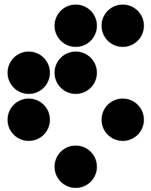

Quantum mechanical characterization of possible self-assembled nanostructures of 1H-benzotriazole on copper

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Jožef Stefan Institute, Ljubljana, Slovenia

in cooperation with
Anton Kokalj

RSE – SEE, Beograd, June 2010

Scientific motivation

Benzotriazole (BTAH):

- One of the best corrosion inhibitors for copper.
- Well experimentally studied over 40 years, yet still some issues are unresolved.

Among open questions: detailed atomic structure of adsorbed BTAH.

- Structures studied with STM.[1,2]
- Interpretation of STM images is not trivial.

Goal:

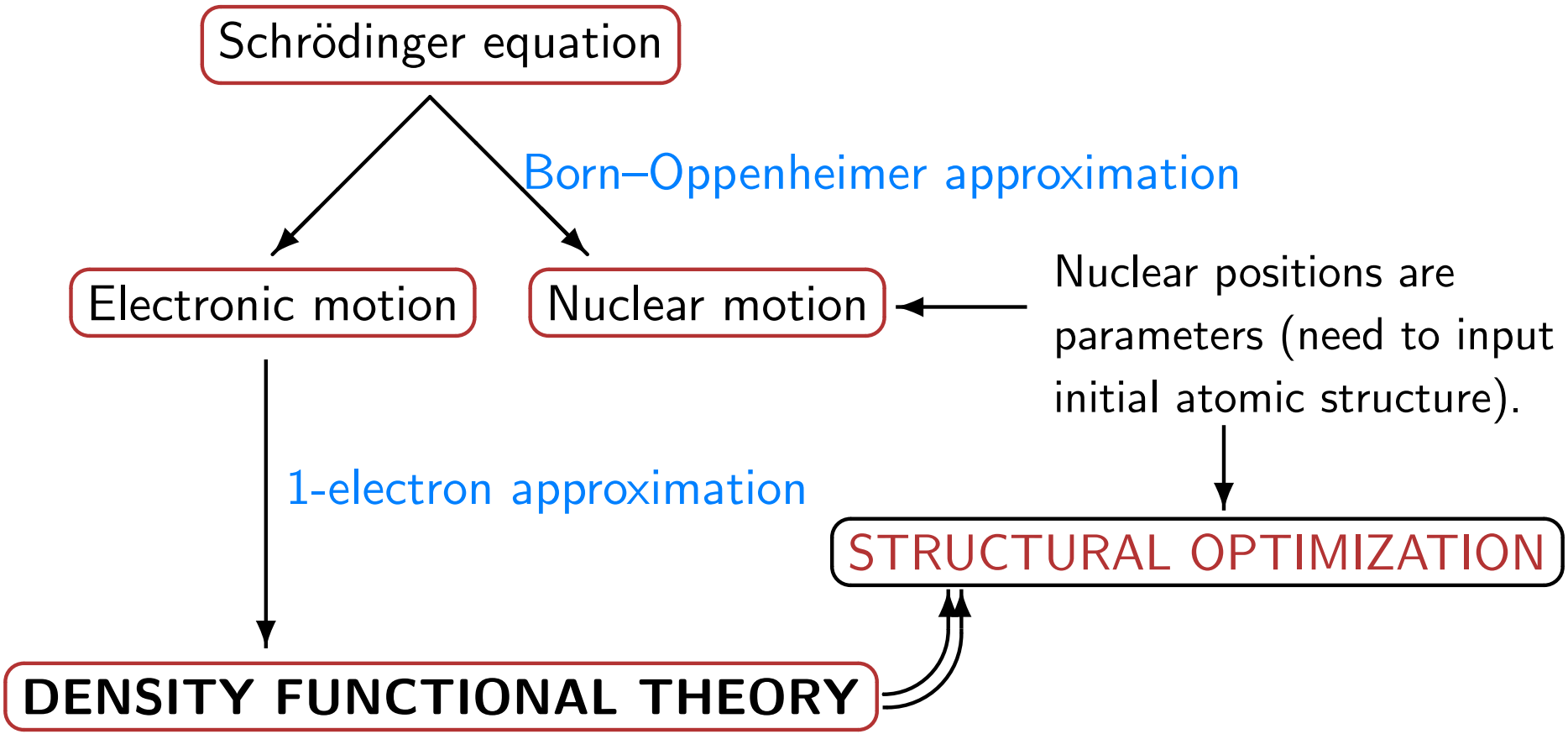
- To help explain STM images by atomistic computer simulations.

[1] Sugimasa, M., *et al.*, *J. Electrochem. Soc.*, **2002**, *149*, E367–E373.

[2] Vogt, M. R., *et al.*, *J. Electrochem. Soc.*, **1997**, *144*, L113–L116.

Ab-initio computer simulations

Starting from first principles (no experimental parameters):



Computational methods

Calculations based on density functional theory (DFT) within generalised gradient approximation (GGA).

Functionals:

PBE: for chemisorption.

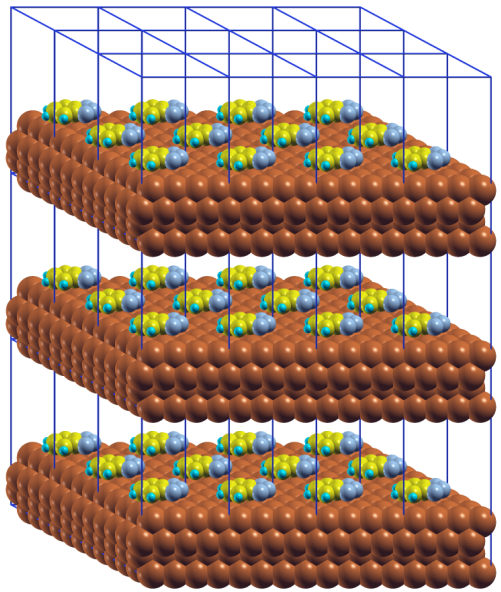
PBE-D: PBE + semiempirical correction for van der Waals interactions for physisorption.[3]

Basis set: plain waves + ultrasoft pseudopotentials.

Code: *PWscf @ Quantum ESPRESSO*
`http://www.quantum-espresso.org/`

Visualization: *XCrySDen*
`http://www.xcrysden.org/`

Periodic slab model



Adsorption calculations at vacuum/metal interface.

[3] Grimme, S., *J. Comp. Chem.*, **2006**, *27*, 1787–1799.

How STM images are calculated?

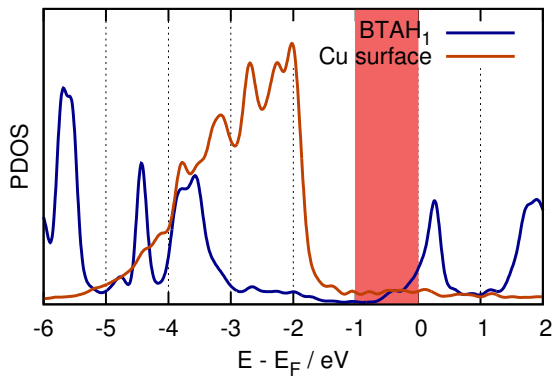
START
initial guess structure

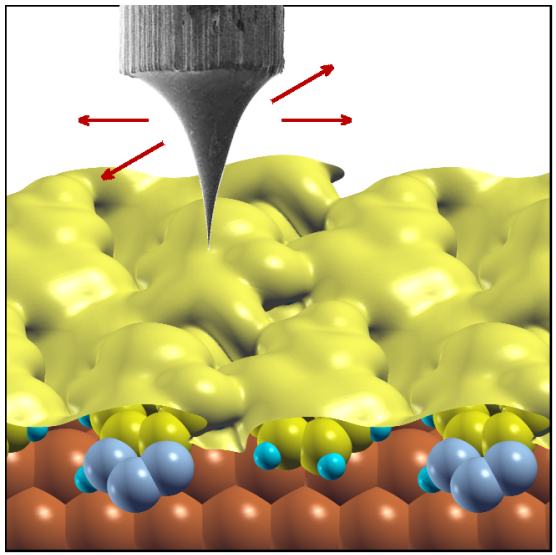
Optimize atomic positions

OPTIMIZED STRUCTURE → Local minimum

Analyze it's electronic structure

STM current $\propto$ LDOS around Fermi level[4]

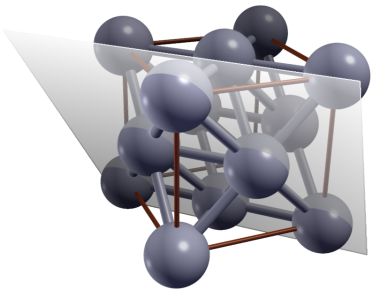


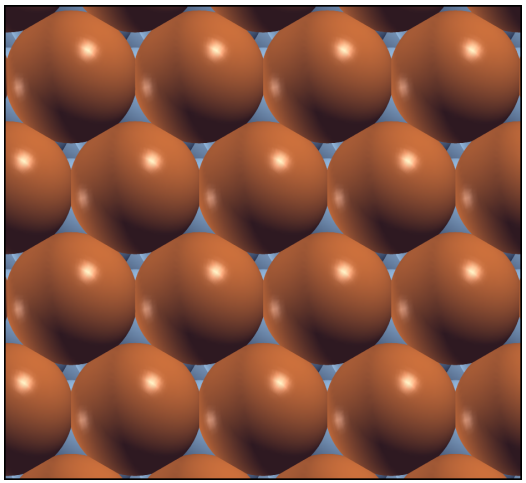


[4] Tersoff, J., Hamann D. R., *Phys. Rev. B.*, **31**, 805.

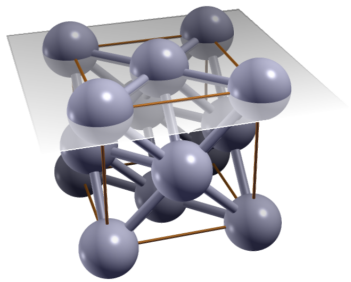
Low Miller index Cu surfaces

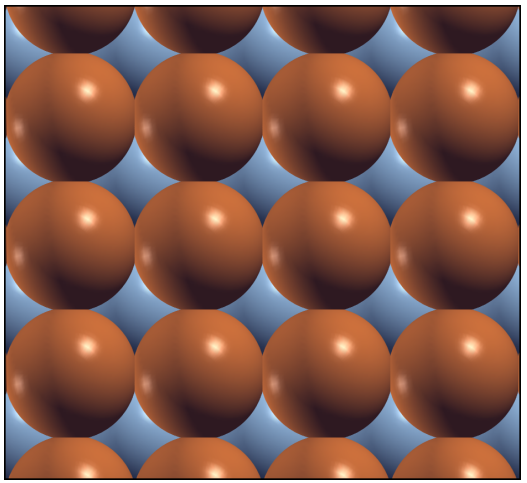
Cu(111)



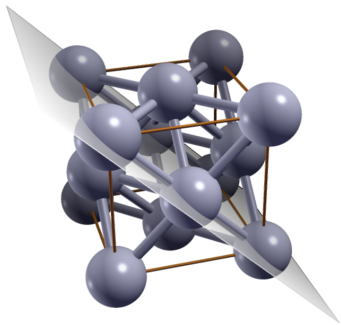


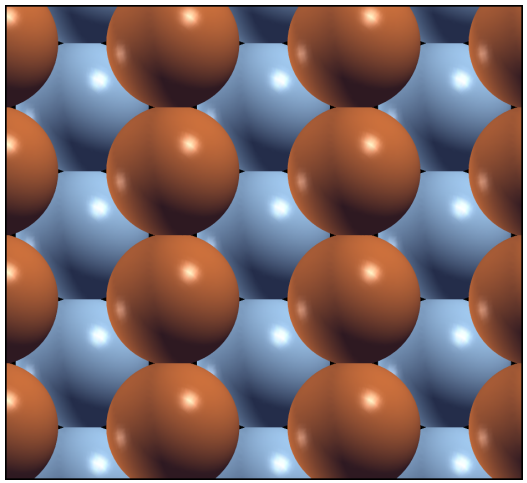
Cu(100)





Cu(110)

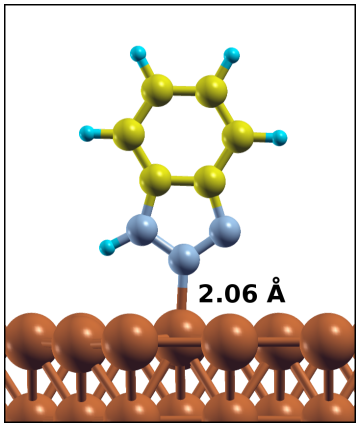


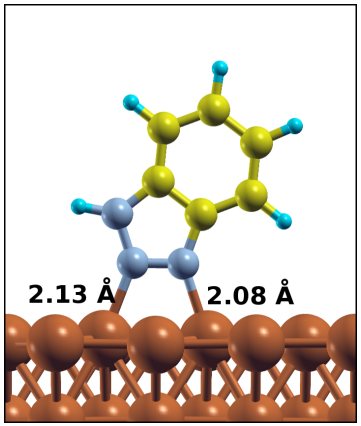


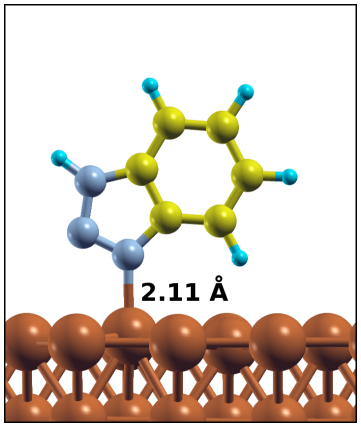
Adsorption of stand-alone molecules ($\Theta \leq 1/15$ ML)

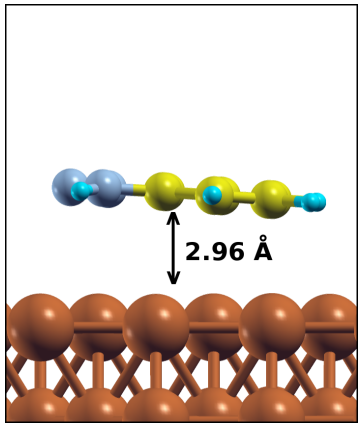
Chemisorbed mode

Physisorbed mode

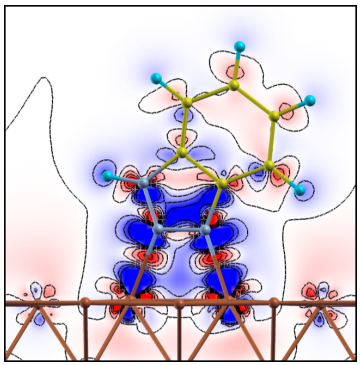




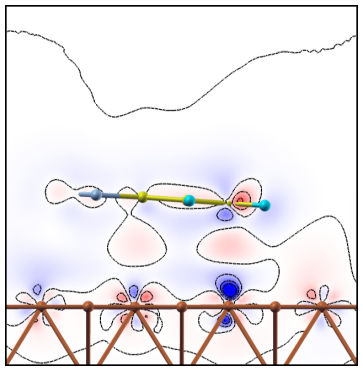




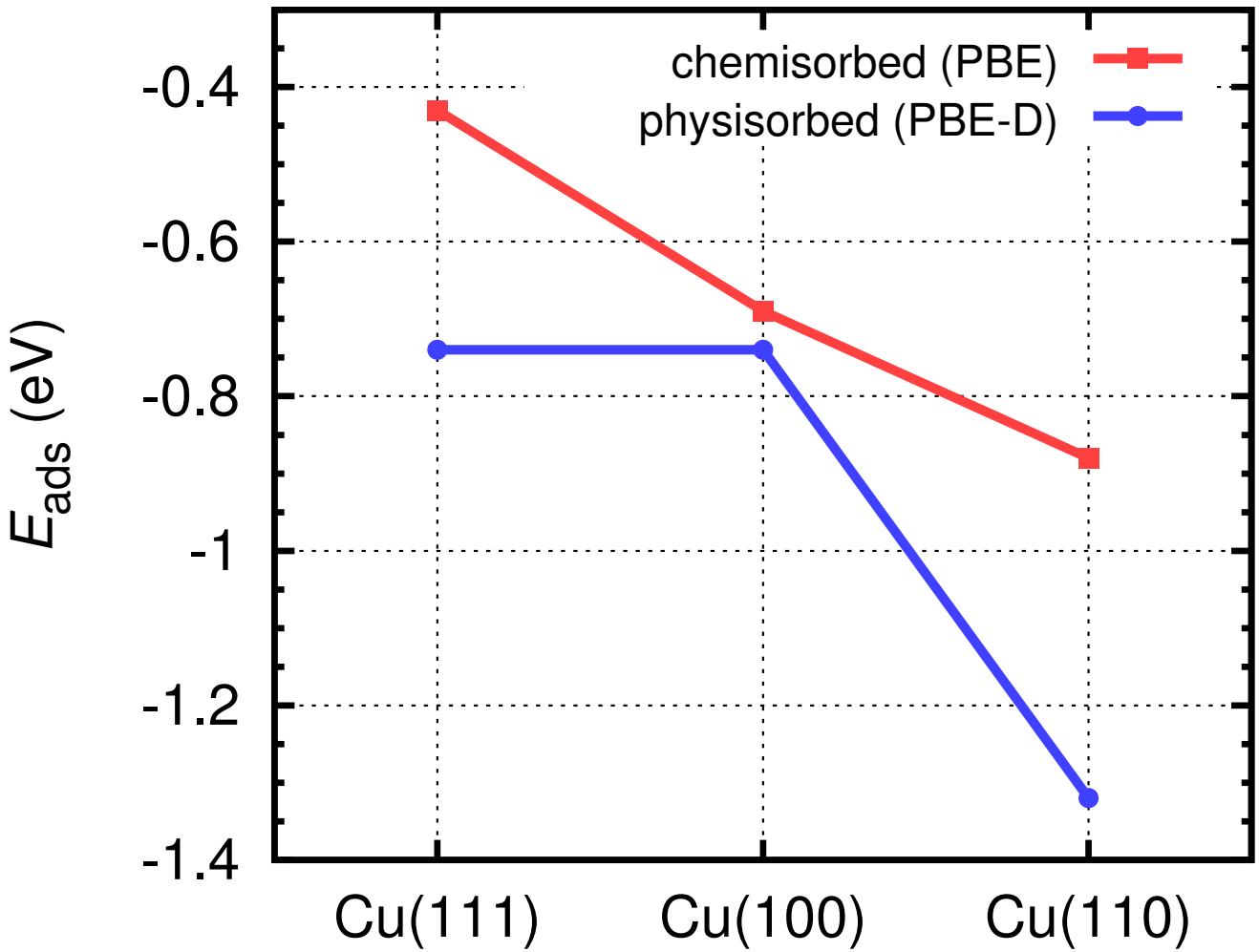
Formation of molecule-surface chemical bond.



No chemical bond – van der Waals dispersion interaction.

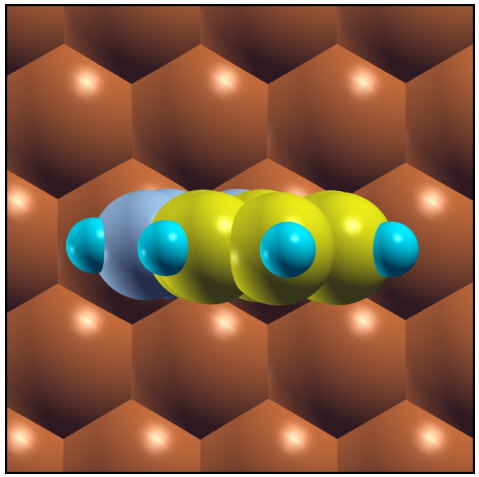


Adsorption energies – stand-alone molecules

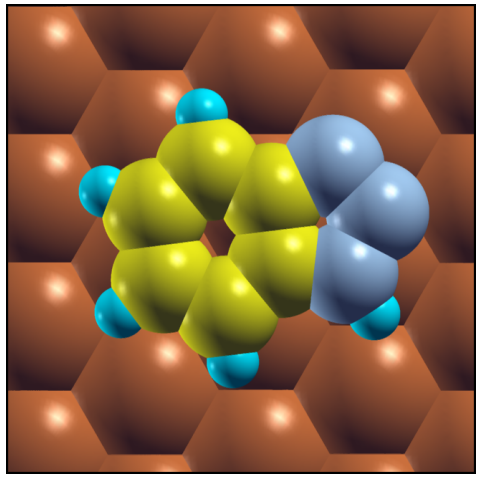


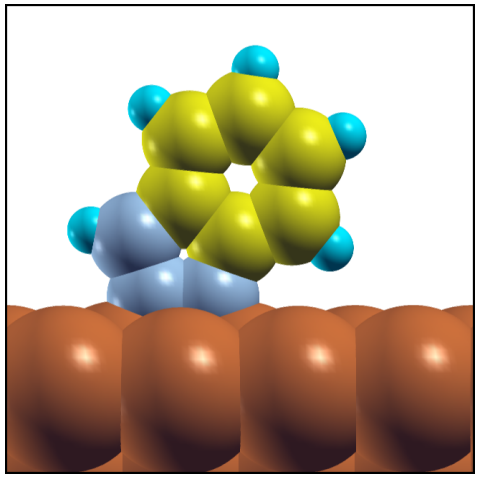
STM of stand-alone molecules

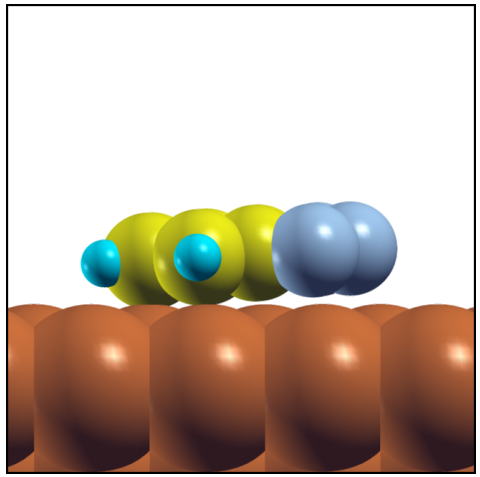
chemisorbed



physisorbed



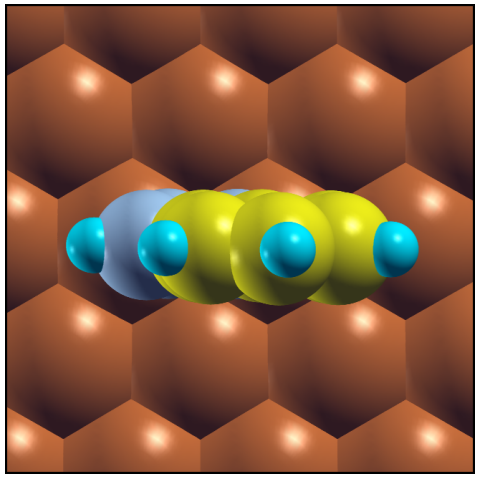


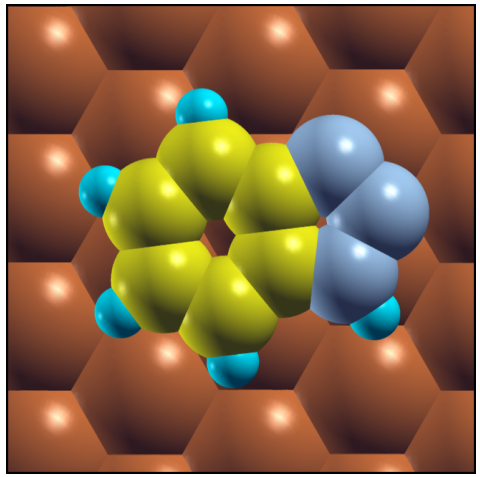


STM of stand-alone molecules

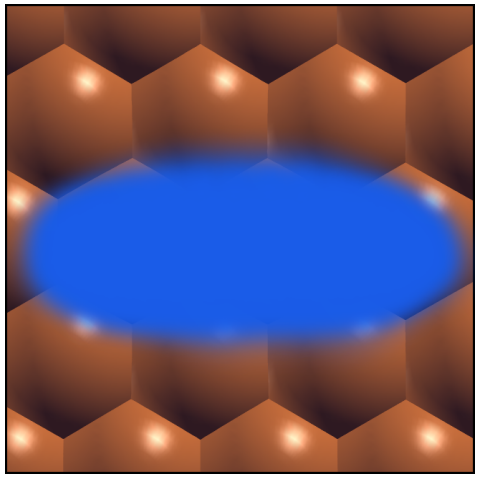
chemisorbed

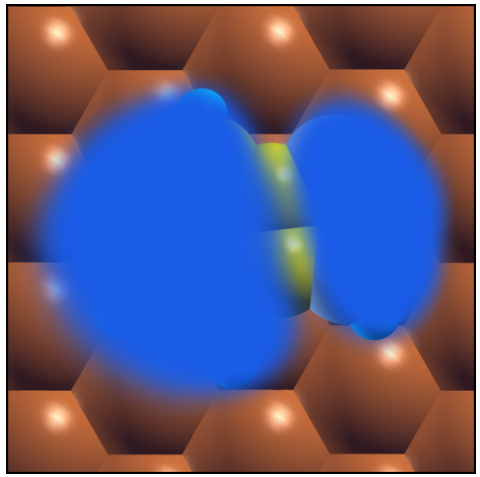
physisorbed





Intuitively expected STM image.

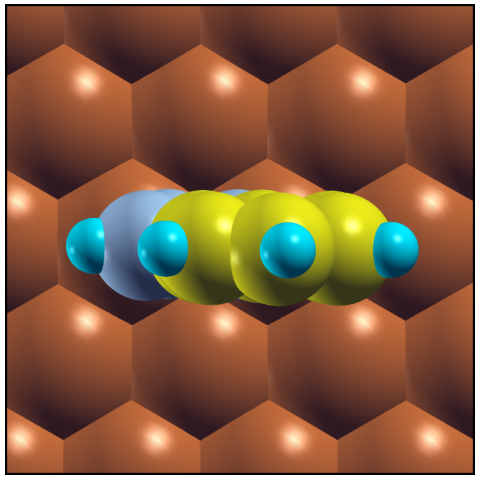


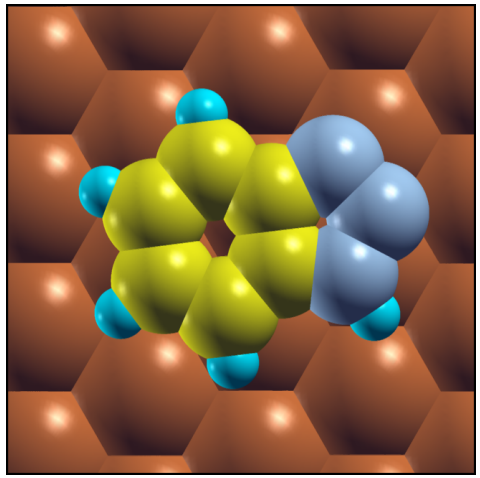


STM of stand-alone molecules

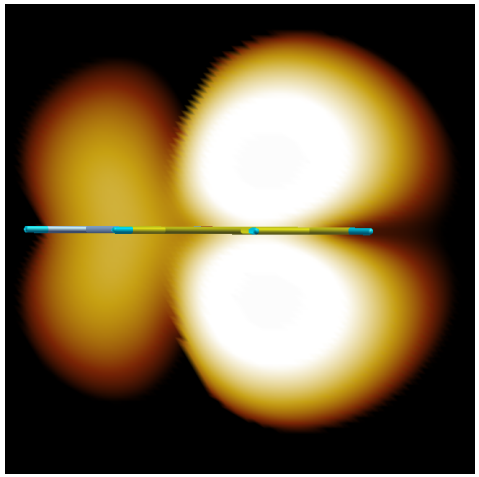
chemisorbed

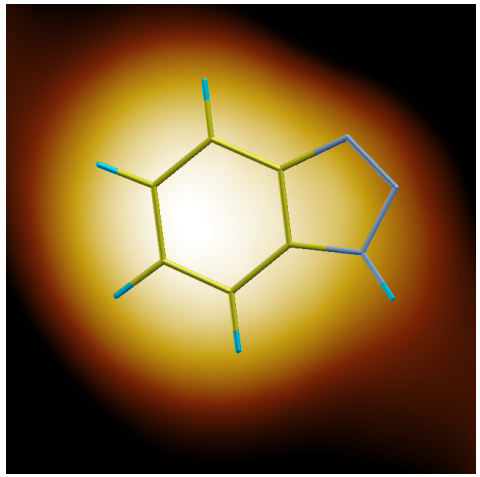
physisorbed





Calculated STM image.





STM images @ Cu surfaces

Out of approximately 15 different studied structures:

1

Experimental image.

2

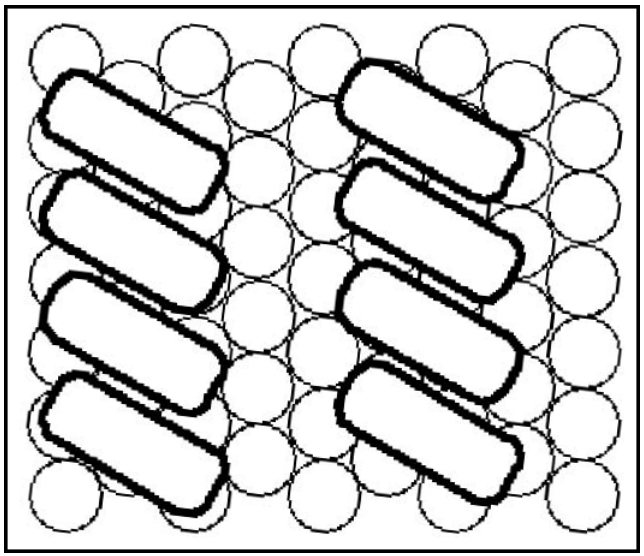
Image based on experimental model.

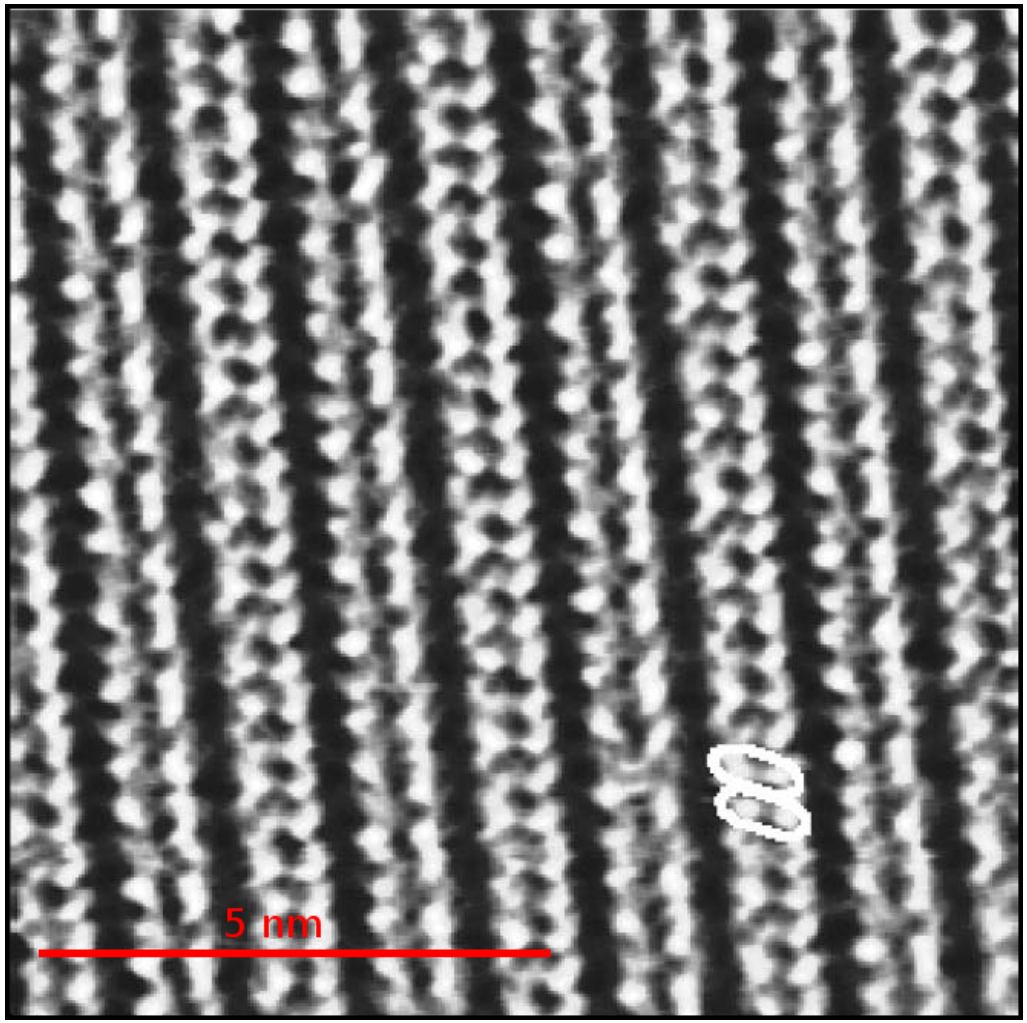
3

Image of most stable structure.
–OR–
Best agreement with experimental picture.

STM @ Cu(111) – experimental

Experimental STM image of BTAH@Cu(111)





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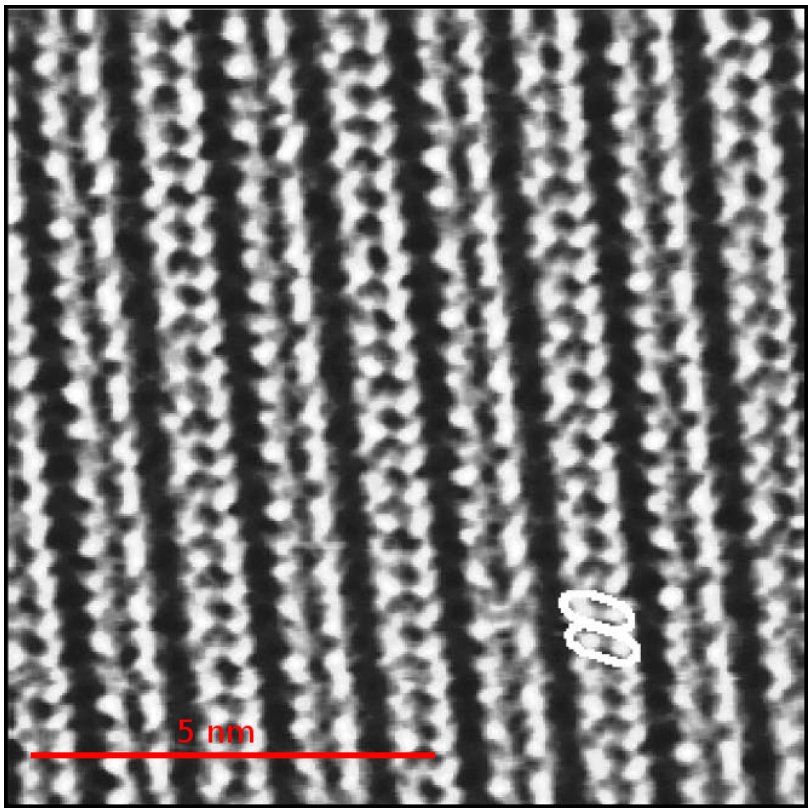
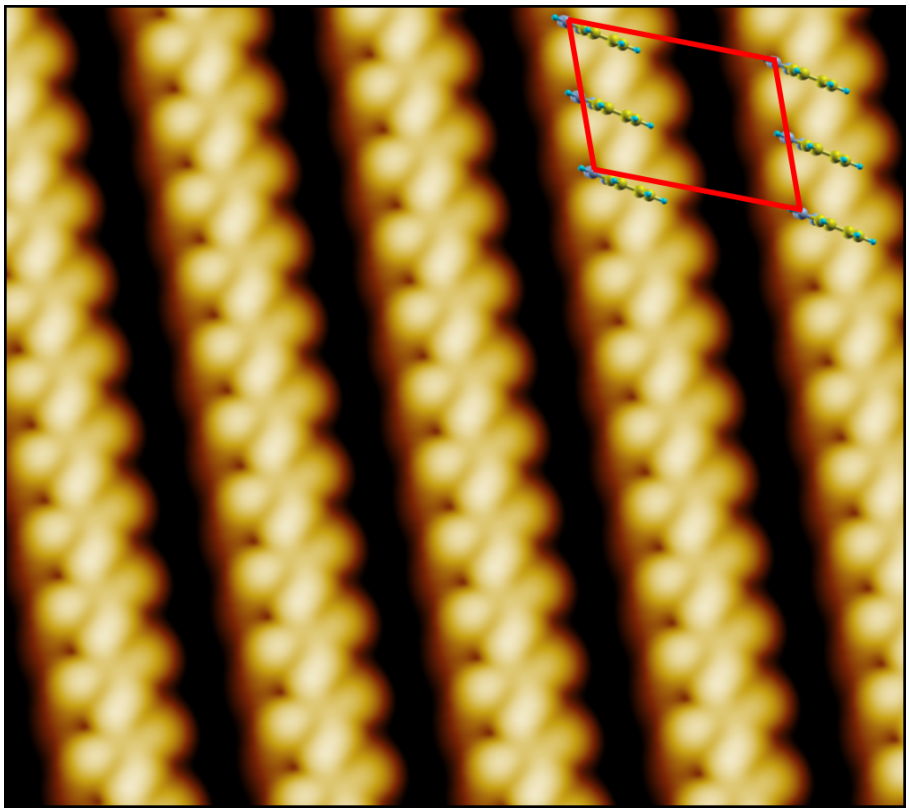
STM @ Cu(111) – experimental vs. calculated

Experimental image



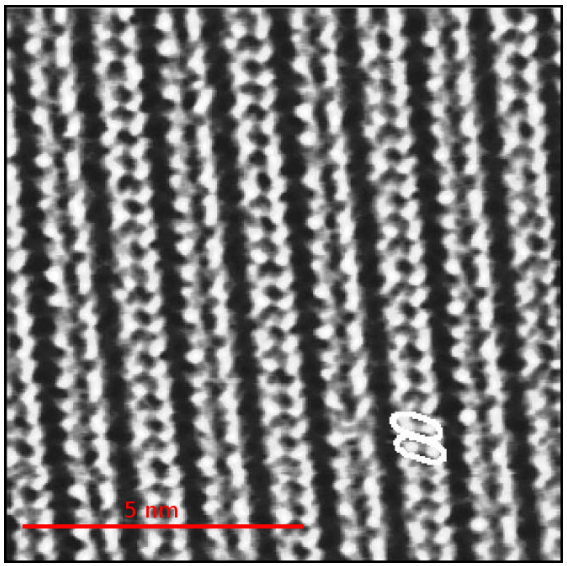
Calculated image of
experimentally proposed structure



Picture reproduced by permission of The Electrochemical Society.

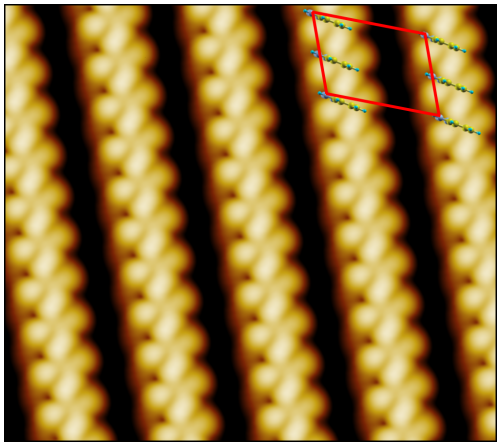
STM @ Cu(111) – most stable structure

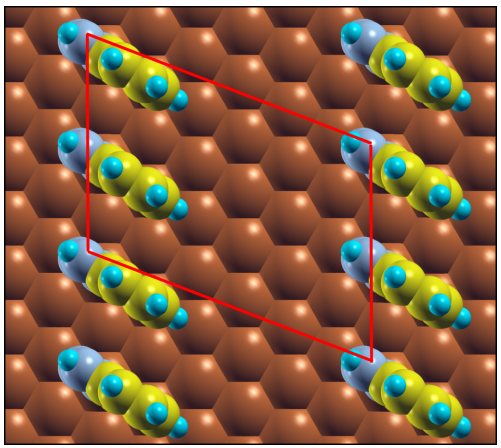
Experimental image



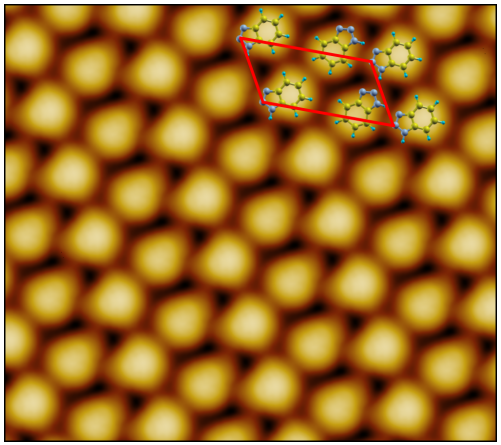
Calculated images

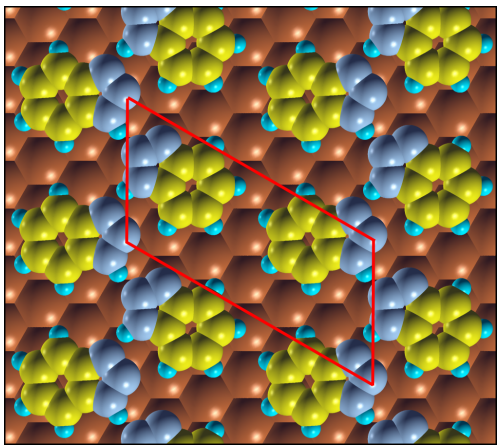
$E_{\mathrm{ads}} = -0.75eV$





$E_{\mathrm{ads}} = -1.14eV$





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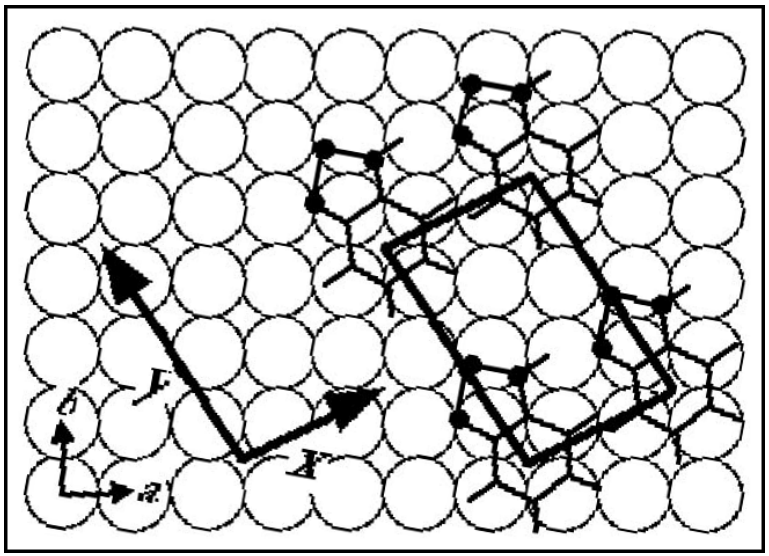
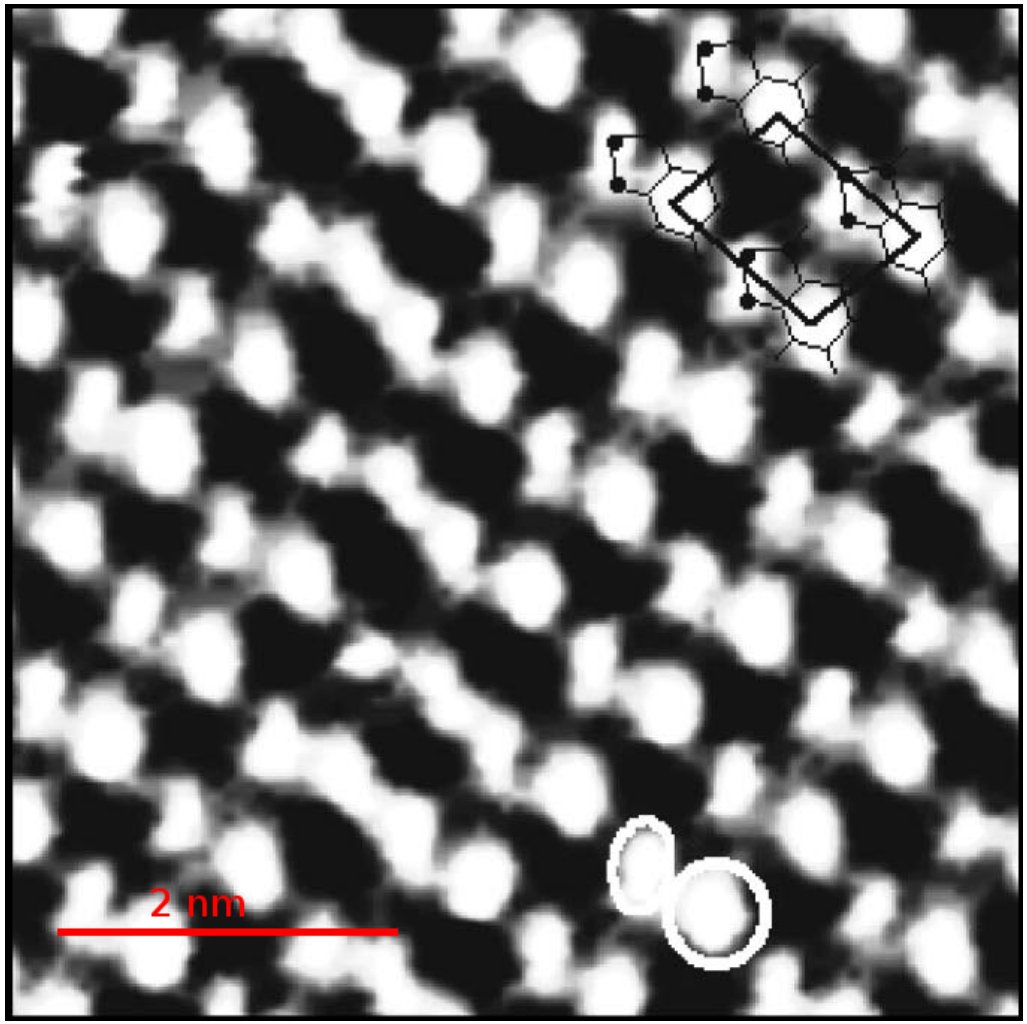
STM @ Cu(100) – experimental

Experimental STM image of BTAH@Cu(100)

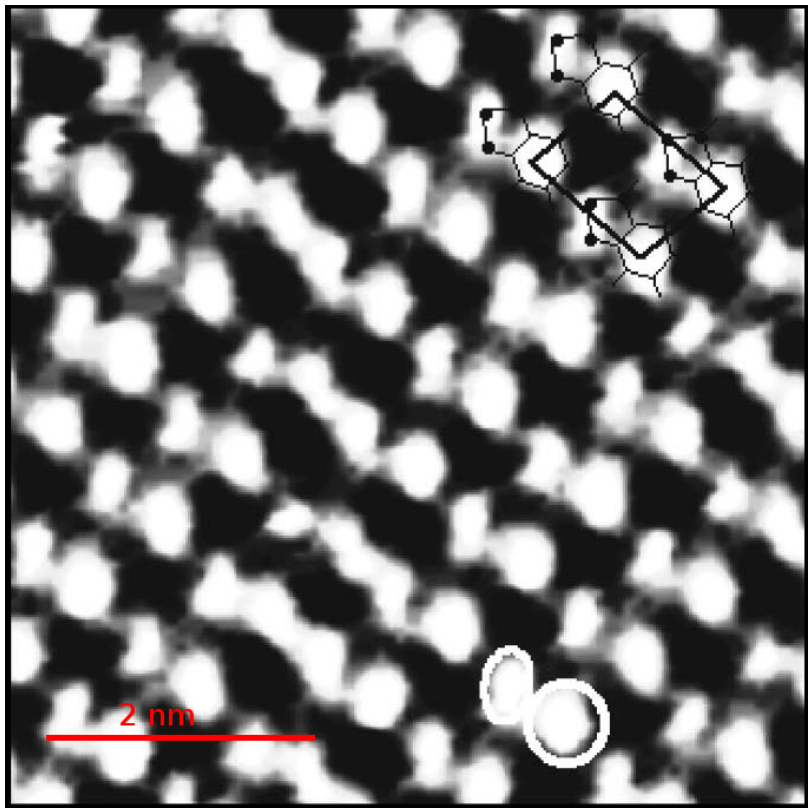




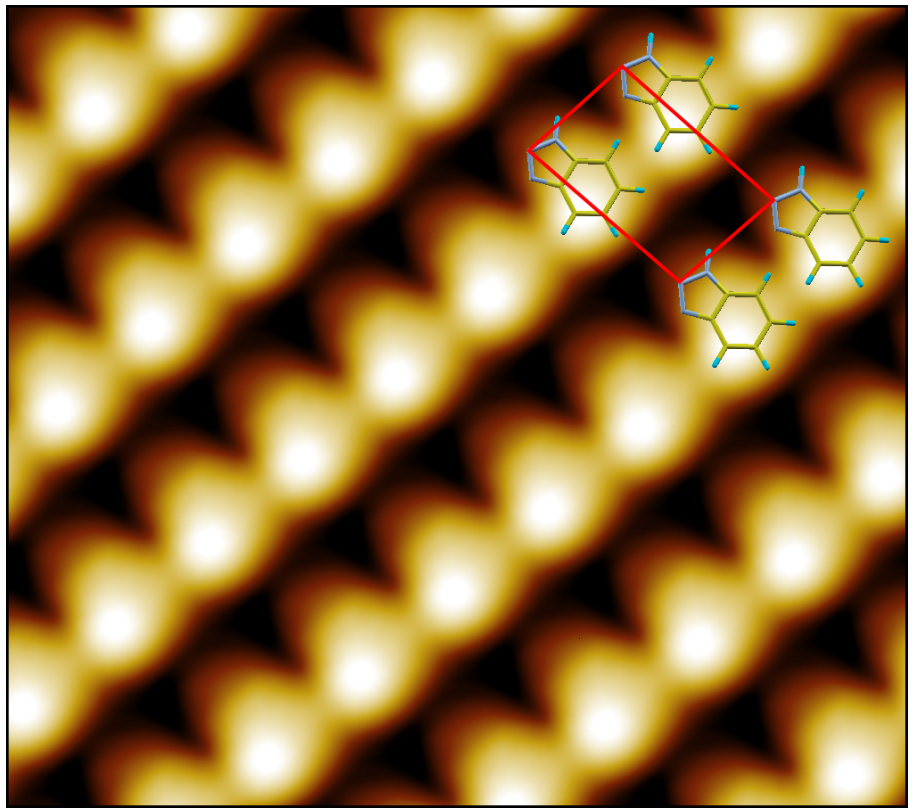
Pictures reproduced by permission of The Electrochemical Society.

STM @ Cu(100) – experimental vs. calculated

Experimental image



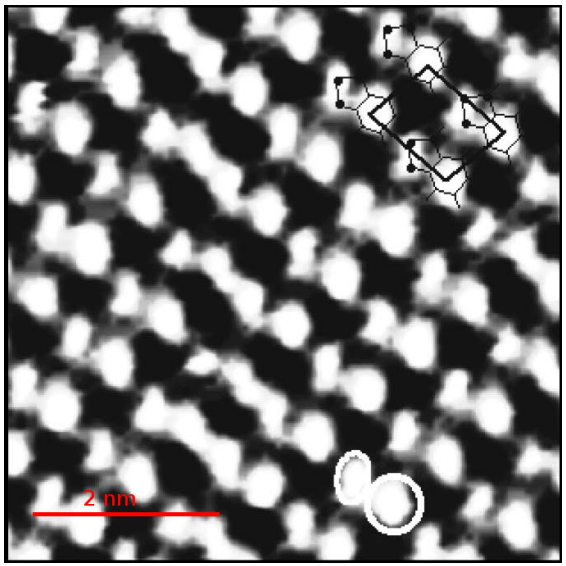
Calculated image of
experimentally proposed structure



Picture reproduced by permission of The Electrochemical Society.

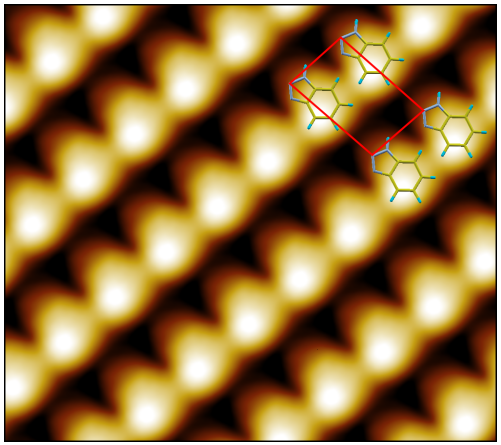
STM @ Cu(100) – most stable structure

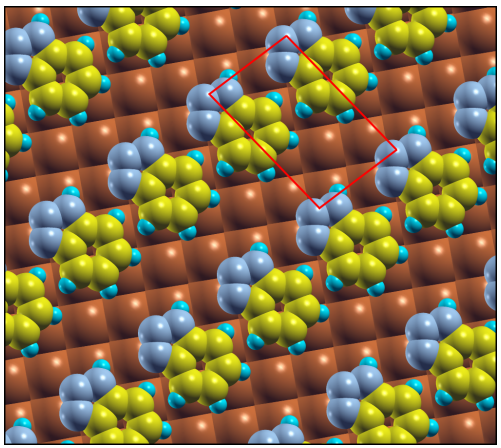
Experimental image



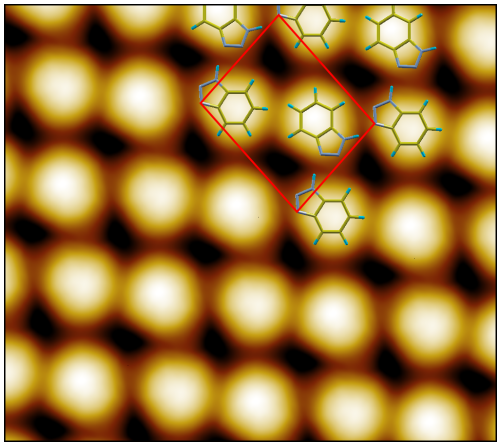
Calculated images

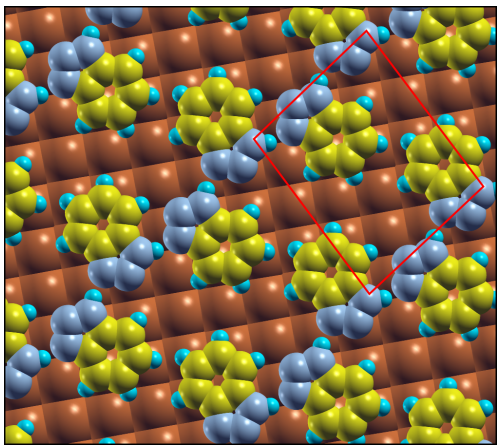
$E_{\mathrm{ads}} = -0.74eV$





$E_{\mathrm{ads}} = -1.14eV$

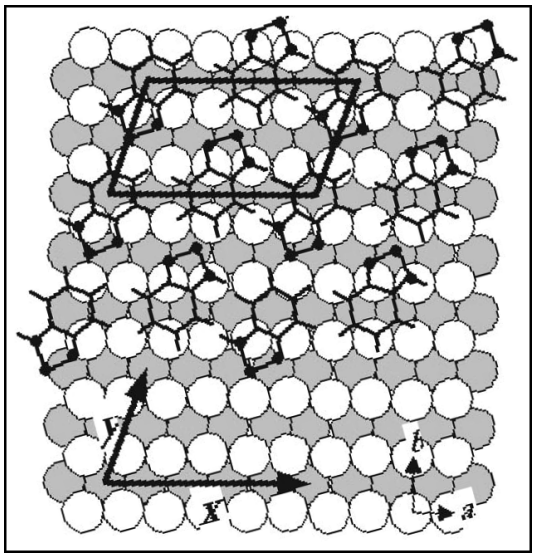


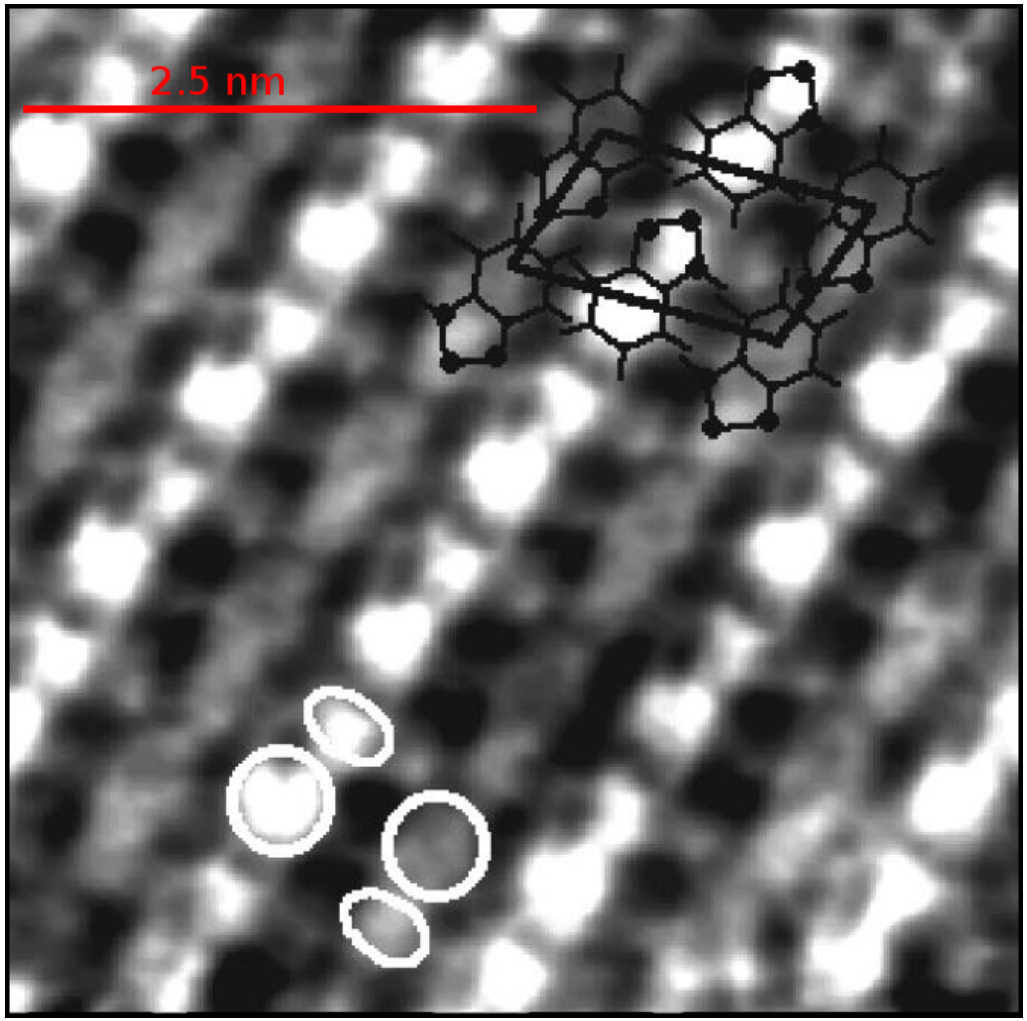


Picture reproduced by permission of The Electrochemical Society.

STM @ Cu(110) – experimental

Experimental STM image of BTAH@Cu(110)





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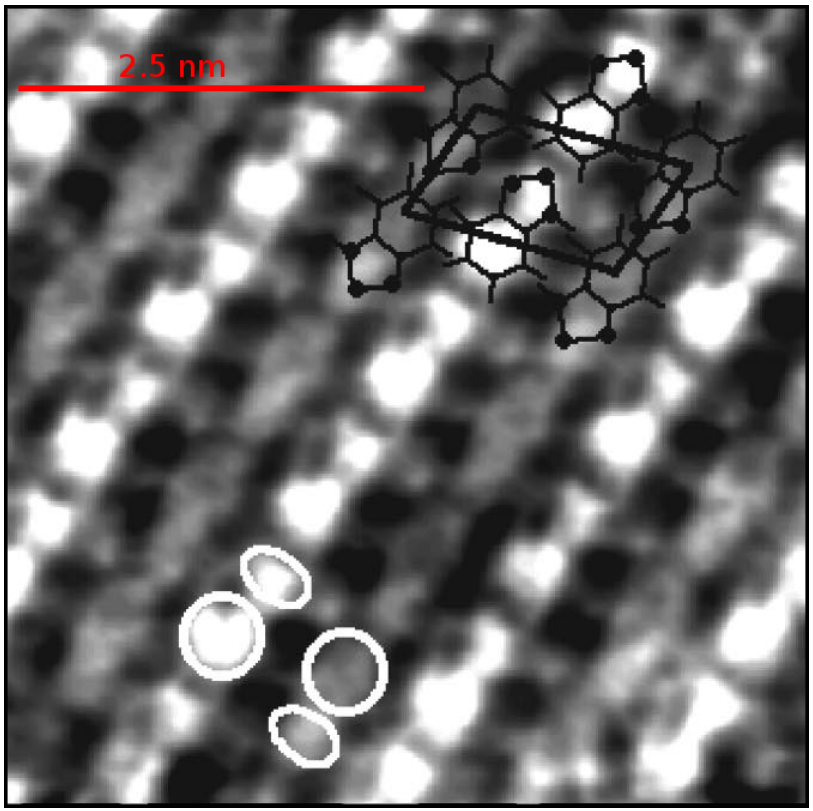
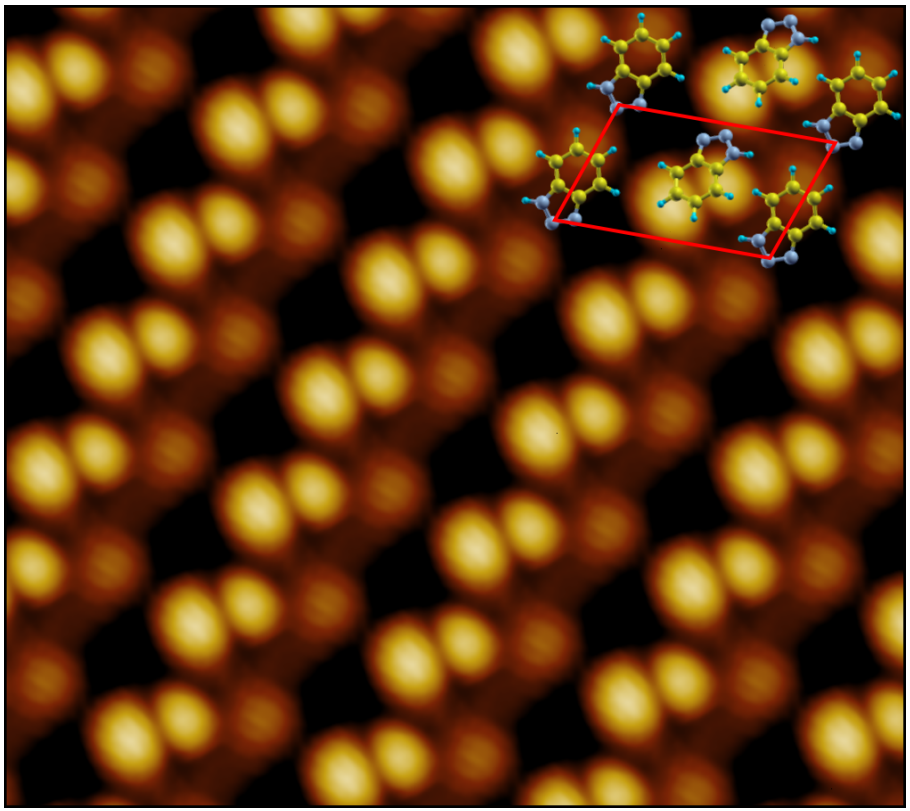
STM @ Cu(110) – experimental vs. calculated

Experimental image



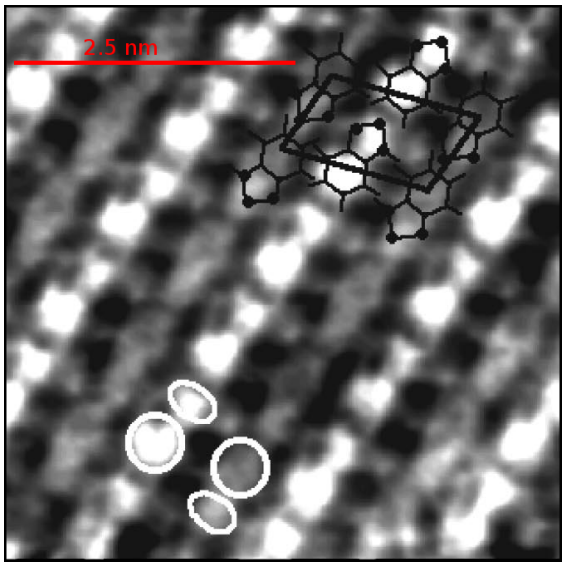
Calculated image of
experimentally proposed structure



Picture reproduced by permission of The Electrochemical Society.

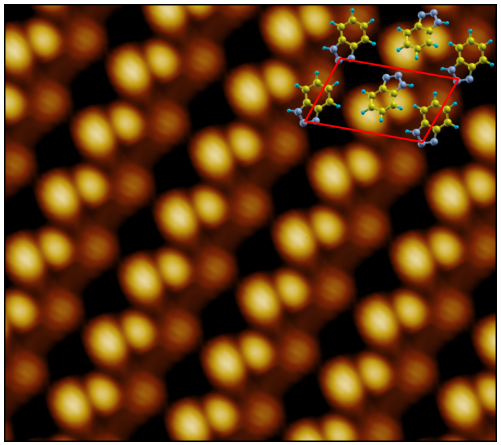
STM @ Cu(110) – best match

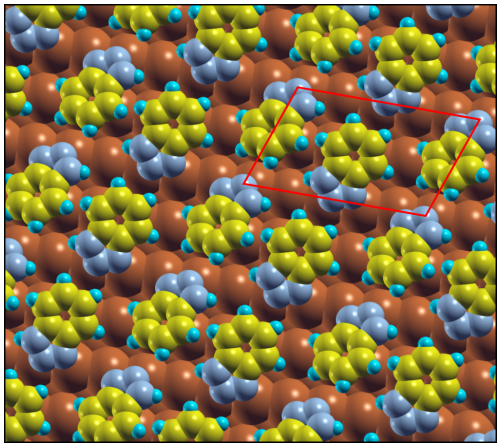
Experimental image



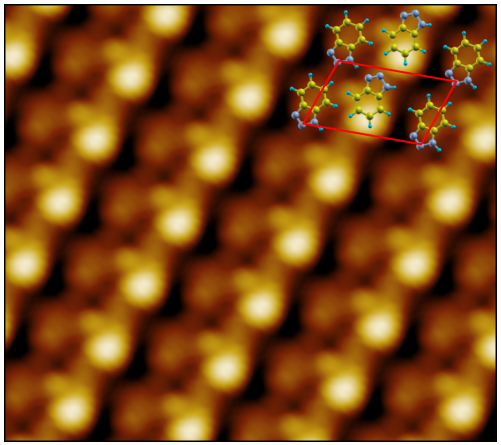
Calculated images

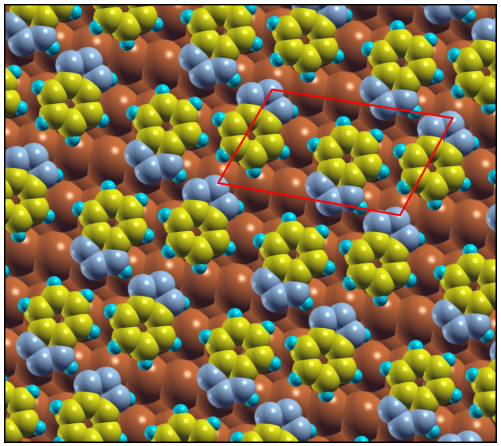
$E_{\mathrm{ads}} = -1.24eV$





$E_{\mathrm{ads}} = -1.15eV$





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Conclusions

Interpretation of STM images is not straightforward–small change of structural detail can alter the image significantly.

Cu(110): our calculations support experimentally proposed structure.

Cu(100): calculated STM image of experimentally proposed structure is neither in good agreement with experimental image nor is the structure among the most stable identified.

Cu(111): calculated STM image of experimentally proposed structure gives good agreement with experimental image, yet other more stable structures were identified computationally.

Reasons for discrepancies:

- Correct structure not yet identified?
- Solvent effects?

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Thank you for your attention!