EMPA

Materials Science & Technology

Stability and dynamics of adatoms and ad-molecules on graphene studied by atomic resolution transmission electron microscopy

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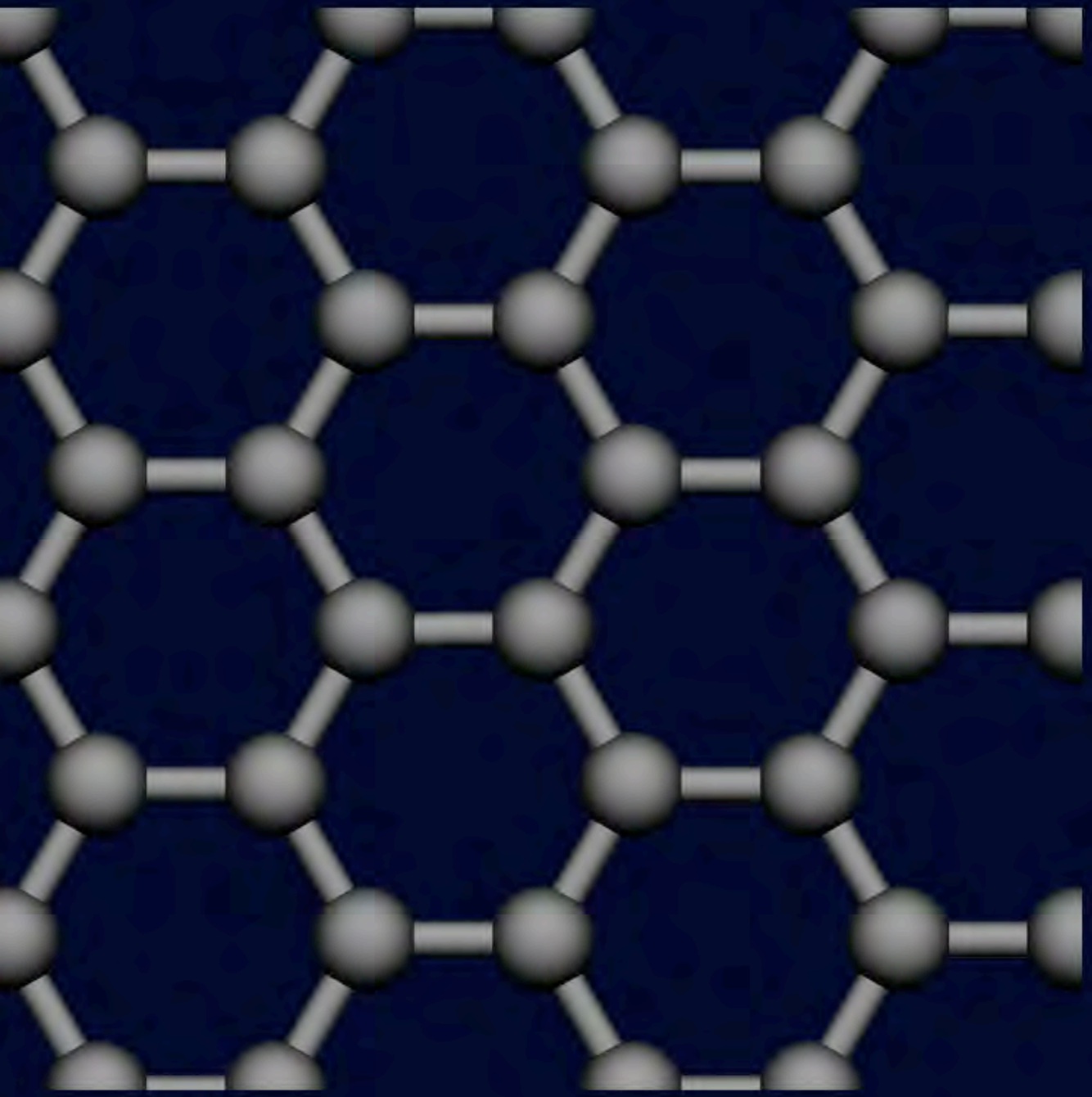
Outline

- Two approaches for aberration-corrected TEM imaging
  - C_S correction + Monochromator
  - C_C/C_S correction
- Dynamics and stability of small molecules on graphene
- Towards an understanding of the atomic structure of graphene oxide

Graphene – A Single Layer of Carbon Atoms



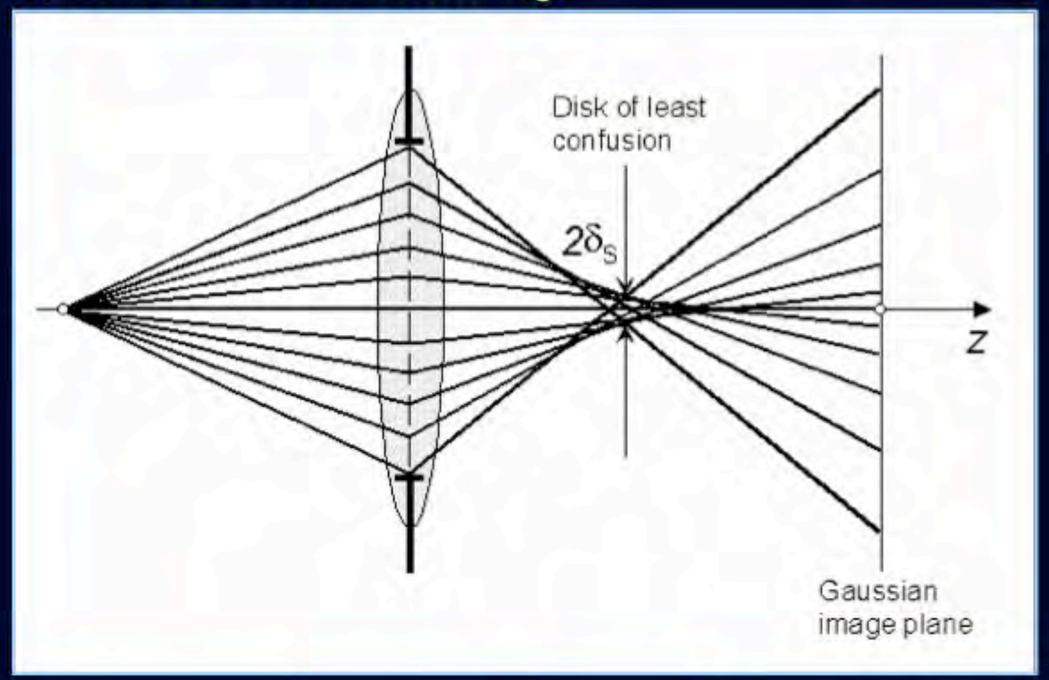
It's a good TEM phase object
Requires: optimized conditions

It's radiation sensitive: knock-on damage
Requires: low high-tension

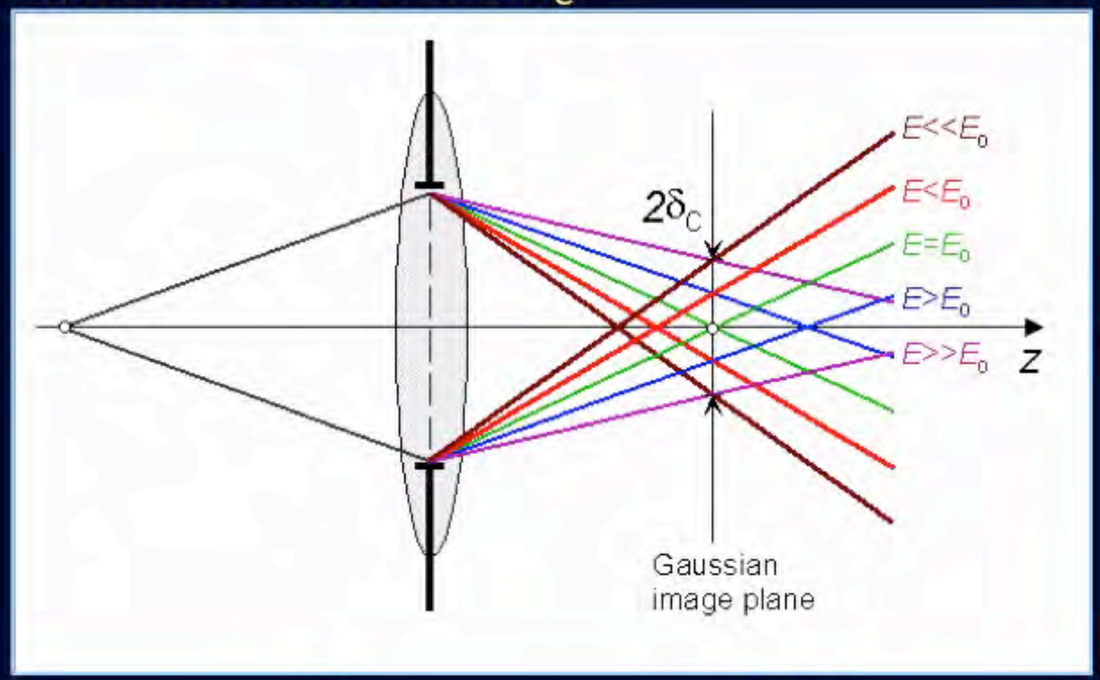
It's a 2D lattice of carbon atoms
Requires: single atom sensitivity

Intrinsic Axial Aberrations of Round Electron Lenses

Spherical Aberration C_S



Chromatic Aberration C_C

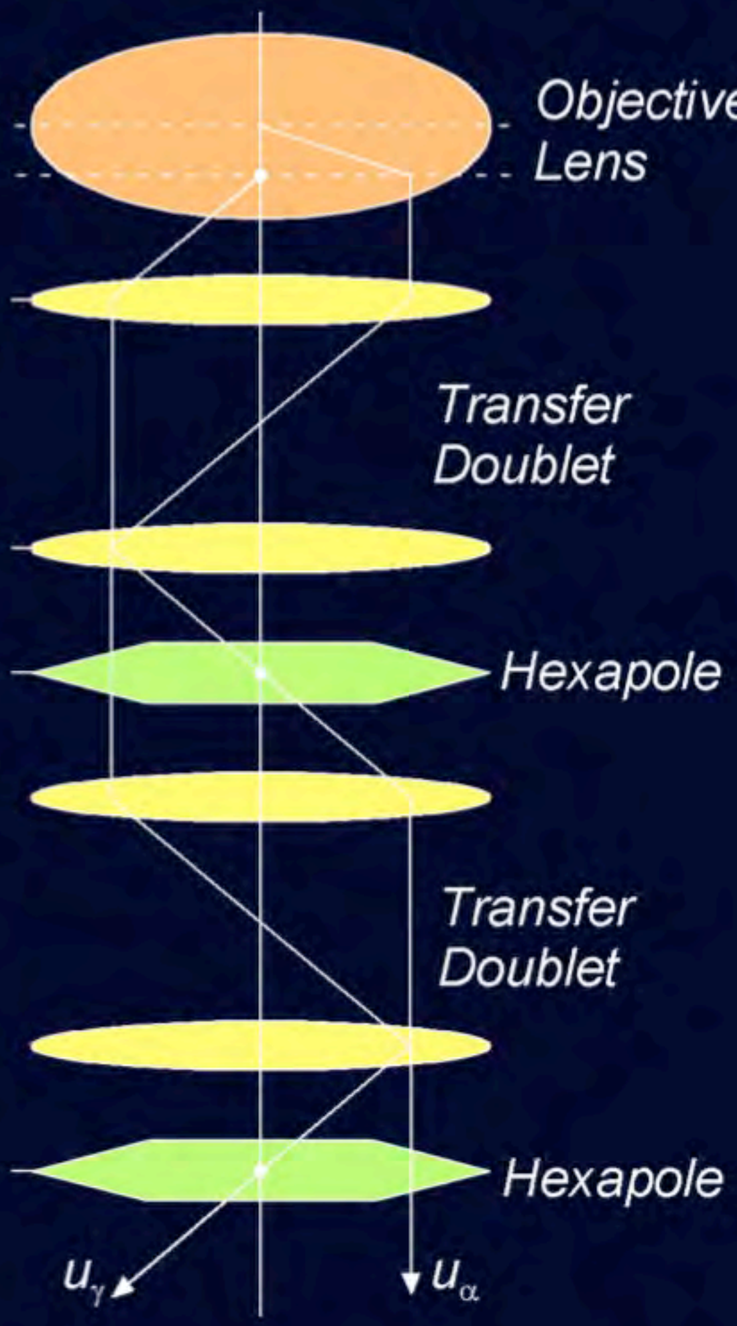


$$2\delta_S = \frac{1}{2} C_S \theta^3$$

$$2\delta_C = C_C \theta \frac{\Delta E}{E}$$

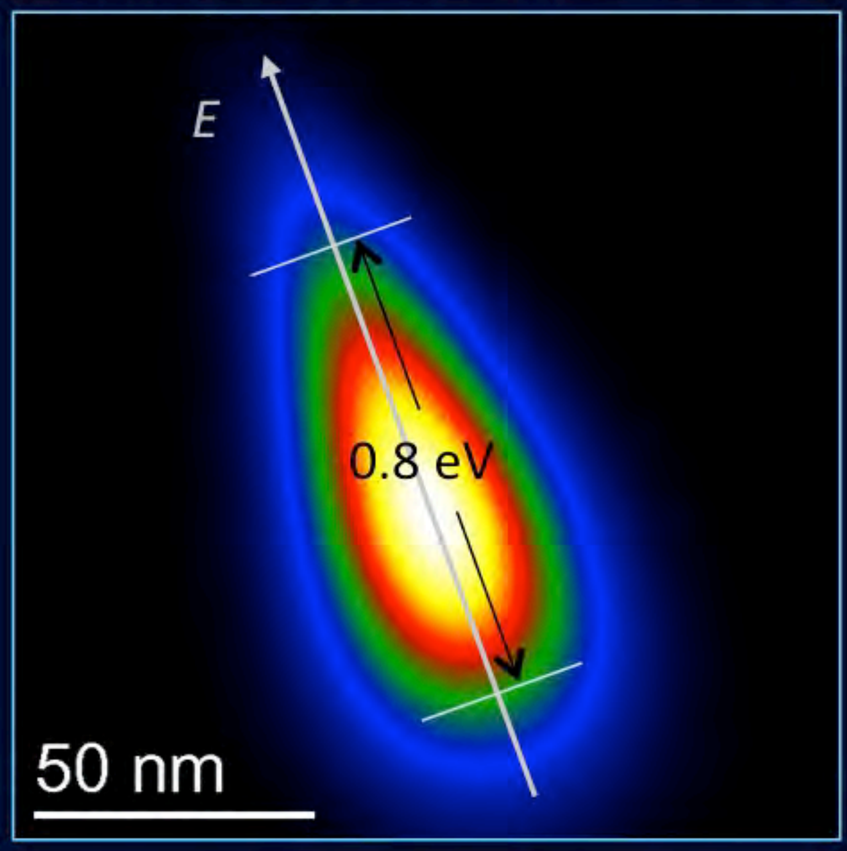
With a demand for increasing resolution (larger θ) and reduced high tension (smaller E), the deleterious effects of C_S and C_C increases.

Strategy 1: C_S corrector + monochromator



Hexapole C_S corrector
(H. Rose, 1990)

Wien-filter monochromator: Rainbow illumination reduces C_C effect for elastically scattered electrons: gain in information limit!



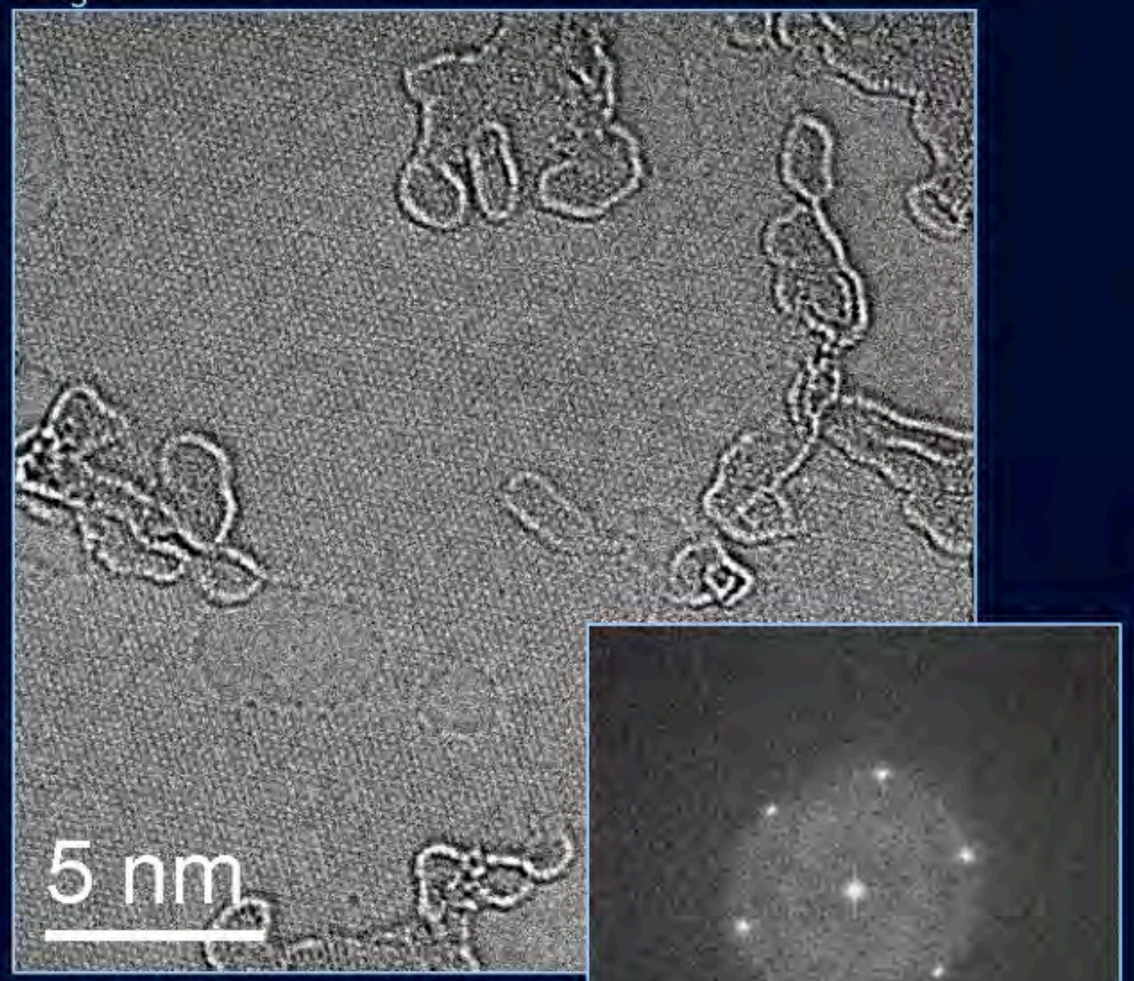
Rainbow-illumination: a dispersed but focused electron probe is used for the illumination in HRTEM

Issues:

- Limited field-of-view
- Inhomogeneous illumination: intensity and energy
- e^--dose is "not" adjustable

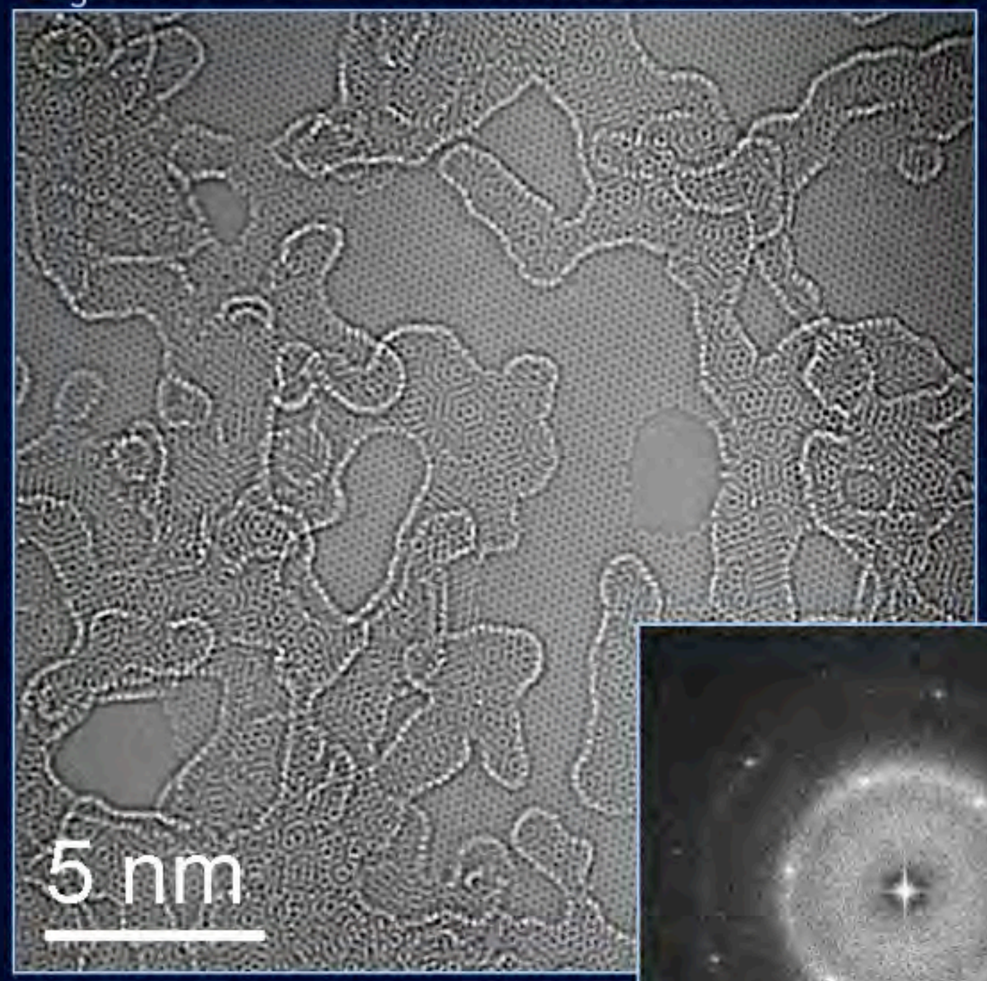
C_S corrector + monochromator

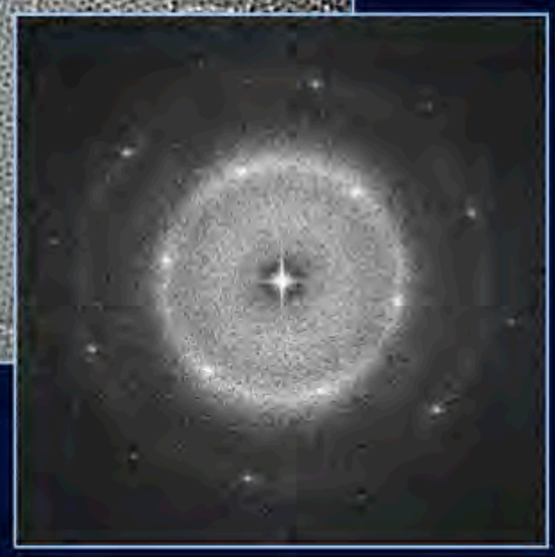
C_S corrected



7'000 counts

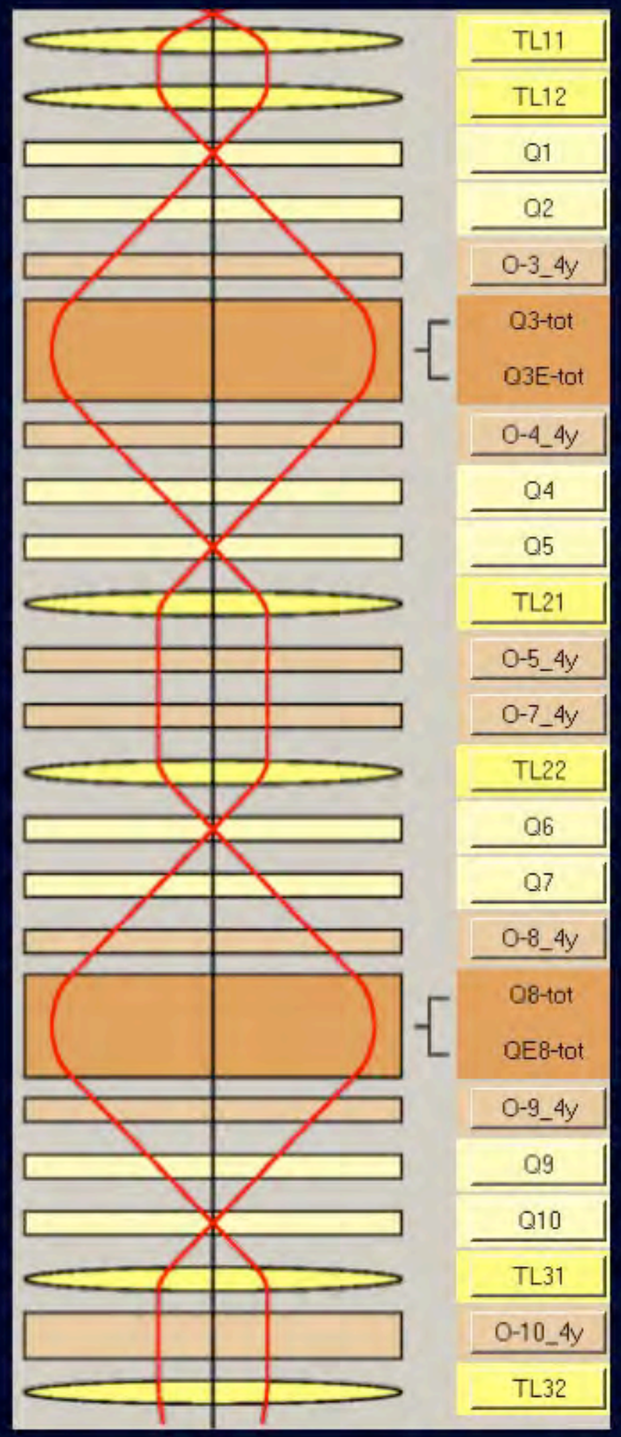
C_S corrected + monochromated





28'000 counts

Strategy 2: C_C / C_S corrector



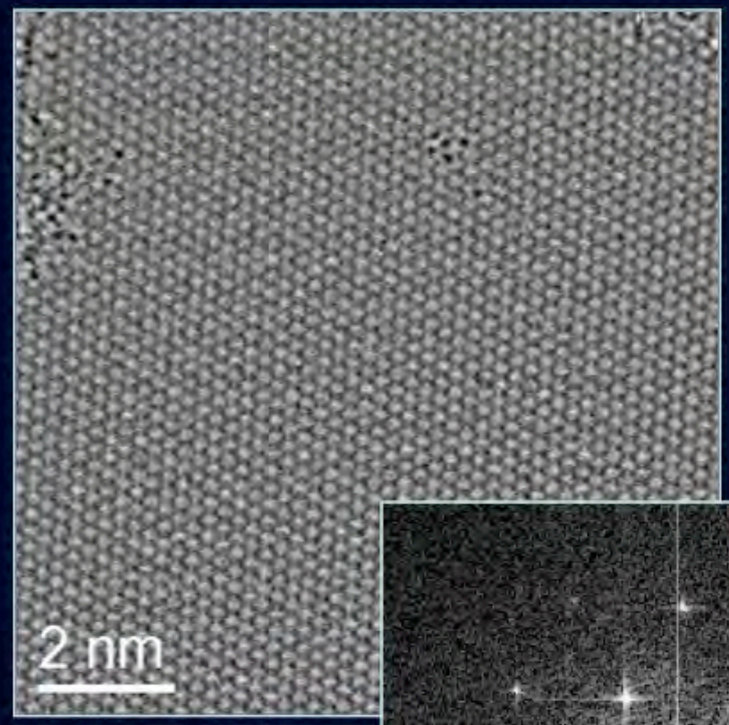
Combined magnetic and electric octupole 1:
C_S and C_C correction

Combined magnetic and electric octupole 1:
C_S and C_C correction

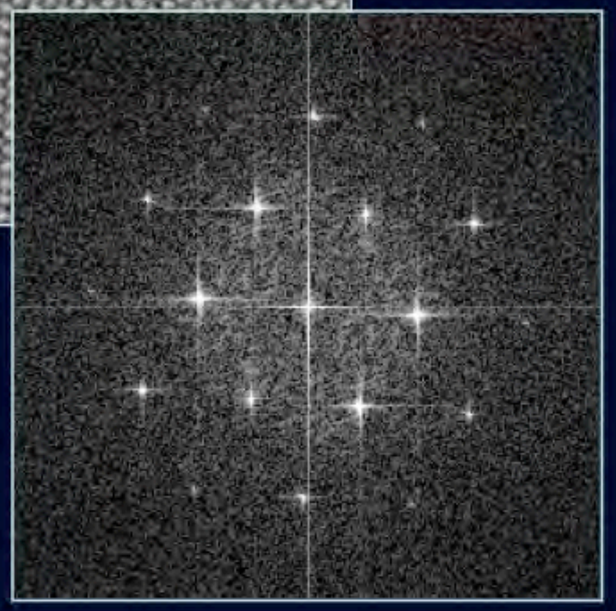
Magnetic octupole:
C_S correction

C_S/mono vs. C_S/C_C corrector

- C_C effect is absent, not minimized
- Primary energy is "uncritical"
- EFTEM: energy window is uncritical
- Illumination and dose are adjustable
- (Off-axial aberrations)



14'000 counts



Beyond Graphene: Scherzer's Chicken

Otto Scherzer: *Die Strahlenschädigung der Objekte als Grenze für die hochauflösende Elektronen-Mikroskopie.* Berichte der Bunsen-Gesellschaft 74 (1970) 1154.

The Object

The Specimen

Electrons cause radiation damage!

The Image

What we expect.

What we don't (want to) expect.

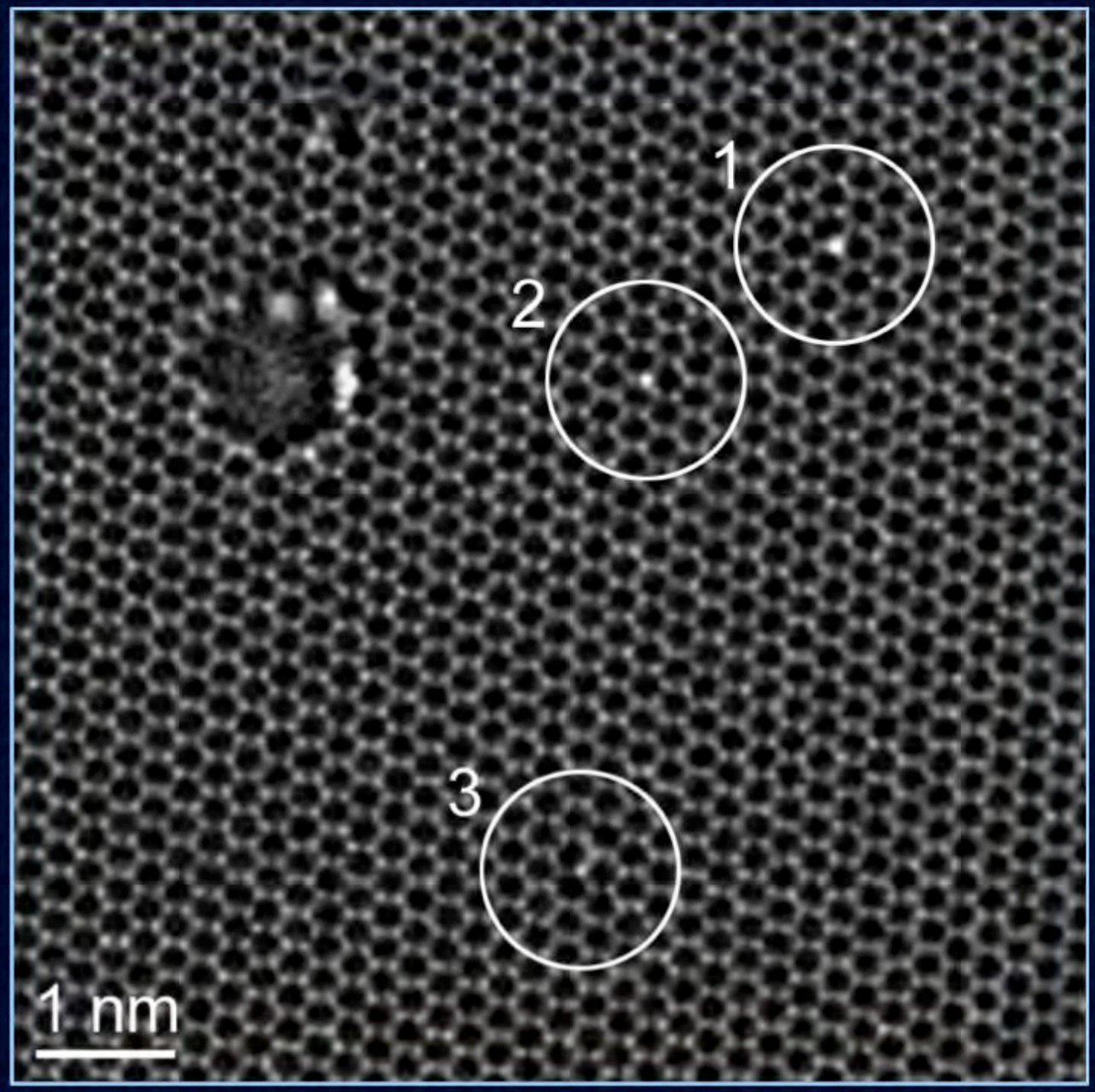
Physics and chemistry on graphene

80 kV
Chromatic and spherical aberration-corrected TEM (TEAM 1)

Electron dose
44.5 A/cm^2
10^4 e^-/s Å^2

Phase of an exit-plane wave restored from a focal series of 11 micrographs.

Phase information provides direct qualitative chemical information-unaffected from the microscope's coherent transfer function.

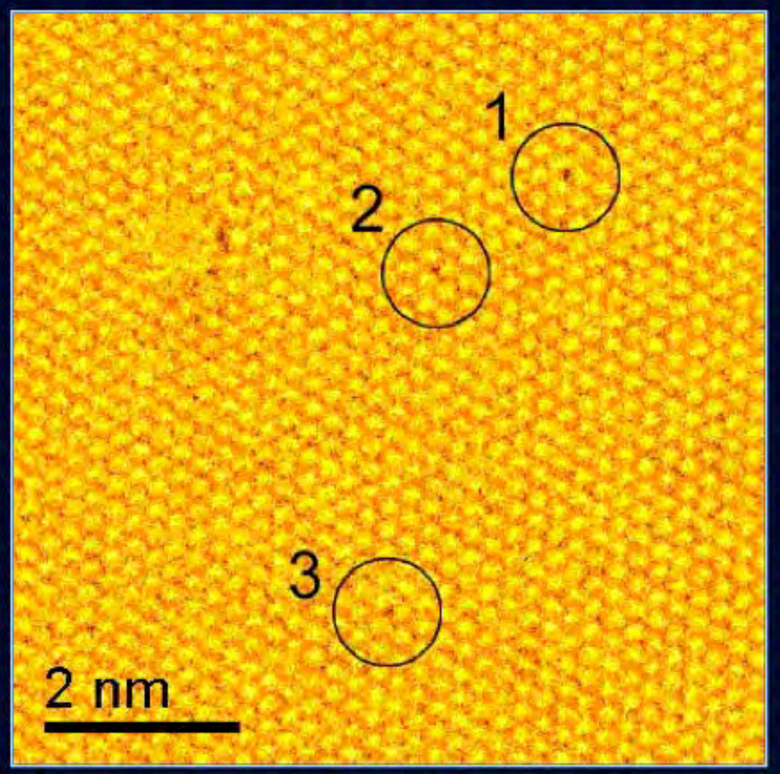


R. Erni, M. D. Rossell, M.-T. Nguyen *et al.*, *PRB* **82** (2010) 165443.

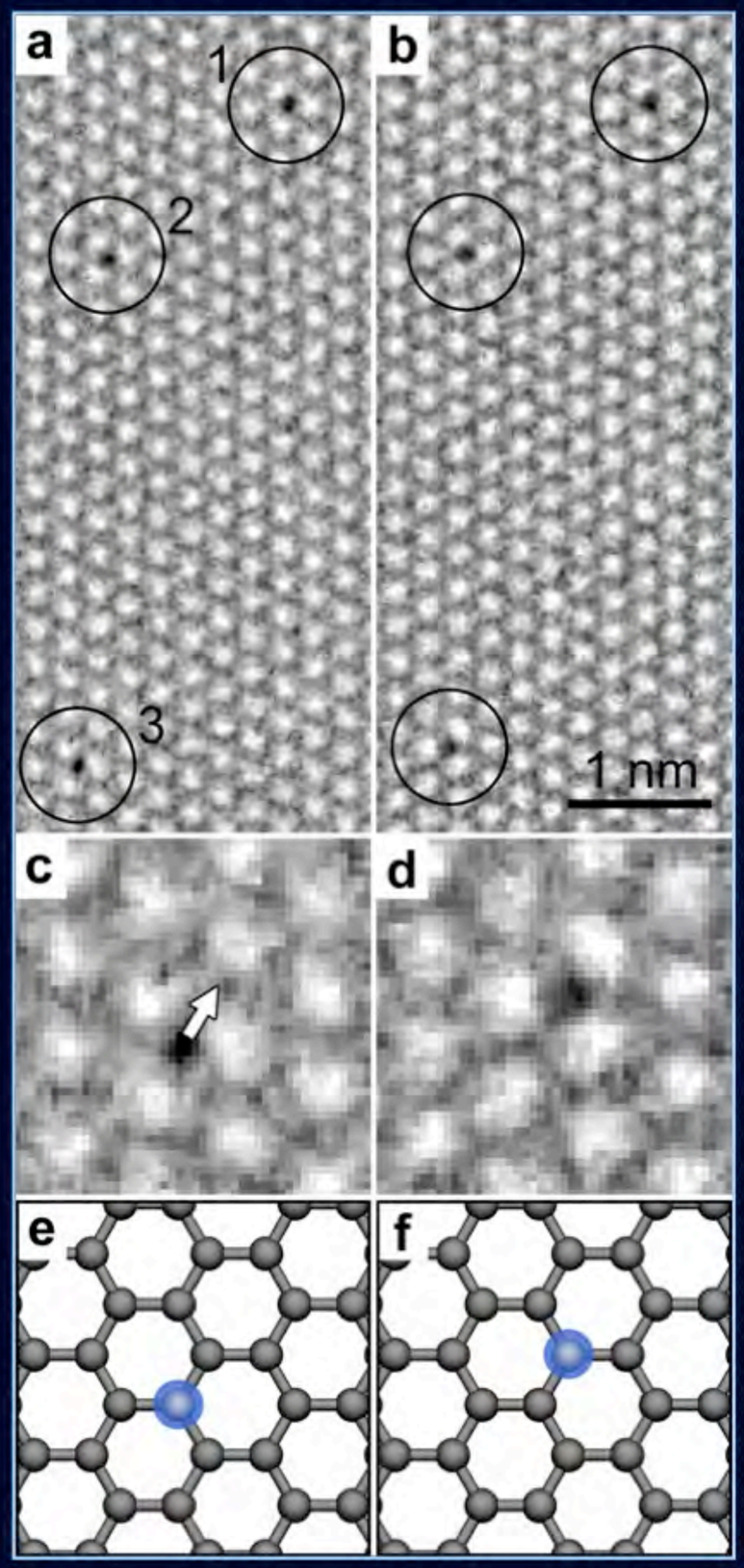
Substitutional or Ad-Atoms?

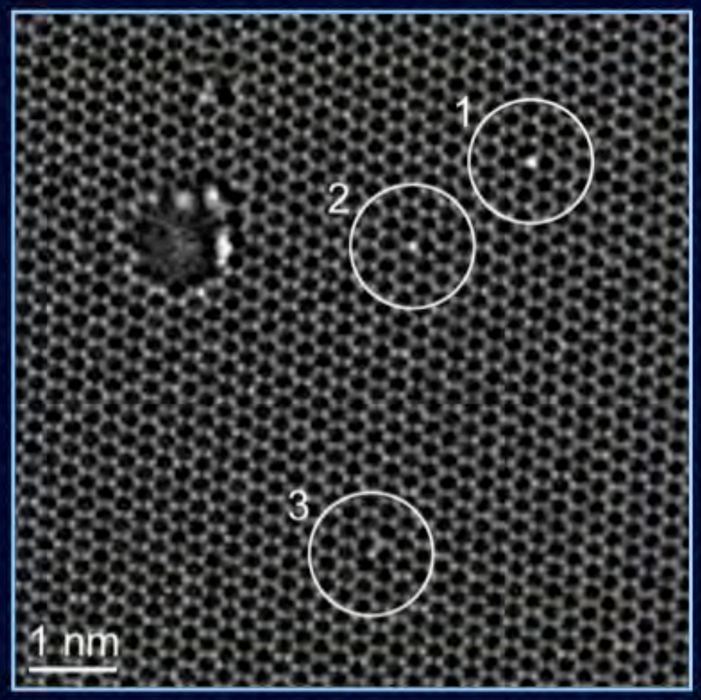
Dynamics helps.

An extract of the focal series…



Atoms appear dark on a bright background.



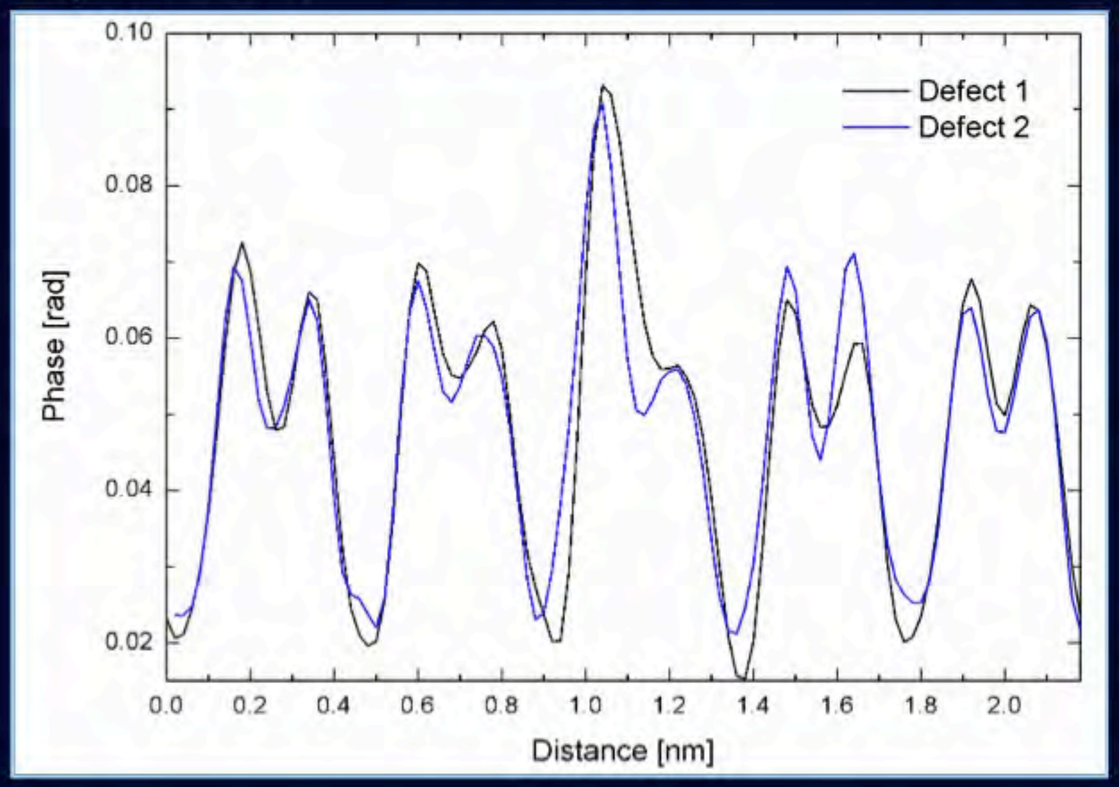


Exposed to 80 keV electrons, substitutional atoms cannot move at room temperature.

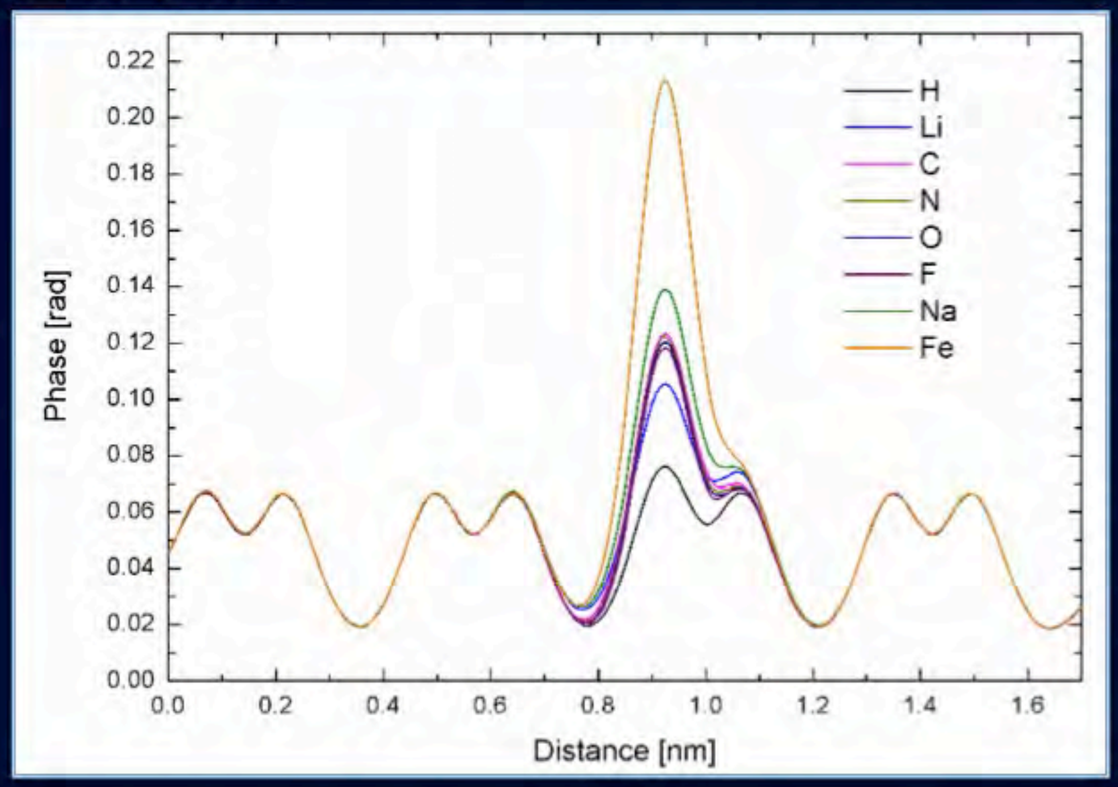
… “ad-atoms”!

What's the nature of the ad-atom?

Experiment



Simulation



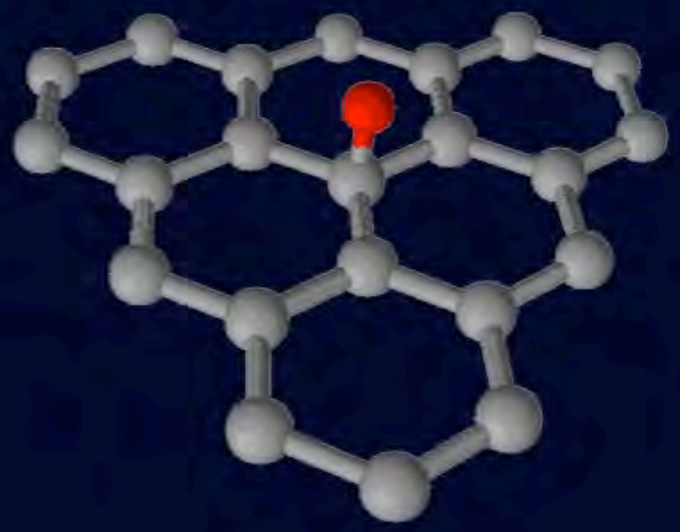
Ad-atoms that give about the right phase shift: Li, Be, B, C, N, O, F, Ne, Na, Mg.

1. The ad-atom must be in the range of Li to Mg!
2. We don't see hydrogen in our data.

Elements present in the system: H, C, N, O!

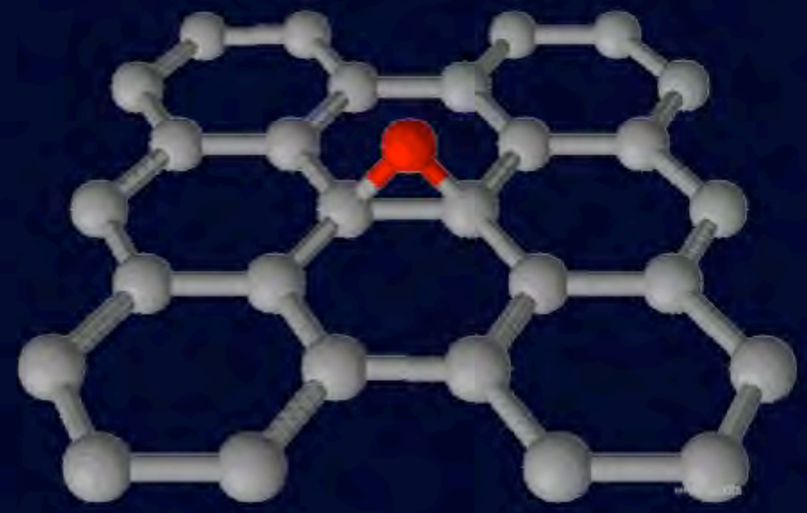
It's not an ad-atom, it must be an ad-molecule!

***T*-site** for "most" atoms not stable.



Li, Be, B,
C, N, O,
F, Ne,
Na, Mg?

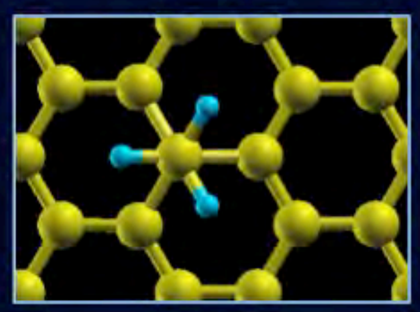
***B*-site** "stable".

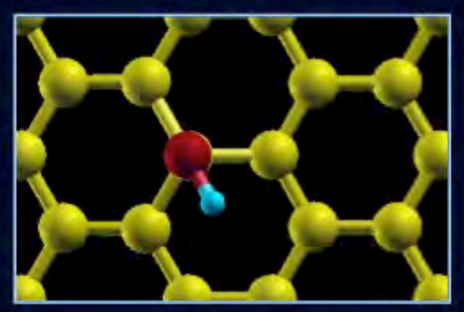


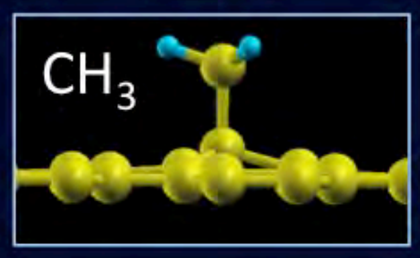
Only fluorine finds a stable position on a *T*-site: but it's presence can't be explained.

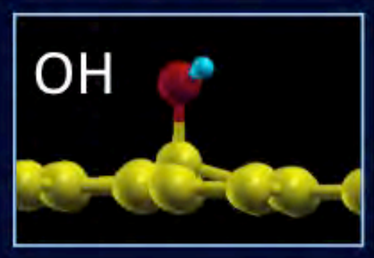
C, N or O do not attach to *T*-sites!

OH, NH_2 and CH_3 do attach to *T*-sites.





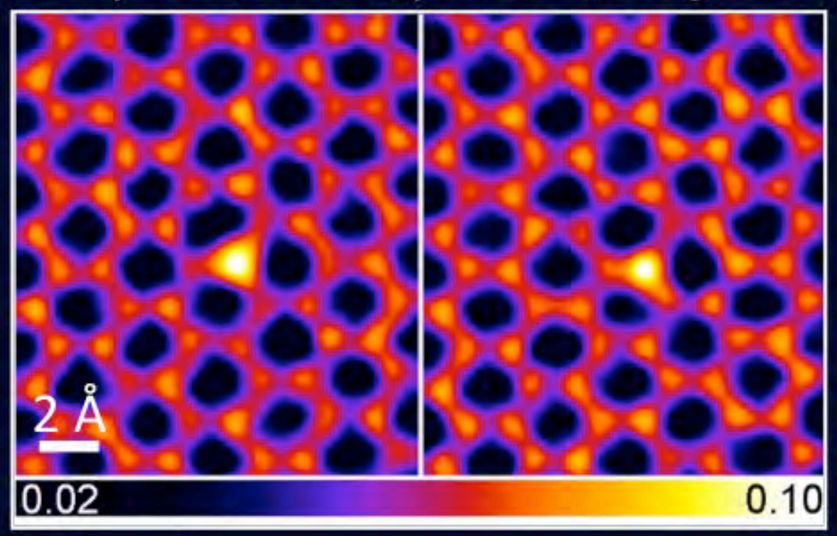




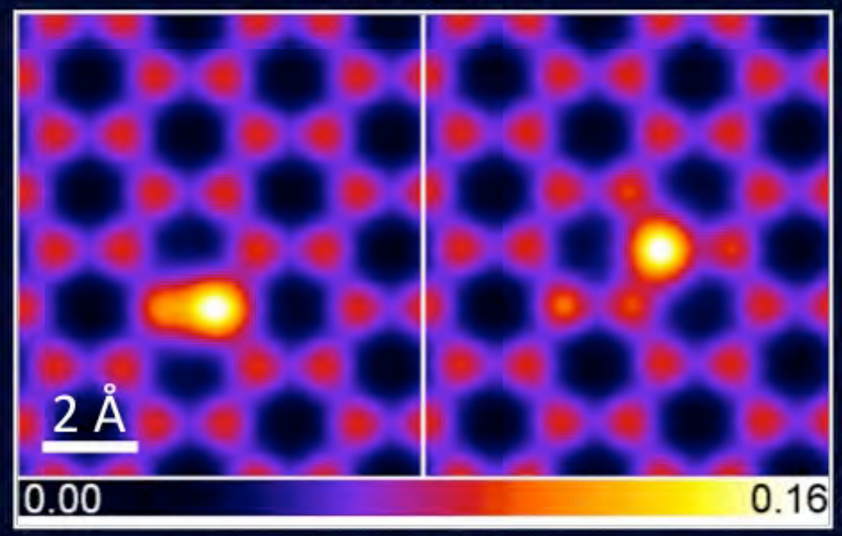
Other possible molecules, like NH_3, H_2O, CO, CO_2 are not on *T*-sites.

Simulation vs. Experiment

Experimental phase image



Simulation



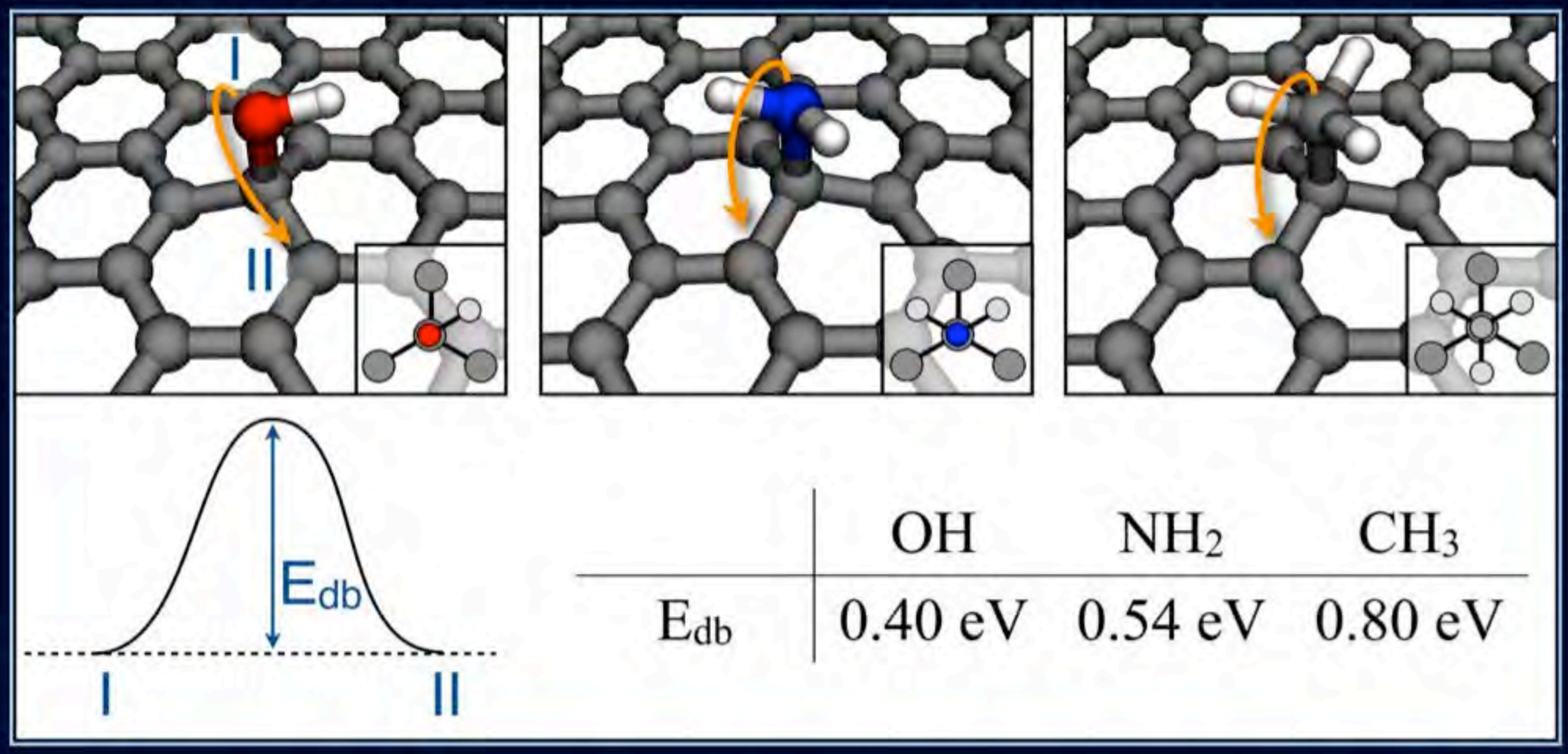
OH, CH_3 on graphene

Hydrogen atoms are not visible.

Good qualitative and quantitative match between simulations and experiments.

The theoretical models provide a possible solution for the experimental observations.

Considerations about stability



	OH	NH_2	CH_3
E_{db}	0.40 eV	0.54 eV	0.80 eV

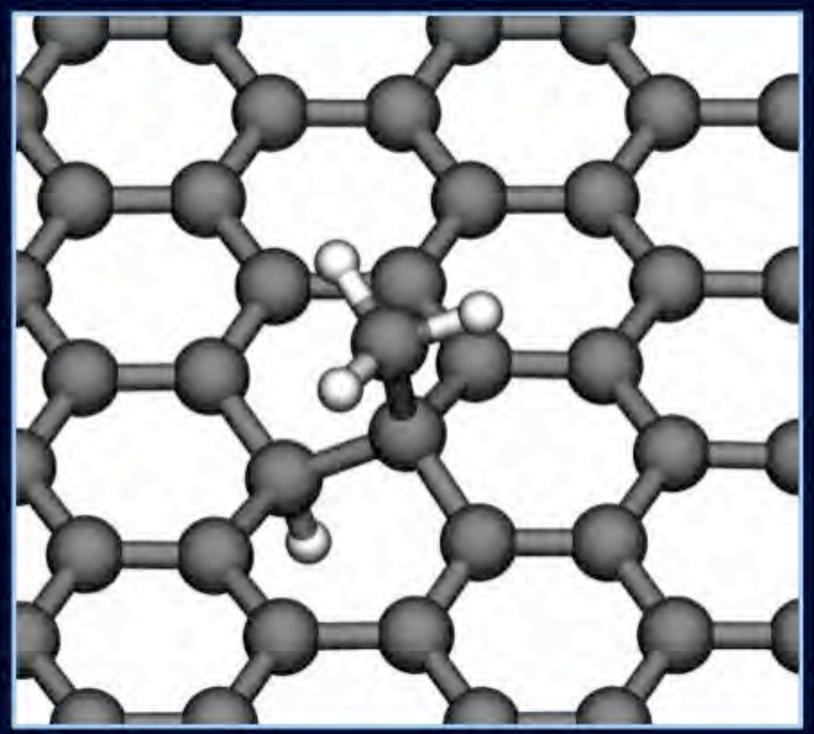
The migration barrier of a hydrogen atom on graphene is about 1.2 eV! = Stable!

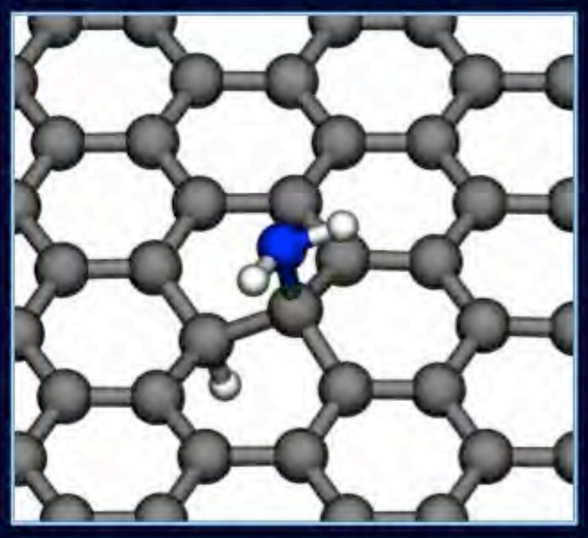
The migration barriers of OH, NH_2 and CH_3 are clearly smaller.
Migration probabilities are more than 10^6 larger than the probability of H!

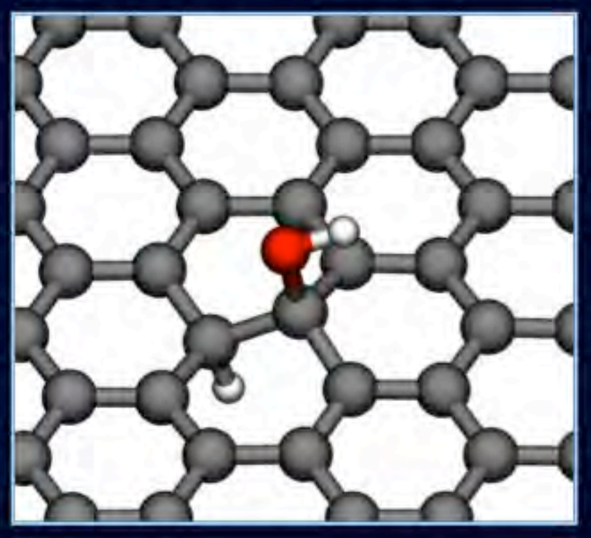
OH, NH_2 and CH_3 are largely mobile at room temperature!

Does this contradict the experiments?

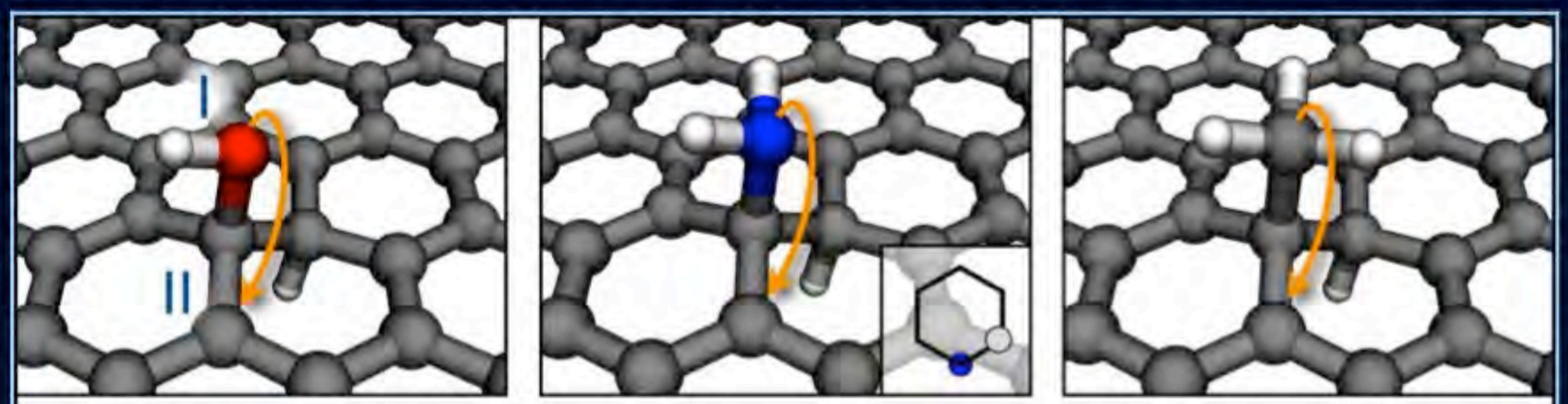
Stable ad-molecules on graphene at RT







Adding an "invisible" species: hydrogen.

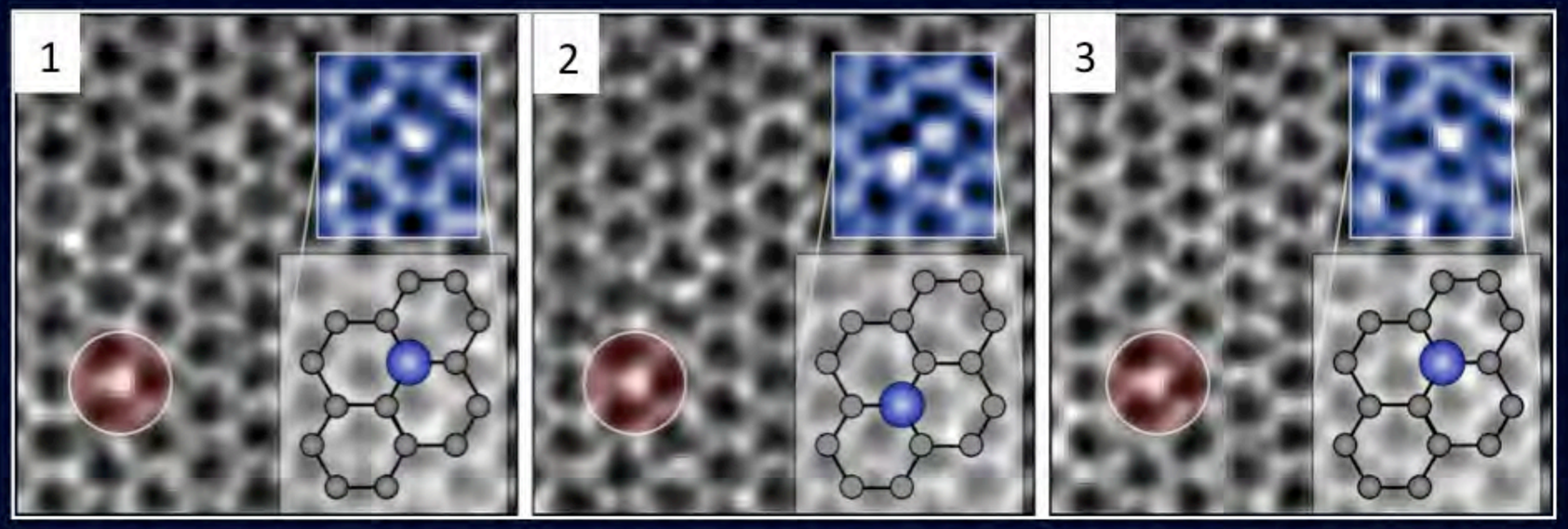


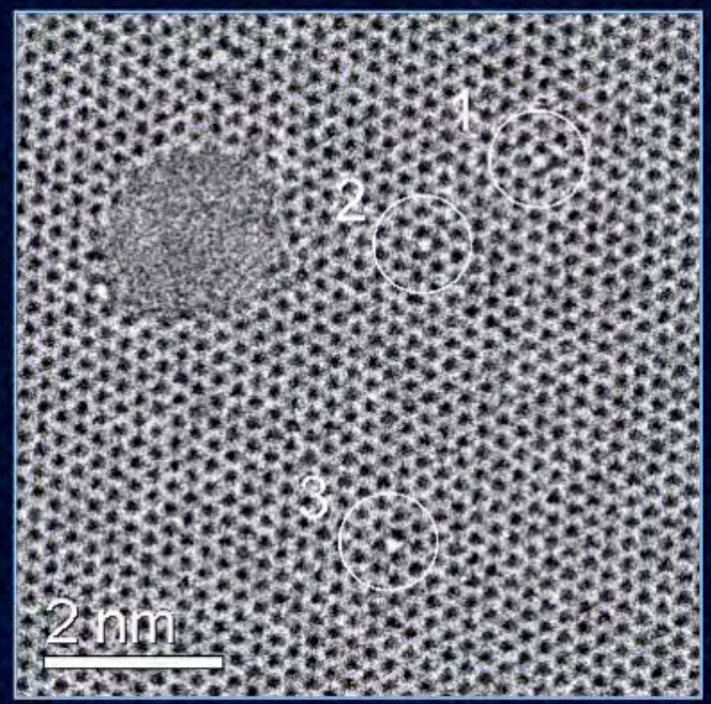
	OH	NH_2	CH_3
E_{db}	1.67 eV	2.00 eV	2.24 eV
E_B	1.46 eV	1.56 eV	1.73 eV

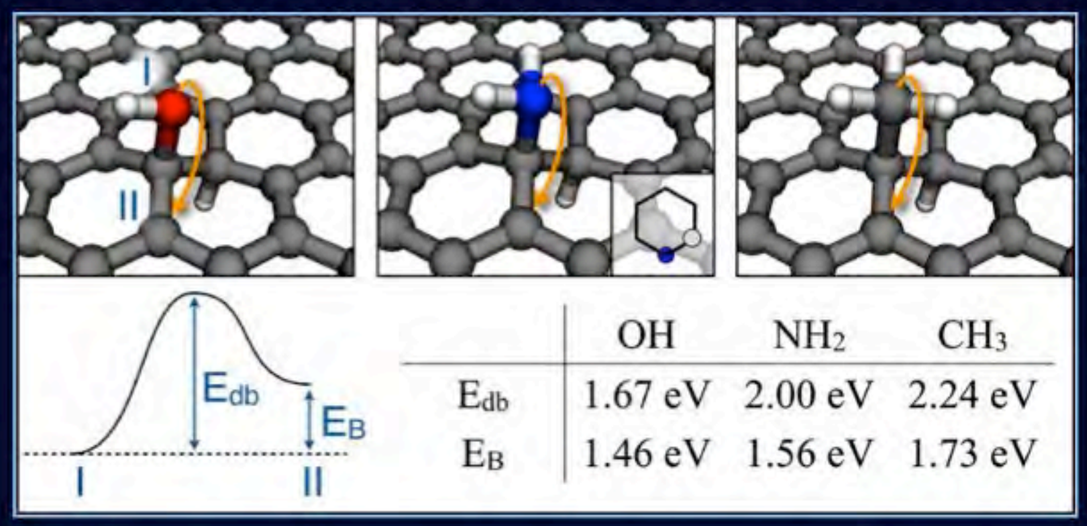
Trapping mechanism
Hydrogen atoms can trap molecules on adjacent *T*-sites.

Dynamics takes place… under the e^--beam

Ad-molecule displaced from its stable position bounces back to the original site.







	OH	NH_2	CH_3
E_{db}	1.67 eV	2.00 eV	2.24 eV
E_B	1.46 eV	1.56 eV	1.73 eV

Energy barriers: Molecule bounces back to I.

OH: 0.2 eV

NH_2: 0.4 eV

CH_3: 0.7 eV

Alternative paths:

i) The molecule continues its diffusion path.

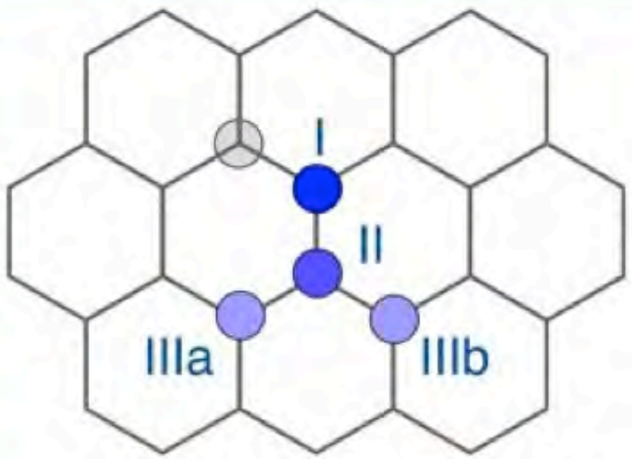
ii) The hydrogen atom follows the molecule.

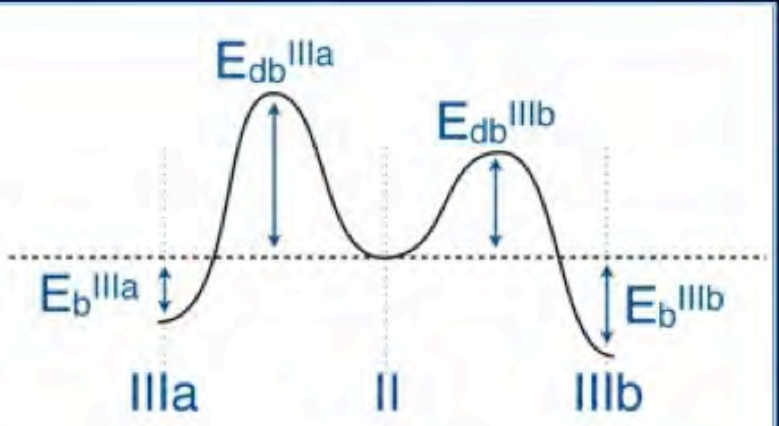
Dynamics that depends on chemistry

Energy barriers
Hydrogen follows the molecule
OH: 0.2 eV
NH_2: 0.2 eV
CH_3: 0.1 eV

?

Energy barriers
Molecule bounces back to I.
OH: 0.2 eV
NH_2: 0.4 eV
CH_3: 0.7 eV





	OH	NH_2	CH_3
E_{db}^{IIIa}	0.61 eV	0.82 eV	0.96 eV
E_{db}^{IIIb}	0.48 eV	0.95 eV	0.94 eV
E_b^{IIIa}	-0.24 eV	-0.33 eV	-0.53 eV
E_b^{IIIb}	-0.64 eV	-0.72 eV	-0.89 eV

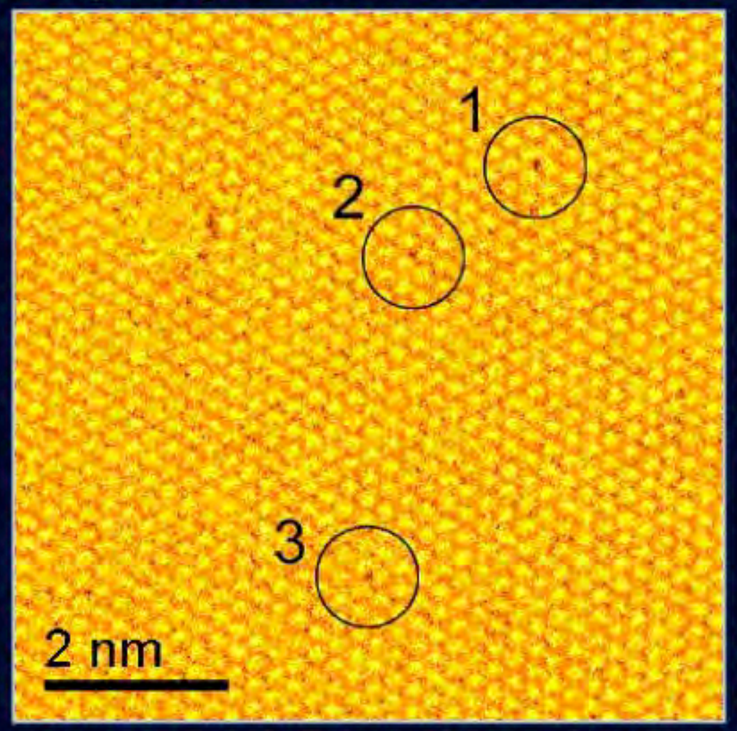
Hydrogen controls the motion of the molecule.

Only OH likely bounces back to the original site!

For NH_2 and CH_3 it is more likely that H follows the molecule!

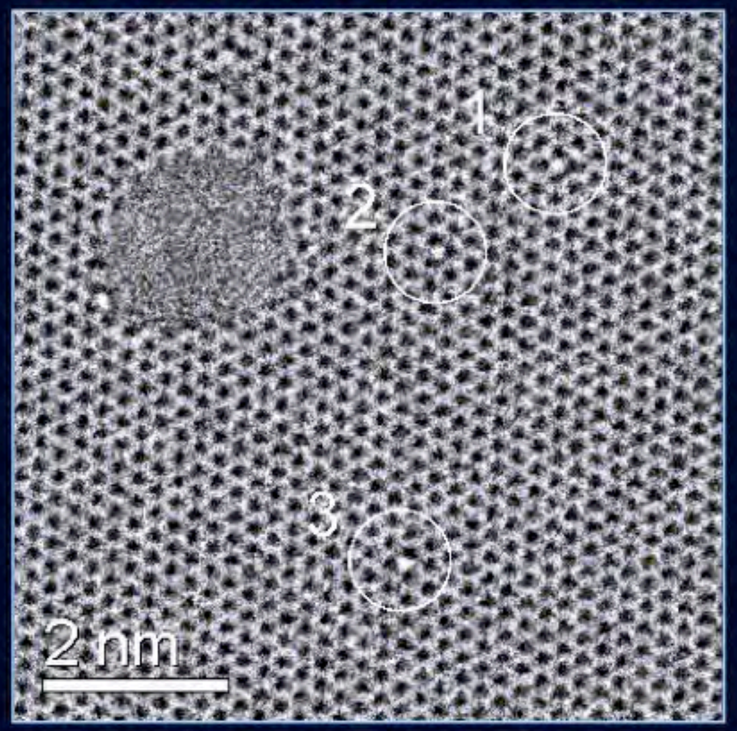
Two cases

Hydrogen follows the molecule



NH_2 or CH_3?

Molecule bounces back



OH?

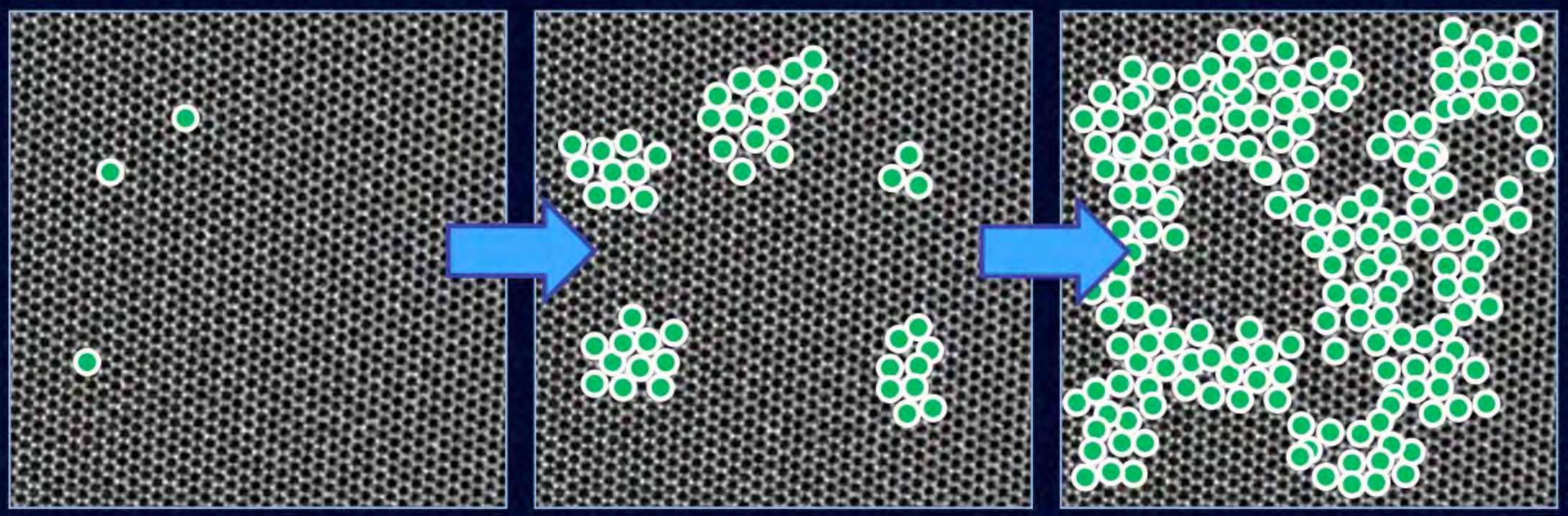
Considering the e^--beam, the situation might be more complex!

The observed dynamics would not take place without electron beam!

H-atoms act as very effective traps for molecules on adjacent sites on graphene.

Implications and Generalization

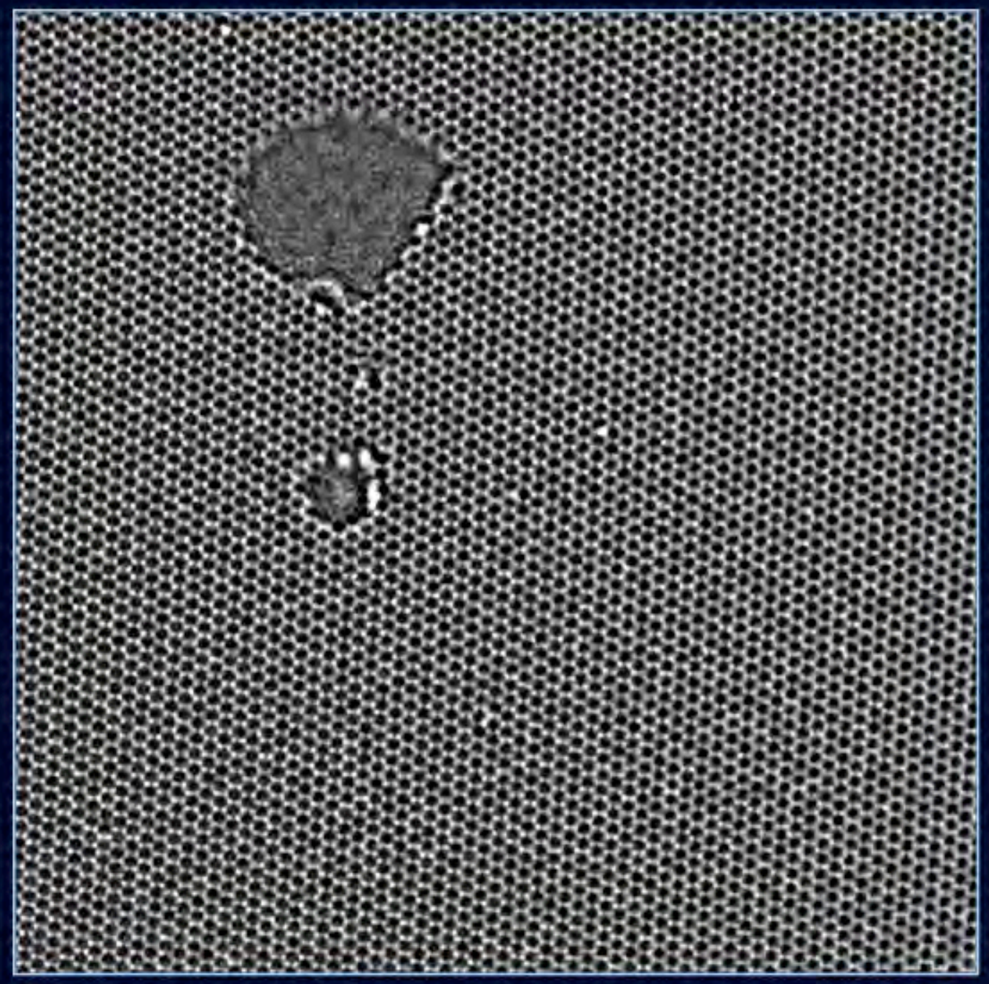
- Species tend to occupy adjacent sites on graphene
- "Damaged" graphene area is energetically attractive for the next occupant
- Functionalizing graphene might occur in a 2D "nucleation-and-growth" mode



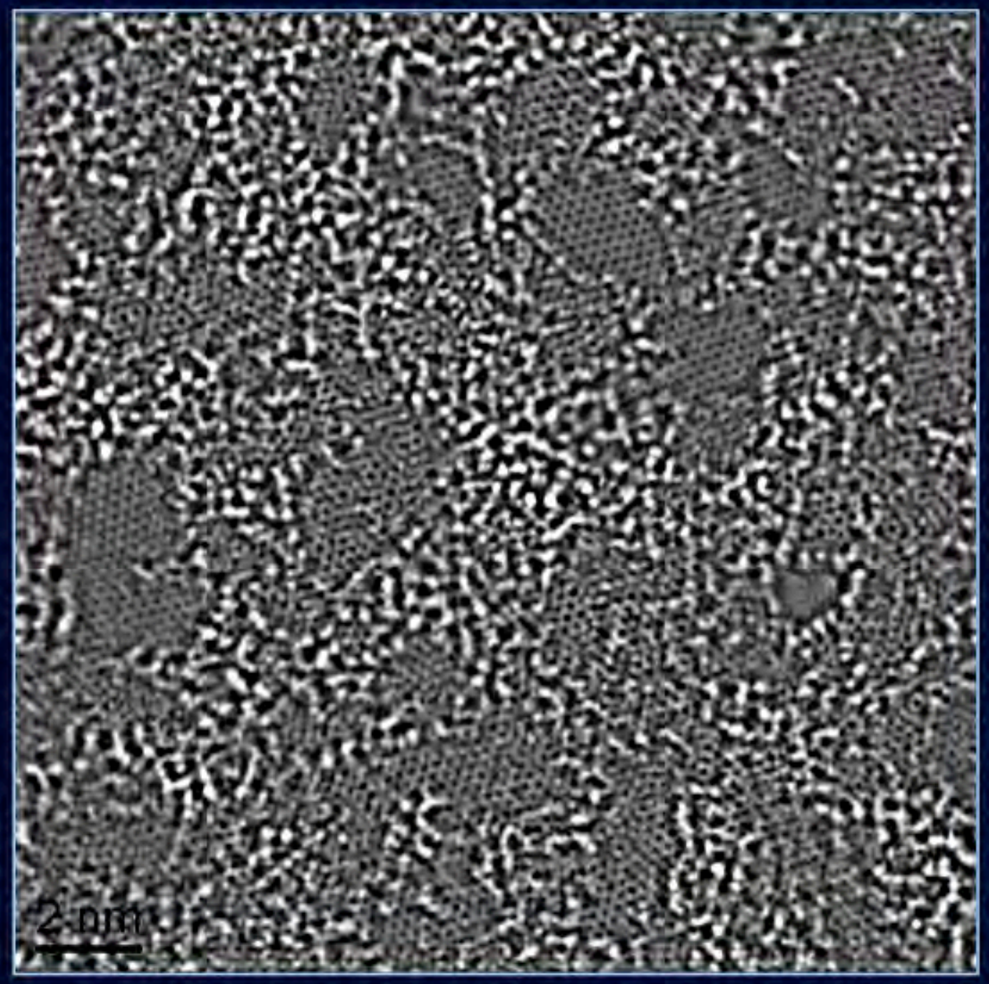
Partial functionalization of graphene: patches of pristine graphene surrounded by functionalized areas: no long range order!

The Structure of Graphene Oxide

Graphene



Graphene Oxide

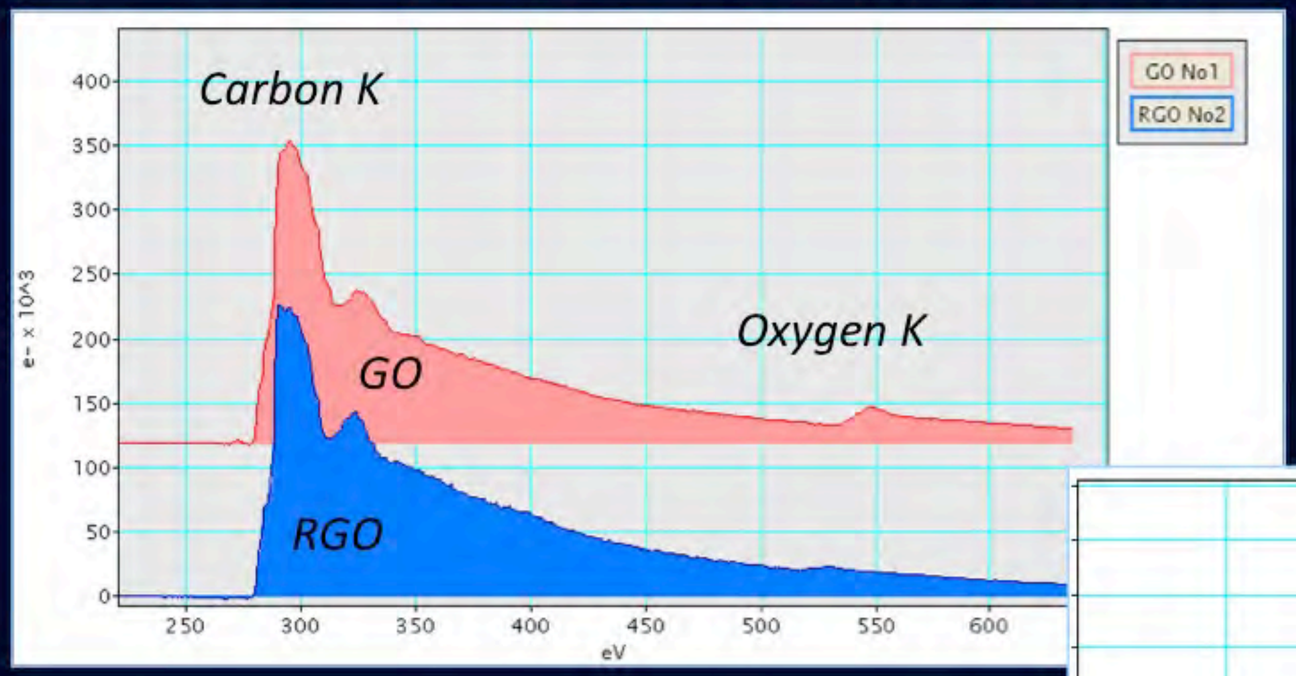


Phase images of reconstructed exit-plane waves

Graphene oxide consists of flakes of perfect graphene surrounded by "defective" areas.
Tuning the functionality of graphene by oxidation means to control the size of the areas of pristine graphene.

K. Erickson, R. Erni, Z. Lee *et al.*, *Adv. Mater.* **22** (2010) 4467.

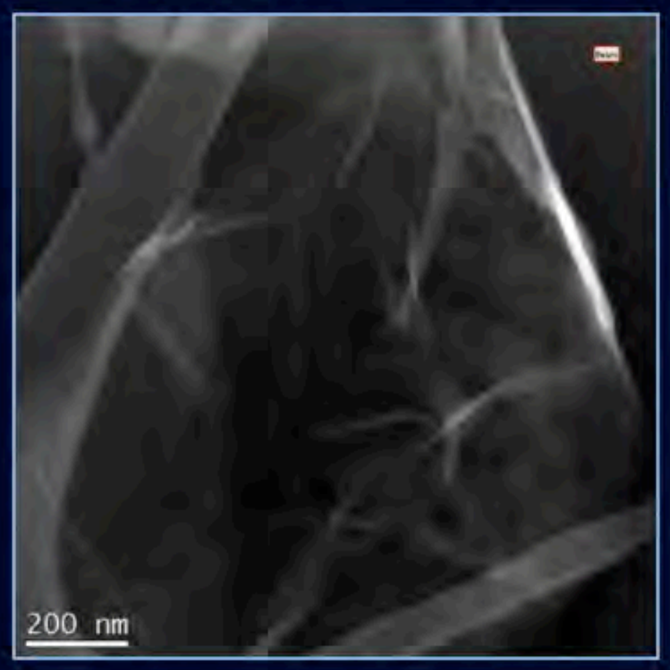
EELS of Graphene Oxide and Reduced GO

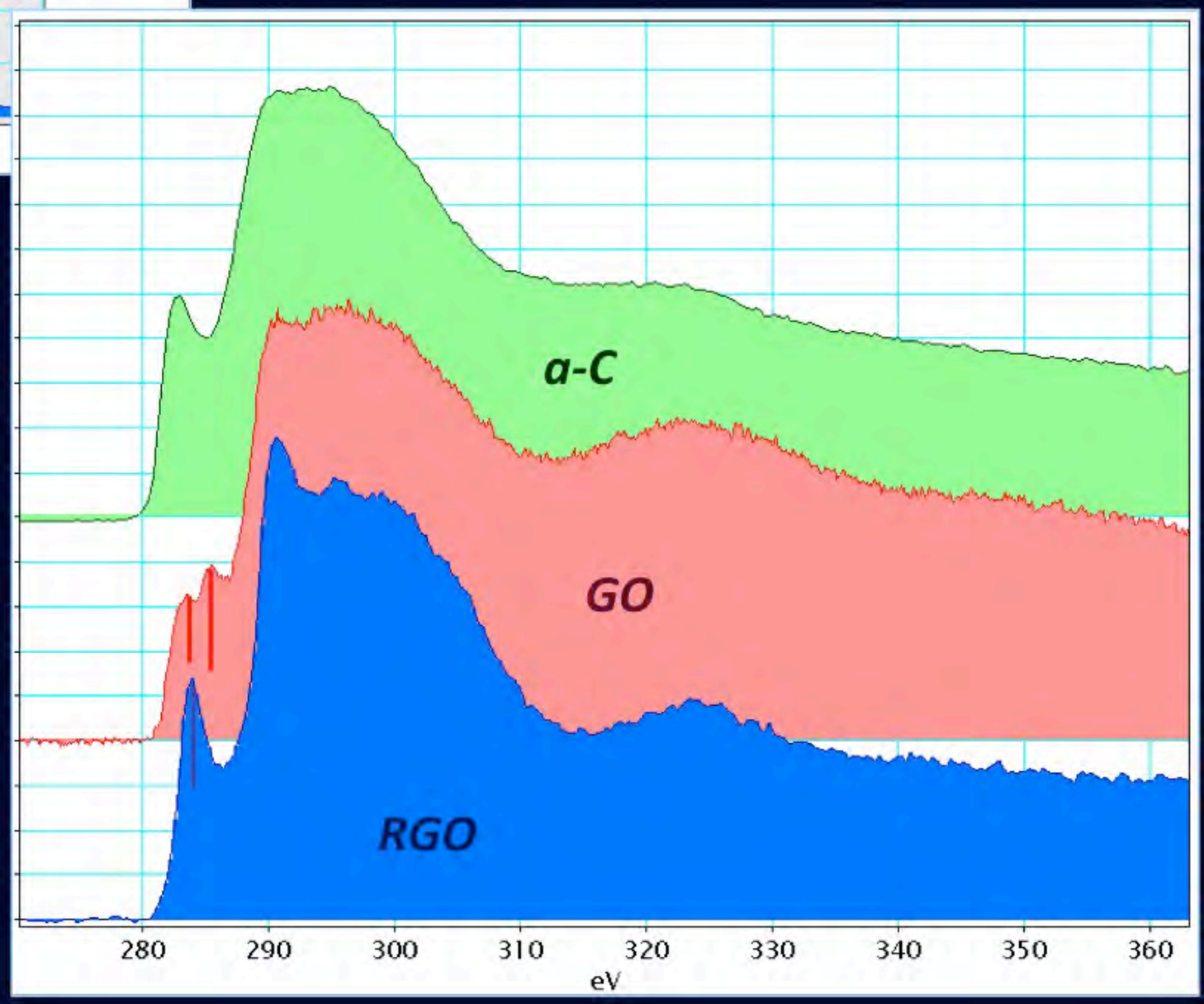


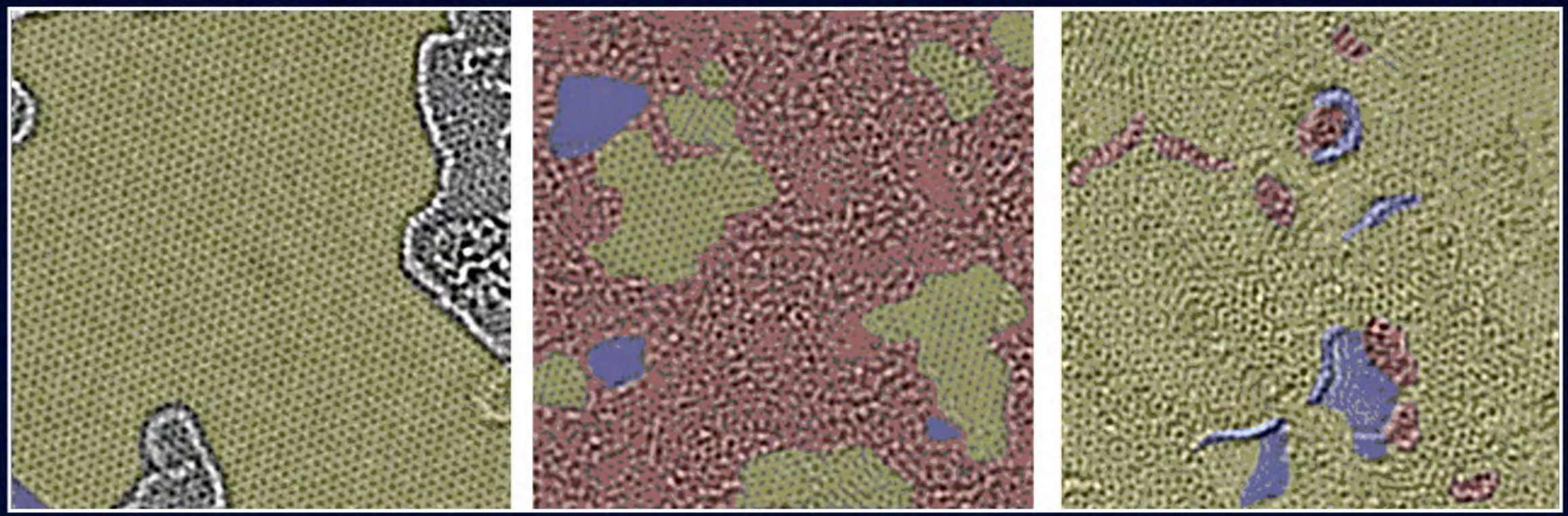
"Non-local" EELS of graphenes
200 kV(!)

Two π peaks in "GO"!*

Graphene oxide seems to be a superposition of Graphene-C and another Carbon configuration.







Graphene | Graphene oxide | Reduced graphene oxide

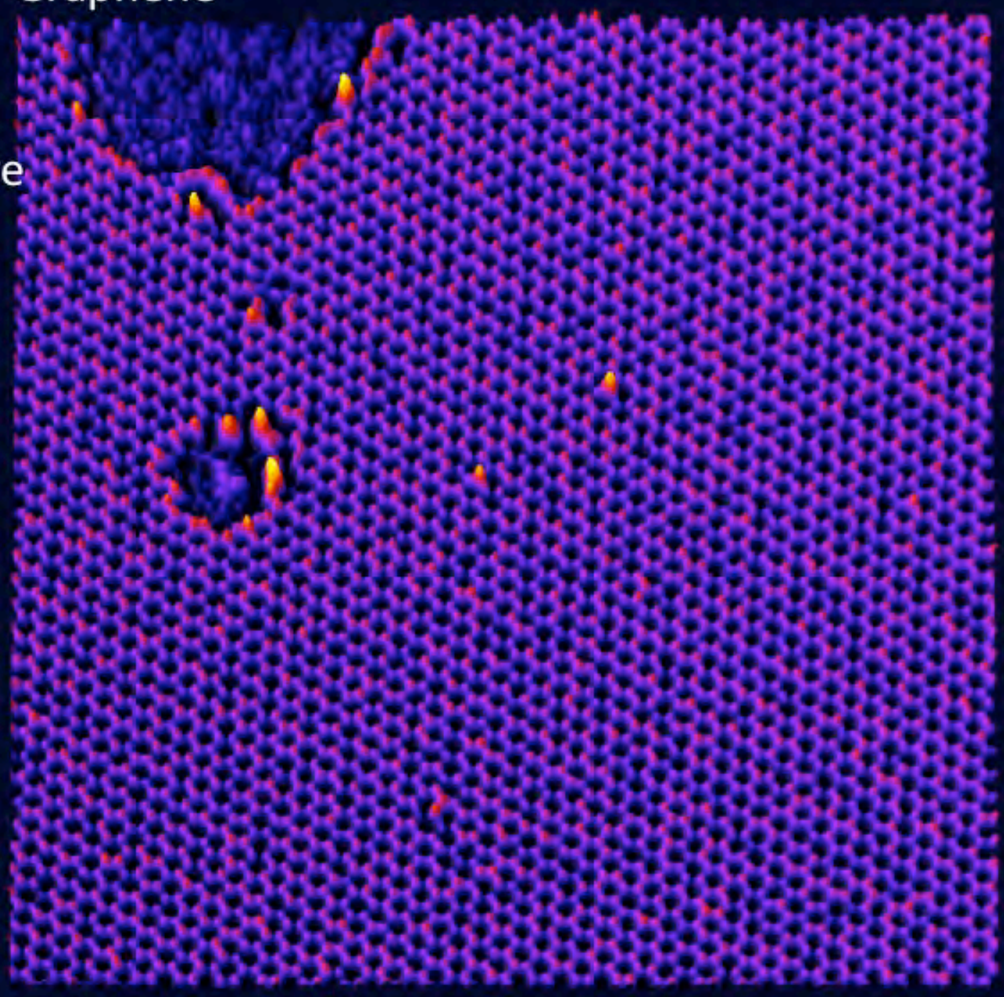
Summary

Materials Science & Technology

- Hydrogen can trap ad-molecules on graphene
- Ad-molecules and ad-atoms mutually attract each other on graphene
- Functionalization of graphene seems to occur in a "nucleation-and-growth" mode
- Explanation for the observed structure of graphene oxide

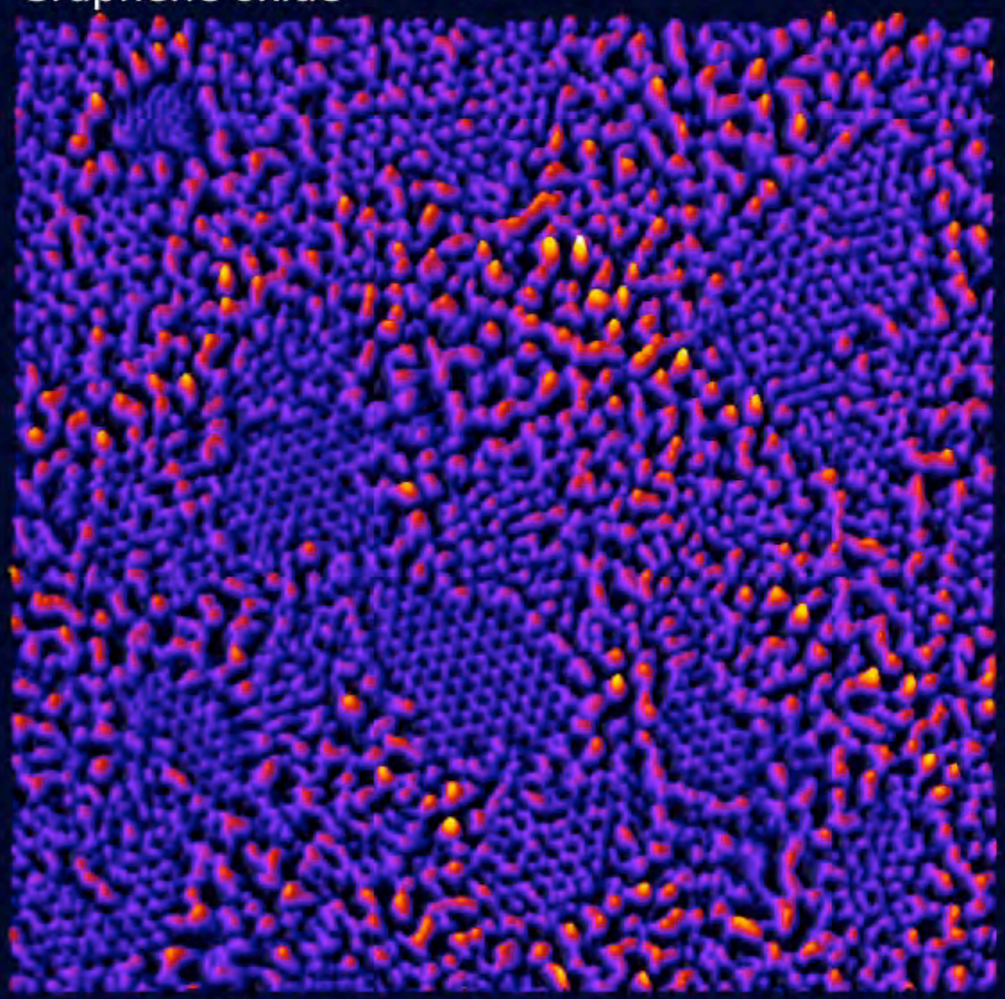
Phase of the reconstructed exit-plane wave

Graphene



C_C/C_S corrected

Graphene oxide



Monochromated C_S corrected

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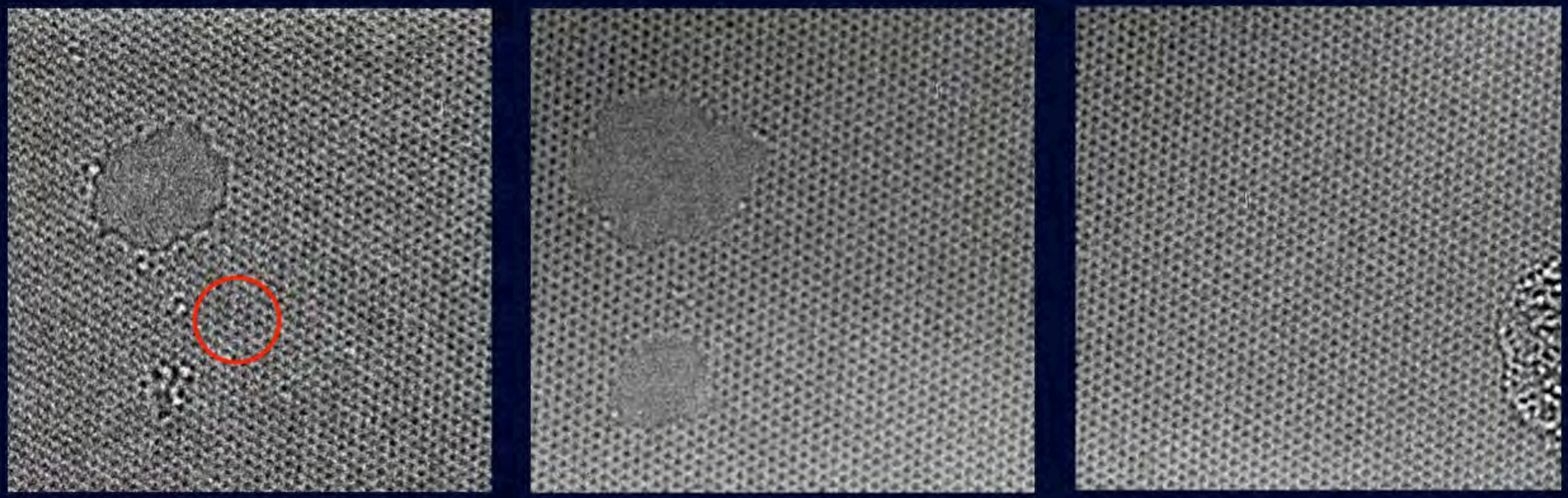
CH-COST office: State Secretariat for Education and Research

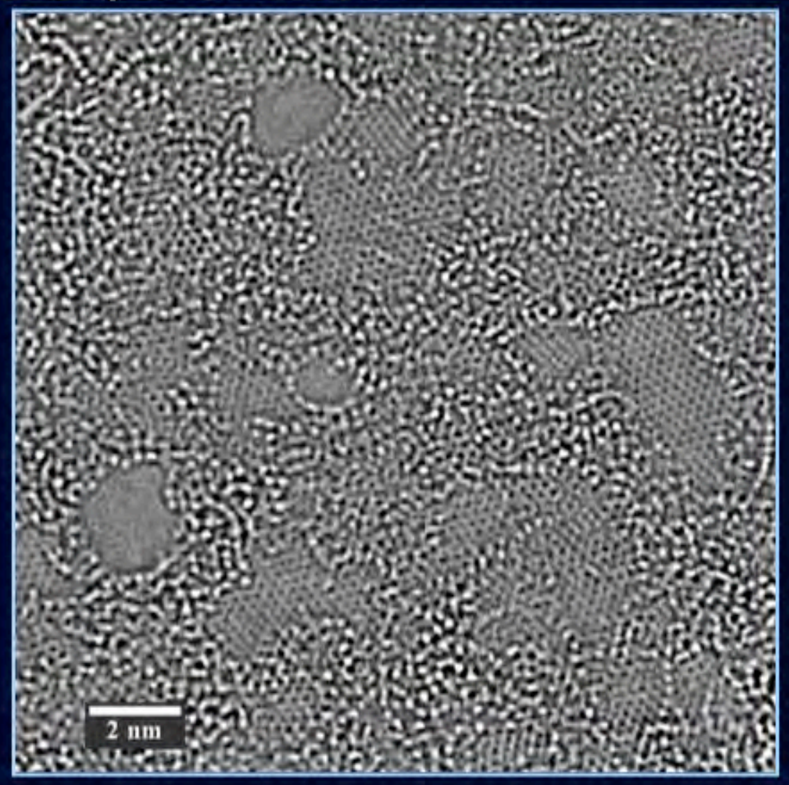
Thank You!



Stability issues

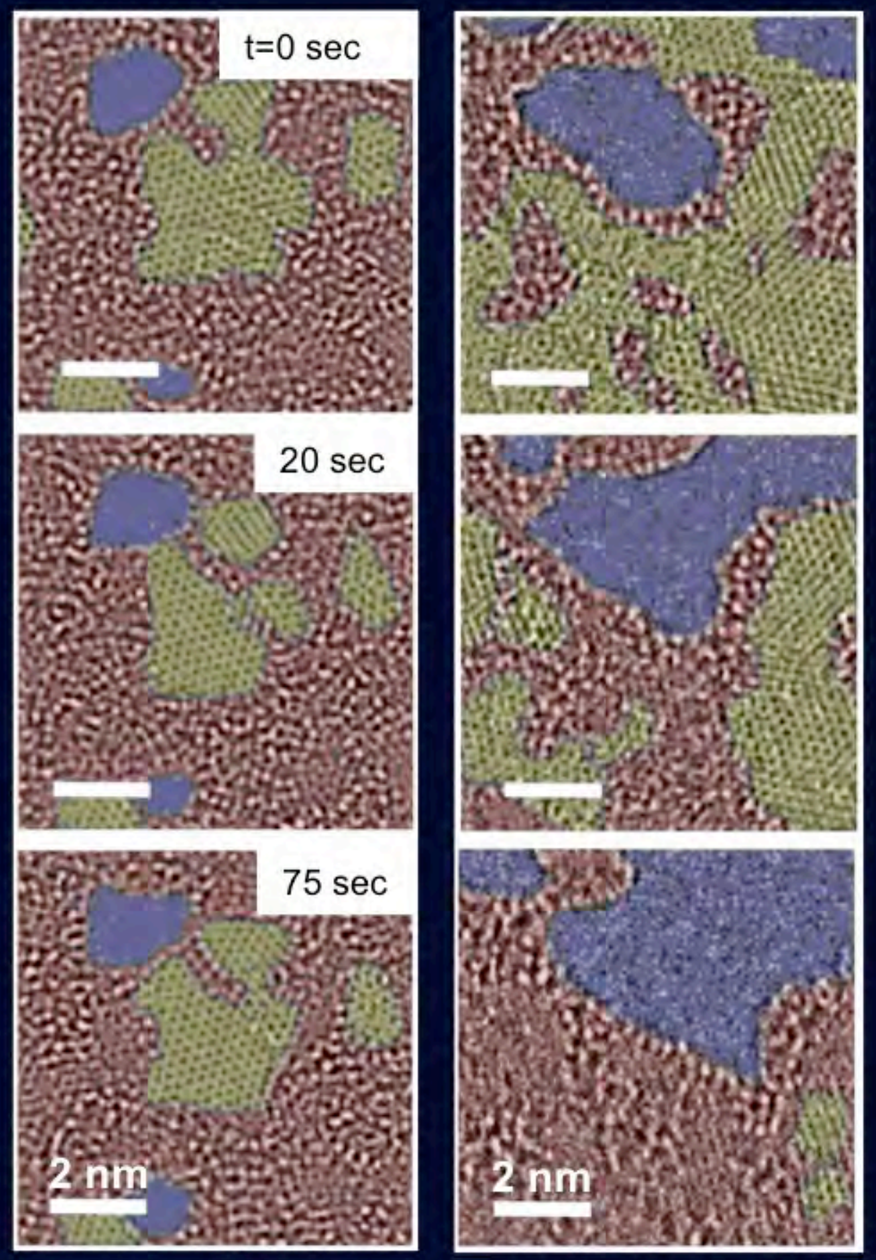
Graphene oxide and reduced graphene oxide exposed to the same electron beam.

Graphene oxide



Reduced graphene oxide

Time series



Reduced graphene oxide is NOT graphene.

The properties of raGO must be different from graphene.

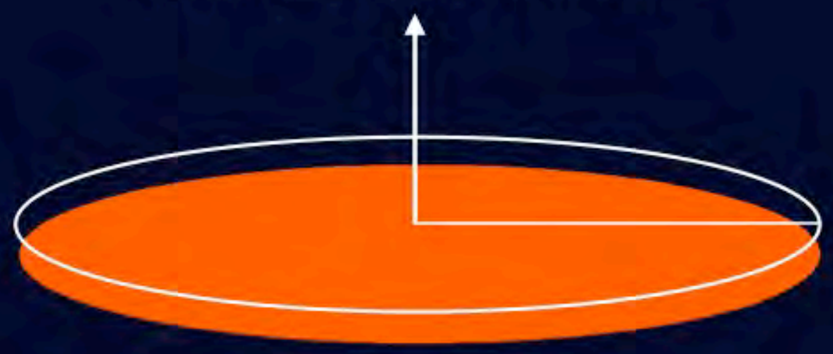
Resolution provides Sensitivity

A single layer of carbon atoms causes an **average** phase shift of

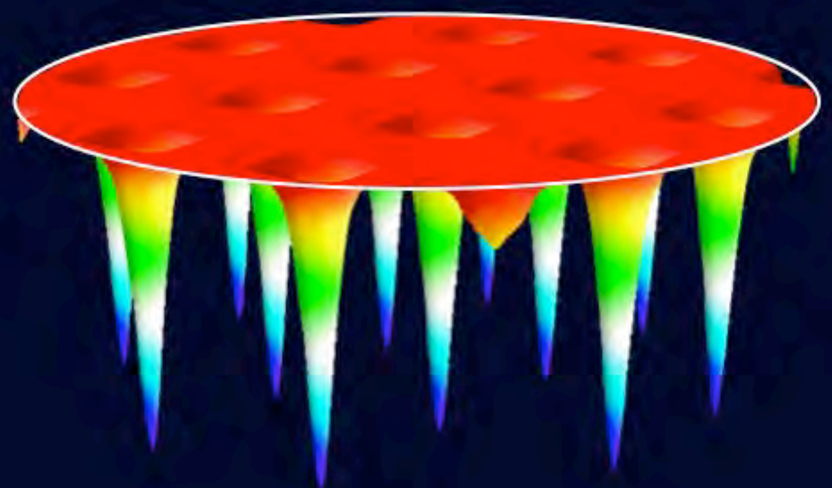
$$\frac{1}{200}\lambda = 21\ \text{fm}$$

(80 kV, λ = 4.2 pm)

Mean crystal potential



Crystal potential

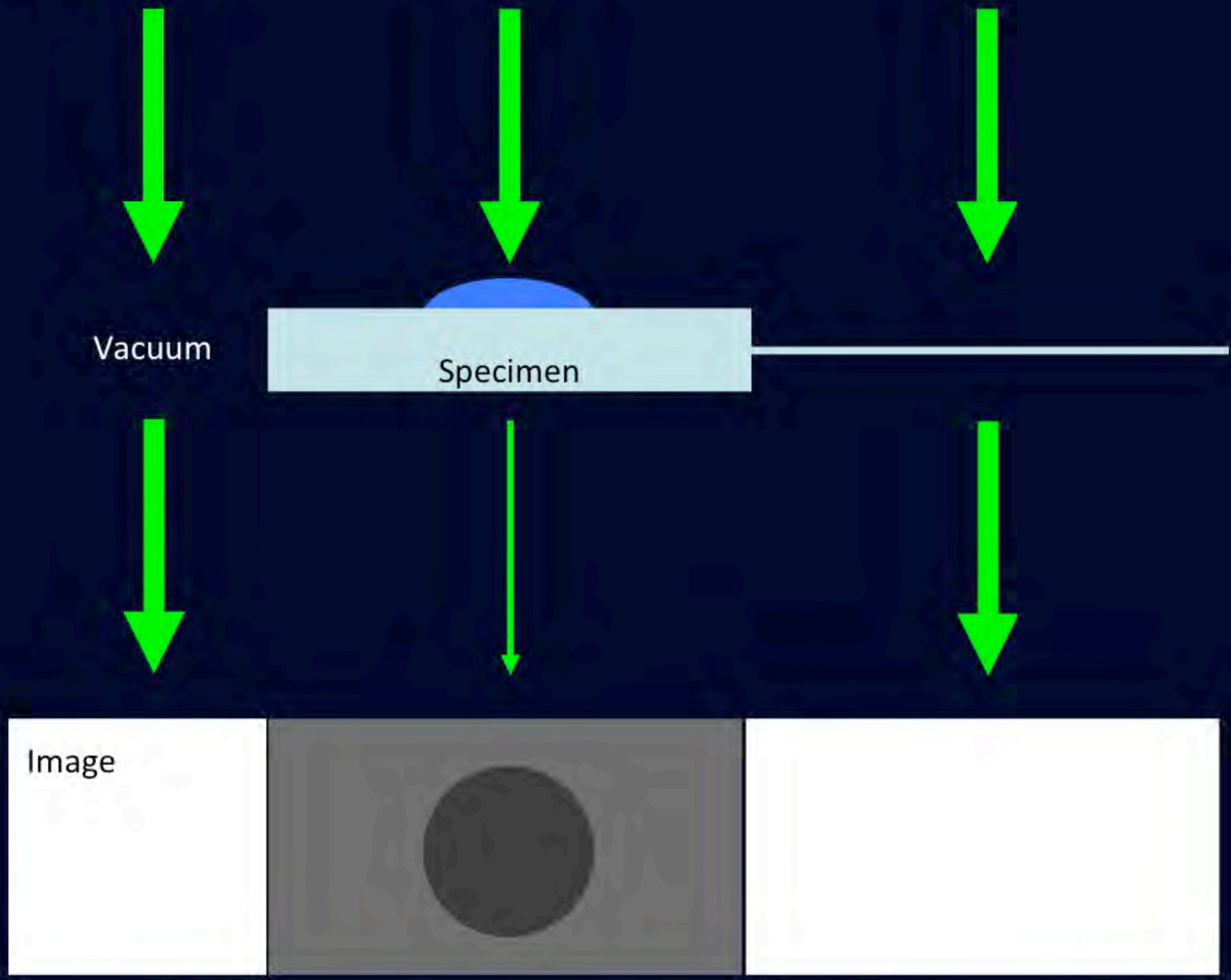


With increasing resolution, the imaging technique becomes more sensitive to the local modulation of the crystal potential.

The better the resolution: the higher the signal to noise ratio!
the higher the sensitivity!

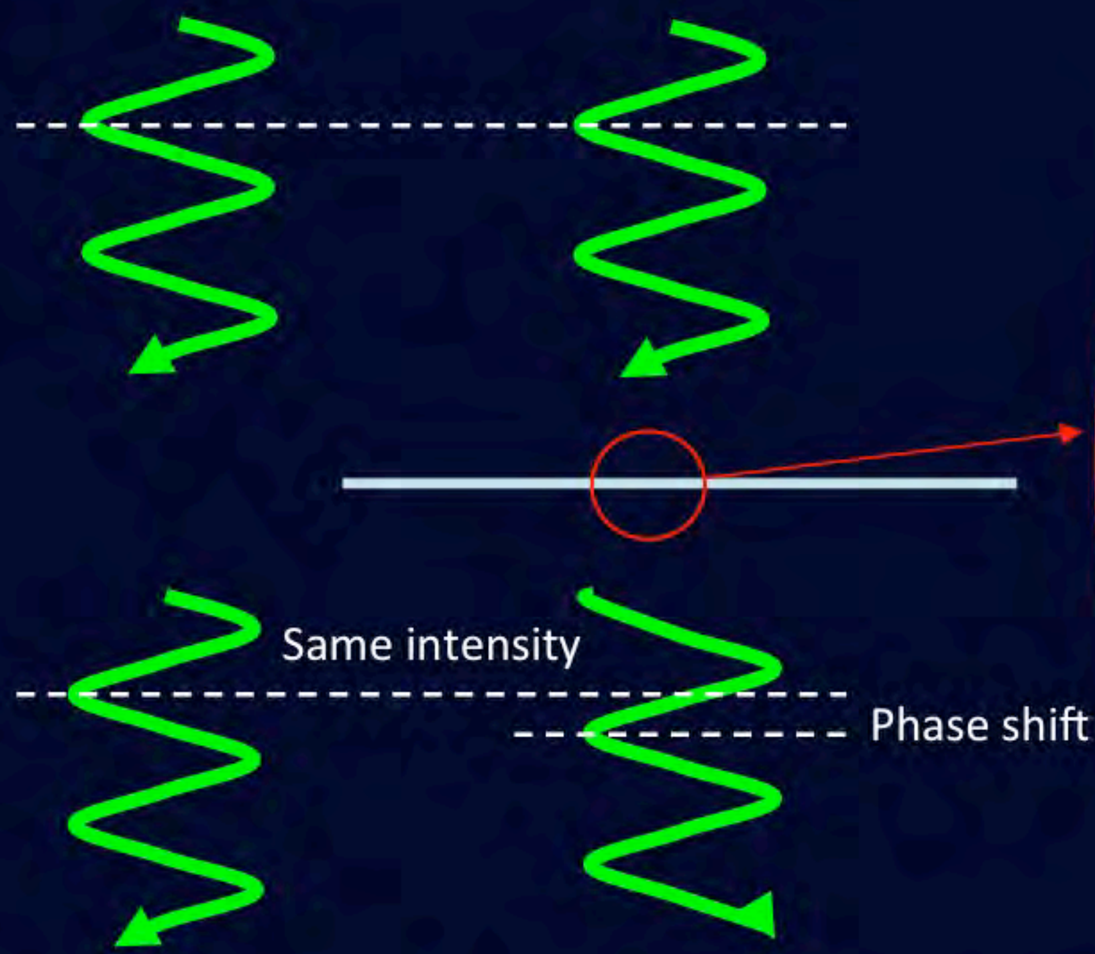
Image formation in TEM

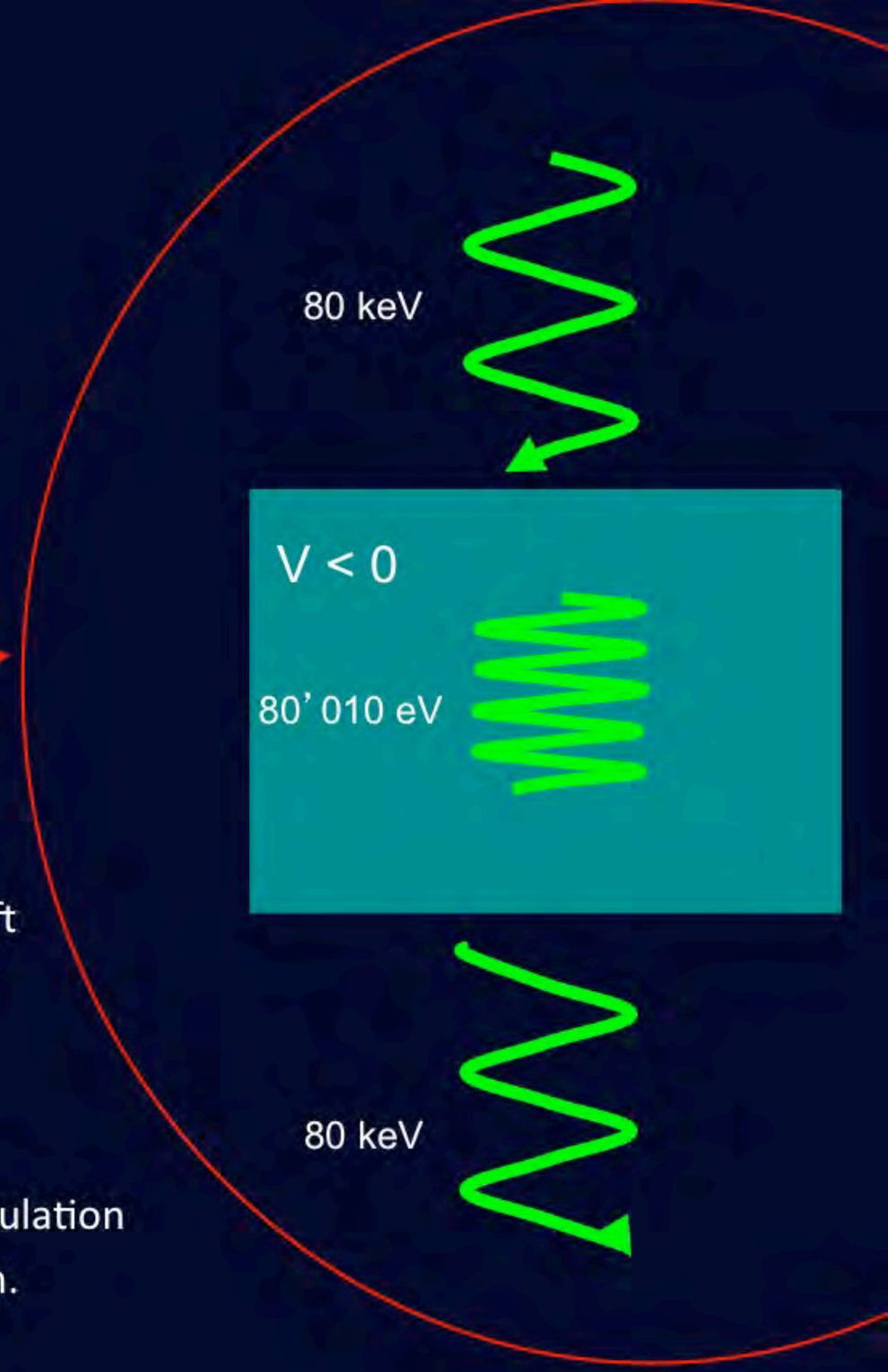
Amplitude Contrast



The “shadow” of a thin specimen is weak! – Amplitude contrast is not suitable.

Phase Contrast





Translation of the phase modulation
into an amplitude modulation.

The imaging characteristics of the "aberrated" TEM translates the phase shift into an amplitude modulation.

Phase Contrast Imaging

... is about optimizing the phase contrast transfer function.

Phase contrast transfer function

$$t_{\mathrm{PC}}(\theta) = \sin\left(-\frac{2\pi}{\lambda}\chi(\theta)\right)$$

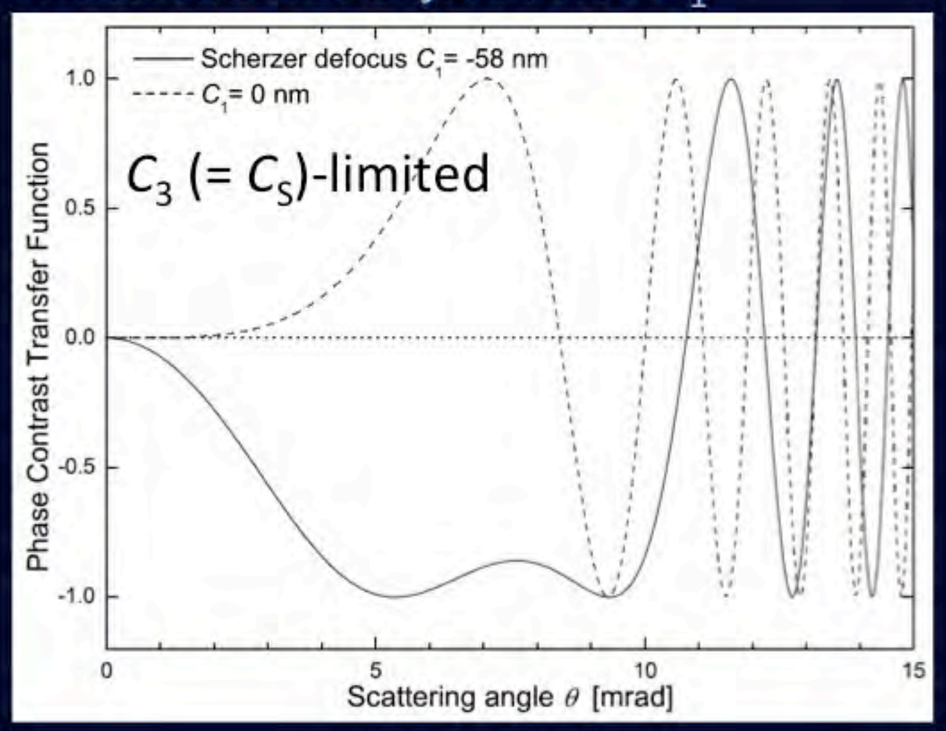
Axial aberration function (isotropic)

$$\chi_{\mathrm{iso}}(\theta) = \frac{1}{2}C_1\theta^2 + \frac{1}{4}C_3\theta^4 + \frac{1}{6}C_5\theta^6 + O(\theta^8)$$

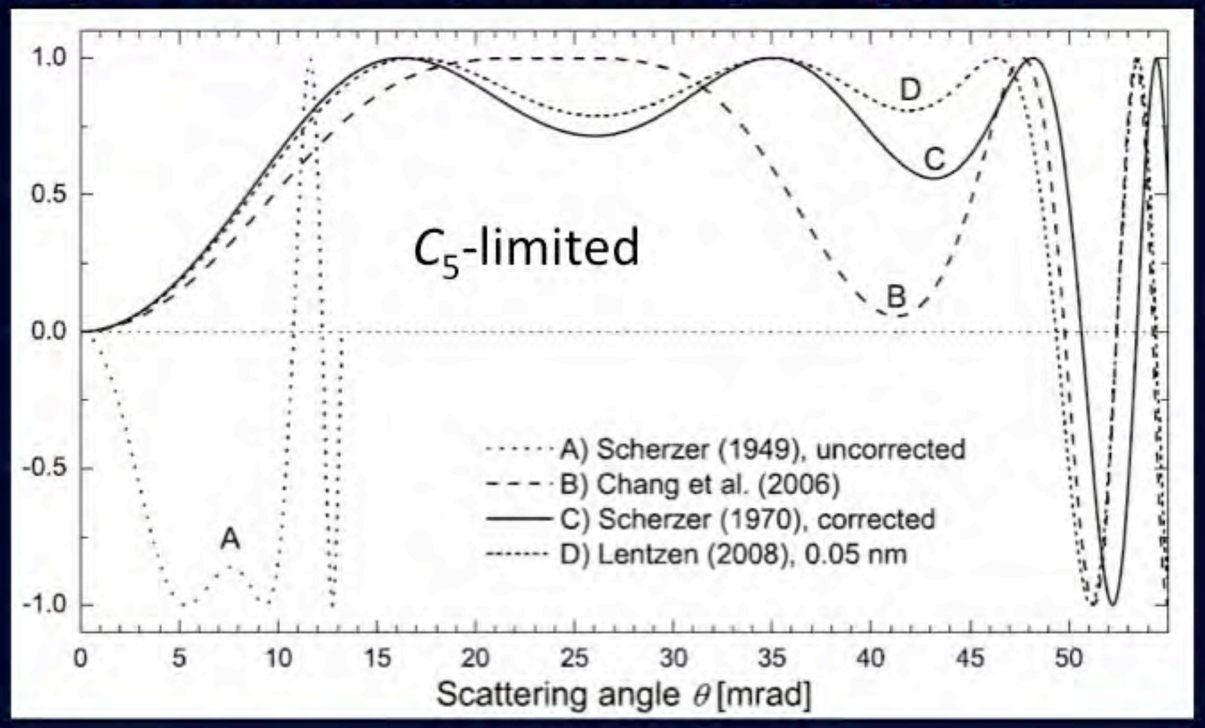
No aberrations = No phase contrast

Criteria: maximize phase contrast, maximize resolution

Conventional: adjust focus C_1



C_S-"corrected": adjust focus C_1 and C_3 (= C_S)



B. First-principles calculations

TEM experiments were complemented with density-functional theory (DFT) calculations. These first-principles calculations were performed with the Gaussian and plane-waves (GPWs) (Ref. 22) approach using the Perdew-Burke-Ernzerhof[23] exchange-correlation functional and periodic boundary conditions implemented in CP2K.[24] The electron-ion interaction was described by the norm-conserving pseudopotentials of Goedecker-Teter-Hutter[25] and for most elements a TZV2P basis set was used, optimized for molecular systems.[26] The van der Waals interaction was considered using a semiempirical scheme in the form of C_6/R^6 proposed by Grimme.[27] Diffusion barriers were calculated with GPW in its spin-polarized formulation using the climbing-image nudged elastic band method, CI-NEB.[28] For each NEB calculation, 12 images are used to calculate the diffusion barrier accurately. The graphene sheet is represented by a 21.34×19.71 Å^2 rectangular supercell containing 160 carbon atoms.