Scanning probe microscopy of graphene with a CO terminated tip

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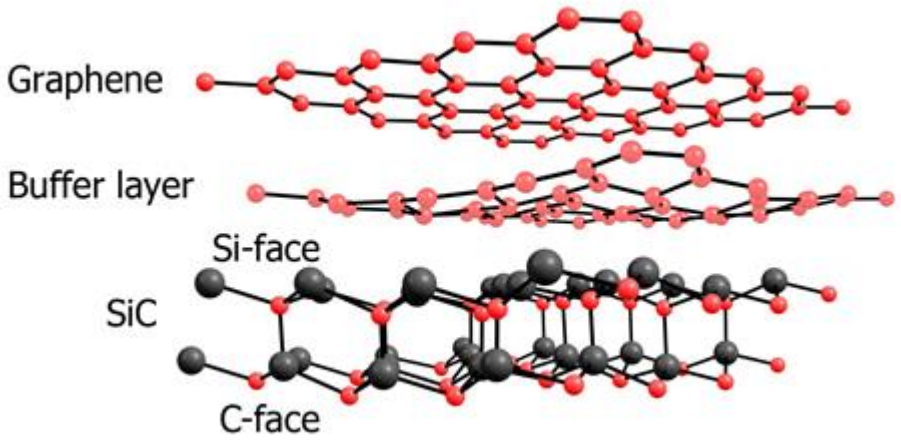
The sample



from the home page of the group of B. J. van Wees

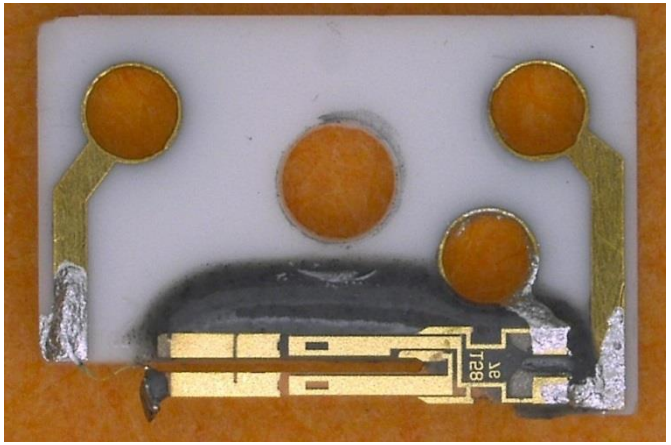
K.V.Emtsev, T.Seyller et al. *Nature Materials* **8**, 203 (2009)

- Graphene monolayer (?)
- Epitaxial growth on the Silicon face of a SiC crystal
- Heating of the crystal in Argon atmosphere
- The pi conjugation is broken in the buffer layer due to covalent bonds to Si in the crystal
- The graphene monolayer is n-doped as determined by ARPES

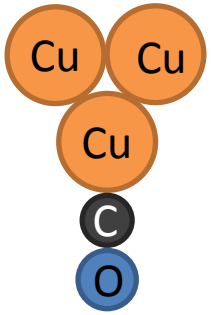
$$E_F \approx 0.4eV$$

The experiment

- Combined Scanning Tunnelling and Atomic Force Microscopy
- Experiment realized in Ultra High Vacuum at a temperature of 4.6 K
- Tip mounted on a qPlus sensor with:
  - Stiffness $k = 1800\,\mathrm{N/m}$
  - Frequency $f_0 = 26660.3\,\mathrm{Hz}$
  - Amplitude $A = 50\,\mathrm{pm}$
- The Cu tip is terminated with a CO molecule



from the hompage of the group of F. Gießibl



Basics on STM

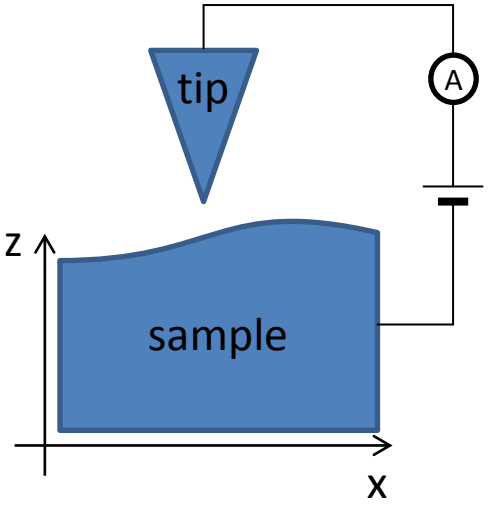
- The signal is the tunnelling current between a metallic tip and the conducting sample

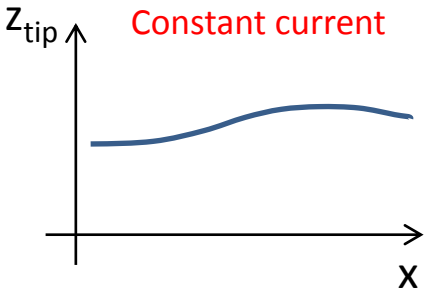
- The tunnelling amplitude depends exponentially on the tip-sample distance

$$I_t = I_0 e^{-2\kappa z} \qquad \kappa = \sqrt{2m\phi}/\hbar$$

- The microscope can be used in two fundamental modes: constant height or constant current.

- Naively one expects to record in both cases the **topography** of the sample



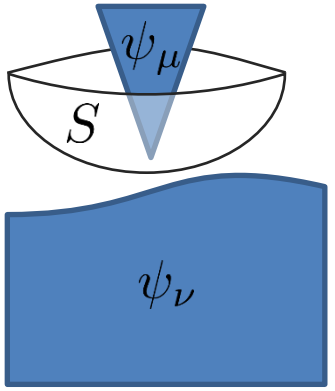


Tersoff-Hamann

- When both tip and sample have a continuous spectrum, the tunnelling current reads:

$$I = \frac{2\pi e}{\hbar} \sum_{\mu\nu} f(E_\mu)[1 - f(E_\nu + eV)]|M_{\mu\nu}|^2 \delta(E_\nu - E_\mu)$$

$$M_{\mu\nu} = \frac{\hbar^2}{2m} \int \mathrm{d}\vec{S} \cdot (\psi_\mu^* \vec{\nabla} \psi_\nu - \psi_\nu^* \vec{\nabla} \psi_\mu)$$



- In the limit of small bias and low temperature

$$I = \frac{2\pi}{\hbar} e^2 V \sum_{\mu\nu} |M_{\mu\nu}|^2 \delta(E_\nu - E_F)\delta(E_\mu - E_F)$$

J. Tersoff' and D. R. Hamann, *PRB* **31**, 805 (1985)
J. Bardeen, *PRL* **6**, 57 (1961)

Chen's derivative rule

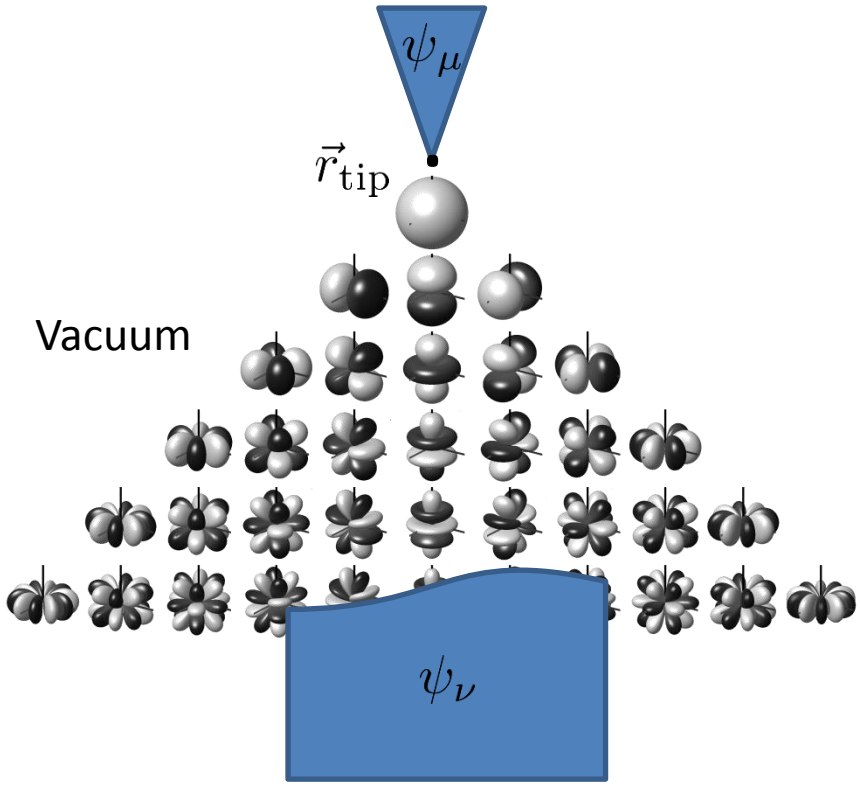
By expanding the vacuum tail of the tip wave function into spherical harmonics one obtains an expression for the Bardeen matrix element $M_{\mu\nu}$

$$M_{s\nu} \propto \psi_\nu(\vec{r}_{\mathrm{tip}})$$

$$M_{p_x\nu} \propto \frac{\partial}{\partial x}\psi_\nu(\vec{r}_{\mathrm{tip}})$$

$$M_{p_y\nu} \propto \frac{\partial}{\partial y}\psi_\nu(\vec{r}_{\mathrm{tip}})$$

$$M_{p_z\nu} \propto \frac{\partial}{\partial z}\psi_\nu(\vec{r}_{\mathrm{tip}})$$

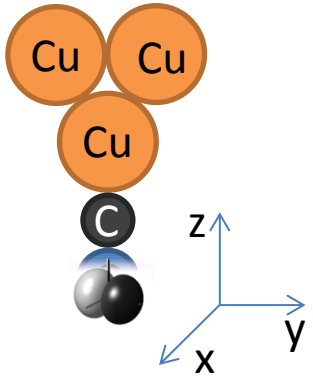


C. J. Chen, *PRB* **42**, 8841 (1990)

Current formulas

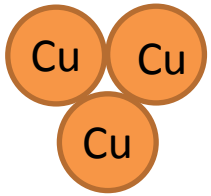
- The π^* orbitals of the CO molecule dominate the symmetry of the tip wave function:

$$I_{\mathrm{CO}}(\vec{r}_{\mathrm{tip}}) \propto \sum_{n\vec{k}} \left[\left| \frac{\partial \psi_{n\vec{k}}(\vec{r}_{\mathrm{tip}})}{\partial x} \right|^2 + \left| \frac{\partial \psi_{n\vec{k}}(\vec{r}_{\mathrm{tip}})}{\partial y} \right|^2 \right] \delta(E_F - E_{n\vec{k}})$$



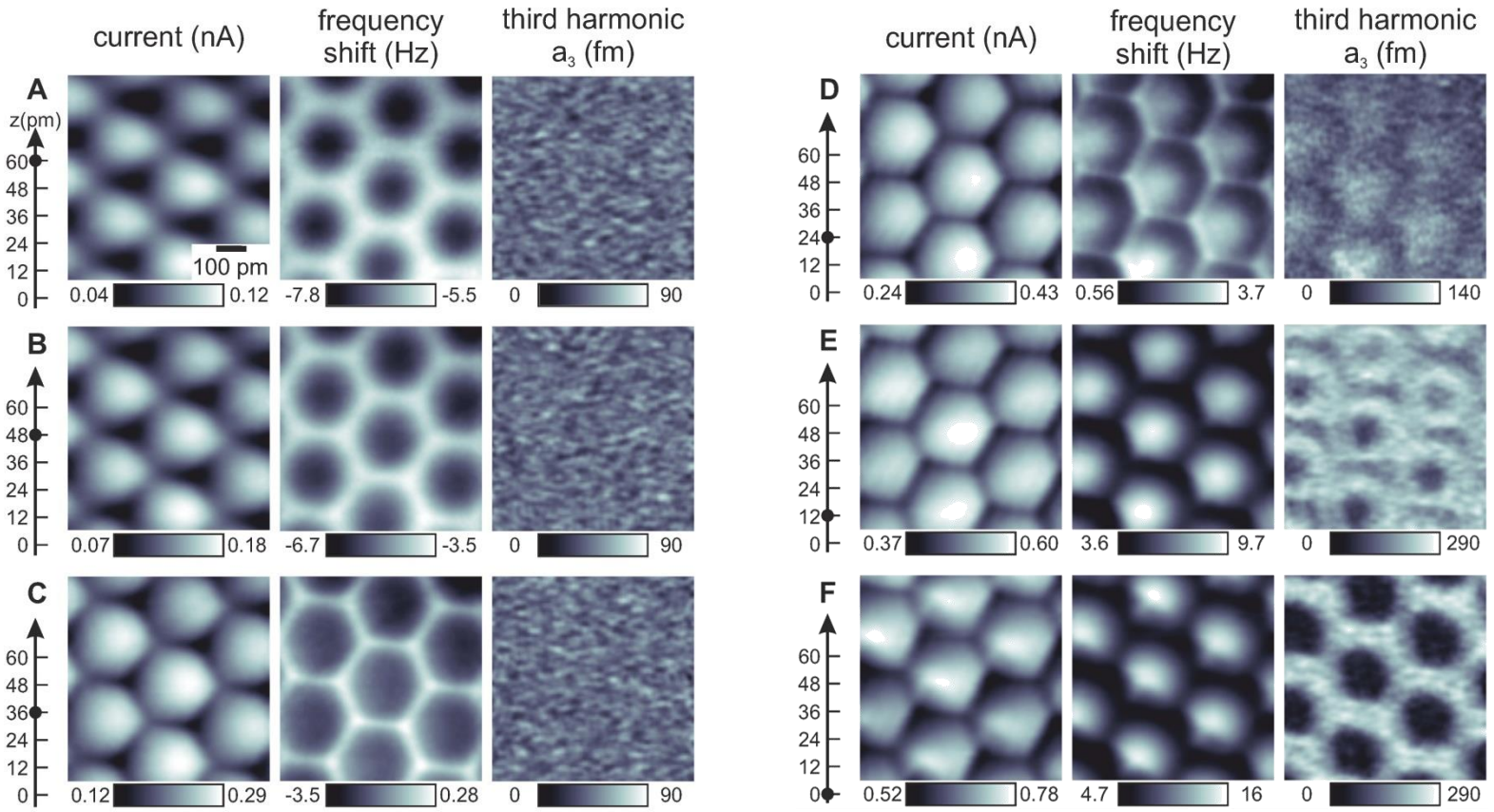
- The wave function of the Cu tip has instead an *s* character:

$$I_{\mathrm{Cu}}(\vec{r}_{\mathrm{tip}}) \propto \sum_{n\vec{k}} \left| \psi_{n\vec{k}}(\vec{r}_{\mathrm{tip}}) \right|^2 \delta(E_F - E_{n\vec{k}})$$



The current is proportional to the local density of states (LDOS)

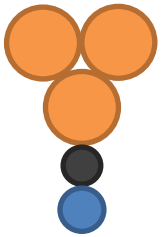
Experimental images



Challenges of the CO termination

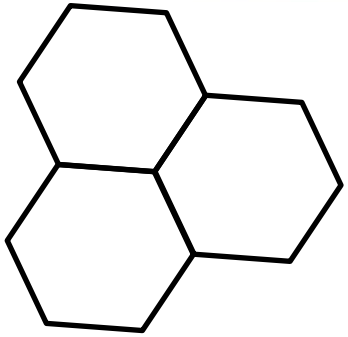
- In the STM images of graphene:
  - Maximum of the current with tip in the hollow position
  - Asymmetry in the A-B sublattice
  - Sharpening of the minima around top position when lowering the tip
- In the AFM images of graphene:
  - Contrast inversion of the frequency shift when lowering the tip
  - Large third harmonic component in the tip dynamics

Maximum in the hollow position

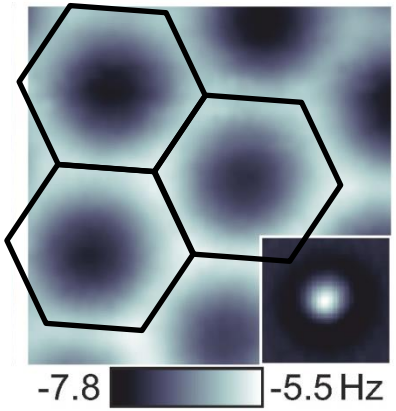


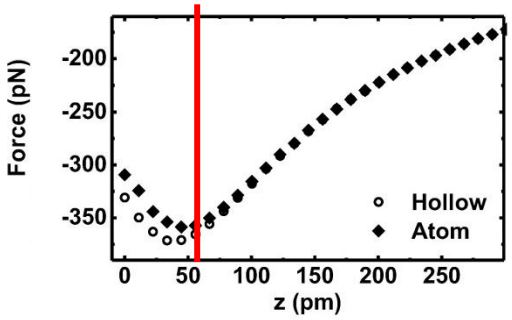
CO tip

STM



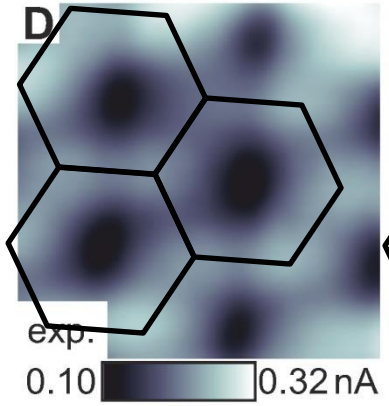
AFM



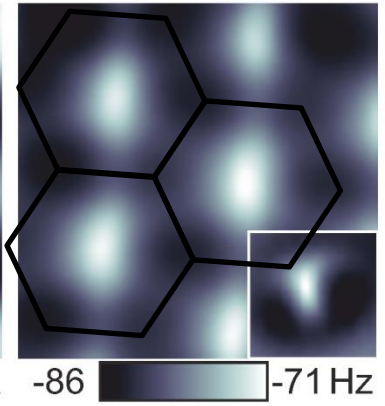


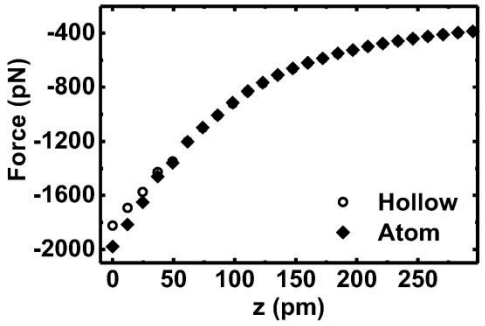
Cu tip

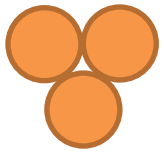
STM



AFM

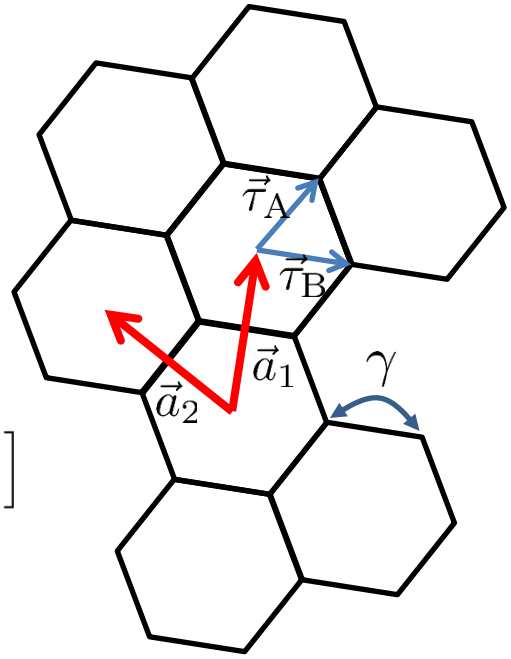






Tight-binding graphene

I calculate the spectrum and eigenstates of graphene
in the nearest neighbours tight-binding approximation



The eigenstates read

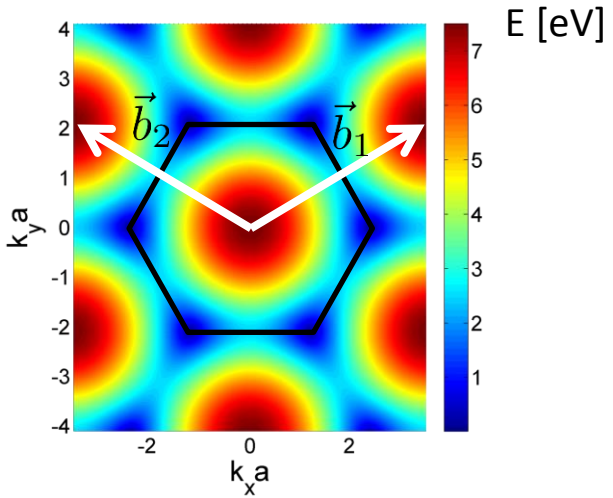
$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{2N_{\text{cell}}}} \sum_{\vec{R}} \mathrm{e}^{i\vec{k}\cdot\vec{R}} \left[p_z(\vec{r} - \vec{R} - \vec{\tau}_{\text{A}}) - n\mathrm{e}^{-i\phi(\vec{k})} p_z(\vec{r} - \vec{R} - \vec{\tau}_{\text{B}}) \right]$$

where

$$\phi(\vec{k}) = \arg(1 + \mathrm{e}^{i\vec{k}\cdot\vec{a}_1} + \mathrm{e}^{i\vec{k}\cdot\vec{a}_2})$$

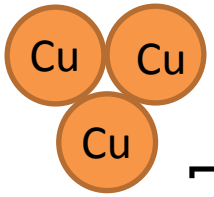
The corresponding eigenenergies are:

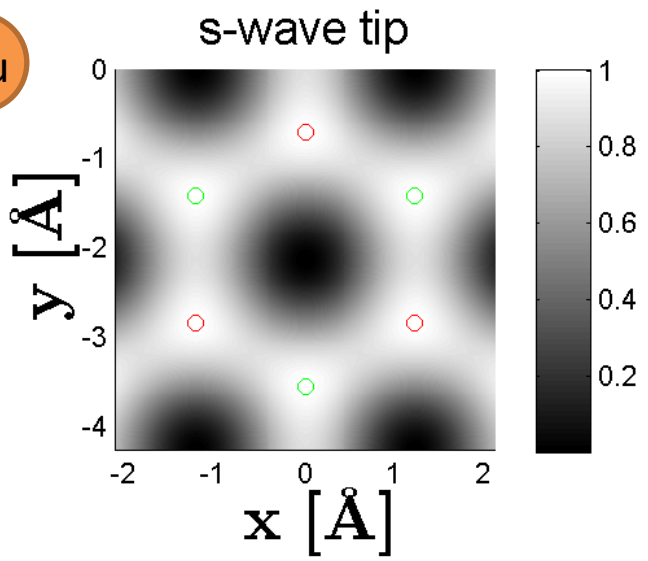
$$E_{n\vec{k}} = n\gamma|1 + \mathrm{e}^{i\vec{k}\cdot\vec{a}_1} + \mathrm{e}^{i\vec{k}\cdot\vec{a}_2}|$$

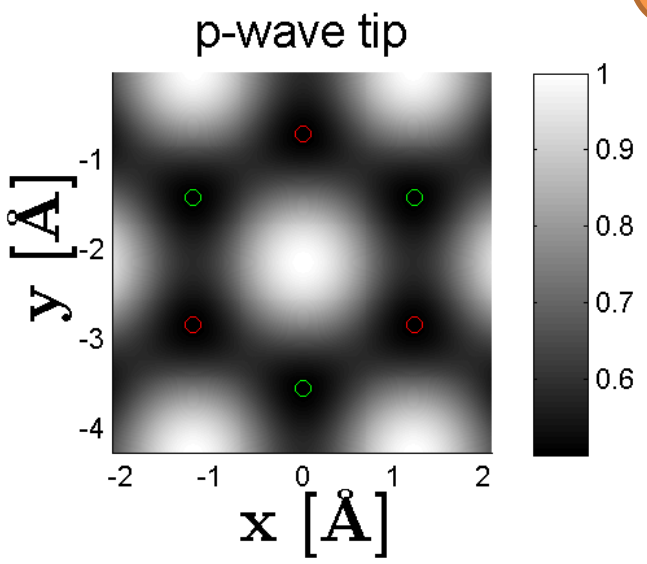


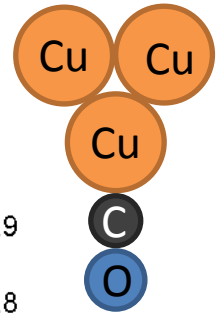
Current maps

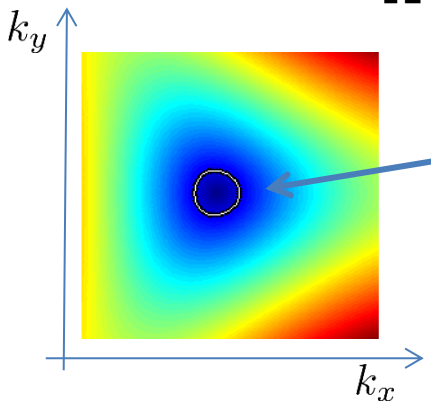
$$I_{\mathrm{Cu}}(\vec{r}_{\mathrm{tip}}) \propto \sum_{n\vec{k}} \left|\psi_{n\vec{k}}(\vec{r}_{\mathrm{tip}})\right|^2 \delta(E_F - E_{n\vec{k}})$$





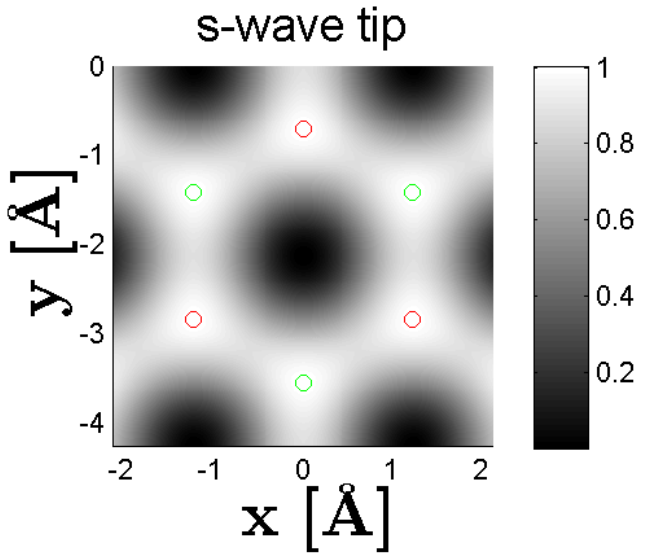






$$I_{\mathrm{CO}}(\vec{r}_{\mathrm{tip}}) \propto \sum_{n\vec{k}} \left[\left|\frac{\partial\psi_{n\vec{k}}(\vec{r}_{\mathrm{tip}})}{\partial x}\right|^2 + \left|\frac{\partial\psi_{n\vec{k}}(\vec{r}_{\mathrm{tip}})}{\partial y}\right|^2\right] \delta(E_F - E_{n\vec{k}})$$

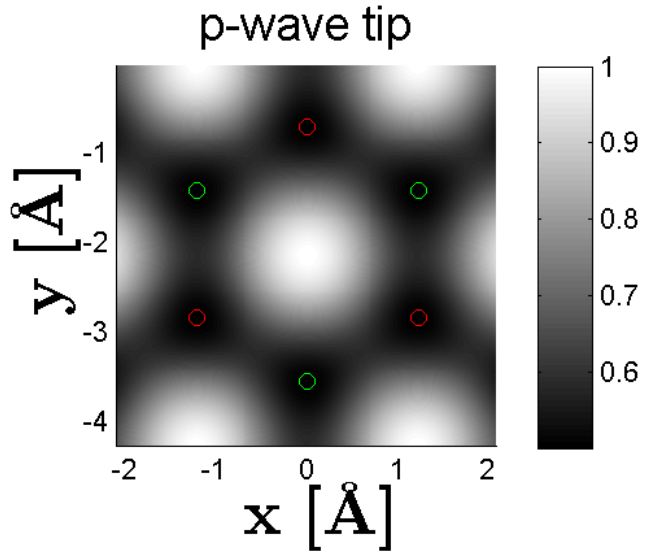
Numerical findings



- The calculated current has an exact zero in the hollow positions and maxima in the top positions

$$I_s(hollow) = 0$$

- The normalized current map is independent of the position of the Fermi energy

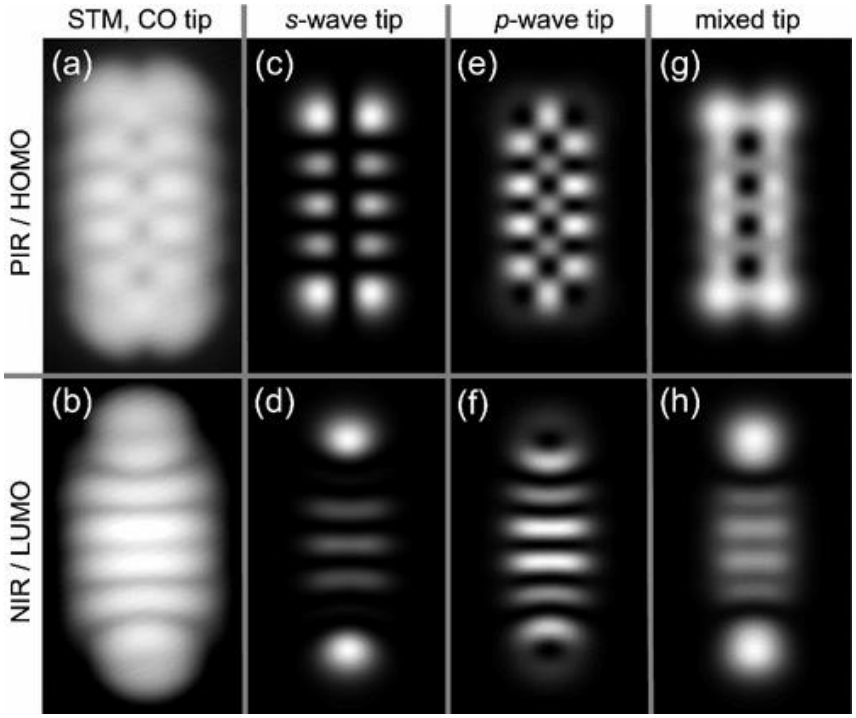


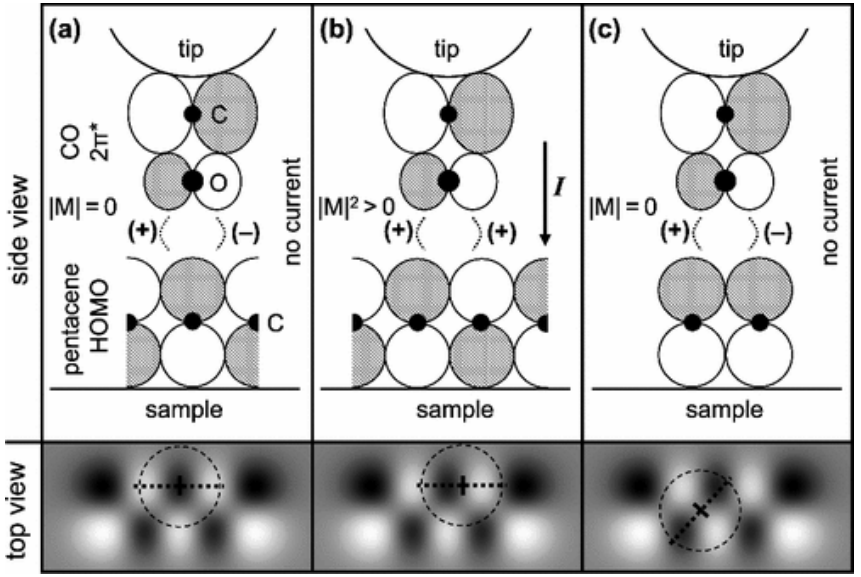
- The calculated current in the hollow positions is two times large that the one in the top positions

$$I_p(hollow) = 2 \times I_p(top)$$

- The normalized current map is independent of the position of the Fermi energy

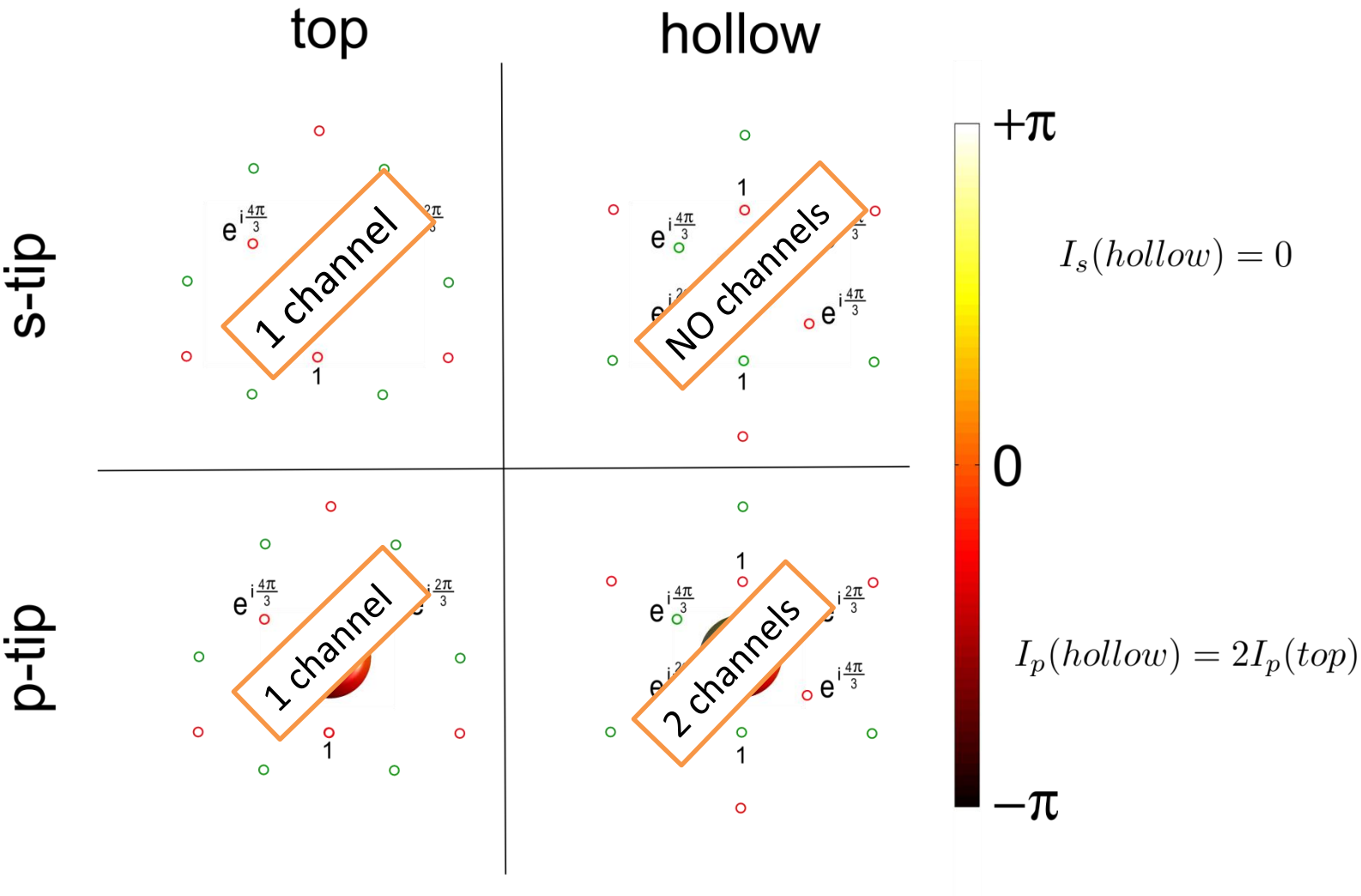
CO tip and molecular nodal planes





L. Gross, et al. *PRL* **107,** 086101 (2011)

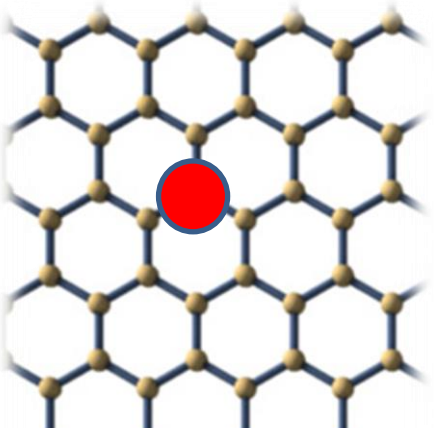
Phase matching



Group theoretical analysis

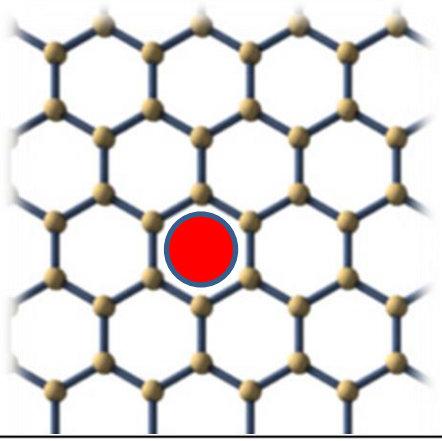
The presence of the tip lowers the symmetry of the graphene lattice to point symmetry groups. In particular

TOP



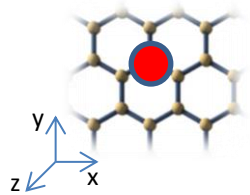
C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

HOLLOW



C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	−1	−1
B_1	1	−1	1	−1	1	−1
B_2	1	−1	1	−1	−1	1
E_1	2	1	−1	−2	0	0
E_2	2	−1	−1	2	0	0

Fermi states representation



- The Fermi states for neutral graphene are 4 (x2 for the spin).

$$|\vec{k}_{\mathrm{F}_1} A\rangle \; |\vec{k}_{\mathrm{F}_2} A\rangle \; |\vec{k}_{\mathrm{F}_1} B\rangle \; |\vec{k}_{\mathrm{F}_2} B\rangle$$

- The representation of the simmetry operations in C_{3v} read, in the basis

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$C^{+}_{3,A} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & e^{-i2\pi/3} & 0 \\ 0 & 0 & 0 & e^{i2\pi/3} \end{pmatrix}$$

or

$$C^{+}_{3,B} = \begin{pmatrix} e^{i2\pi/3} & 0 & 0 & 0 \\ 0 & e^{-i2\pi/3} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_{yz} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

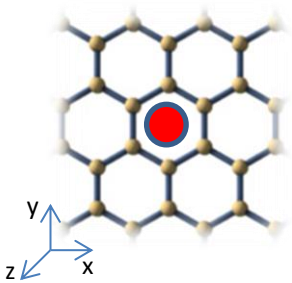
- In both cases (tip on top of A or B) one obtains the decomposition:

$$\Gamma_{\mathrm{F,top}} = \{4, 1, 0\} = A_1 \oplus A_2 \oplus E$$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

Fermi states representation

- Analogously for the point symmetry group C_{6v} , in the same basis $|\vec{k}_{\mathrm{F}_1} A\rangle \; |\vec{k}_{\mathrm{F}_2} A\rangle \; |\vec{k}_{\mathrm{F}_1} B\rangle \; |\vec{k}_{\mathrm{F}_2} B\rangle$



$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad C_6 = \begin{pmatrix} 0 & 0 & 0 & e^{i2\pi/3} \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ e^{-i2\pi/3} & 0 & 0 & 0 \end{pmatrix}$$

$$C_3 = \begin{pmatrix} e^{i2\pi/3} & 0 & 0 & 0 \\ 0 & e^{-i2\pi/3} & 0 & 0 \\ 0 & 0 & e^{i2\pi/3} & 0 \\ 0 & 0 & 0 & e^{-i2\pi/3} \end{pmatrix} \qquad C_2 = \begin{pmatrix} 0 & 0 & 0 & e^{-i2\pi/3} \\ 0 & 0 & e^{i2\pi/3} & 0 \\ 0 & e^{-i2\pi/3} & 0 & 0 \\ e^{i2\pi/3} & 0 & 0 & 0 \end{pmatrix}$$

$$\sigma_{yz} = \begin{pmatrix} 0 & e^{-i2\pi/3} & 0 & 0 \\ e^{i2\pi/3} & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{-i2\pi/3} \\ 0 & 0 & e^{i2\pi/3} & 0 \end{pmatrix} \qquad \sigma_{xz} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

- One obtains the decomposition

$$\Gamma_{\mathrm{F,hollow}} = \{4, 0, -2, 0, 0, 0\} = E_1 \oplus E_2$$

$$\Gamma'_{\mathrm{F,hollow}} = \{4, -2, 0\} = 2E$$

in C_{3v}

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	−1	−1
B_1	1	−1	1	−1	1	−1
B_2	1	−1	1	−1	−1	1
E_1	2	1	−1	−2	0	0
E_2	2	−1	−1	2	0	0

Selection rules

- Also the tip state generates irreducible representation of the simmetry groups C_{3v} and C_{6v}:

$$\Gamma_s = A_1 \qquad\qquad \Gamma_p = E\,(\text{or } E_1)$$

- The tunnelling matrix element between a tip state and a graphene state is not vanishing only if the tensor product of the associated representations contains the trivial representation A_1

$$\Gamma_s \otimes \Gamma_{\mathrm{F,top}} = A_1 \oplus A_2 \oplus E \longrightarrow \text{1 channel}$$

$$\Gamma_s \otimes \Gamma'_{\mathrm{F,hollow}} = 2E \longrightarrow \text{no channel}$$

$$\Gamma_p \otimes \Gamma_{\mathrm{F,top}} = A_1 \oplus A_2 \oplus 3E \longrightarrow \text{1 channel}$$

$$\Gamma_p \otimes \Gamma'_{\mathrm{F,hollow}} = 2A_1 \oplus 2A_2 \oplus 2E \longrightarrow \text{2 channels}$$

Equivalent channels A ↔ B symmetry

Challenges of the CO termination

- In the STM images of graphene:
  - ✓ Maximum of the current with tip in the hollow position
  - ✓ Asymmetry in the A-B sublattice
  - ✓ Sharpening of the minima around top position when lowering the tip

Static CO bending

Dynamical CO bending

- In the AFM images of graphene:
  - ✓ Contrast inversion of the frequency shift when lowering the tip
  - Large third harmonic component in the tip dynamics

Conclusion

- I have shown measurements of SPM of graphene on SiC by means of a metal (Cu) and CO terminated tip
- The Tersoff‘-Hamann approach complemented by the Chen‘s derivative rule allows to reproduce the **contrast inversion in the STM** images when comparing metal and the CO terminated tip
- A **symmetry** analysis based on **group theory** allows to explain quantitatively the numerical STM simulations

Outlook

The sudden appearance of the **third harmonic** in the dynamics of the AFM cantilever suggests the presence of **complex non-linear effects**:

- bending of the whole graphene flake in combination with
- temporal rehybridization with the formation of covalent bonding to the buffer layer

are under consideration.

Thank you for your attention!

Back-up Slides

Basics on non-contact AFM

- The signal is the frequency shift of the oscillating cantilever to which the tip is attached

$$\Delta f(\vec{r}_{\mathrm{tip}}) = f(\vec{r}_{\mathrm{tip}}) - f_0 = \frac{f_0}{2k}\langle k_{\mathrm{TS}}\rangle(\vec{r}_{\mathrm{tip}})$$

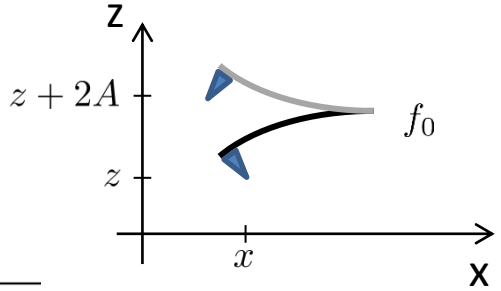
where

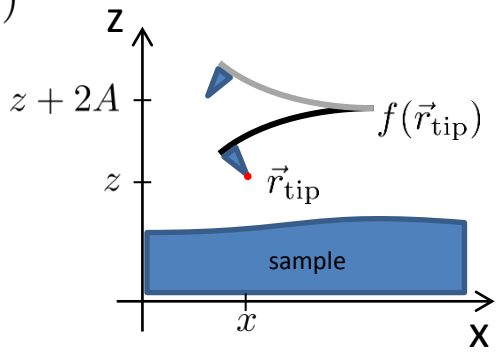
$$\langle k_{\mathrm{TS}}\rangle(x,y,z) = \frac{2}{\pi A^2}\int_0^{2A} \mathrm{d}q\, k_{\mathrm{TS}}(x,y,z+q)\sqrt{A^2-(q-A)^2}$$

and

$$k_{\mathrm{TS}}(x,y,z) = -\frac{\partial}{\partial z}F_{\mathrm{TS}}(x,y,z)$$

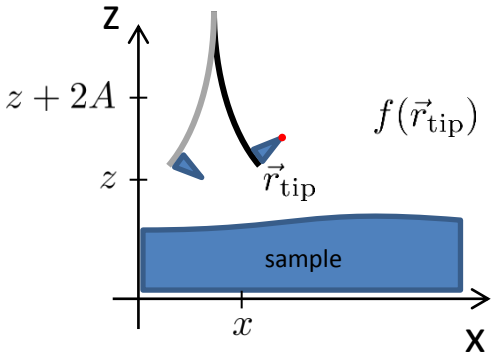
Tip-sample interaction force





- With the same principle, by tilting the cantilever one can measure also lateral forces

$$-\frac{\partial}{\partial x}F_{\mathrm{TS}}(x,y,z) \quad \text{or} \quad -\frac{\partial}{\partial y}F_{\mathrm{TS}}(x,y,z)$$



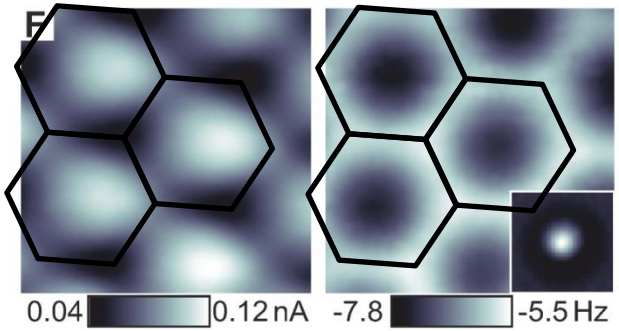
Higher harmonics

- Due to different sources of non-linearities (e.g. anharmonicity of the tip-sample potential, non linear dynamics of the sample) the motion of the tip acquires components with higher harmonics

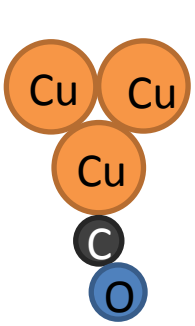
$$q_{\mathrm{tip}}(t) = \sum_{n=0}^{\infty} a_n \cos(2\pi n f t + \phi_n)$$

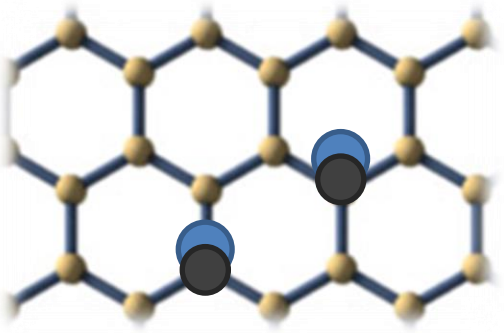
A-B sublattice asymmetry

- According to the measurements of ARPES on the sample there should be no asymmetry in the A-B sublattice. Nevertheless one observes a strong asymmetry in the STM and AFM signal



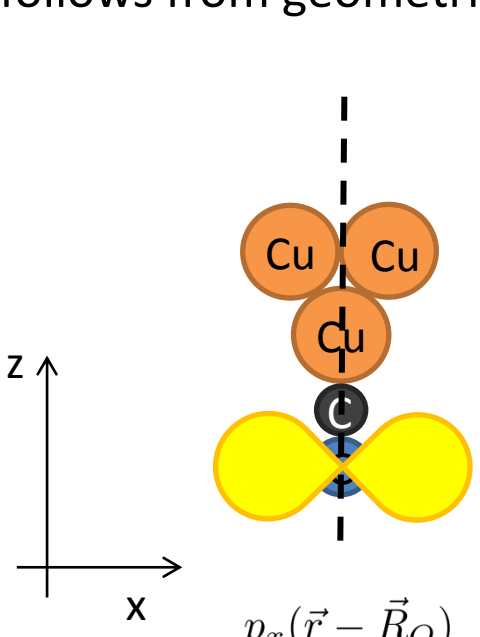
- Hypothesis: The CO molecule does not stand vertical above the graphene surface. Origin: asymmetry of the Cu tip.



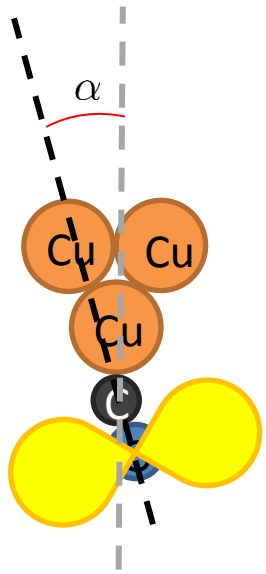


Tilted CO tip

- The numerical implementation of the STM signal with a tilted CO tip follows from geometrical arguments



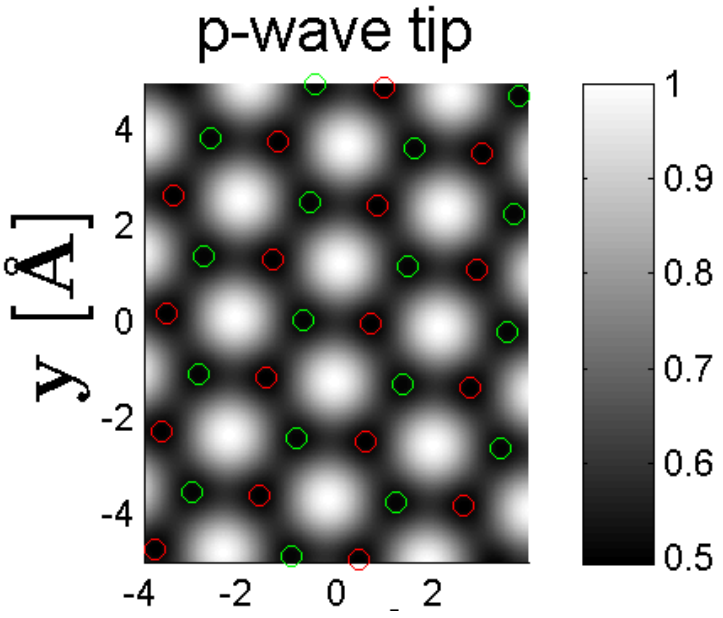
$p_x(\vec{r} - \vec{R}_O)$

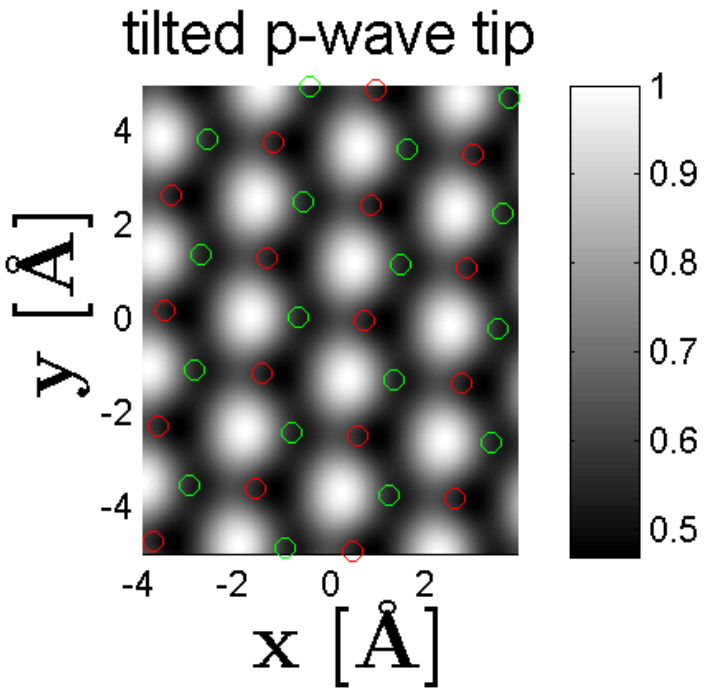


$\cos\alpha\, p_x(\vec{r} - \vec{R}_O) + \sin\alpha\, p_z(\vec{r} - \vec{R}_O)$

- The component p_z is then associated to $\frac{\partial}{\partial_z}\psi_\nu$ by Chen's derivative rule.

Numerical results

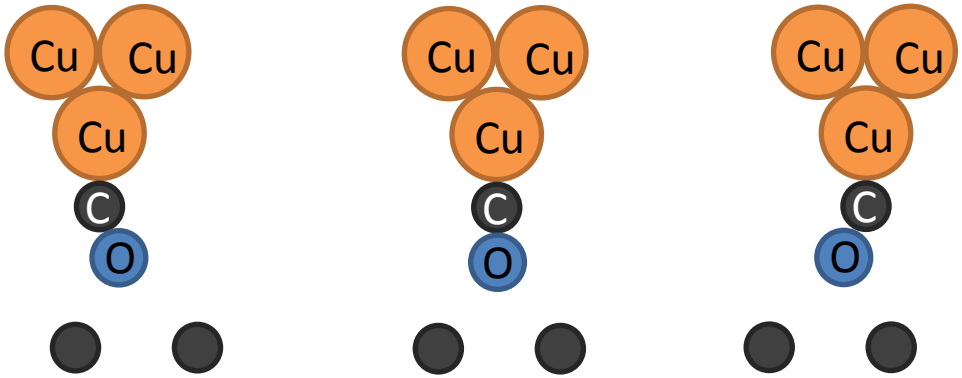




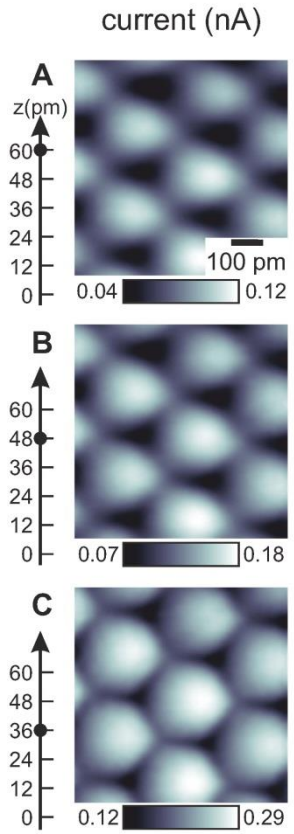
$\theta = 11^\circ \quad \phi = -3^\circ$

Sharpening of the minima

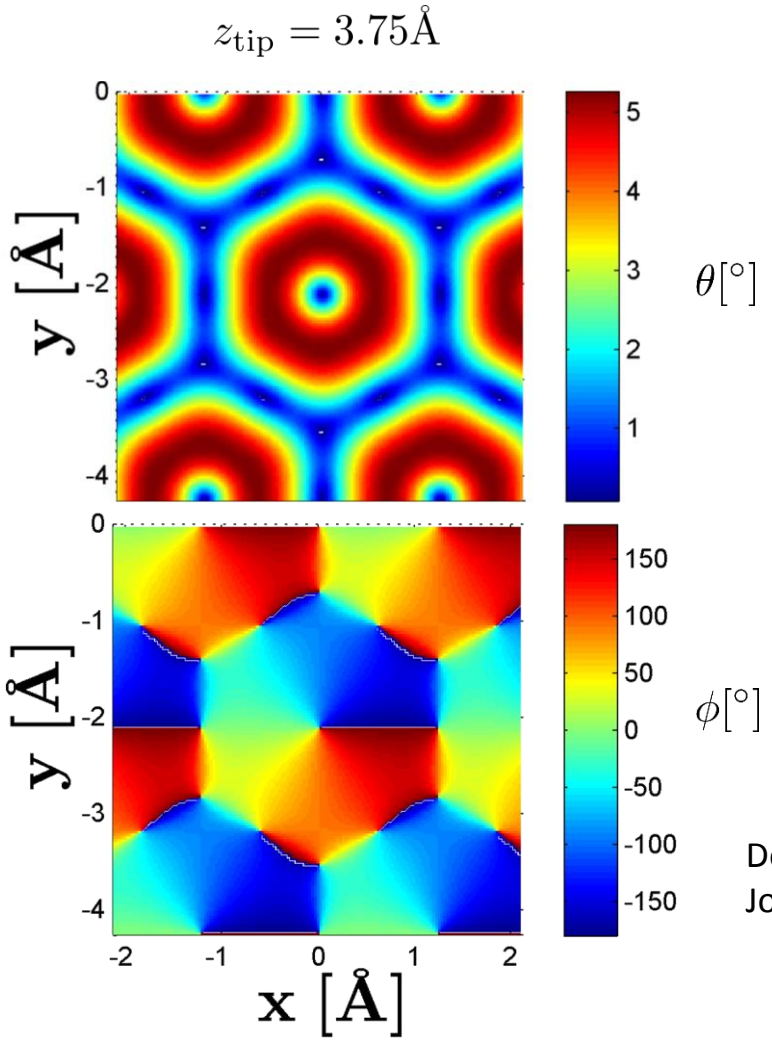
The interaction of the Oxigen of the CO molecule with the Carbon mesh of the graphene causes position dependent deflection

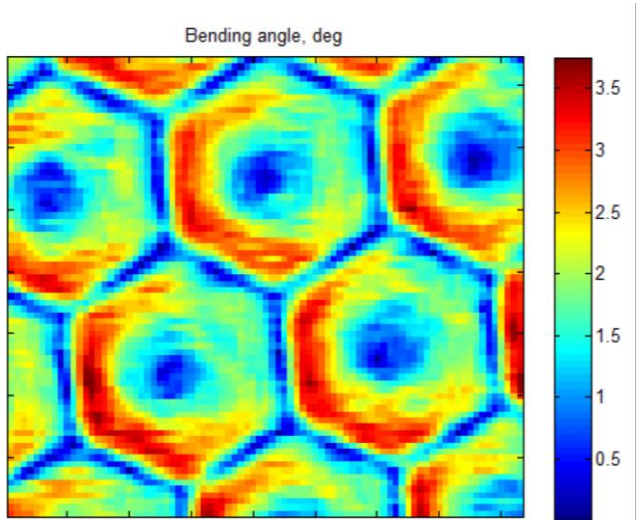


We calulated this interaction using an effective Lennard-Jones potential between the oxigen on the tip and the carbons in graphene.



The deflection maps



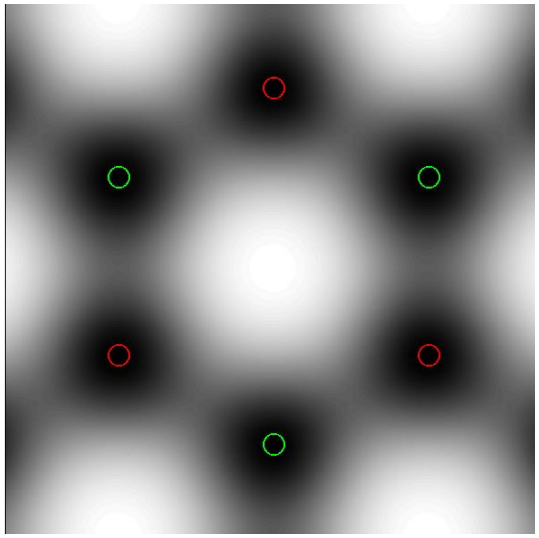


CO deflection angle map obtained from lateral force microscopy measurements

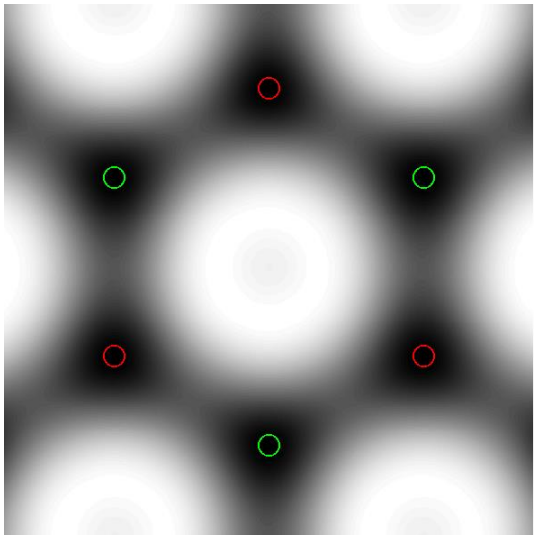
Deflection maps calculated using an effective Lennard-Jones potential

Sharpening of the minima

$z_{\mathrm{tip}} = 4\text{Å}$

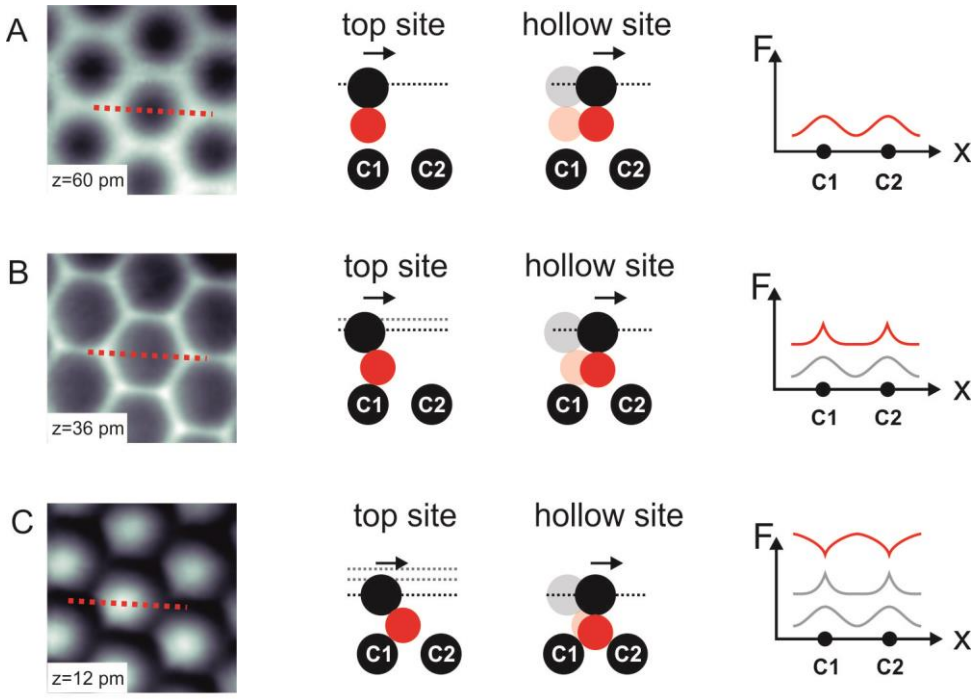


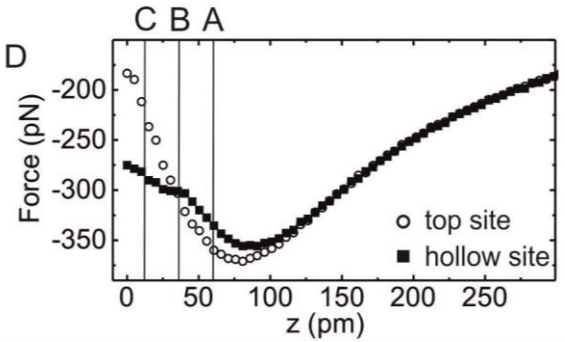
$z_{\mathrm{tip}} = 3.75\text{Å}$



STM constant height current maps calculated taking into account the position dependent deflection of the CO molecule.

Contrast inversion in AFM





A - True image of the graphene lattice

B - The image sharpens due to CO bending

C - The contrast reverse due to Oxigen locking