$Mo(CO)_6$ monolayer adsorption and decomposition on Cu(111) studied by STM

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Valpré (Écully), 2011

Outline

Introduction

- Mo-CO chemical bonds, decomposition; Applications in nanotechnology

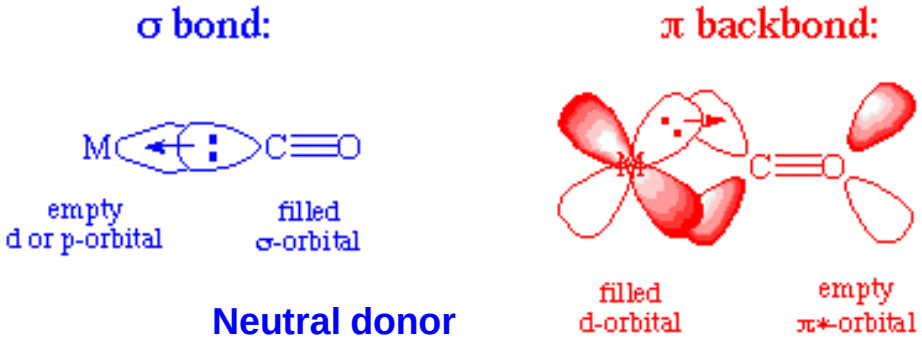
$Mo(CO)_6$ monolayer adsorption on Cu(111)

- Structure interpretation, DFT calculation

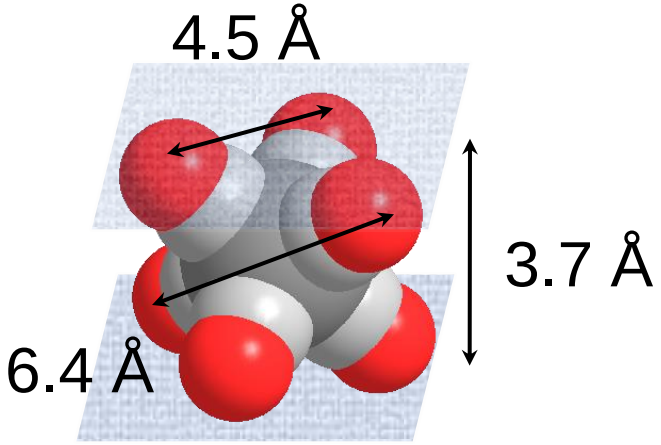
$Mo(CO)_6$ monolayer decomposition

Conclusions

$Mo(CO)_6$ single molecule



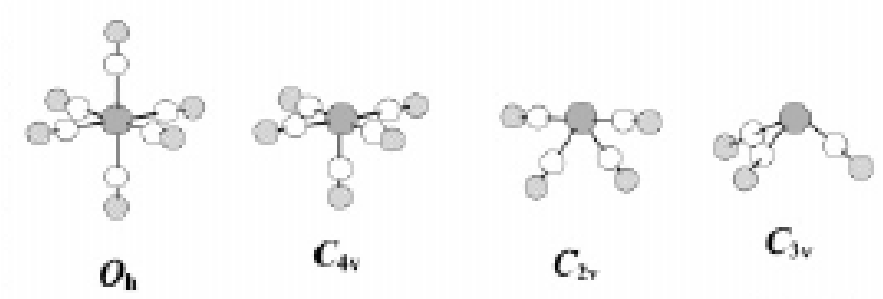
Neutral donor



Mo-C-O 3.2Å

Calculated bond dissociation enthalpies on Mo(CO)*n* (*n* = 6, 5, 4, and 3)

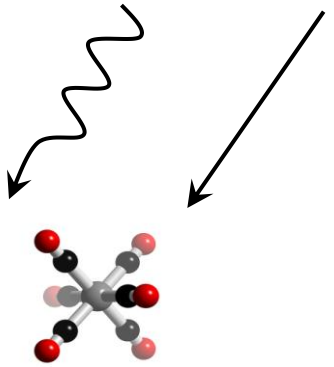
≈1.4 eV/CO



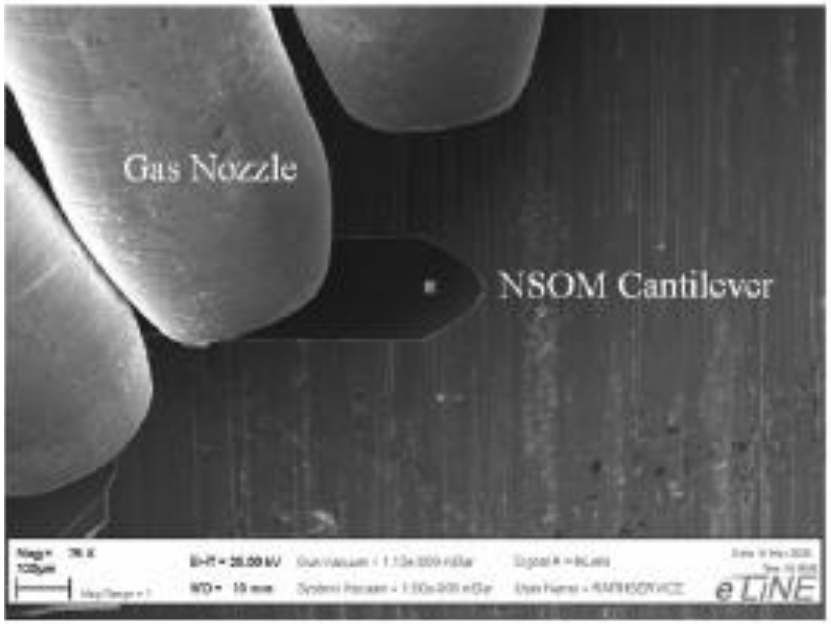
Y.Ishikawa, K.Kawakami,
J. Phys. Chem. A 111 (2007) 9940

Decomposition

hv (UV) **-e**

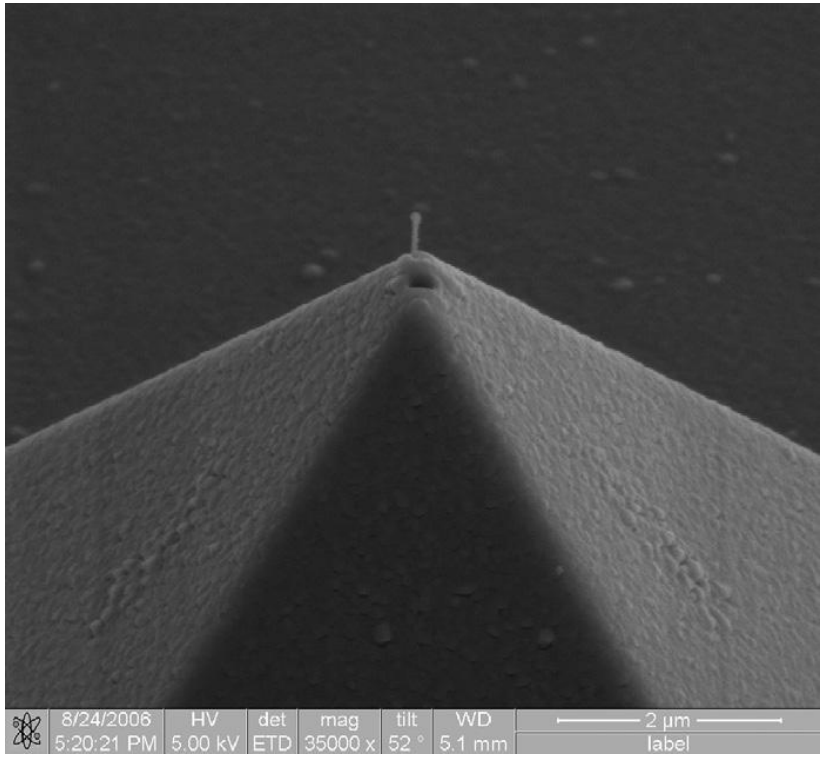


tip-on-aperture SNOM



Parameters for the electron beam-induced deposition process

Parameters	Experimental cond
Precursor gas	$W(CO)_6$
Reservoir temperature	65 °C
Capillary temperature	75 °C
Base pressure	1.3×10^{-6} mbar
Process pressure (global)	4.6×10^{-6} mbar
Acceleration voltage	20 kV
Beam current	257 pA
Dwell time per point	1000 μs
Repeat of e-beam irradiation	$N = 2, 4, 6$

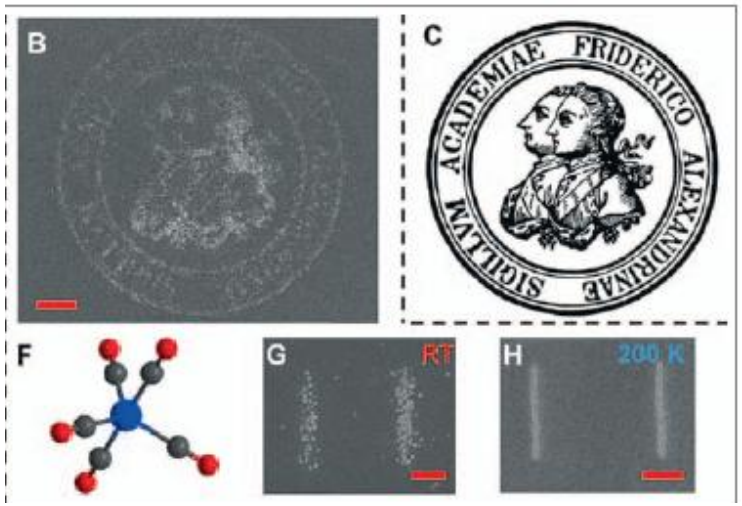


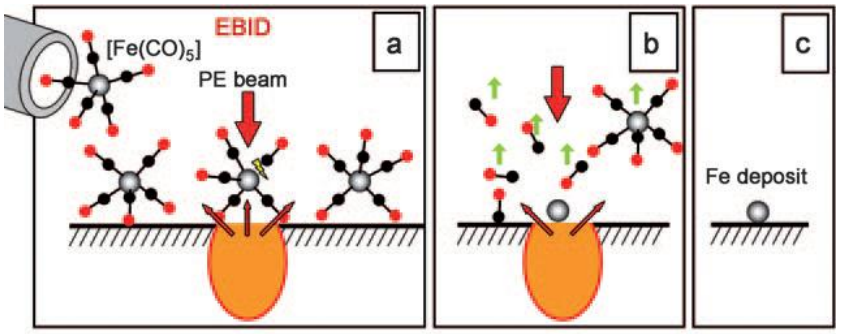
(AFM+SNOM)

W.-S. Chang et al.
***Ultramicroscopy* 108 (2008) 1070–1075**

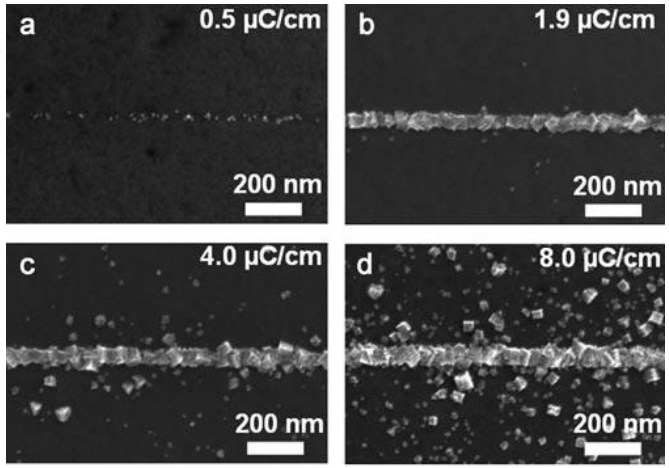
Nanolithography

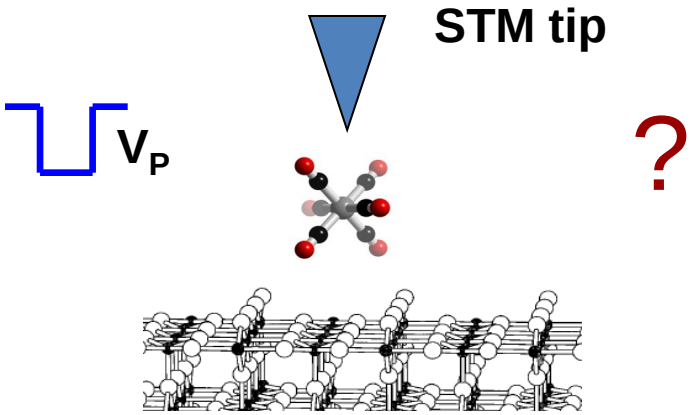
Direct Writing with an Electron-Beam in UHV





T.Lukasczyk, M.Schirmer, M.-M.Walz, F.Vollnhals, H.-P.Steinrück and H. Marbach, *Omicron NanoTech. Newsletter,* Vol. 12 No. 2, 2008





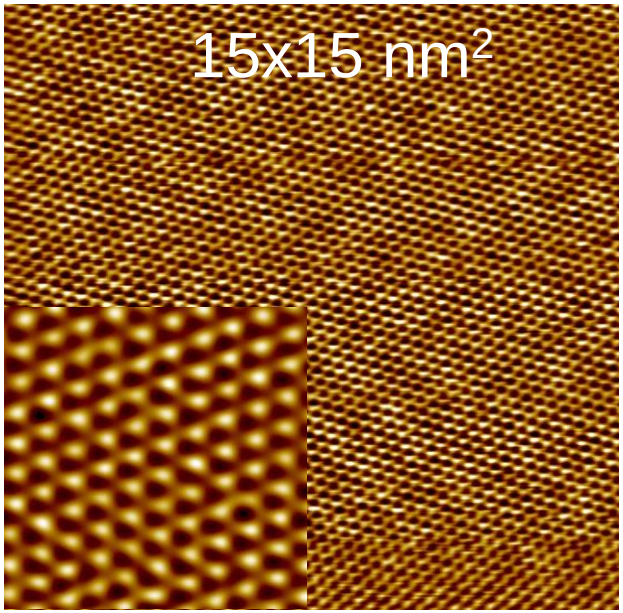
***Angew. Chem. Int. Ed.* 2010, 49,** 4669 –4673

Experimental details

VT STM Omicron Nanotechnology
UHV base pressure 1x10^{-10} mbar
LN cooling system 150÷800 K

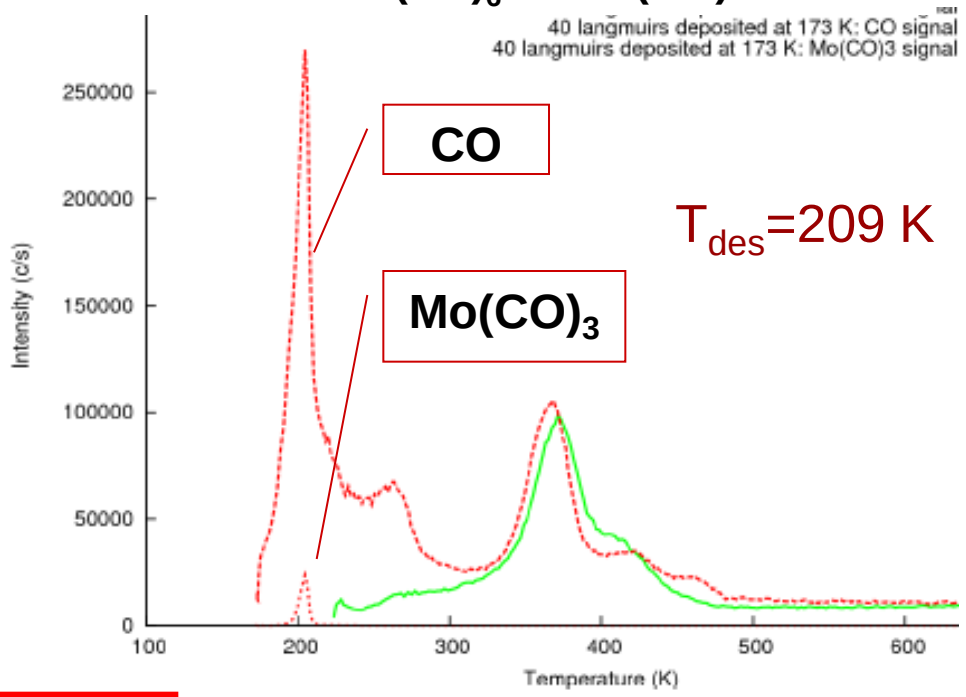
$Mo(CO)_6$ gas by powder evaporation at RT

Cu(111), a=2.55 Å



2.2x2.2 nm²

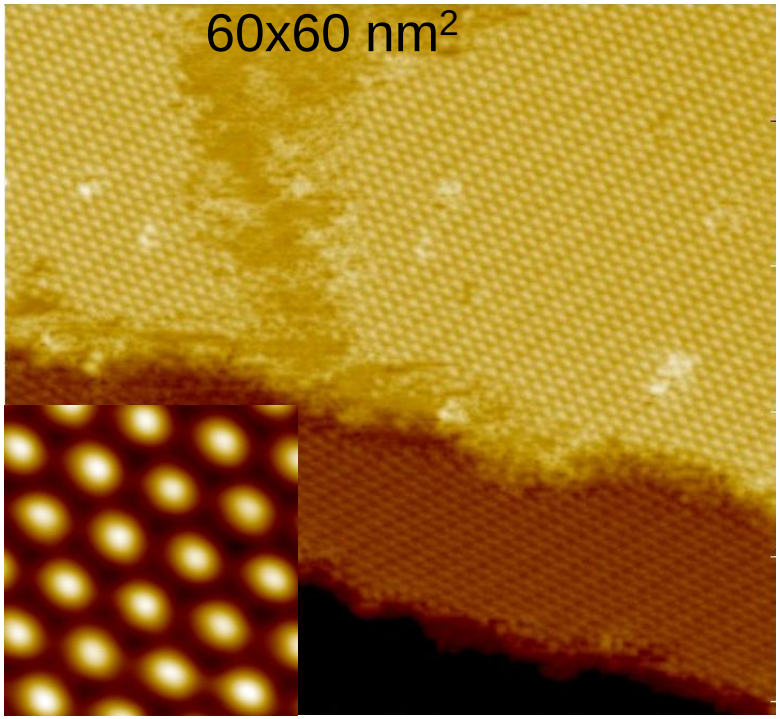
Temperature Programmed Desorption $Mo(CO)_6$ on Cu(111)



T=160 K

$Mo(CO)_6$ monolayer on Cu(111)

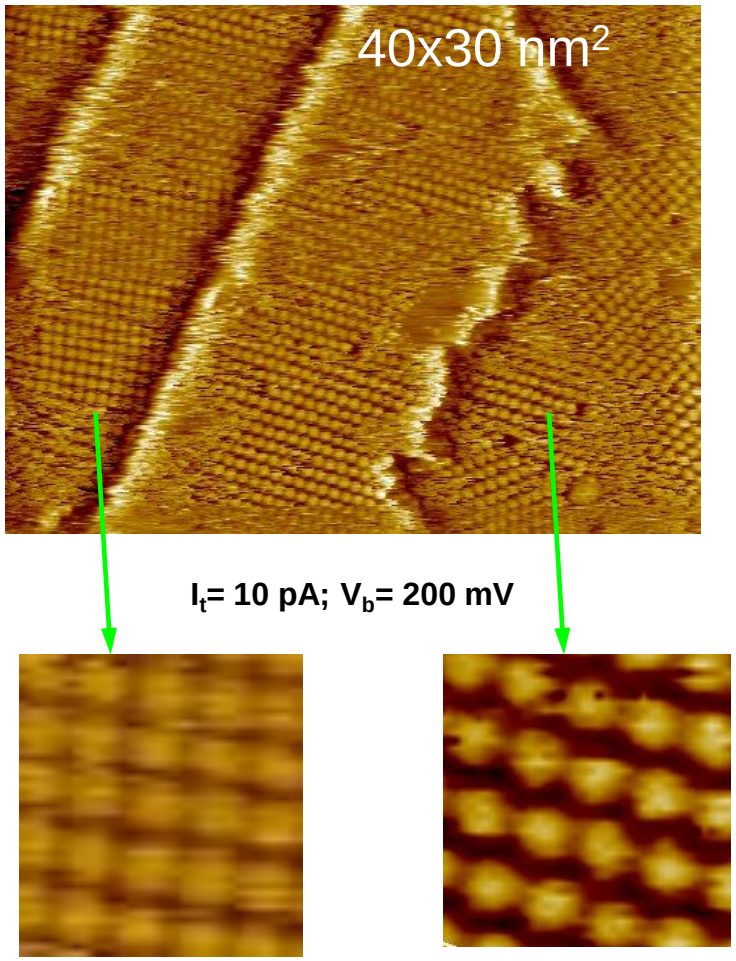
Exposition: 1-2 L



I_t= 5 pA; V_b= 20 mV

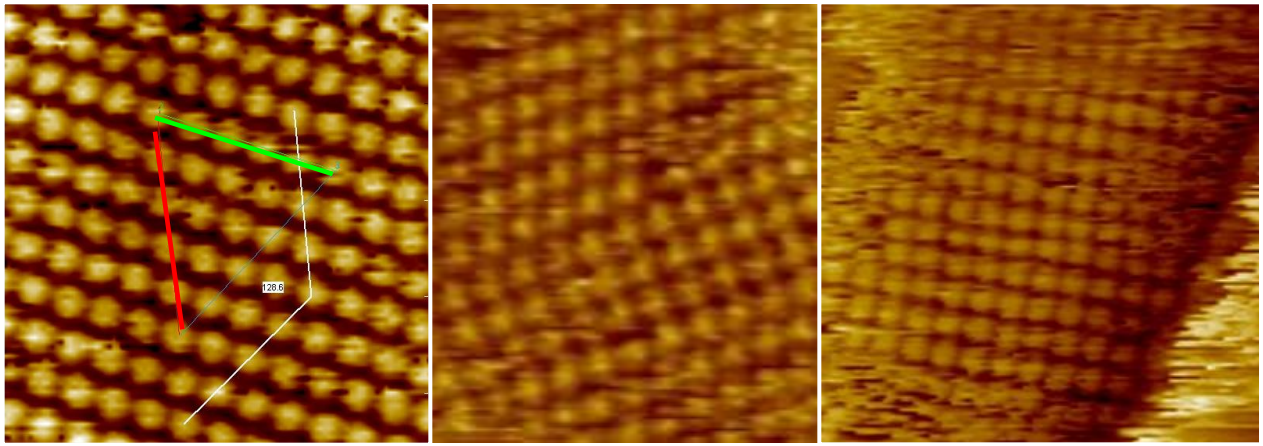
Apparent height ~ 0.6÷0.8 Å ;
Corrugation of ML ~ 0.4 Å

5-10 L



Cu(111) + CO interface

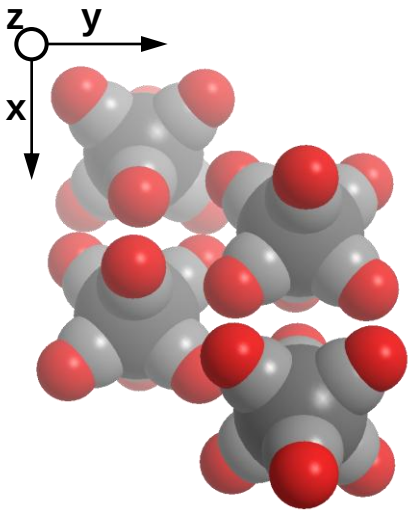
$Mo(CO)_6$ monolayer on Cu(111) (CO)



Hex-like : green 6.8 Å (±0.1)
red 7.4 Å (±0.1)

square-like : 6.8 Å (±0.1)

Bulk: Oh; P_{nma}

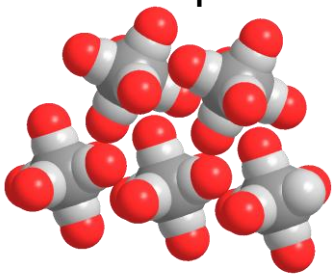


[2-10]
a=7.20; b=6.49 Å; φ=63.2

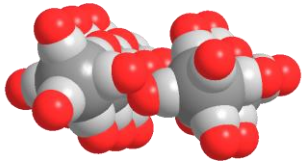
[210]
a=6.53; b=6.49 Å; φ=82.7

x=12.019; y=11.415; z=6.488 Å; N=4.

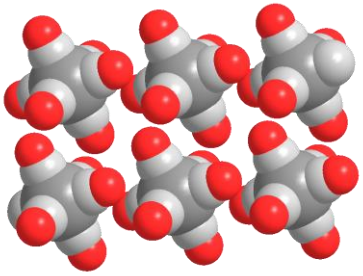
top



side



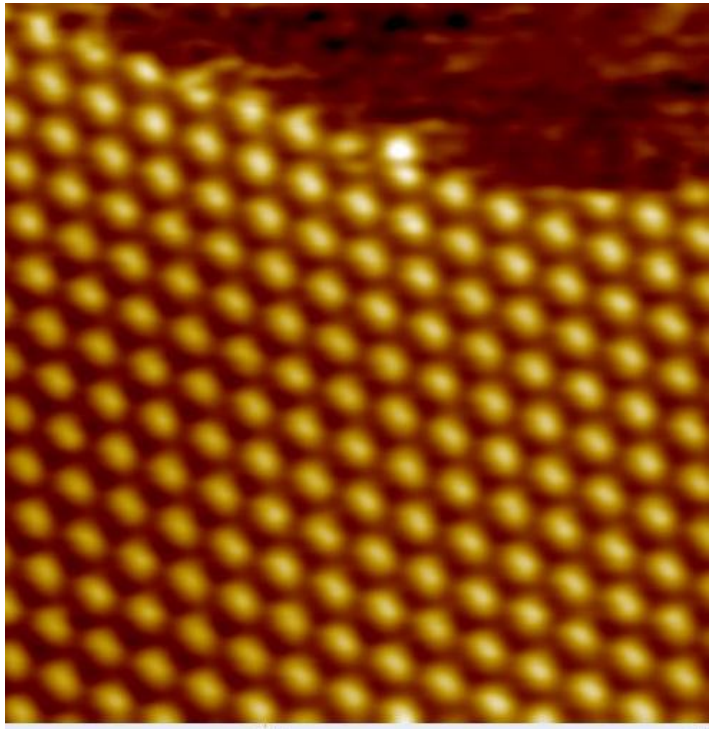
top



T.C.W.Mak,
Zeitschrift für Kristallographie
166 (1984) 277-281

Arrangement is guided by forces between molecules

$Mo(CO)_6$ monolayer on Cu(111)



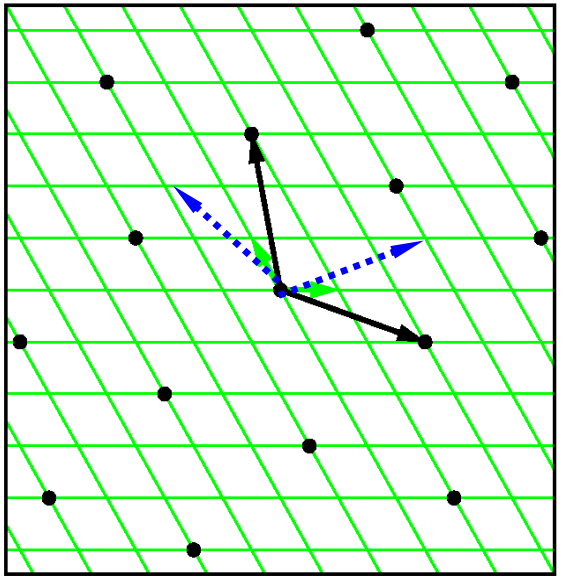
8x8 nm^2; I_t= 10 pA; V_b= 20 mV

Hexagonal a=6.8 Å (±0.1)

Cu(111)+(√7x√7)R19 $Mo(CO)_6$

Basic 2D lattice/group : [14] Hexagonal p3m1
a = 2.55000, b = 2.55000, phi = 120.00
Superlattice/group : (None) Matrix = (2, -1 | 1, 3) [1]
a_s = 6.74667, b_s = 6.74667, phi_s = 120.00, 2 uni
Channel plate distortion = 0.0000

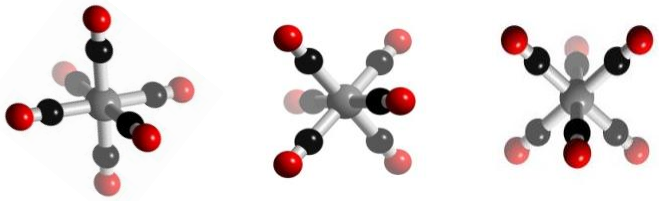
Real lattice



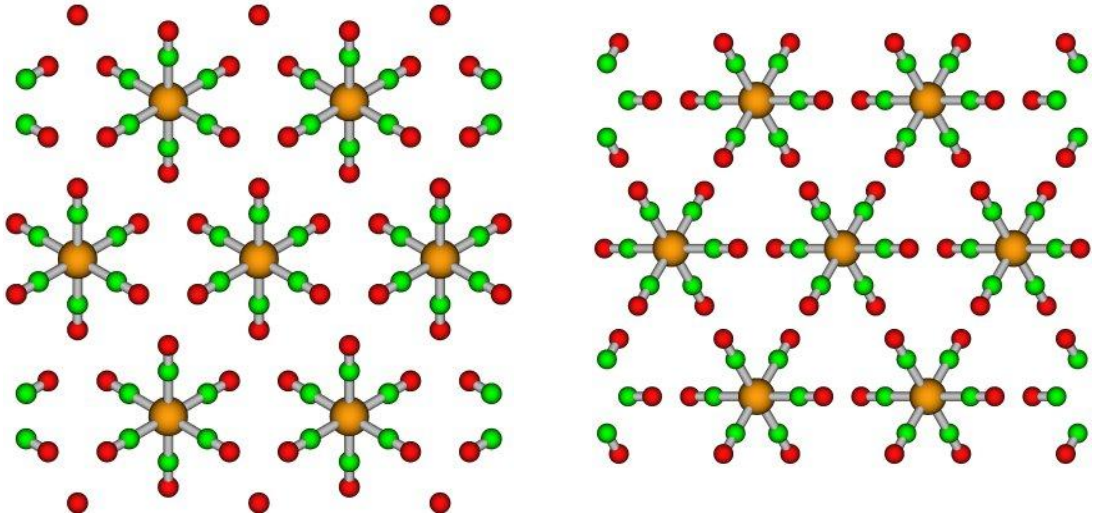
Nucleation site and molecule orientation ?

DFT calculations

Semiempirical GGA-type density functional constructed with a long-range dispersion correction (Van-der-Waals)

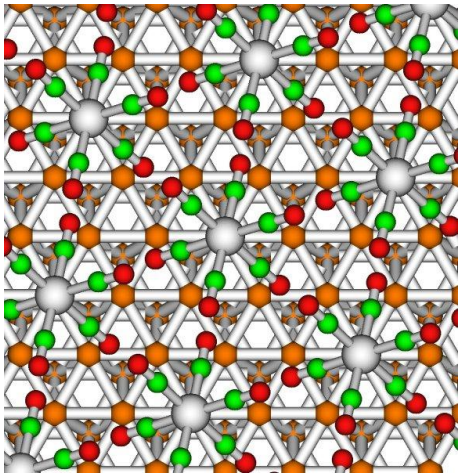


3-leg orientation



“short” O-O distances are avoided

Bulk $Mo(CO)_6$:
$E_{cohesive}$ = -0.58 eV/molecule



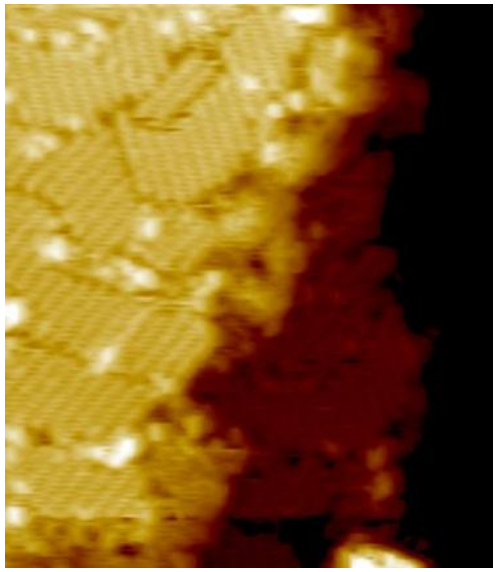
close packed (6.7Å)

on-top nucleation site

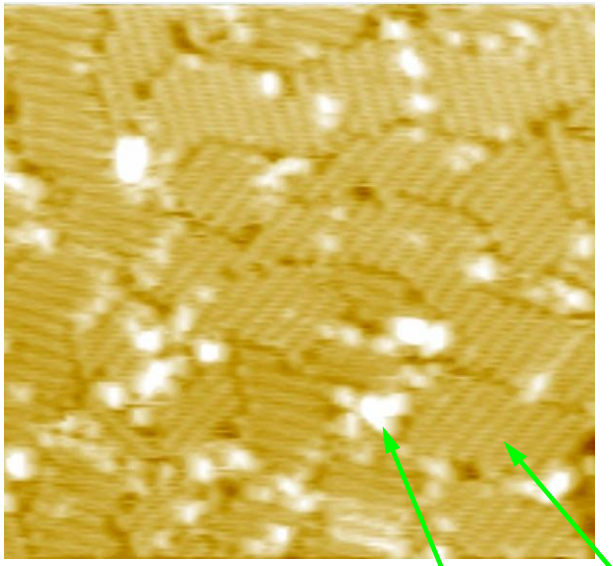
E_{ML} = -0.70 eV/molecule

Cu(111)+(√7x√7)R19 $Mo(CO)_6$ confirmed by calculation

$Mo(CO)_6$ monolayer decomposition only on Cu(111) !



I_t= 10 pA; V_b= 50 mV



Chemistry ?

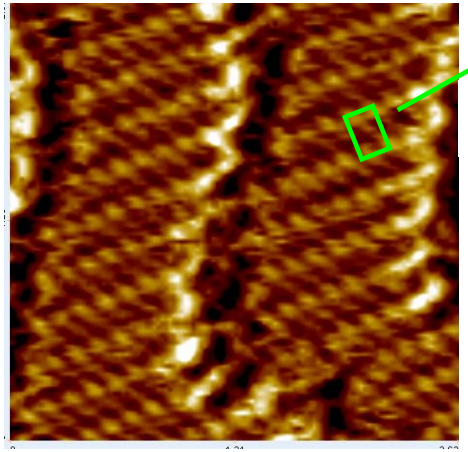
unstable dI/dV

Clusters area =10 %

(√7x√7)
1 ML coverage :
Mo atoms 14 %
CO molecules 86 %

Mo clusters

Adsorbed CO domaines



5x5 nm; I_t= 0.12 nA; V_b= 100 mV

2.6 x 4.4 Å²

Cu(111) (1x2)CO !

$$Mo(CO)_6 \xrightarrow[Cu(111)]{\text{STM tip}} Mo + CO$$

Conclusions

- **Monolayer adsorption of $Mo(CO)_6$ was studied by STM and DTF calculations**
- **STM tip generate decomposition of $Mo(CO)_6$ monolayer on Cu surface.**

Perspectives

- **Controlled decomposition conditions; nanostructures**
- **Scanning tunneling spectroscopy**
- **Multi layers growth**

Acknowledgements

Pierre Pauffert ***PhD Student, Université de Bourgogne, Dijon***

ANR Project :
"Electronic **L**ithography through **S**elf **A**ssembly"

$Mo(CO)_6$ monolayer on Cu(111)