Institute of Physics
National Academy
of Sciences of Ukraine

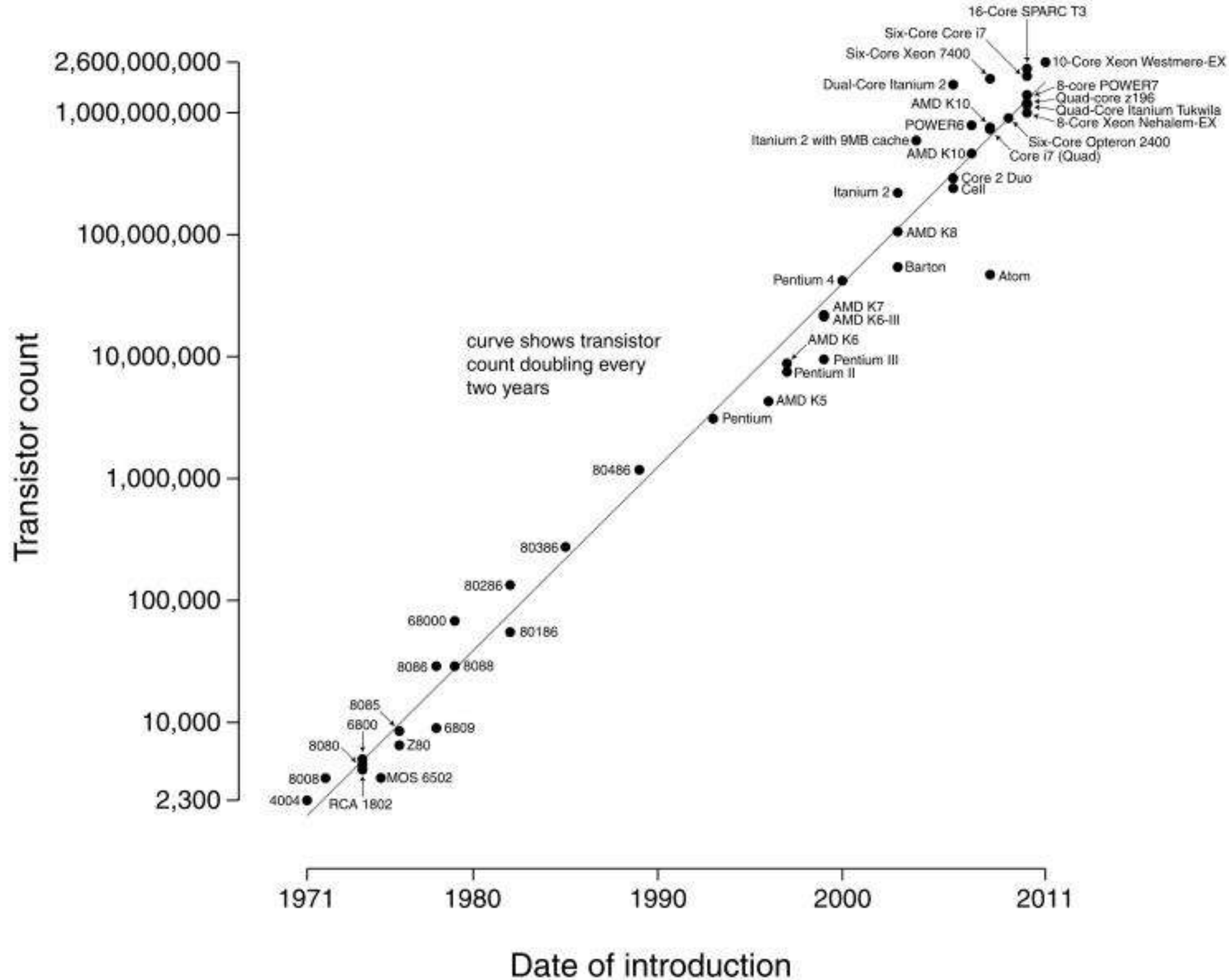
STM-investigation of adsorption of long chain aliphatic compounds on atomically flat surfaces

A.I. Senenko

STM-AFM team

- **A.A. Marchenko**
- **V.V. Cherepanov**
- **D.V. Stryzheus**
- **A.G. Naumovets**

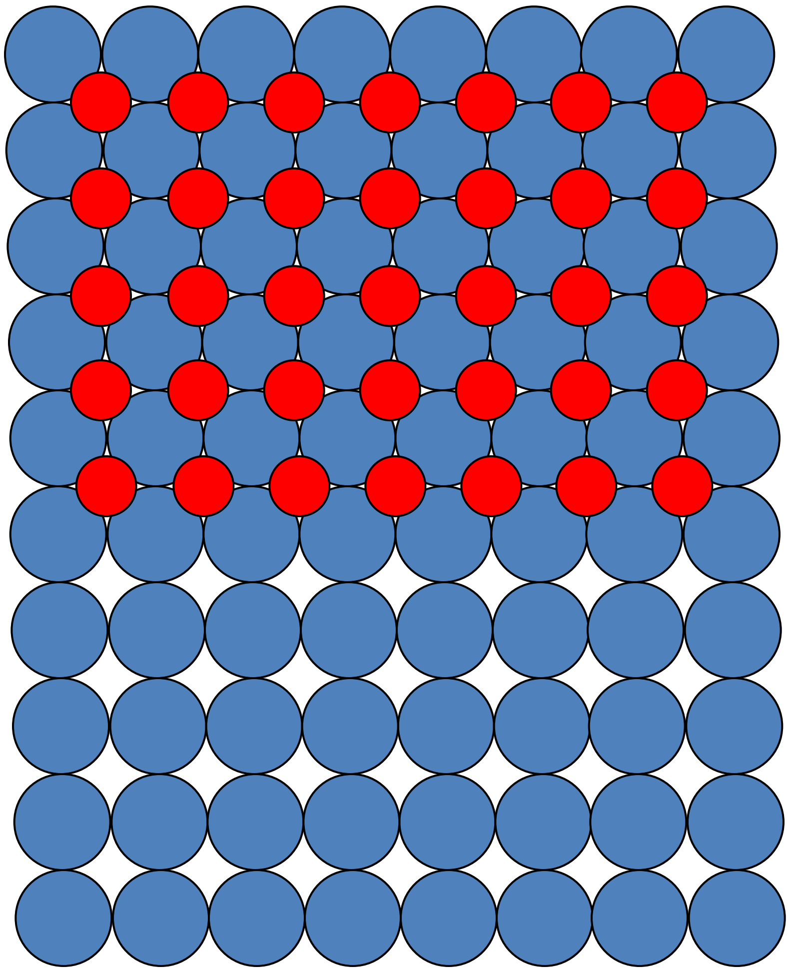
Microprocessor Transistor Counts 1971-2011 & Moore's Law



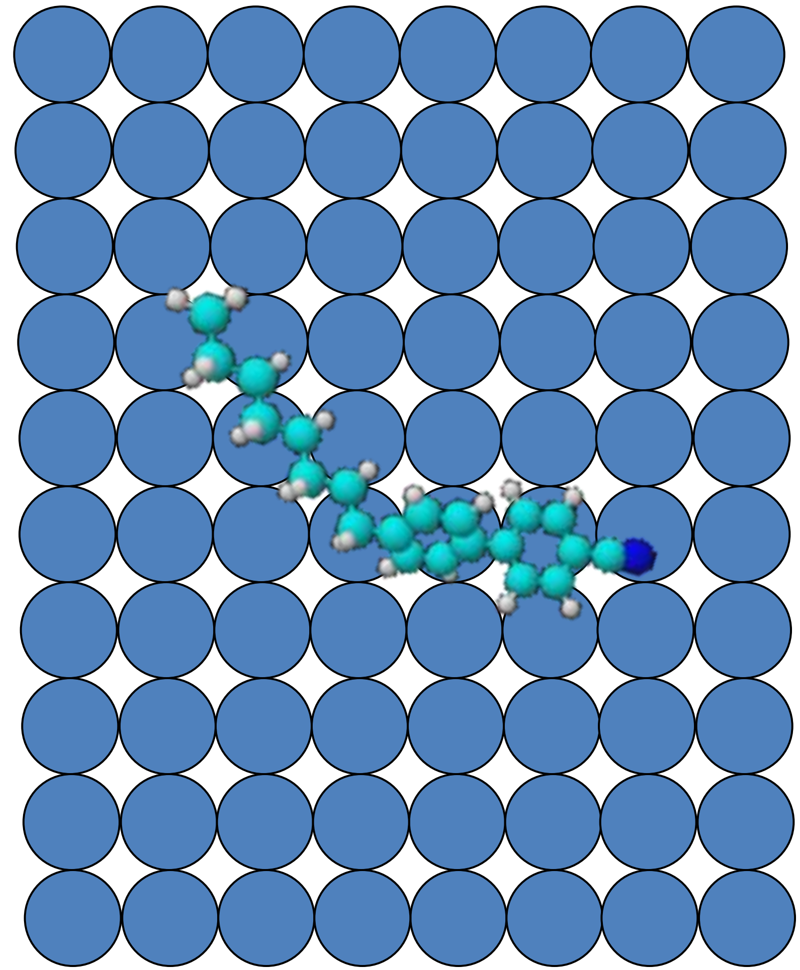
EPITAXY

”επι“ — *on*, ”ταξισ“ — *order*

Adsorption of atoms

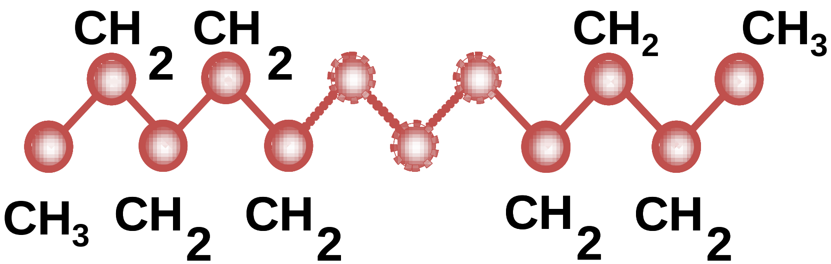


Organic adsorbates



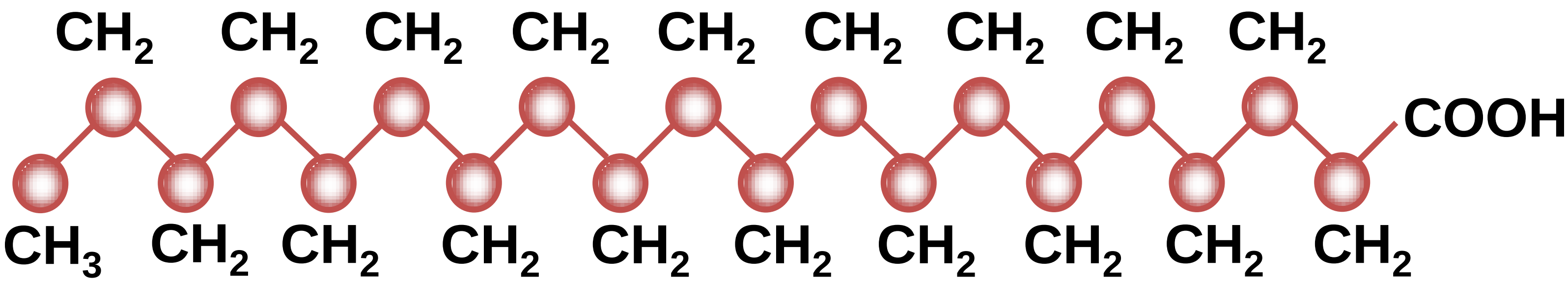
?

Investigated compounds



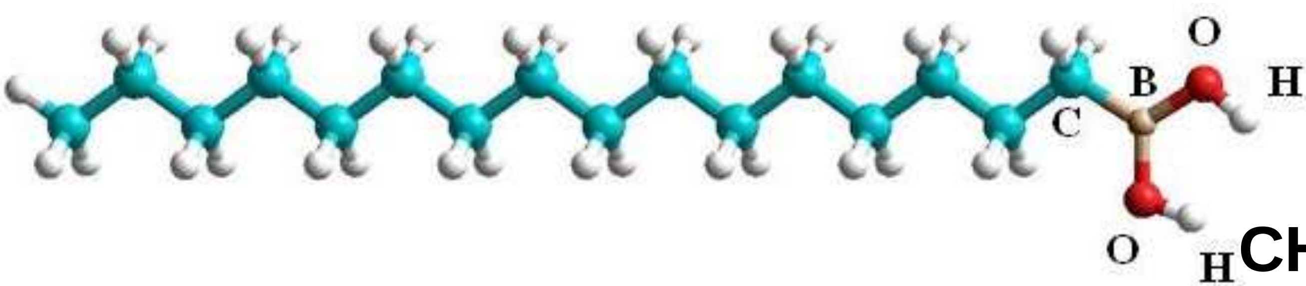
n-alkanes

C_nH_{2n+2} (*n*=10-50)



Arachidic acid

CH_3-$(CH_2)_{18}$-COOH



Hexadecyl boron acid

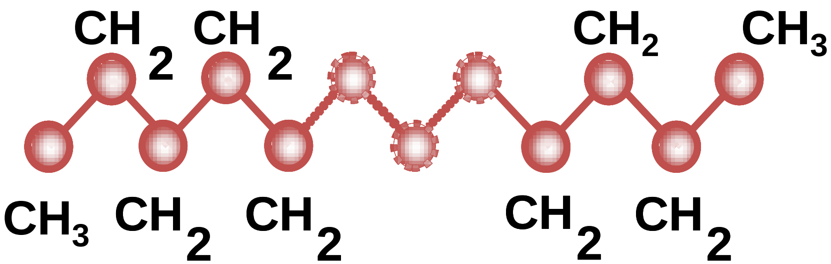
CH_3–$(CH_2)_{15}$–$B(OH)_2$

Aims:

- the study of monolayer films of long chain aliphatic compounds (acids) on atomically-flat substrate (graphite);

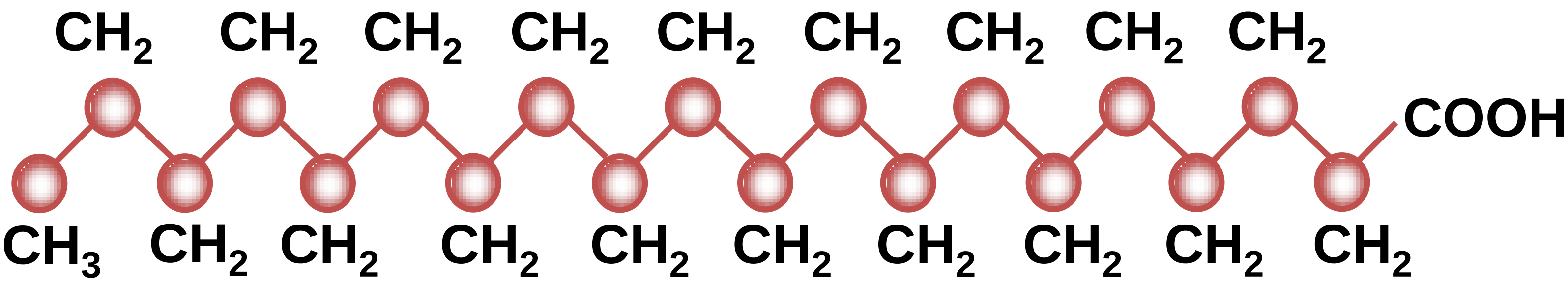
- the elucidation of influence of functionalization on monolayer structure (carboxylic and boron groups)

Investigated compounds



n-alkanes

C_nH_{2n+2} (n=10-50)



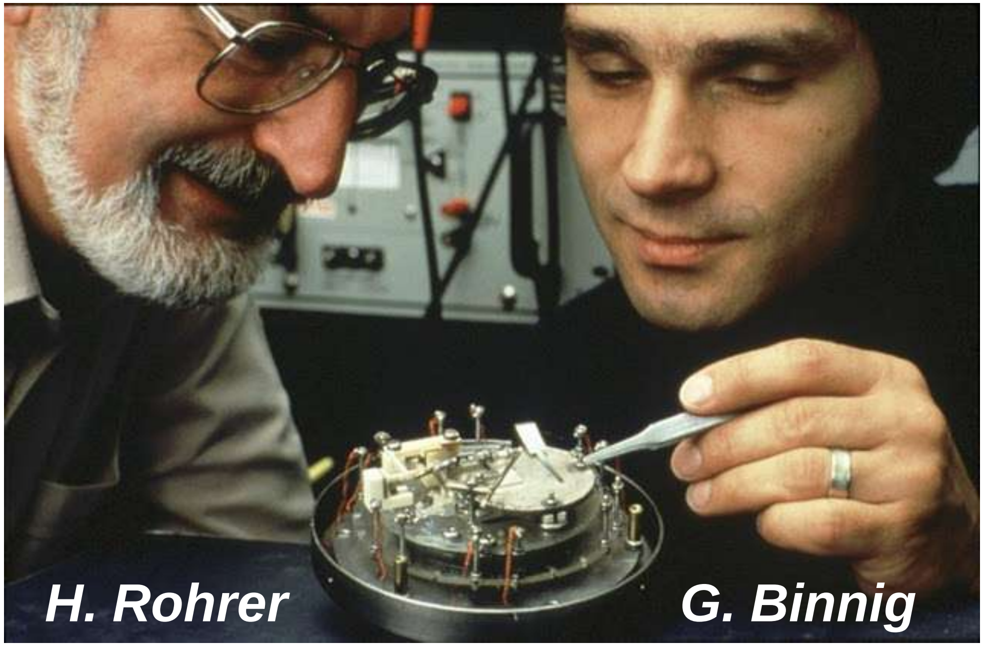
Arachidic acid

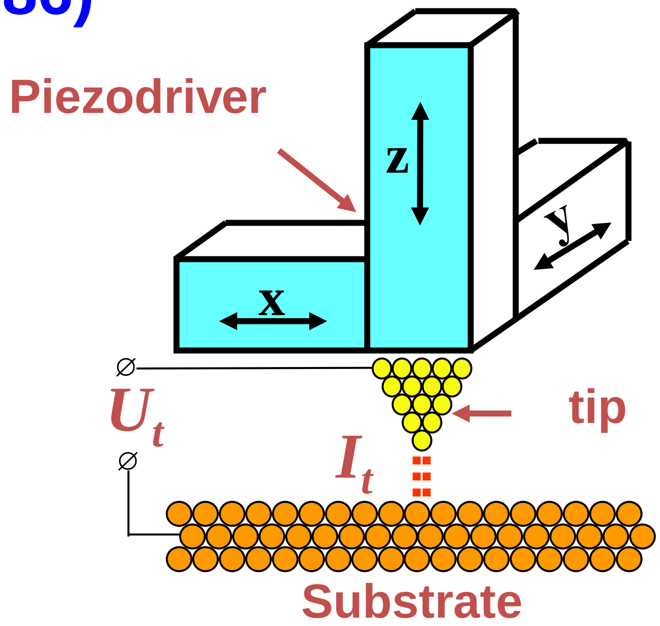
CH_3-$(CH_2)_{18}$-COOH

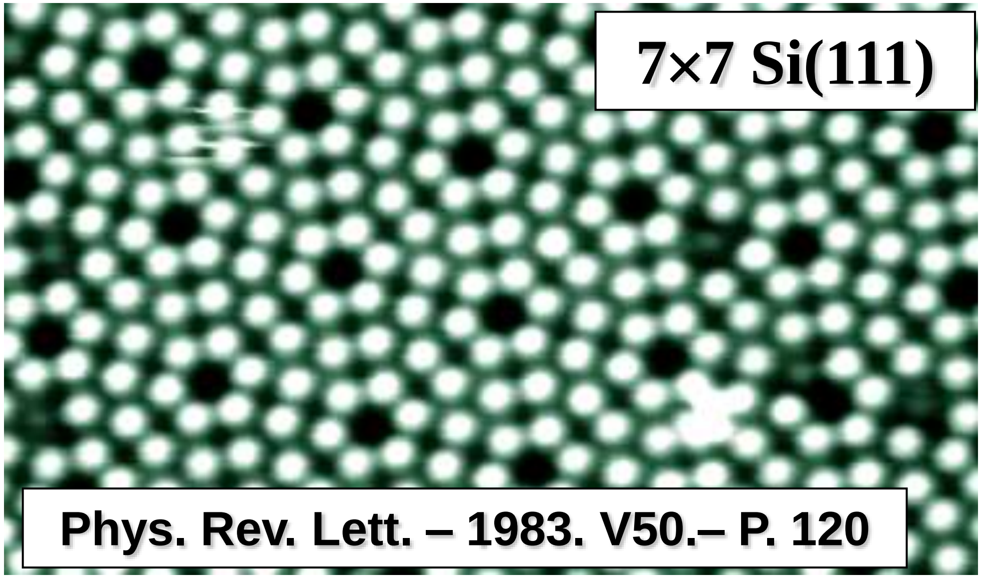
Hexadecyl Boron acid

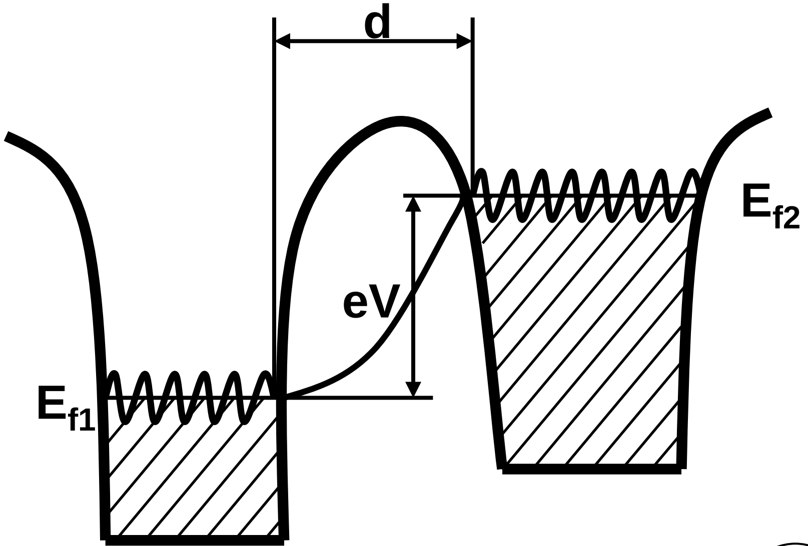
CH_3–$(CH_2)_{15}$–$B(OH)_2$

1982 – Invention of the Scanning Tunneling Microscopy (Noble prize 1986)

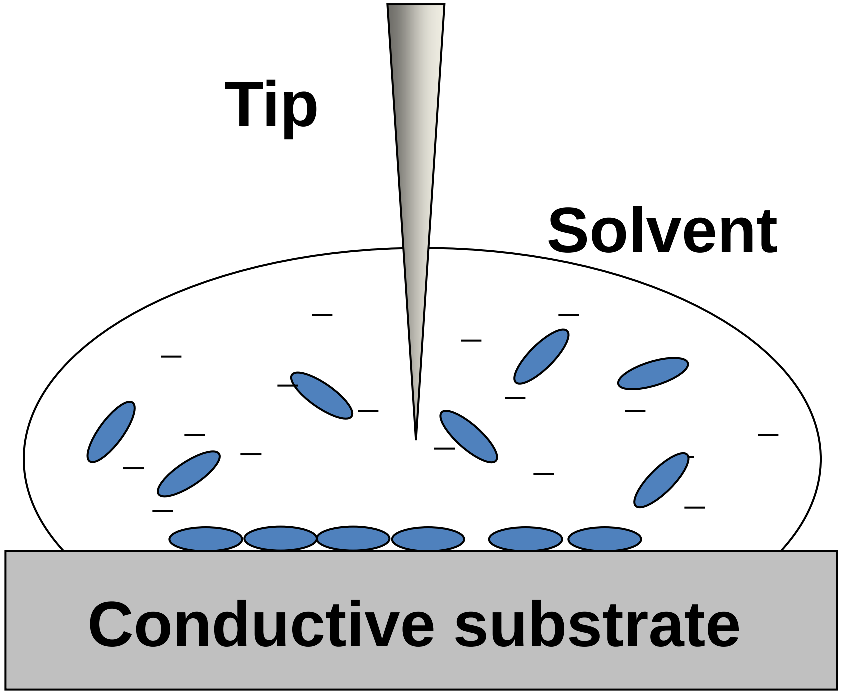






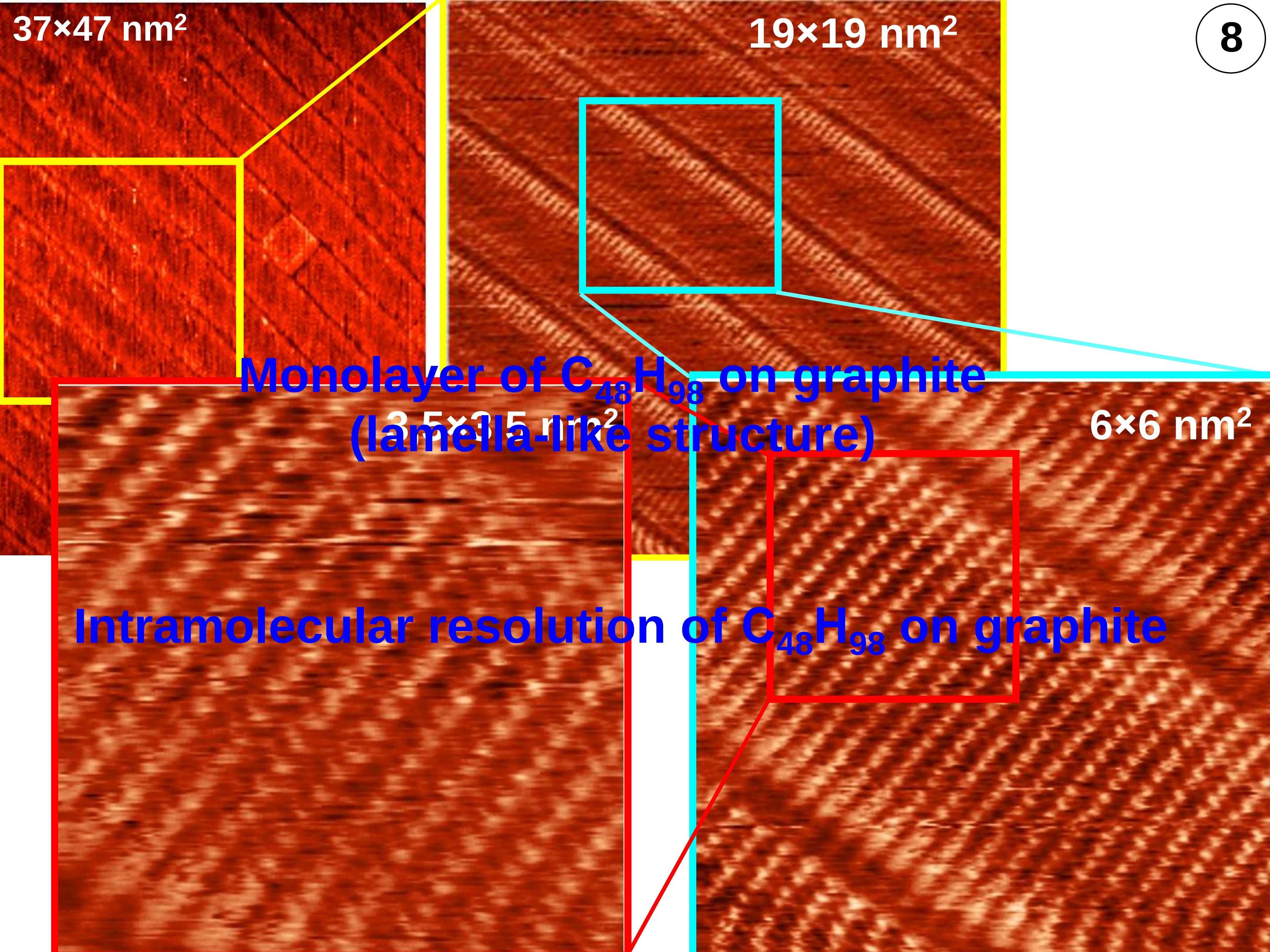


Principle of STM in liquid-solid interface

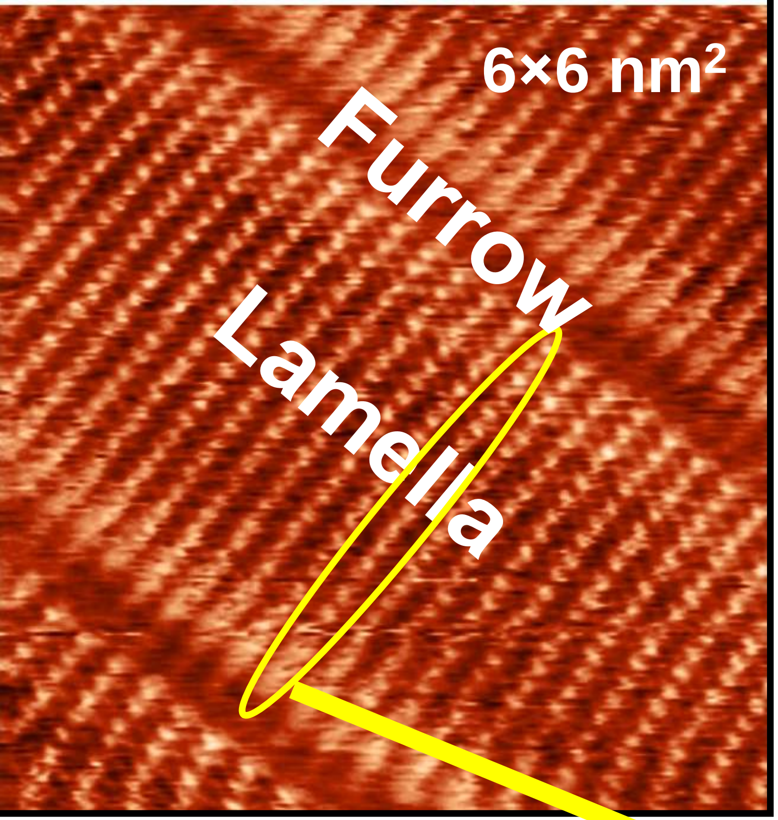


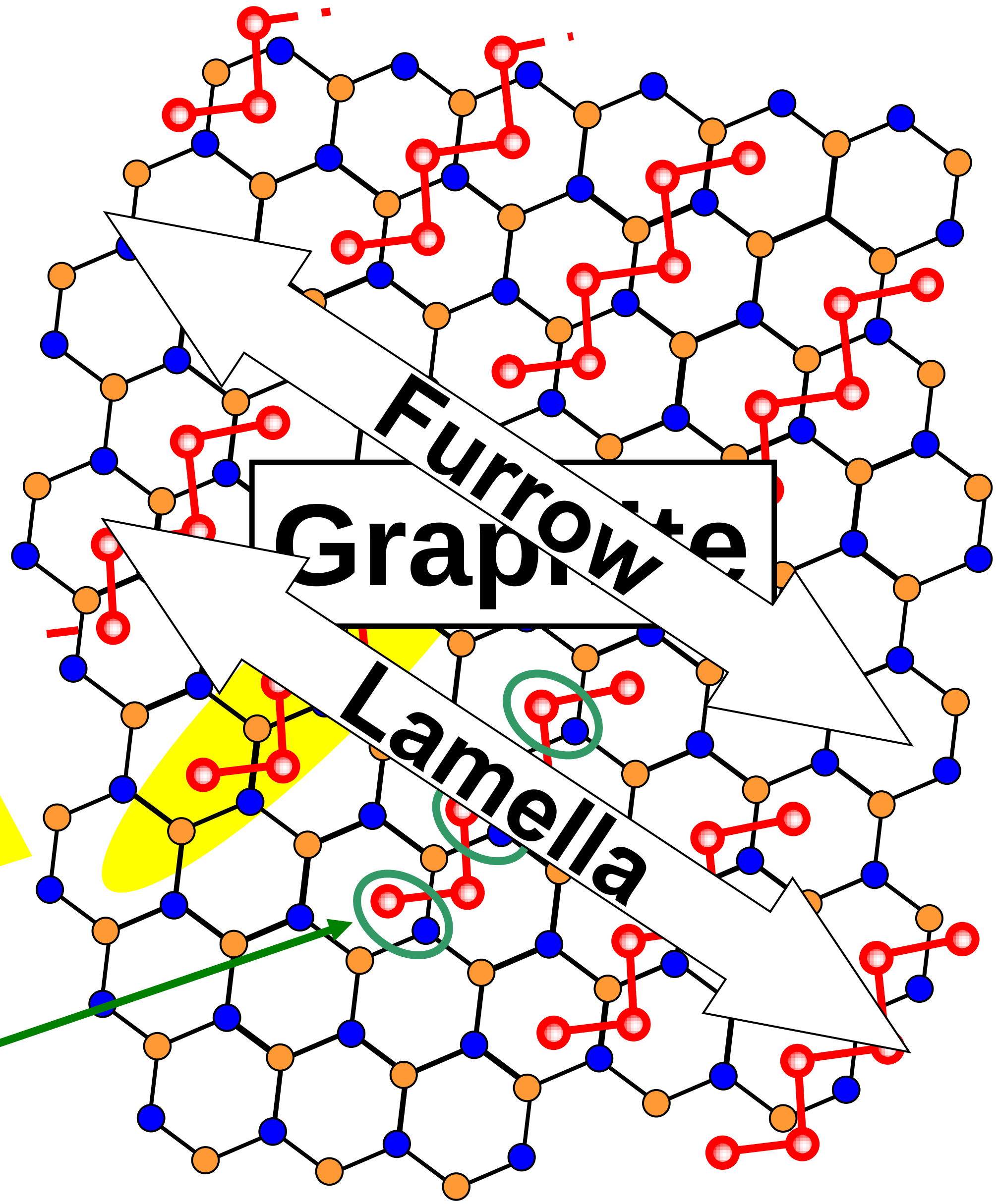
Advantages

- high performance of the method
- a diversity of adsorption systems
- the possibility of investigation of biological objects



37×47 nm2
19×19 nm2
8
Monolayer of C48H98 on graphite
(lamella-like structure)
3.5×3.5 nm2
6×6 nm2
Intramolecular resolution of C48H98 on graphite



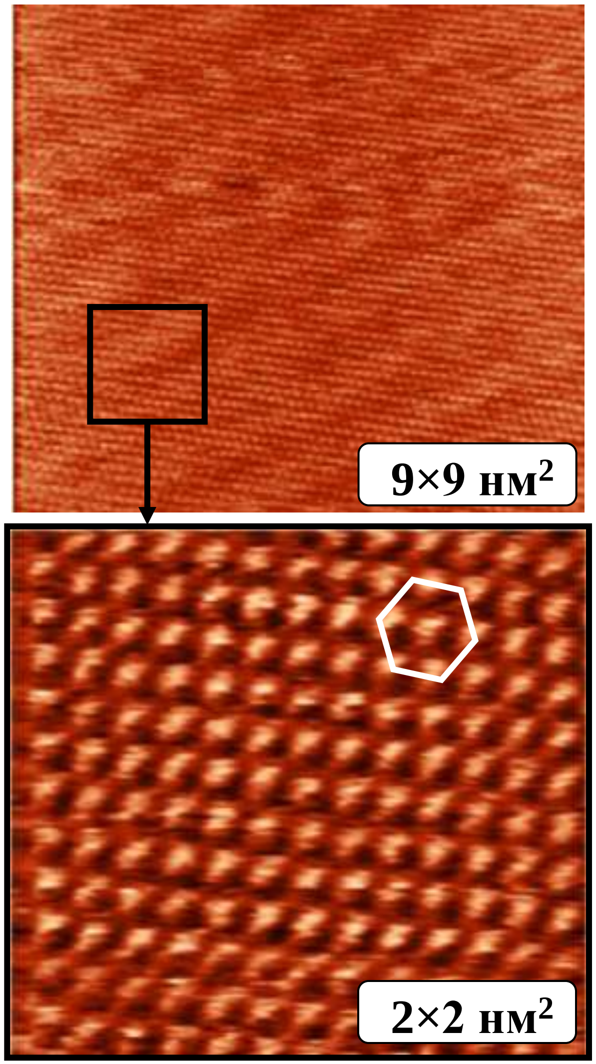


Schematic model of lamella formation

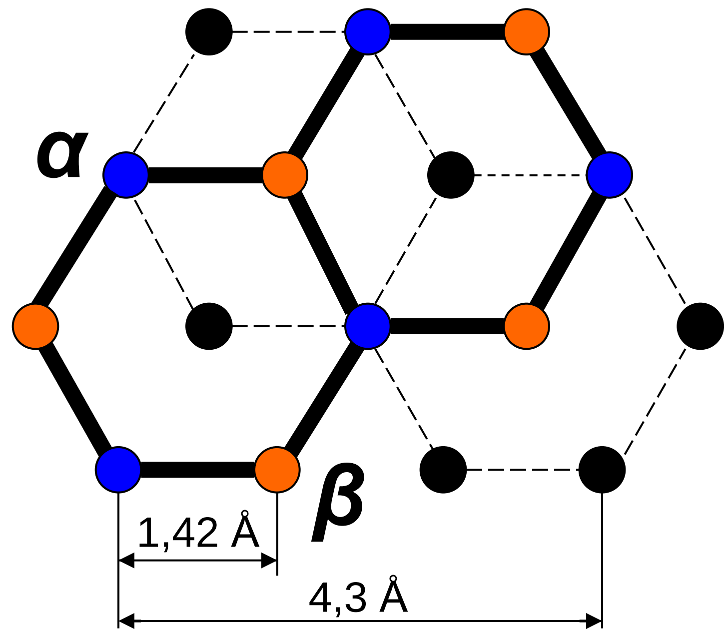
enlighted STM contrast

-CH_2

Highly Oriented Pyrolytic Graphite



Two kinds of carbon atoms in the first layer

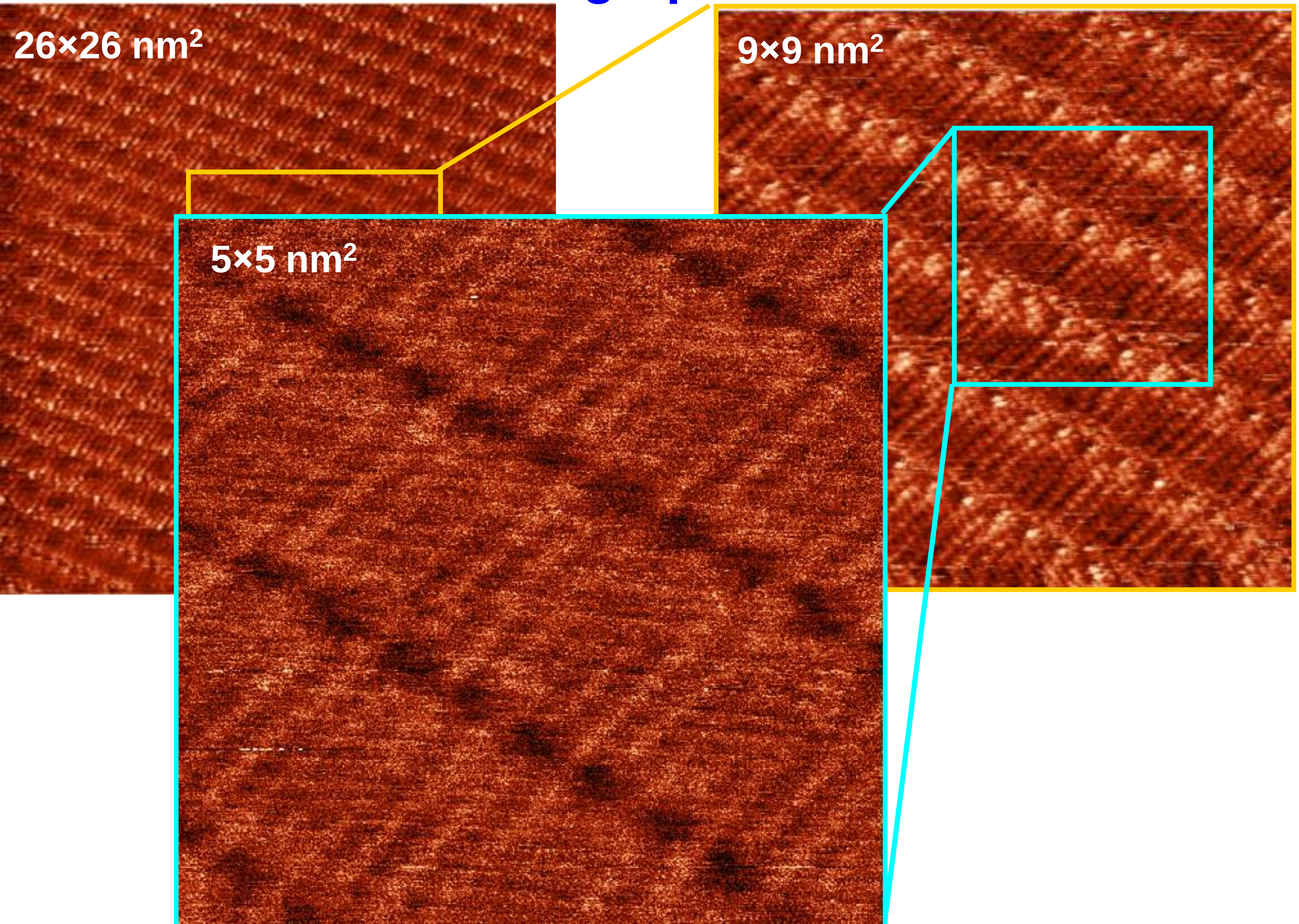


α - atoms have neighbours in the second layer

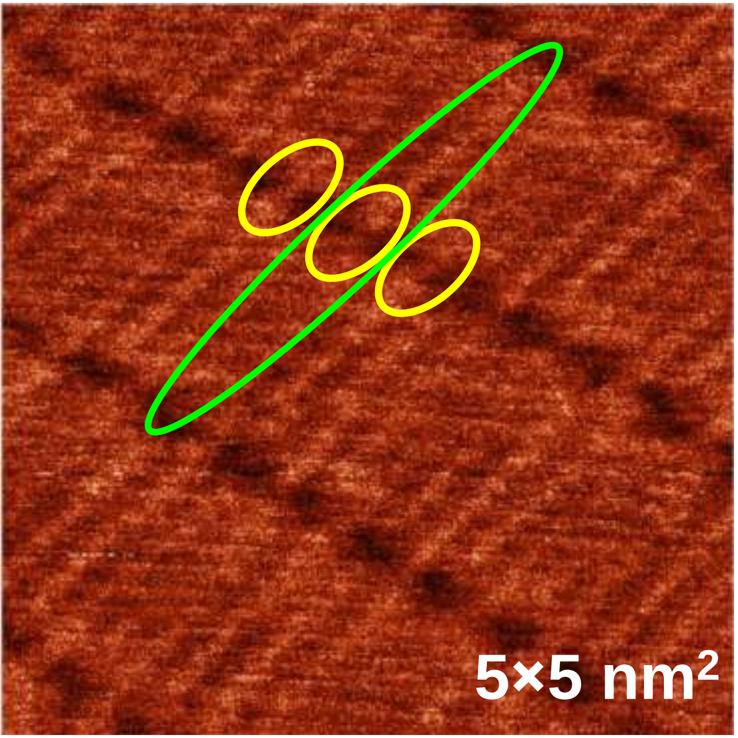
β **- atoms don`t have the neighbouring atom in the second layer**

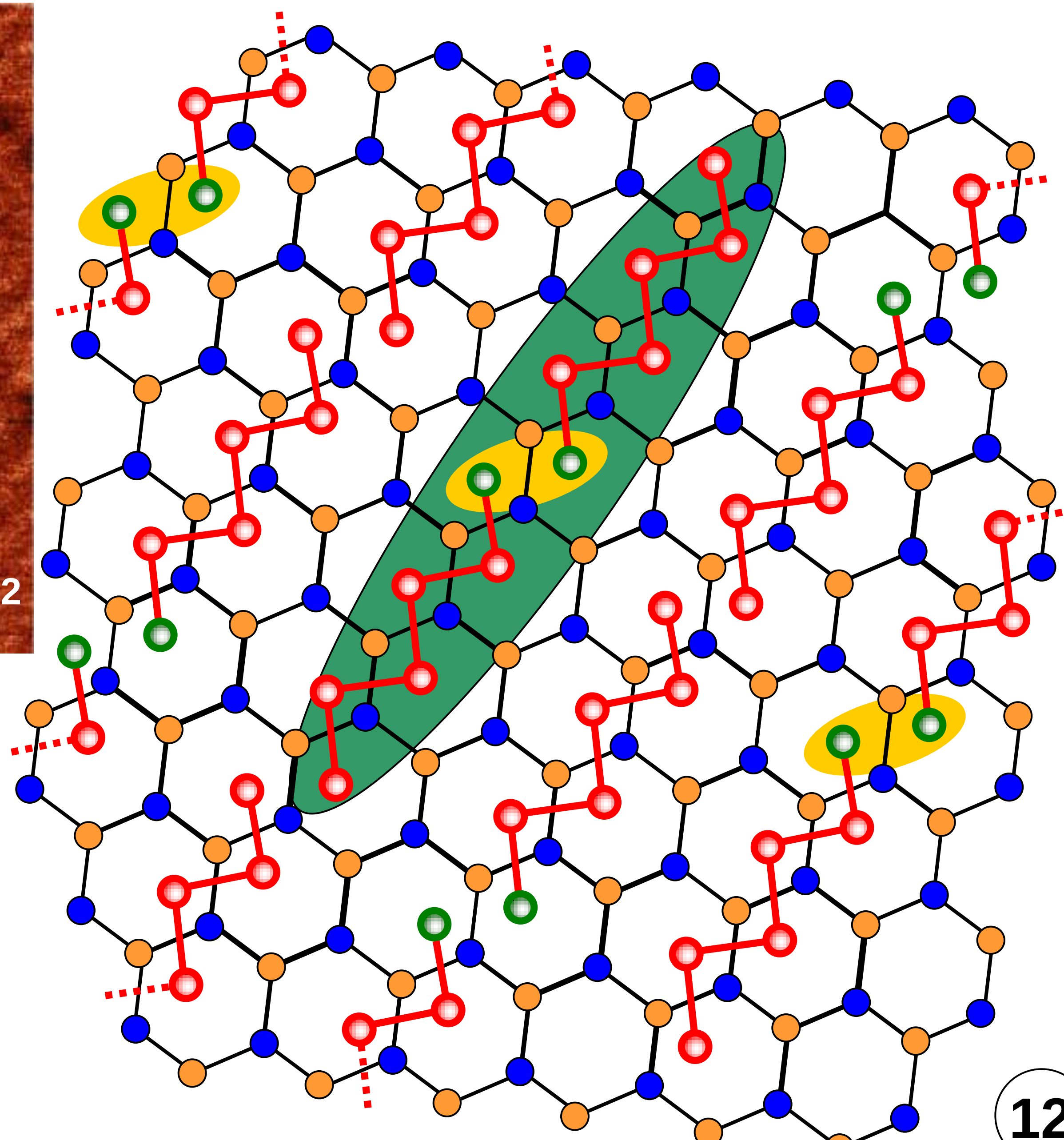
Intramolecular resolution of $C_{20}H_{40}O_2$ on graphite

Monolayer of $C_{20}H_{40}O_2$ on graphite



Dimer structure of $C_{20}H_{40}O_2$ on graphite

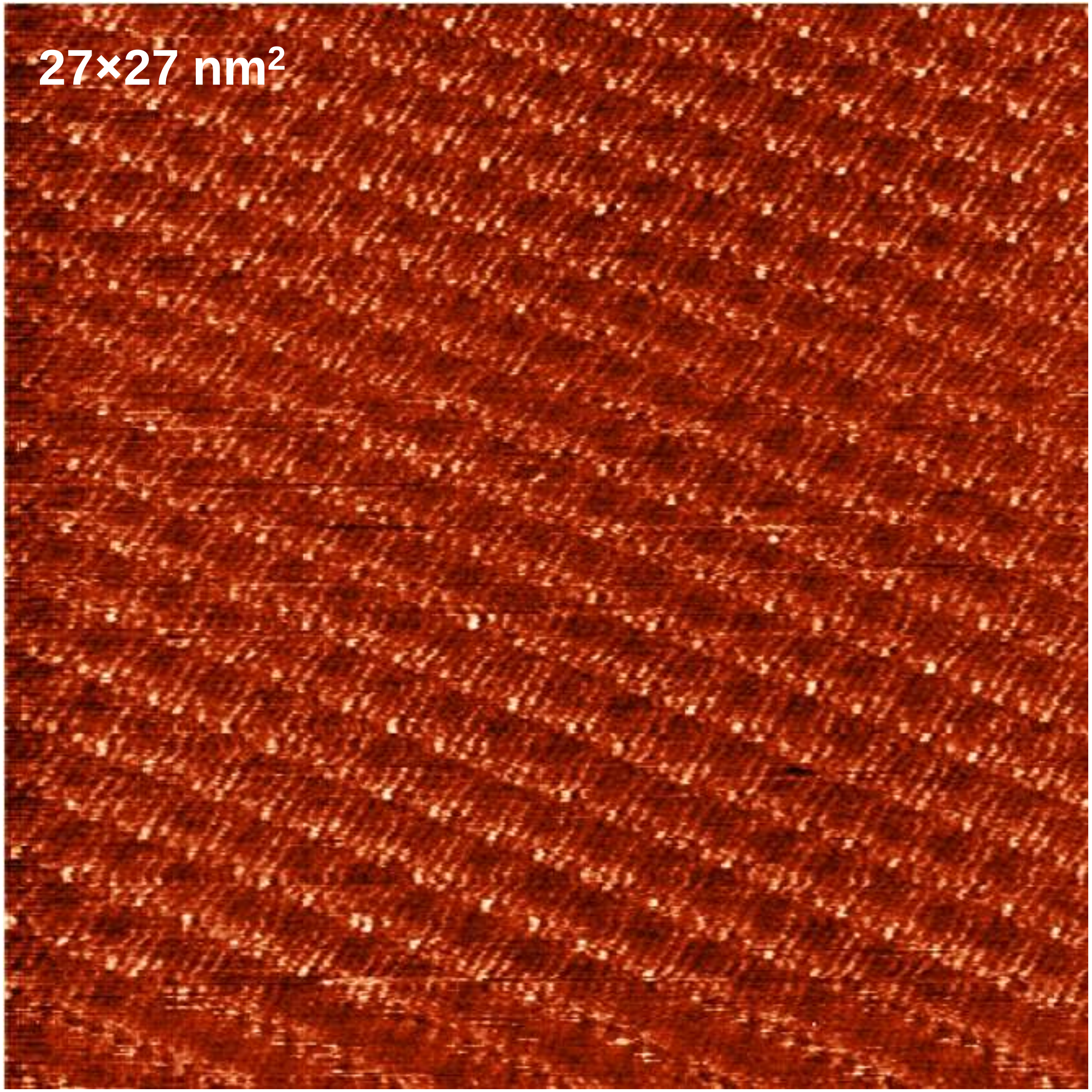




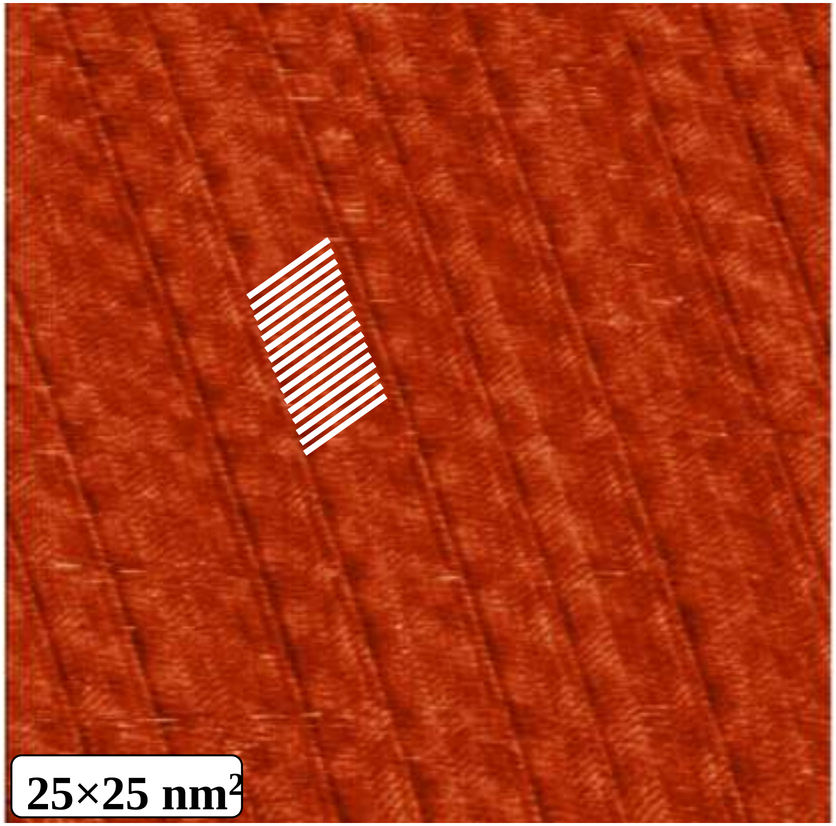
Schematic model of dimer formation

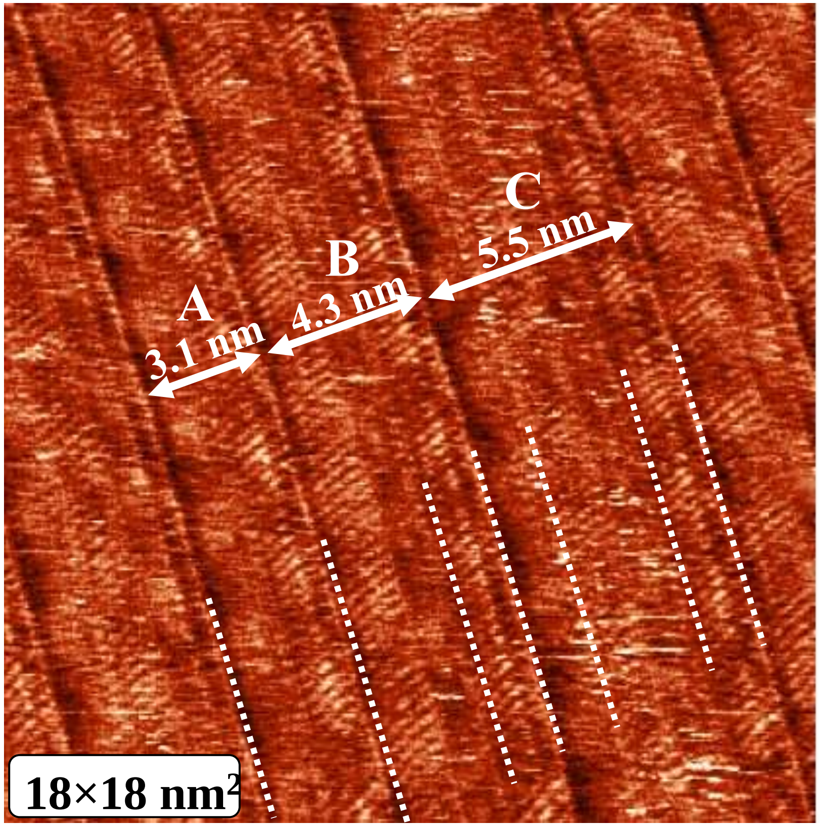
- CH_2-group
- COOH-group

Monolayer of $C_{20}H_{40}O_2$ on graphite

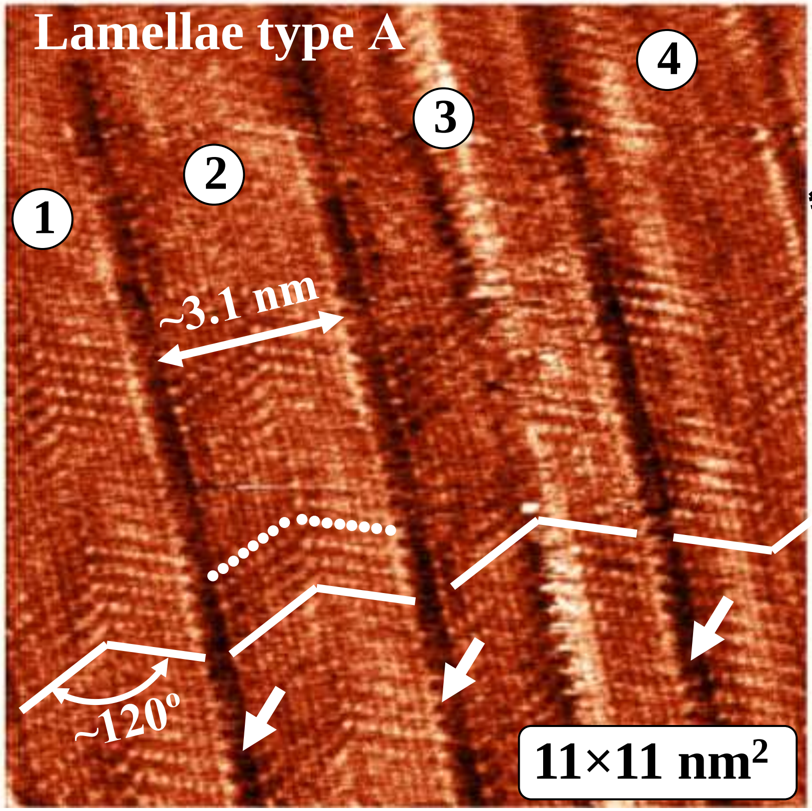


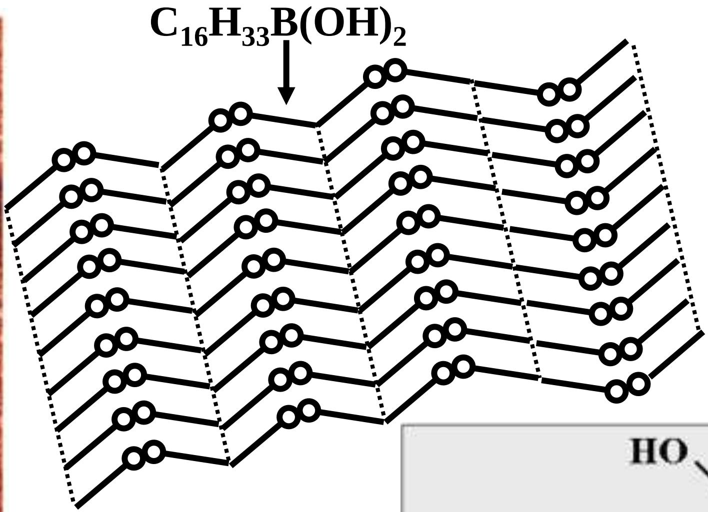
Monolayer of $C_{16}H_{33}B(OH)_2$ on graphite

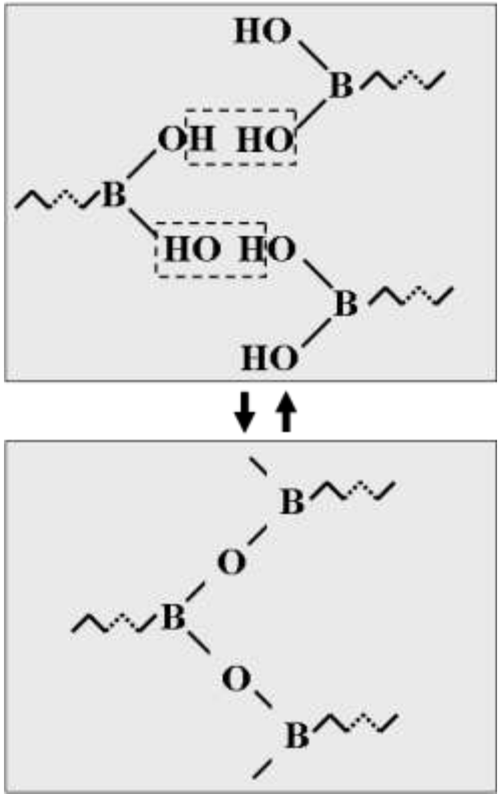




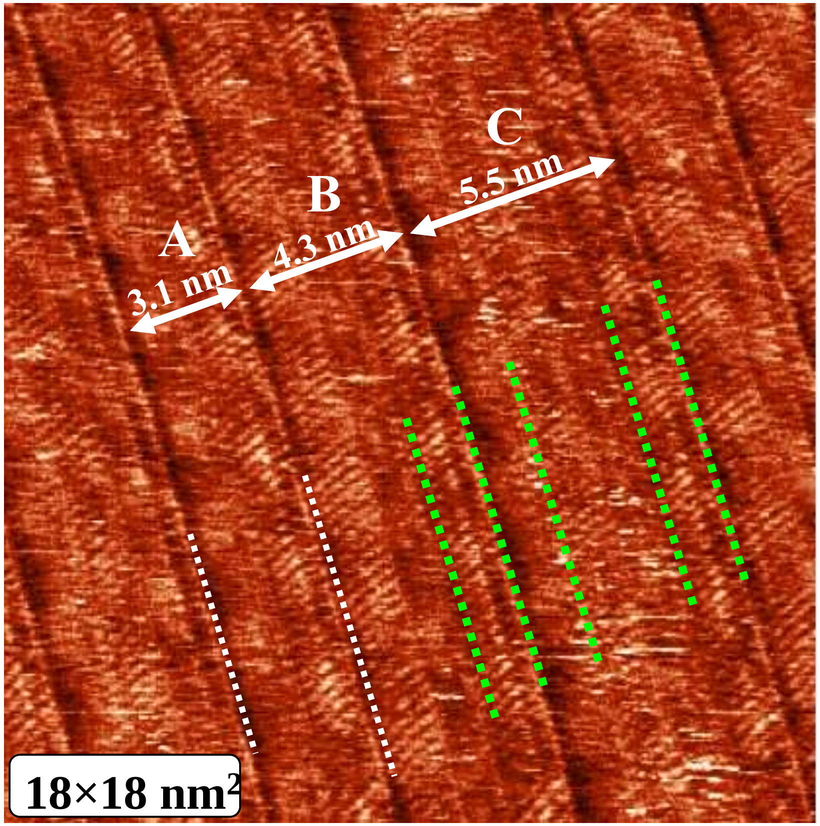
Monolayer of $C_{16}H_{33}B(OH)_2$ on graphite

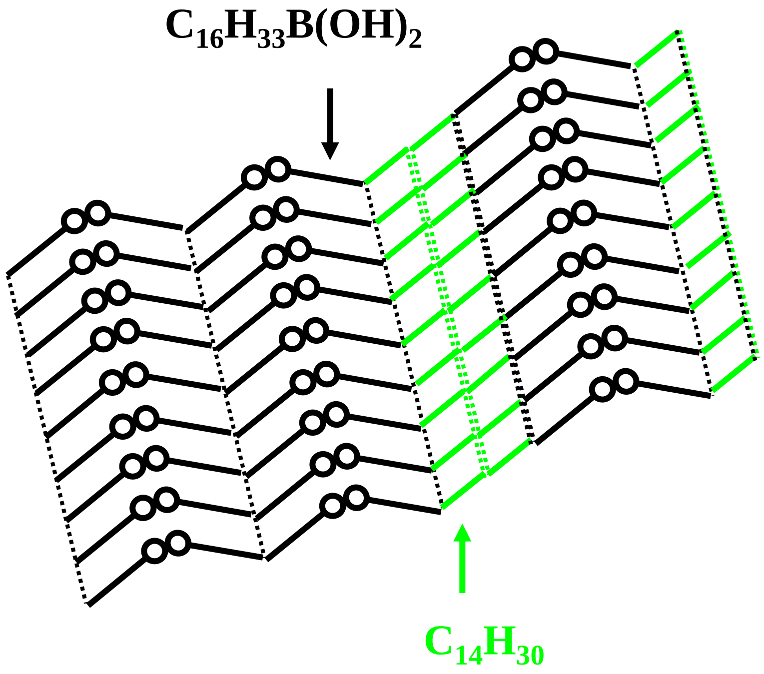






Monolayer of $C_{16}H_{33}B(OH)_2$ on graphite





Conclusions

- highly ordered lamella like monolayers of arachidic acid were obtained on graphite by the deposition from n-tetradecane. Lamellas are composed by dimers. Association of molecules in the dimers is due to interaction between COOH-groups (in contrast to n-alkane monolayers, for which dimmerisation was never observed).

Conclusions

- highly ordered monolayers of boron acid were obtained on graphite by the deposition from n-tetradecane. Monolayers are formed by dimers ($B(OH)_2$-groups are responsible for association of molecules within the dimers).
- molecules of solvent n-$C_{14}H_{30}$ can be coadsorbed with molecules of acid at temperature significantly higher than the monolayer melting point of n-tetradecane on graphite.

Perspectives

1) Templating of atomically flat surfaces by functionalized aliphatic compounds

2) Surface modification of Au-nanocrystals ("nanoprisms") for incorporation in biological cells

3) Control of plasmon resonance in Au-nanocrystals (by adsorbed monolayers)

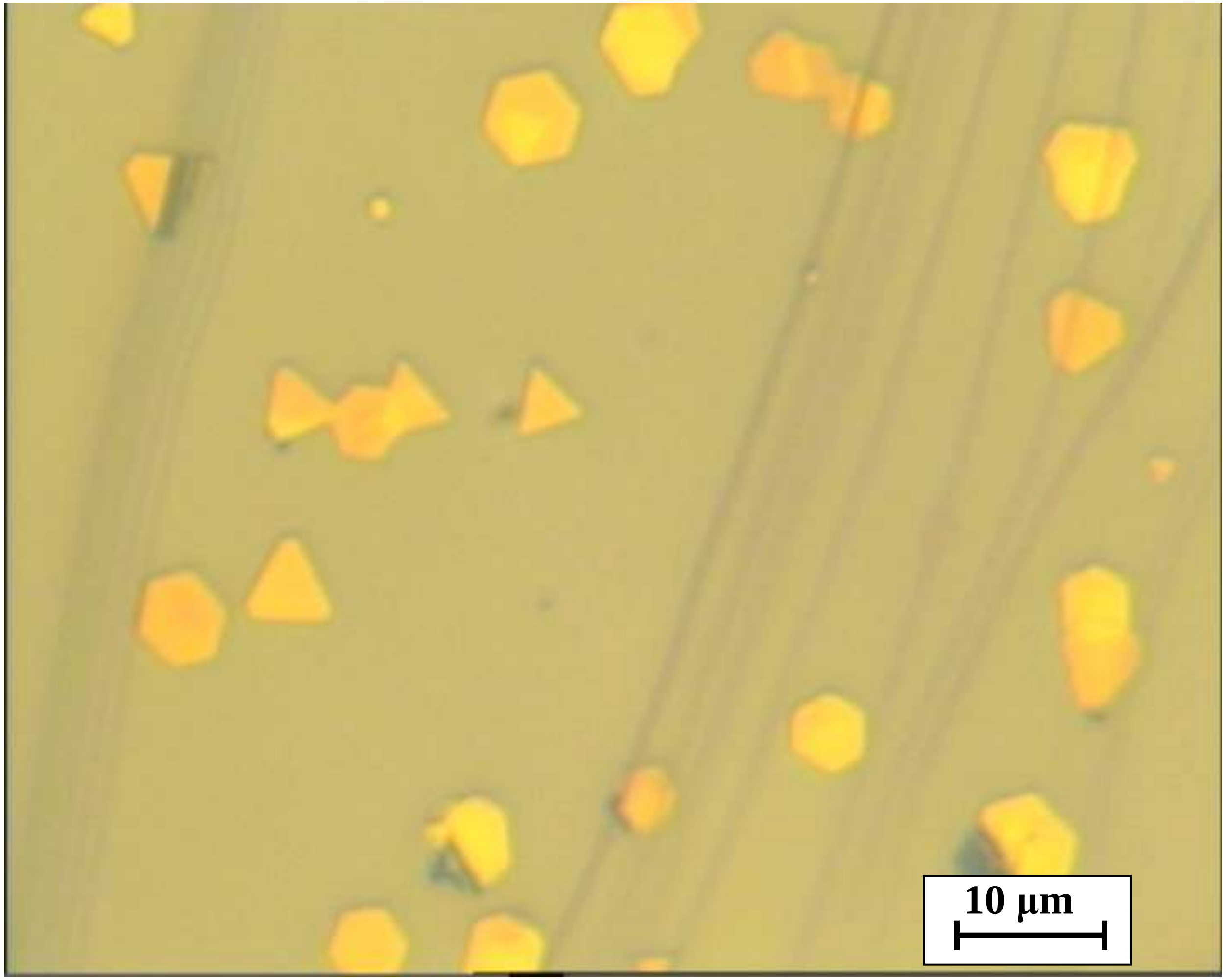
4) Control of lateral conductivity in organic monolayers (realization of field transistor effect)

Growth of Au nanoprisms

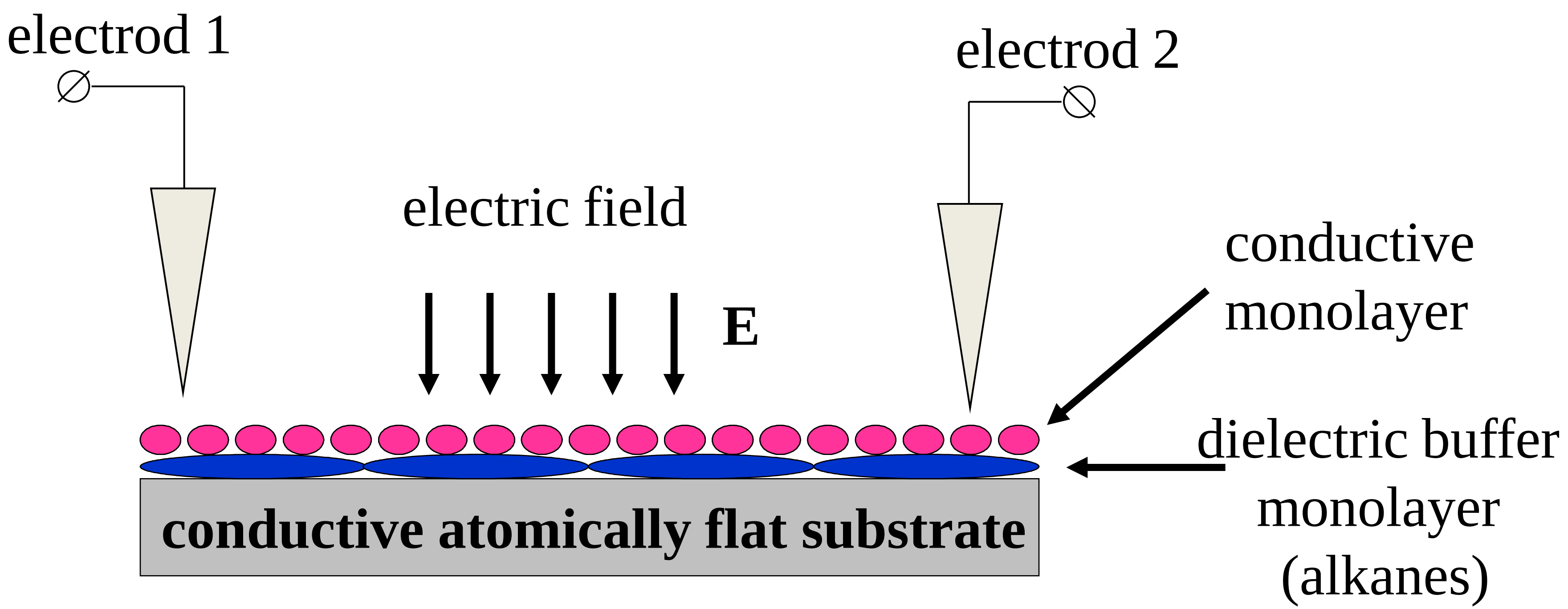
In collaboration with

Dr. Estrella-Llopis and T. Borodinova

Institute of biocolloidal chemistry (Kiev, Ukraine)



Control of lateral coonducivity in organic monolayers
(field transistor effect)



Problems: - contacts

- creation of long range ordered structure

Acknowledgements

O. Varzatskiy

Vernadsky Institute of General and Inorganic Chemistry NAS of Ukraine

for synthesis of hexadecyl boron acid

Department of Physics and Astronomy of NAS of Ukraine for financial support

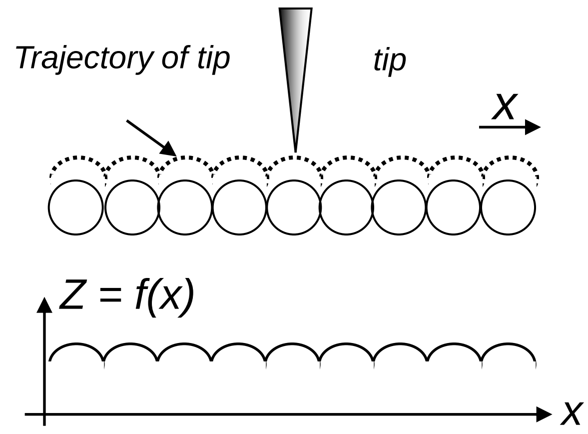
Thank you!

The operating regimes of STM

a)

Constant current mode

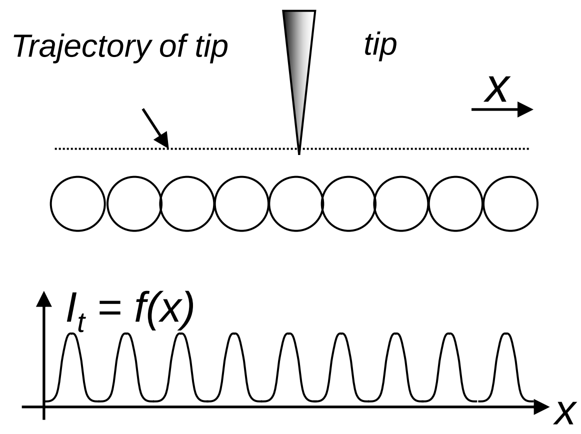
I_t =const, $Z = f(x)$



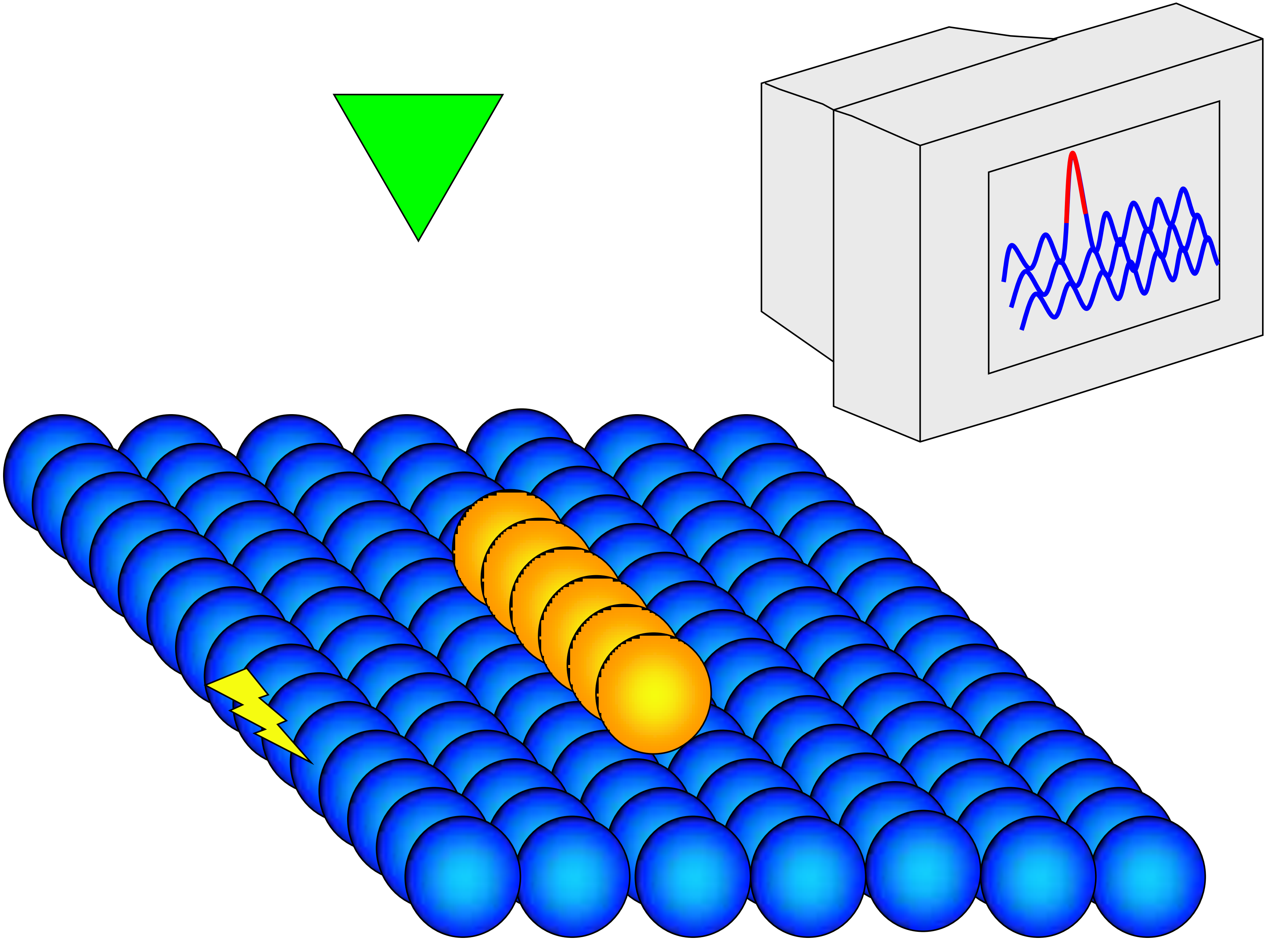
b)

Constant hight mode

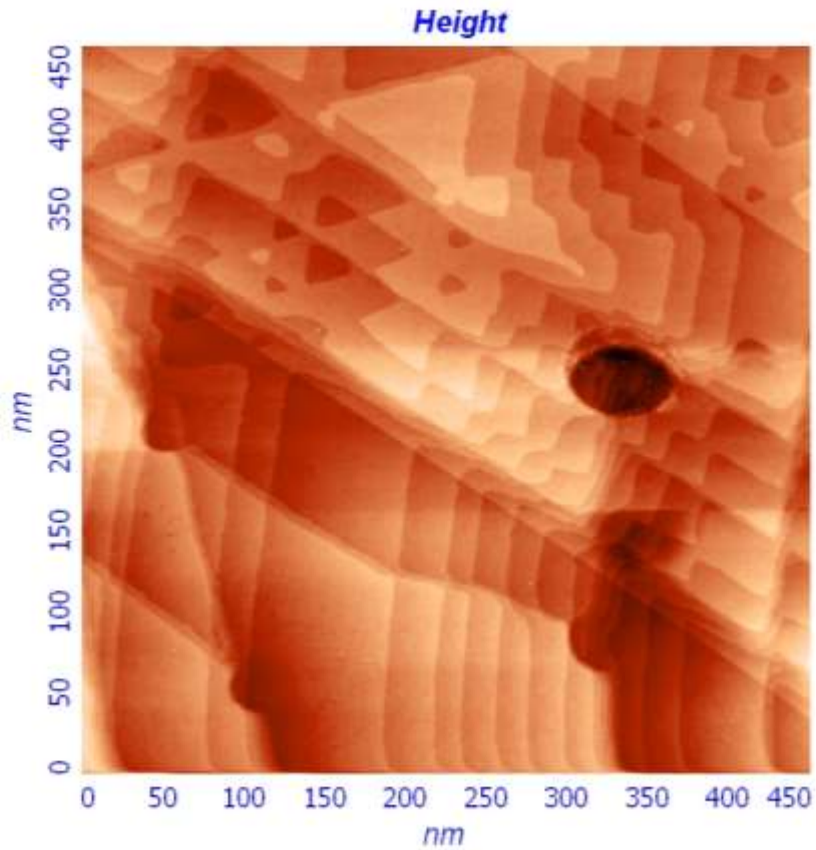
Z = const, $I_t = f(x)$

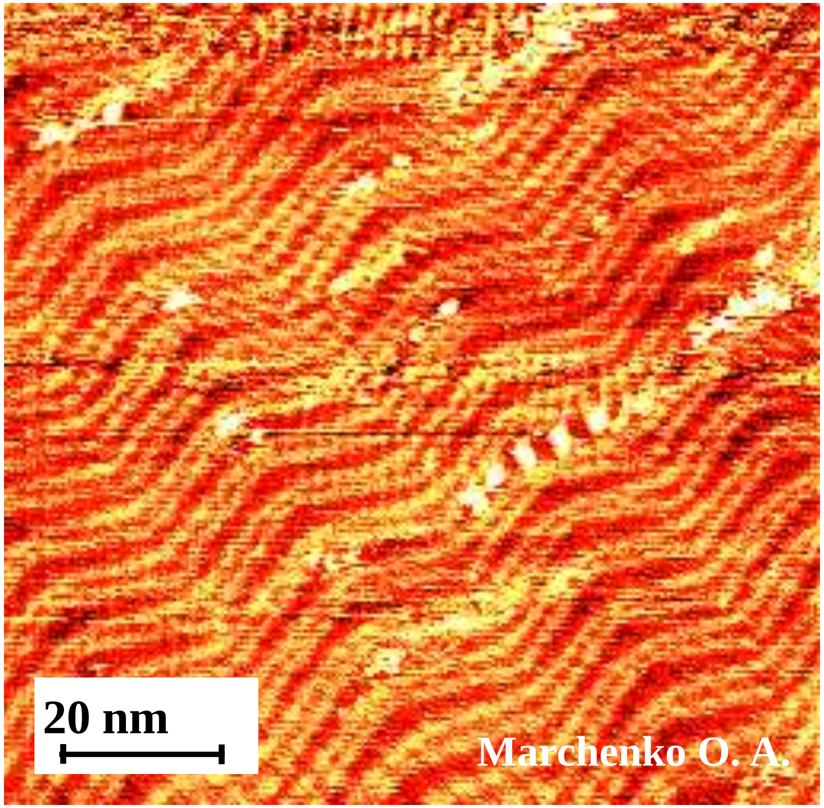


The mechanism of the STM

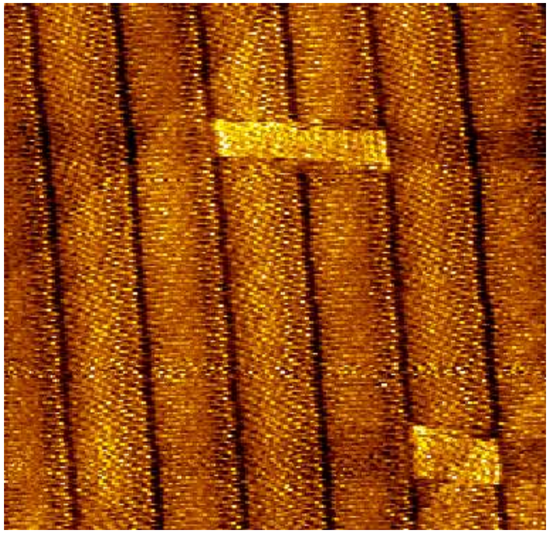


Reconstruction of Au(111) substrate

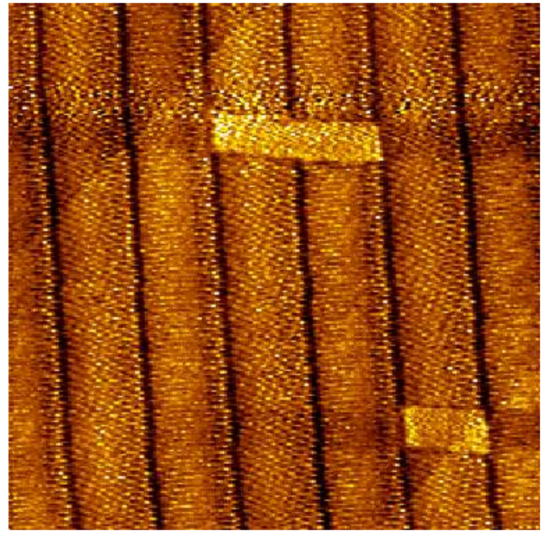




A Diffusion of “magic”-clusters



509 ◄-13, 10► 63×63 nm^2



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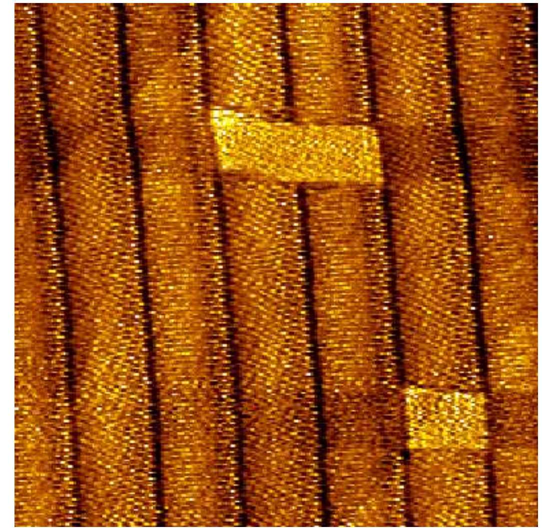

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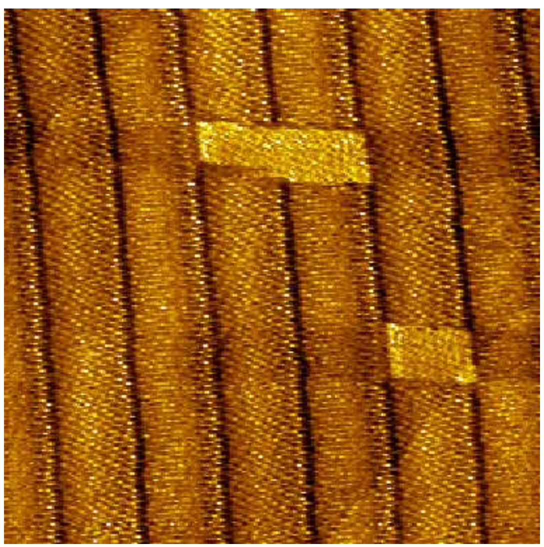

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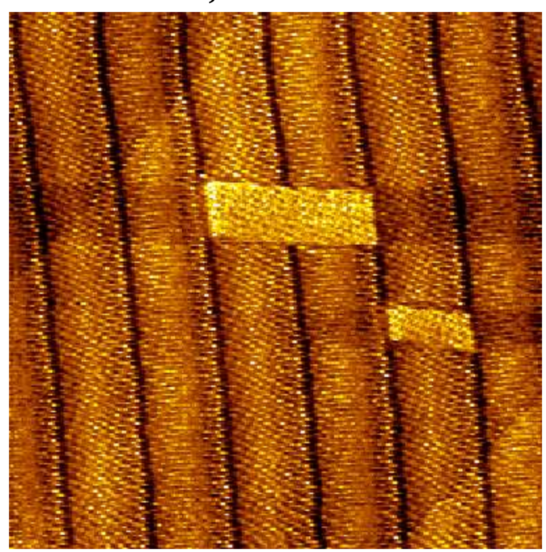
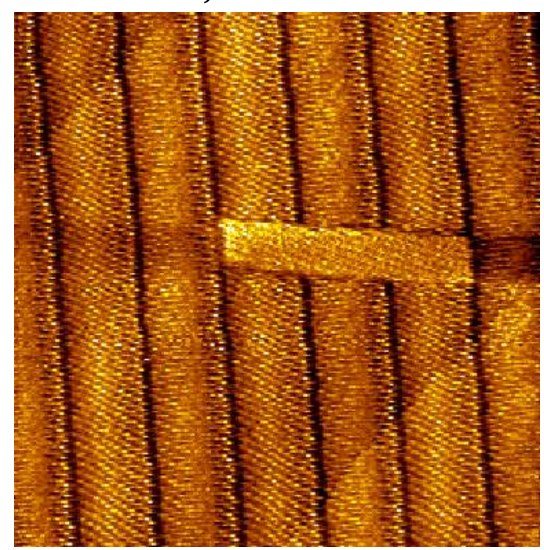
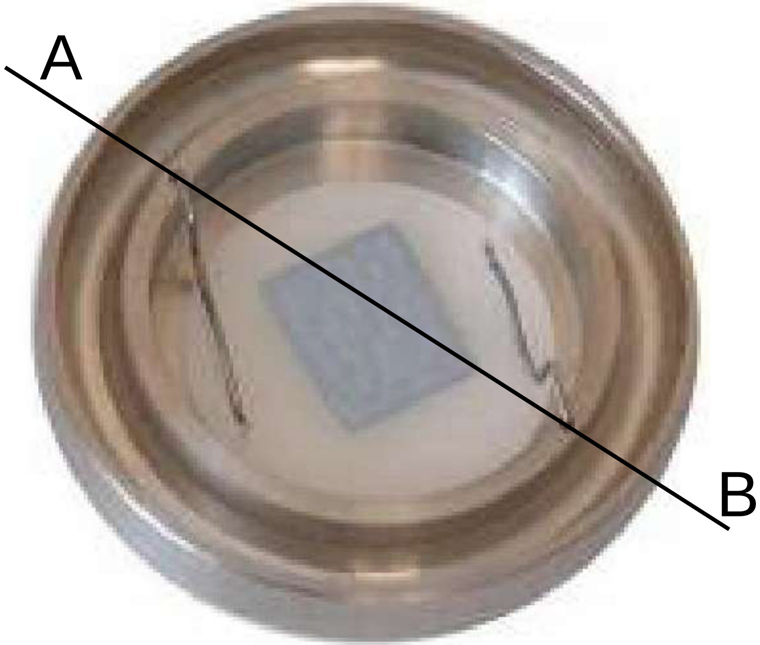


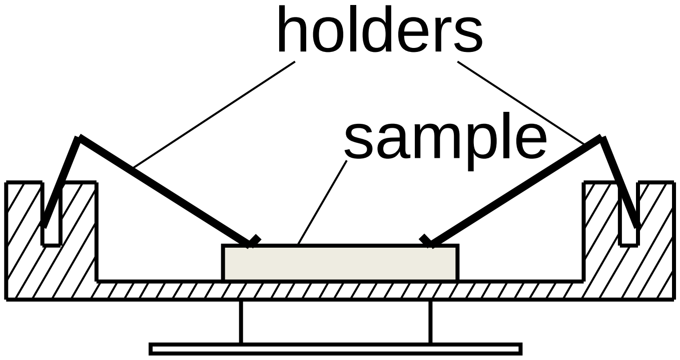
529 ◄-13, 10► 63×63 nm^2



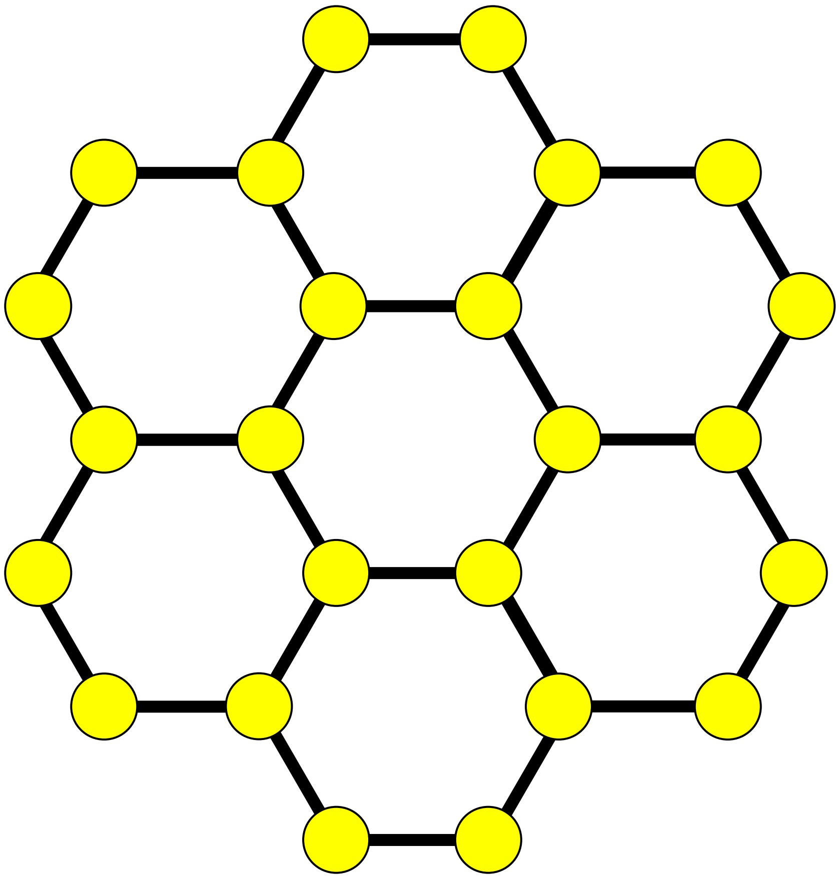
538 ◄-13,10► 63×63 nm^2

Liquid cell



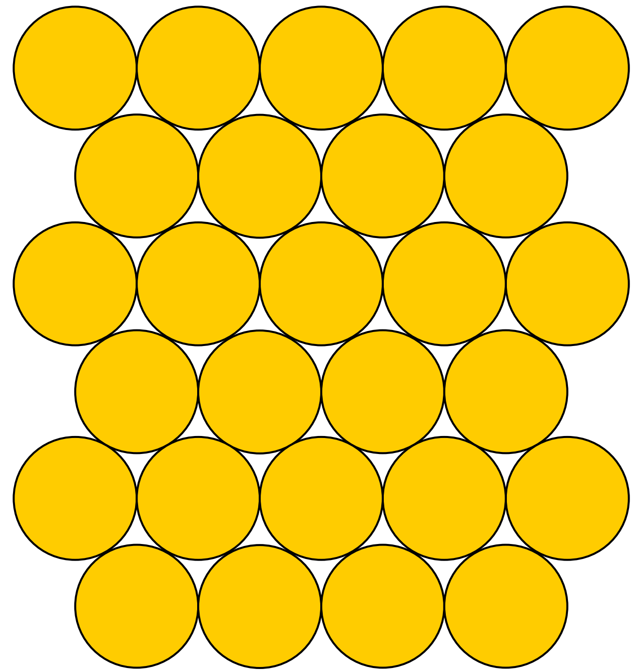


Highly Oriented Pirolitic Graphite



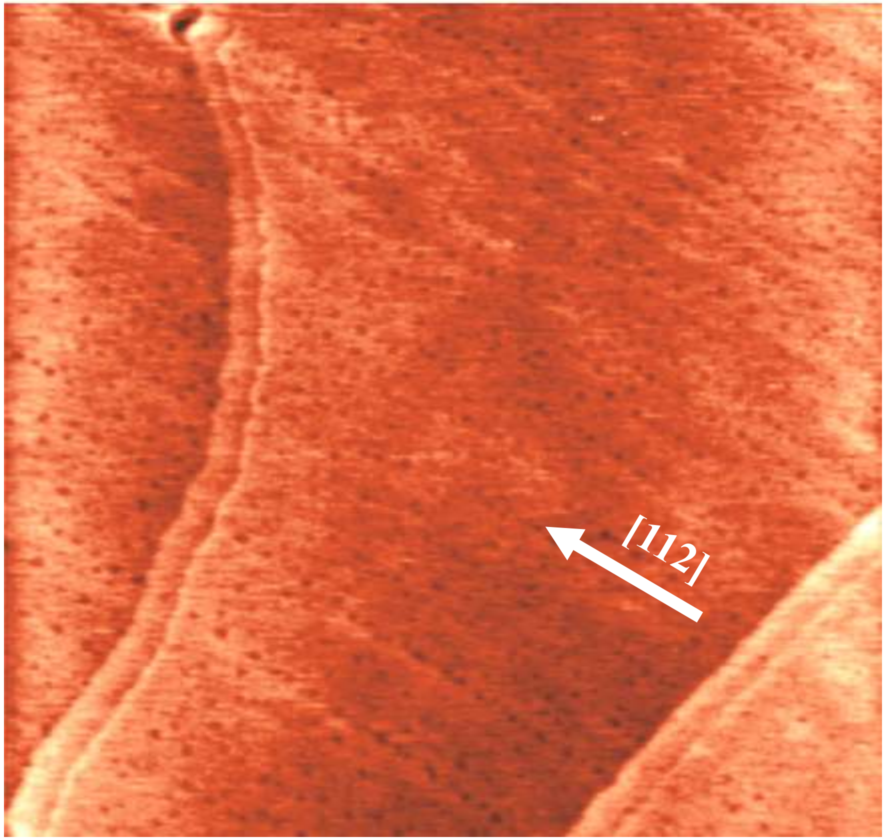
Honeycomb packing

Au (111)

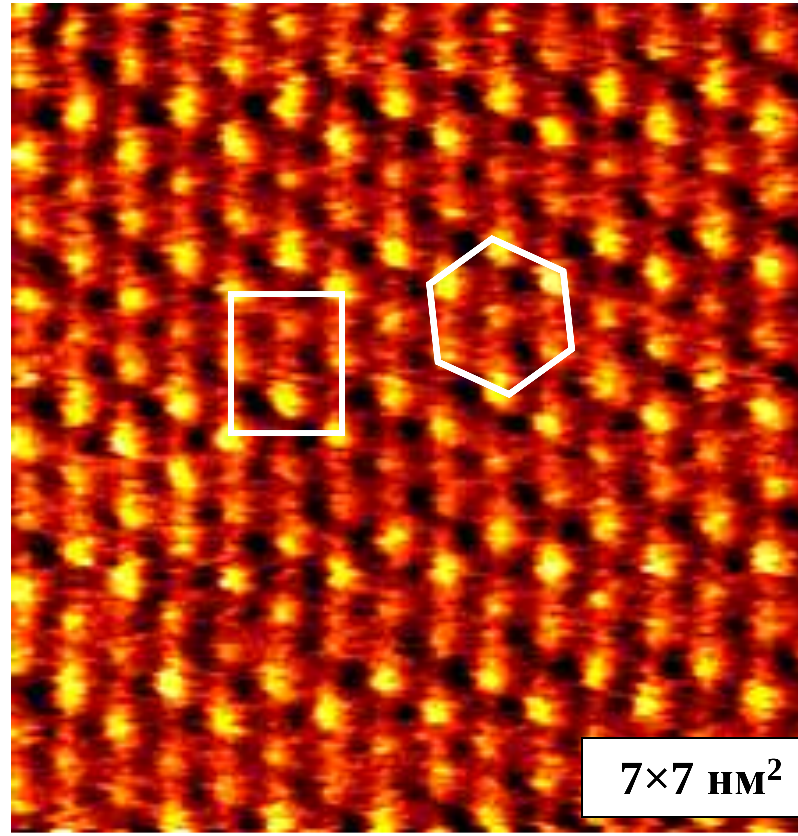


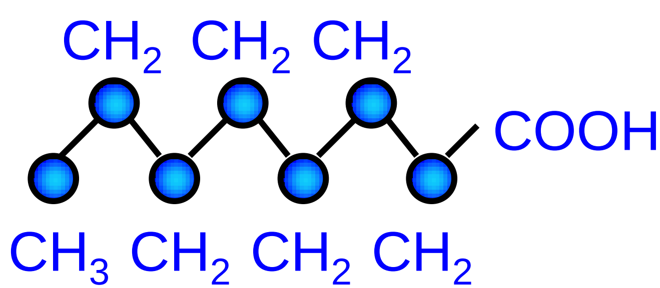
Densely packing

Monolayer of n-octane acid $C_8H_{16}O_2$ on Au(111)



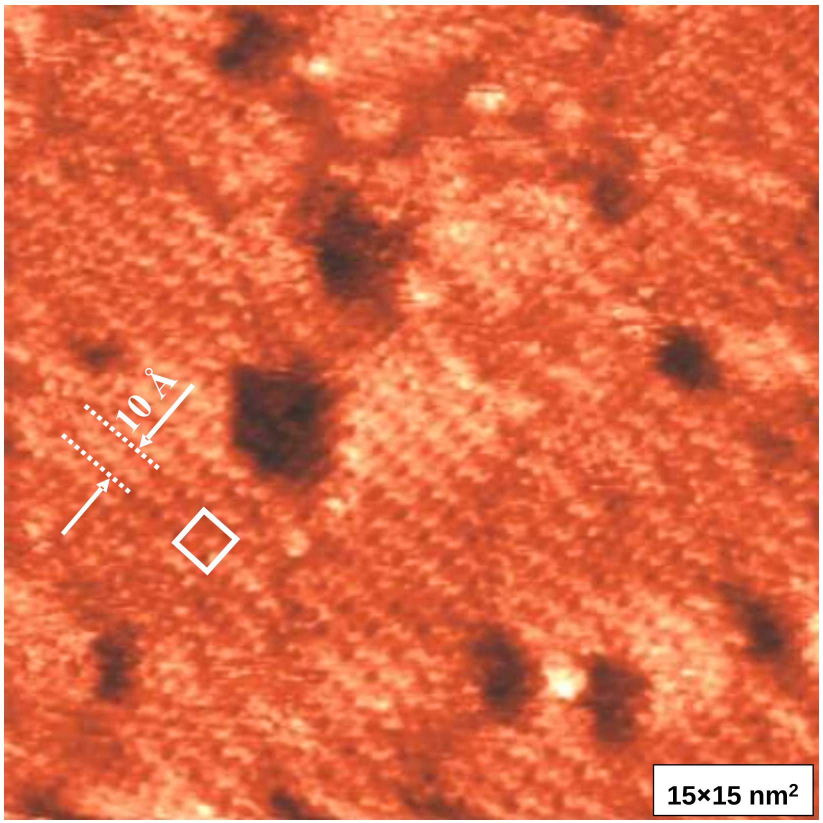
180×180 nm^2, I_t= 0,4 nA, U_t= 0,6 V

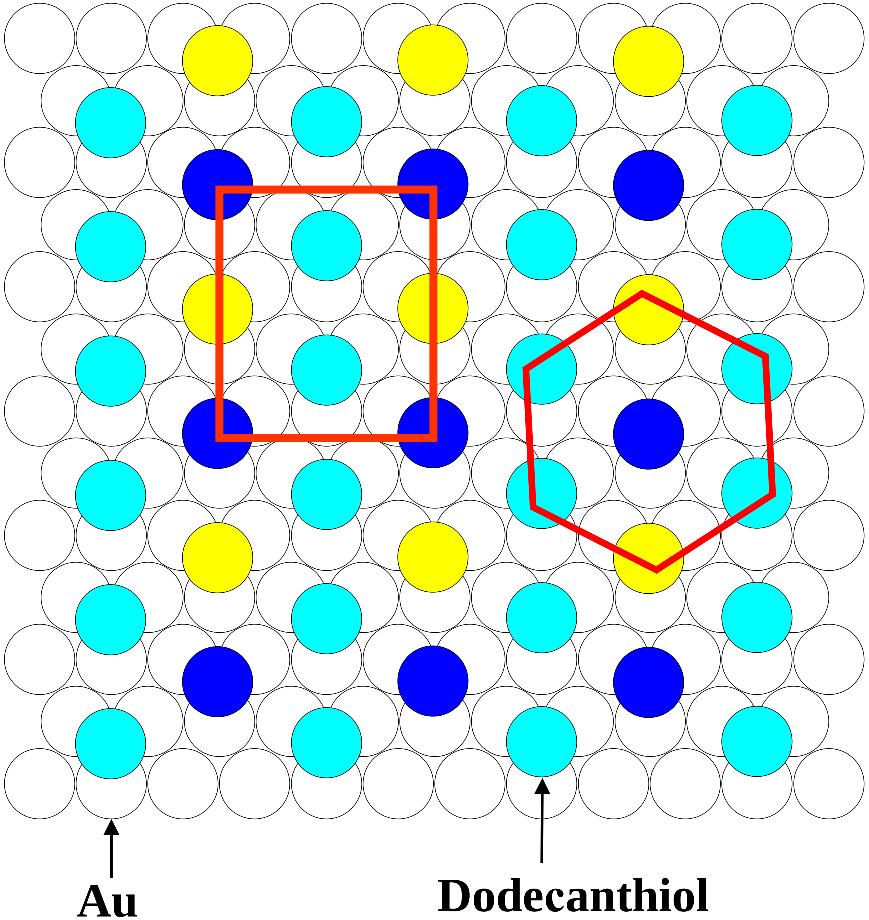


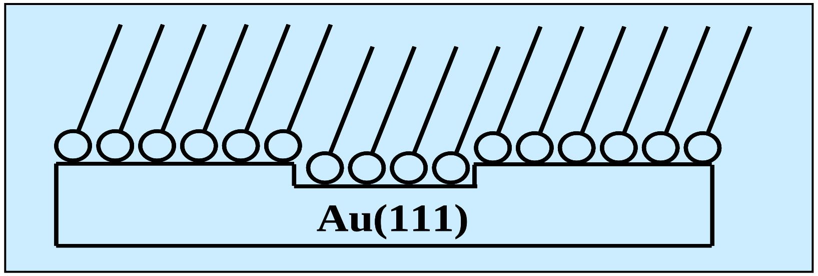


Monolayer of Dodecanthiol $C_{12}H_{25}SH$ on Au(111)

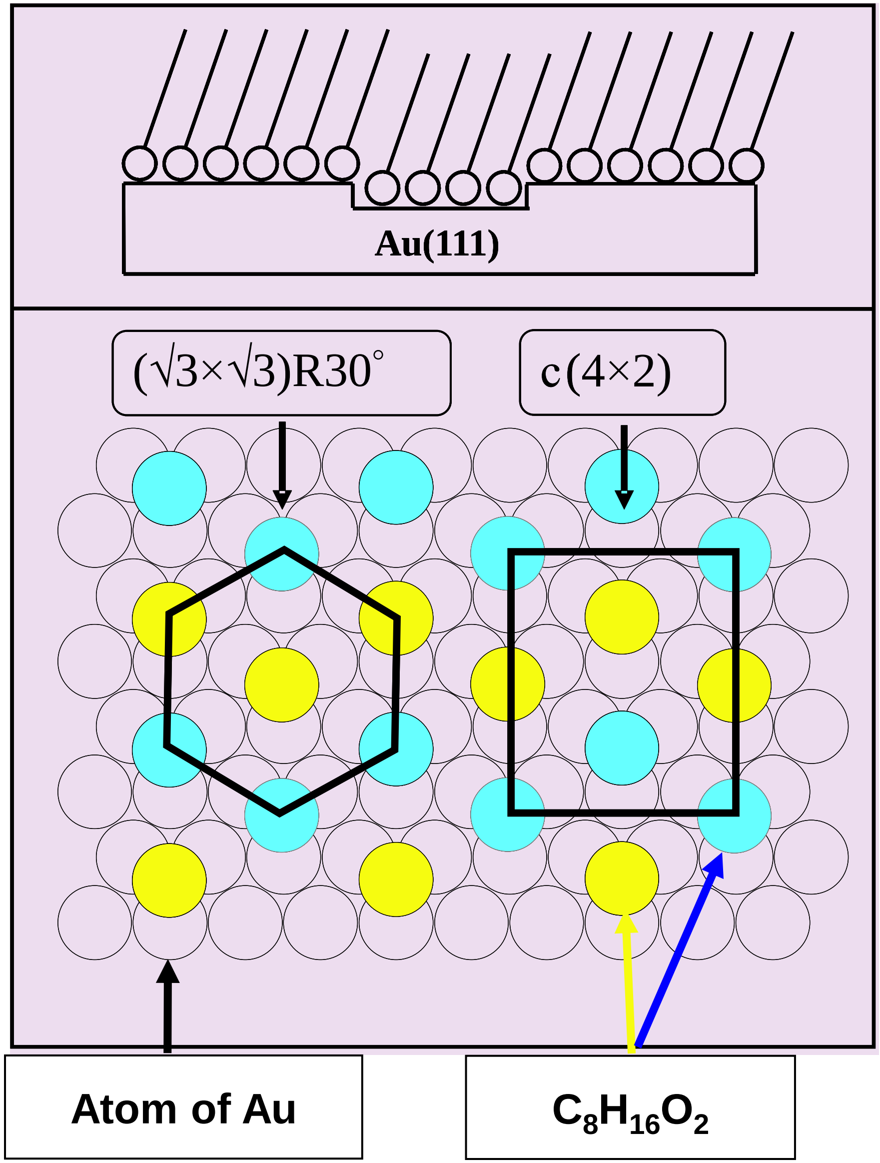
Packing (√3×√3)R30º,
superstructure c(4×2)



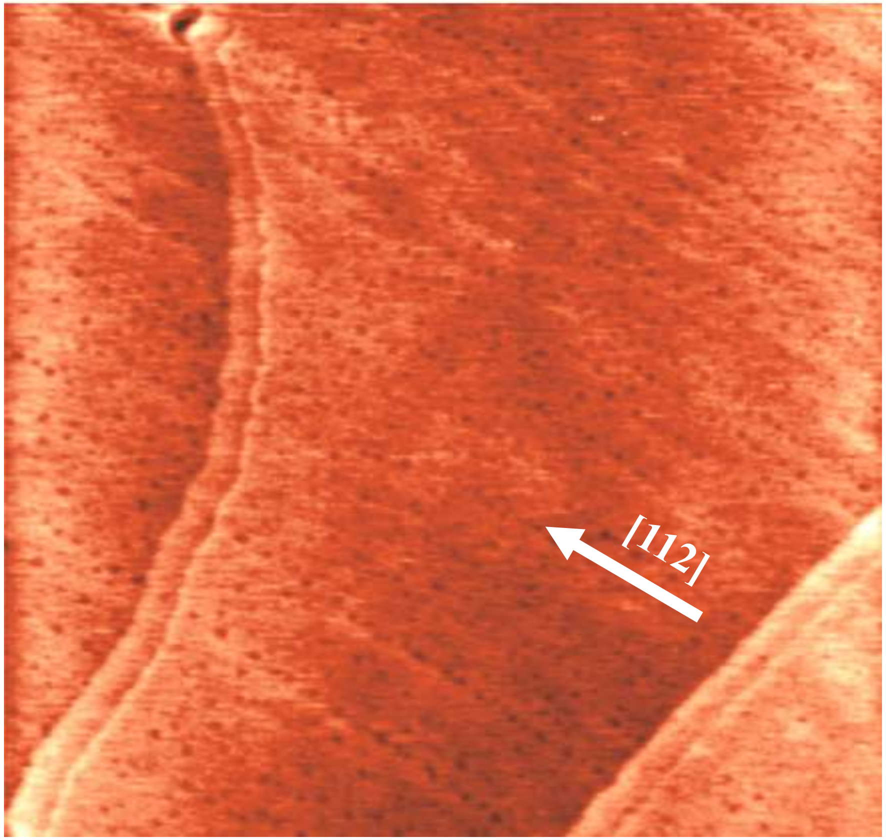




Packing $(\sqrt{3}\times\sqrt{3})R30^{o}$, superstructure $c(4\times2)$ of n-octane acid $C_8H_{16}O_2$ on Au(111)



Monolayer of n-octane acid $C_8H_{16}O_2$ on Au(111)



180×180 nm^2, I_t= 0,4 nA, U_t= 0,6 V