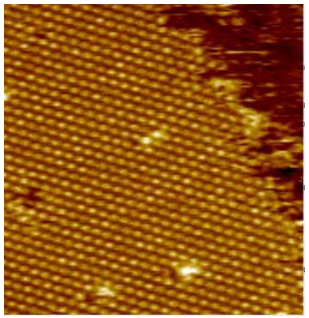
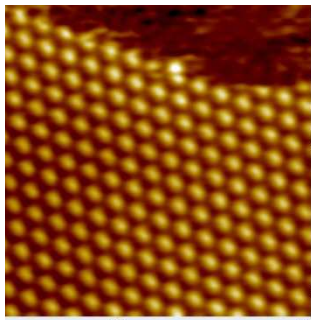
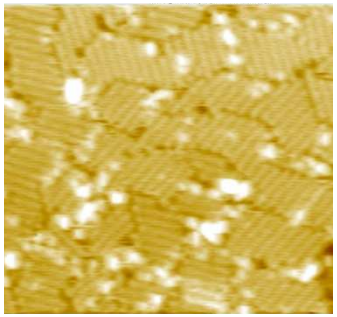
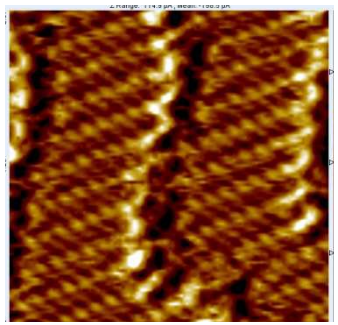
Hexacarbonyl de Molybdène adsorption et décomposition étudiée par TPD, XPS et STM

Mikhail Petukhov

ICB, Université Bourgogne Franche-Comté, Dijon

« Molécules Organiques et UHV », Strasbourg, octobre 2015

Outline

Introduction

- Metal Carbonyls, $Mo(CO)_6$
- Decomposition and Applications

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

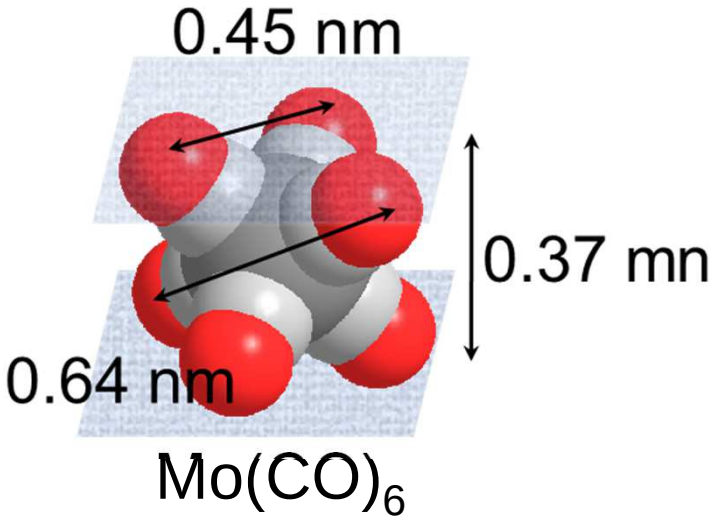
- Temperature Programmed Desorption (TPD)
- X-ray Photoelectron Spectroscopy (XPS)

Scanning Tunneling Microscopy of $Mo(CO)_6$ on Cu(111)

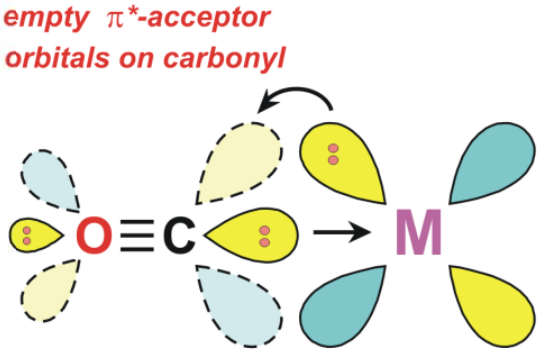
- Monolayer on Cu(111), structure interpretation
- Stimulated dissociation

Conclusions

Metal carbonyls



$Mo(CO)_6$

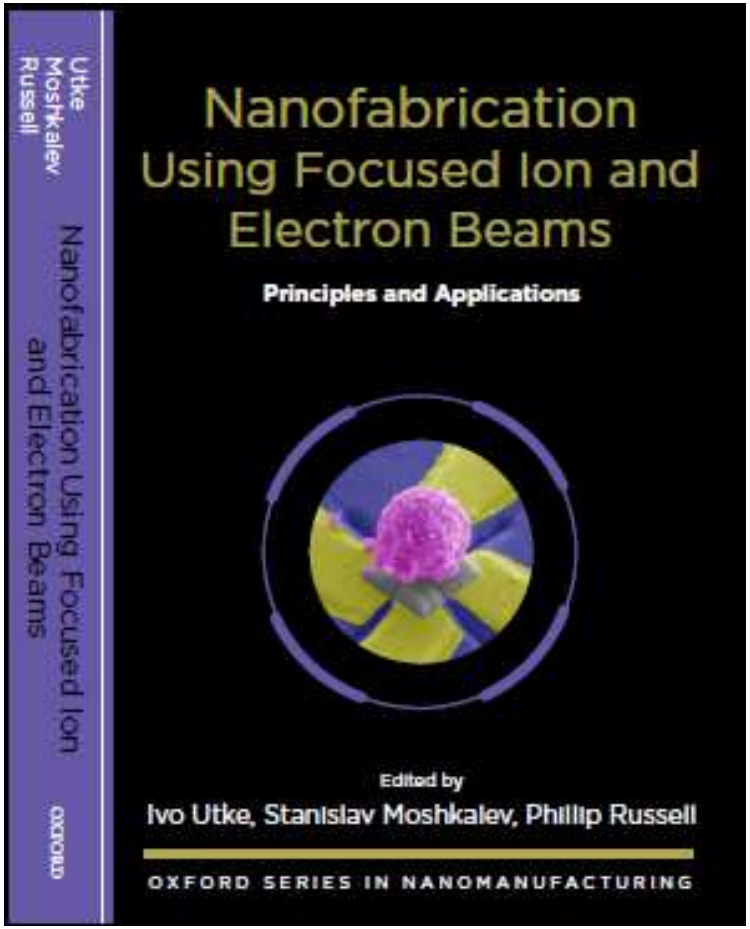


powerful π-acceptor ligand!

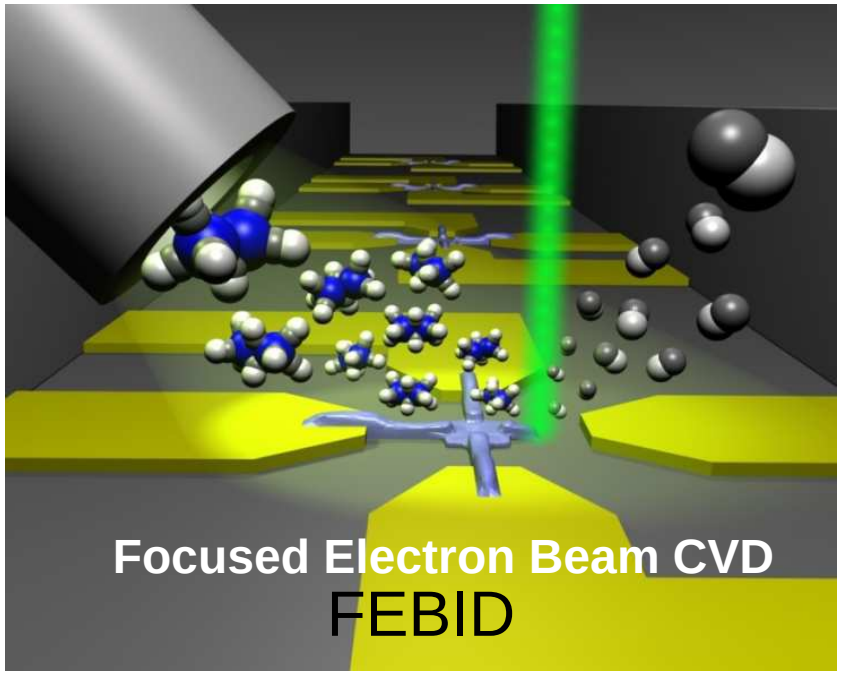
excellent ligand, therefore, for stabilizing electron-rich low-valent metal centers

5	6	7	8	9	10
$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$	$Ni(CO)_4$
	$Mo(CO)_6$	$Tc_2(CO)_{10}$	$Ru(CO)_5$ $Ru_3(CO)_{12}$	$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	
	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_3(CO)_{12}$	$Ir_4(CO)_{12}$	

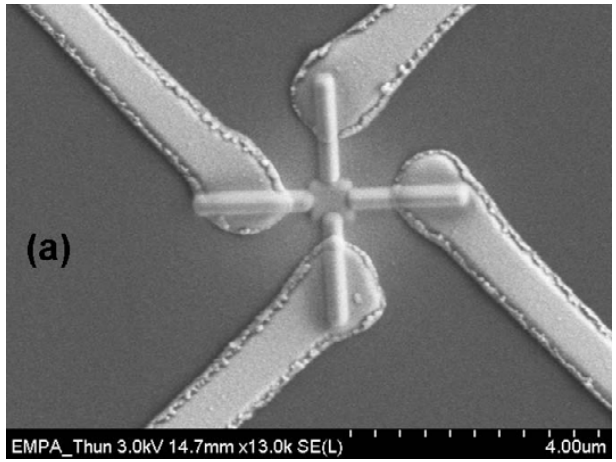
Applications



Oxford University Press **2011 ISBN 9780199734214**



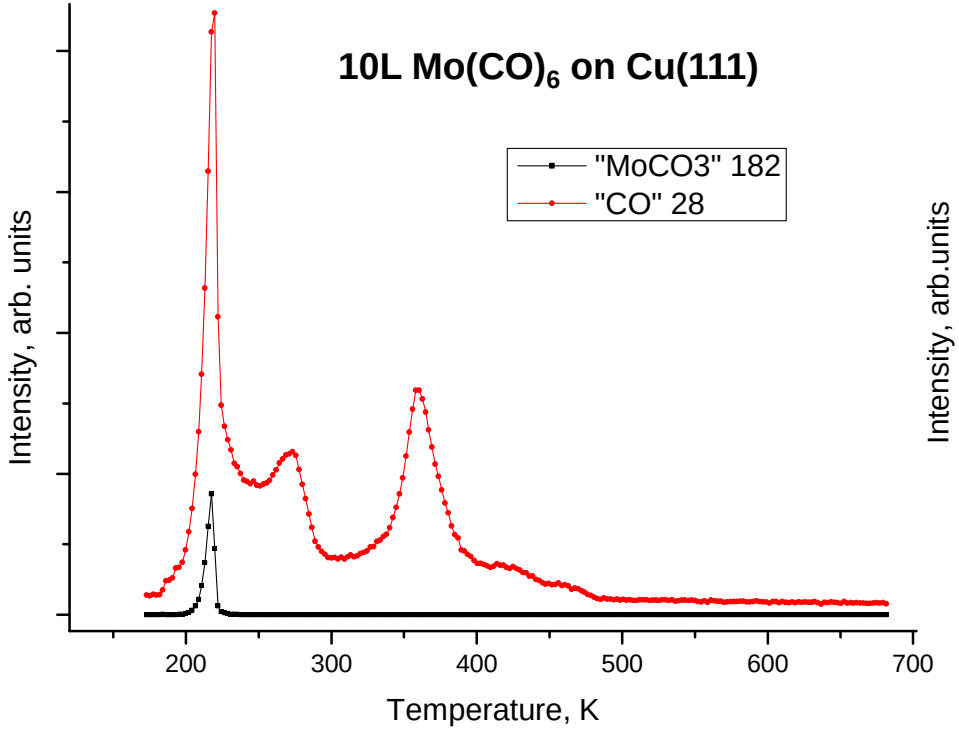
I. Utke and A. Goelzhaeuser, Angewandte Chemie Int. Edition 2010

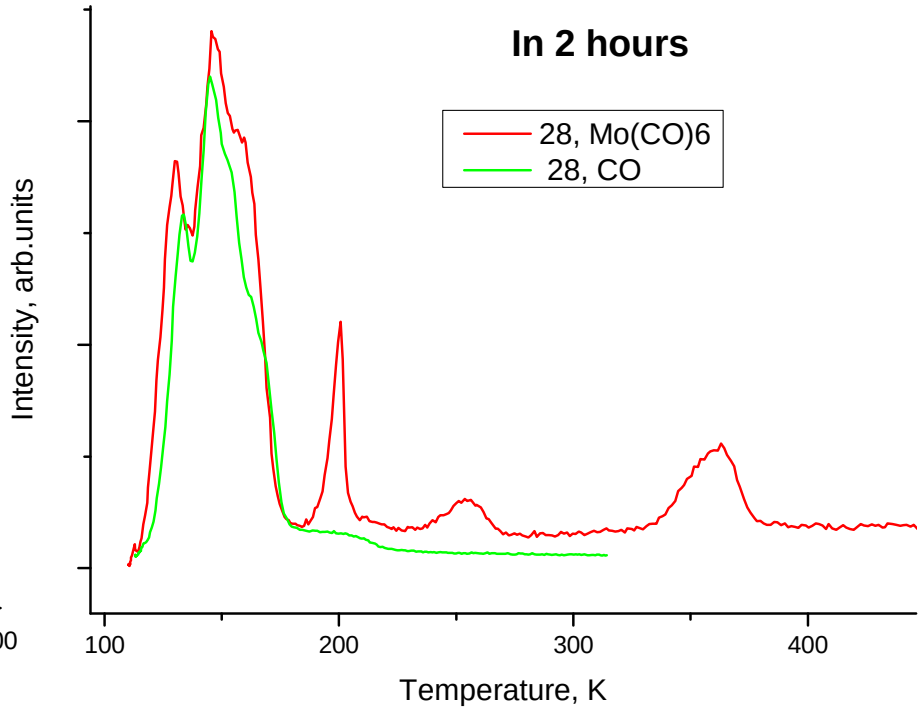


Ideal reaction:

$Me(CO)_n + e^- = Me\downarrow + nCO\uparrow$

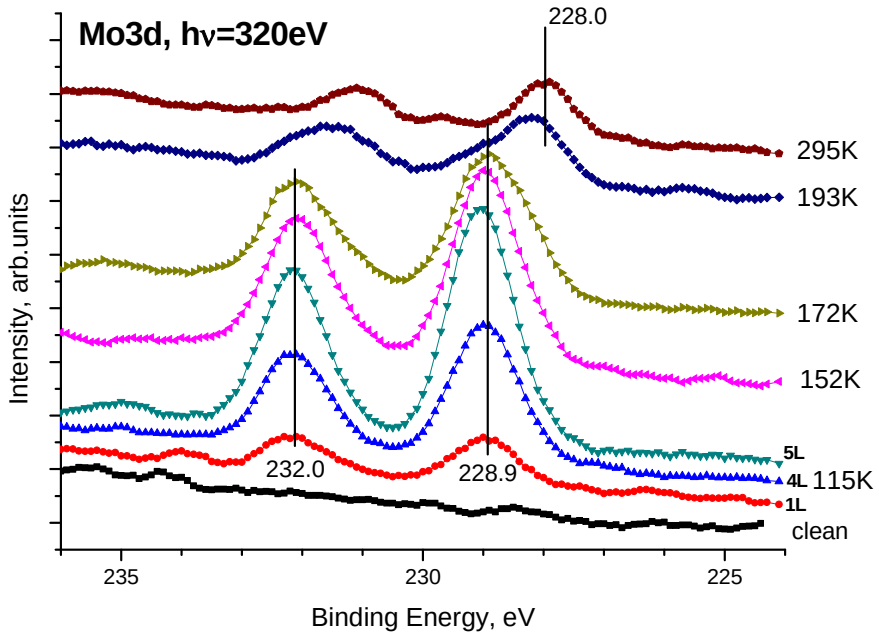
Temperature Programmed Desorption

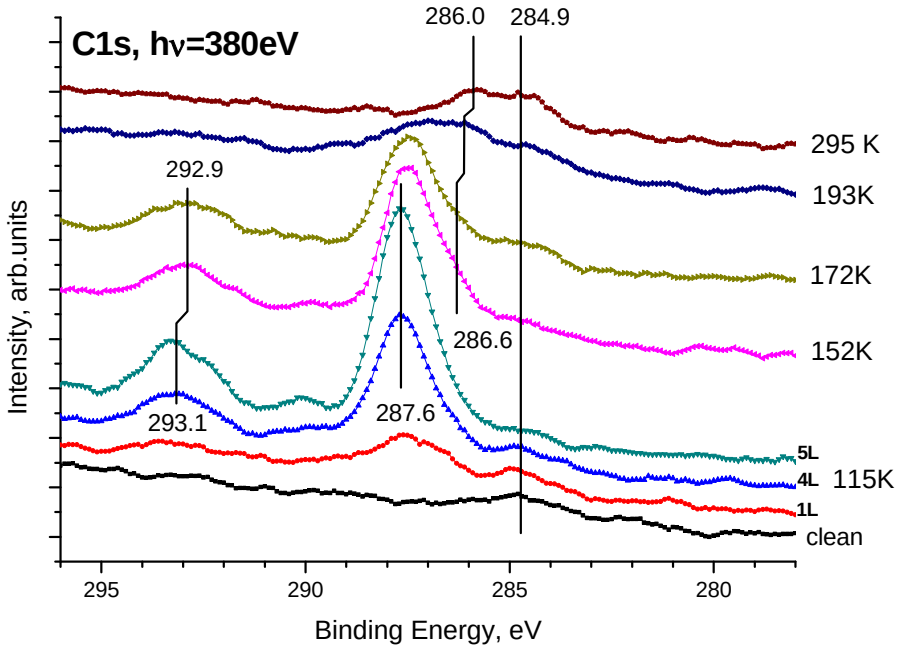


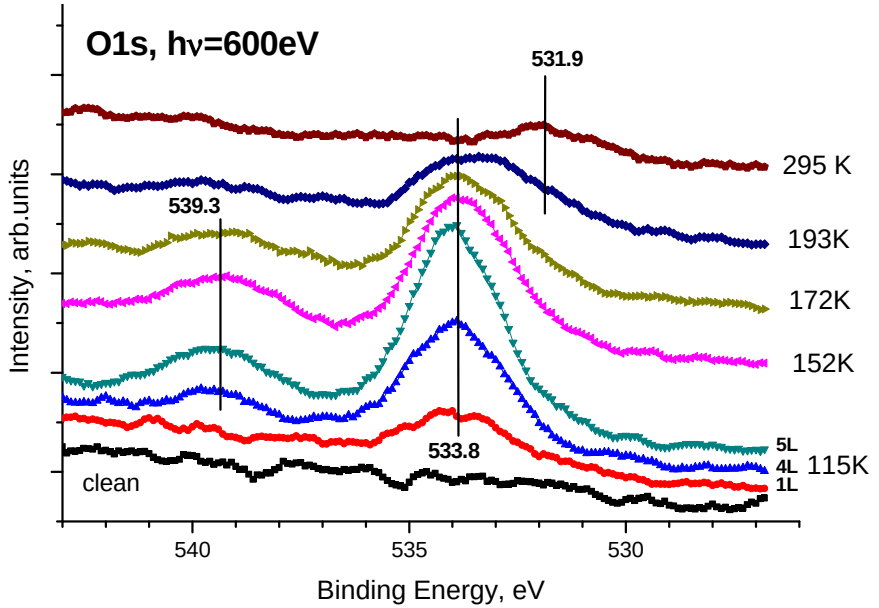


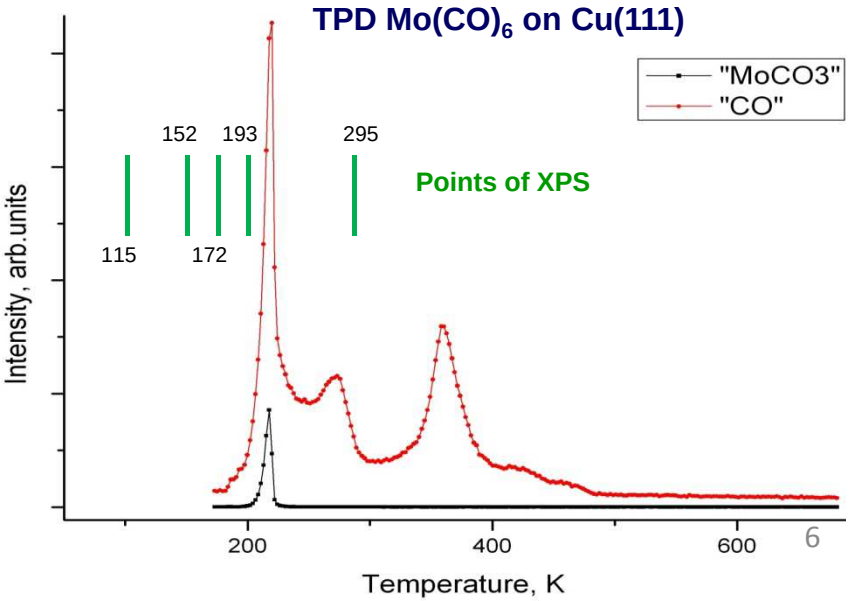
m(CO) = 28;
m(Mo) = 96;
m(MoCO) = 126;
m($Mo(CO)_2$) =154;
m($Mo(CO)_3$) =182;
…

XPS (SR)


Mo3d, hν=320eV
228.0
295K
193K
172K
152K
5L
4L
115K
1L
clean
232.0
228.9
Intensity, arb.units
235
230
225
Binding Energy, eV

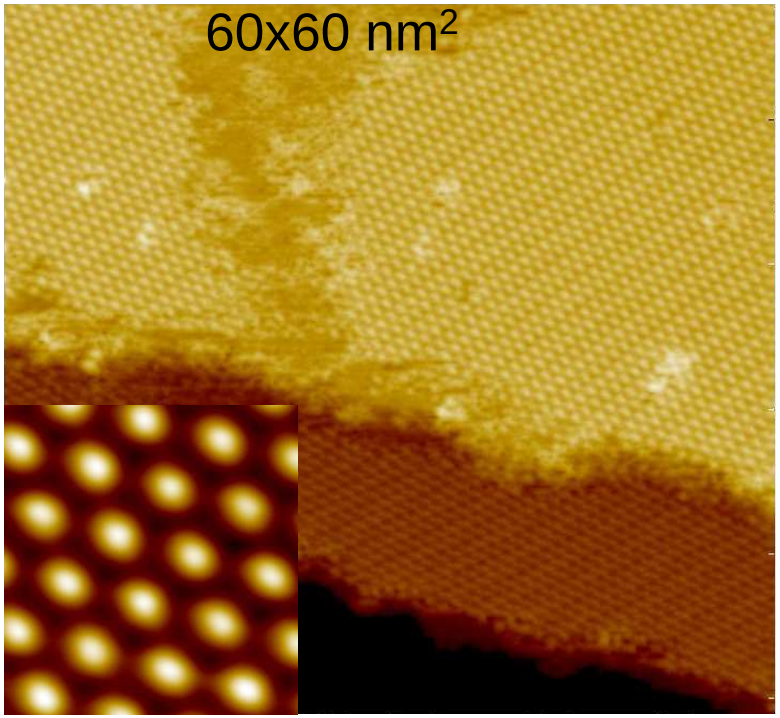

C1s, hν=380eV
286.0
284.9
295 K
193K
172K
152K
5L
4L
115K
1L
clean
292.9
286.6
293.1
287.6
Intensity, arb.units
295
290
285
280
Binding Energy, eV


O1s, hν=600eV
531.9
295 K
193K
172K
152K
5L
4L
115K
1L
539.3
533.8
clean
Intensity, arb.units
540
535
530
Binding Energy, eV


TPD Mo(CO)6 on Cu(111)
"MoCO3"
"CO"
152
193
295
Points of XPS
115
172
Intensity, arb.units
200
400
600
Temperature, K

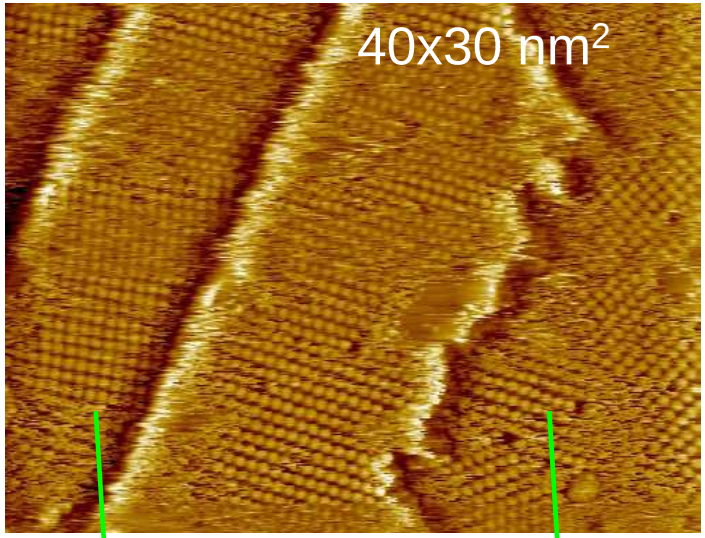
$Mo(CO)_6$ monolayer on Cu(111)

Exposition: 1-2 L

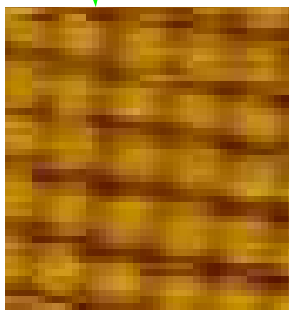


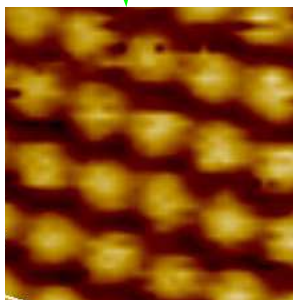
I_t= 5 pA; V_b= 20 mV

5-10 L



I_t= 10 pA; V_b= 200 mV



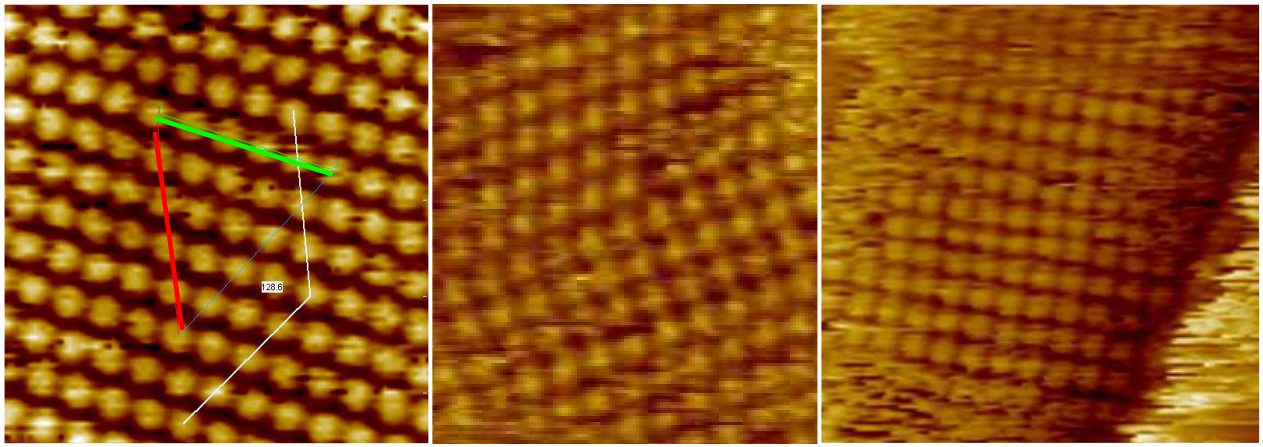


Apparent height ~ 0.06÷0.08 nm ;
Corrugation of ML ~ 0.04 nm

T = 150 K

Cu(111) + CO interface

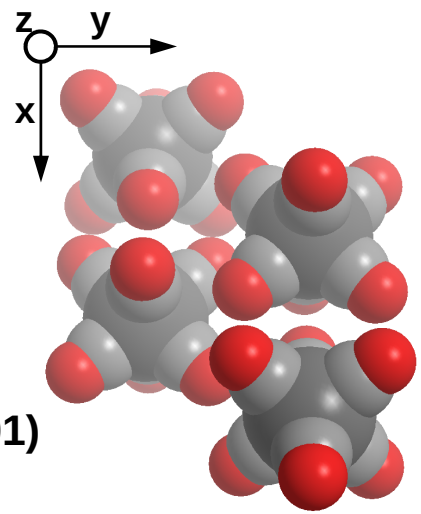
$Mo(CO)_6$ monolayer on Cu(111) (CO)



Hex-like : green 0.68 nm (±0.01)
red 0.74 Å (±0.01)

square-like : 0.68 nm (±0.01)

Bulk: Oh; P_{nma}

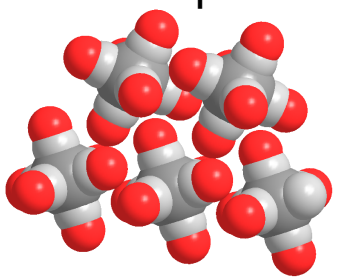


[2-10]
axb=0.72x0.649 nm²; φ=63.2 deg

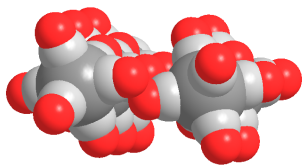
[210]
axb=0.653x0.649 nm²; φ=82.7 deg

x=1.2019; y=1.1415;
z=0.6488 nm; N=4.

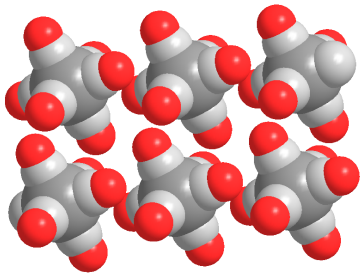
top



side



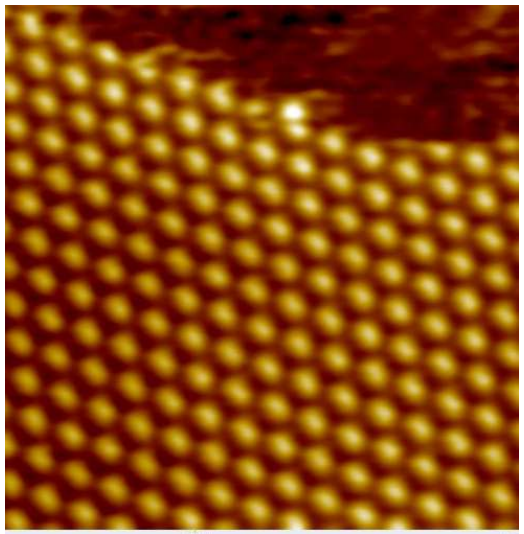
top



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

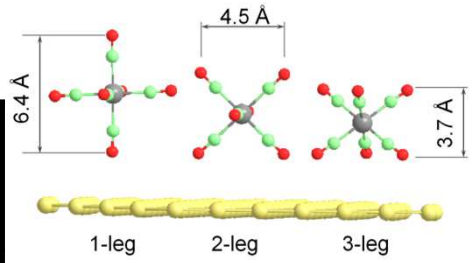
Arrangement is guided by forces between molecules

$Mo(CO)_6$ monolayer structure



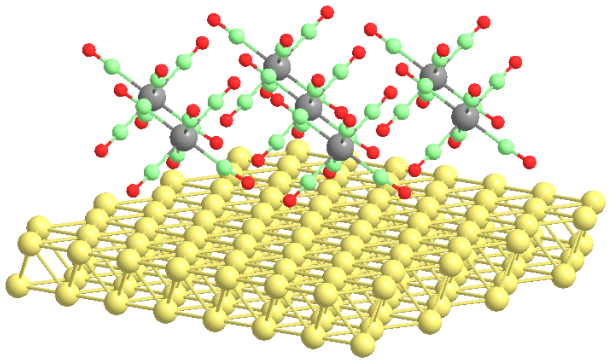
8x8 nm^2; I_t= 10 pA; V_b= 20 mV

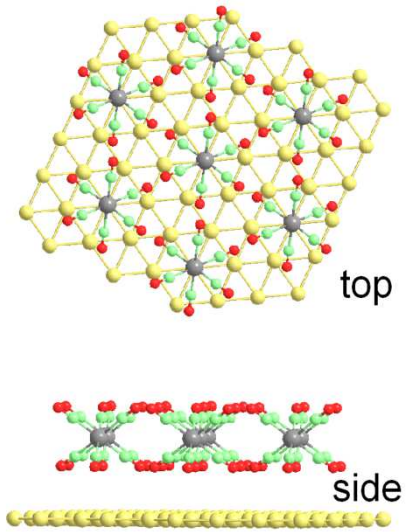
Slab	Adsorption energy, eV/molecul	Cohesive energy, eV/molecule	Layer formation energy, eV/molecule
Cu(111) 5x5x4	-0.77	-0.31	-1.08
Cu(001) 5x5x4	-0.78	-0.31	-1.09

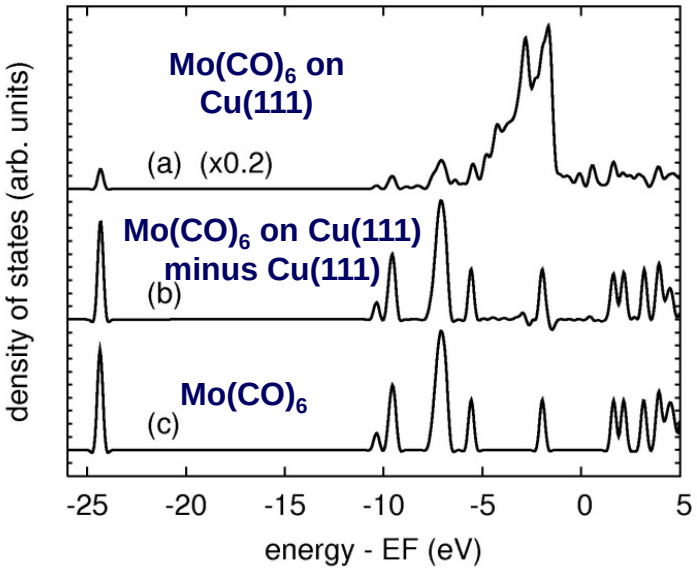


Van-der-Waals forces

Hexagonal a=0.68 nm (±0.01)





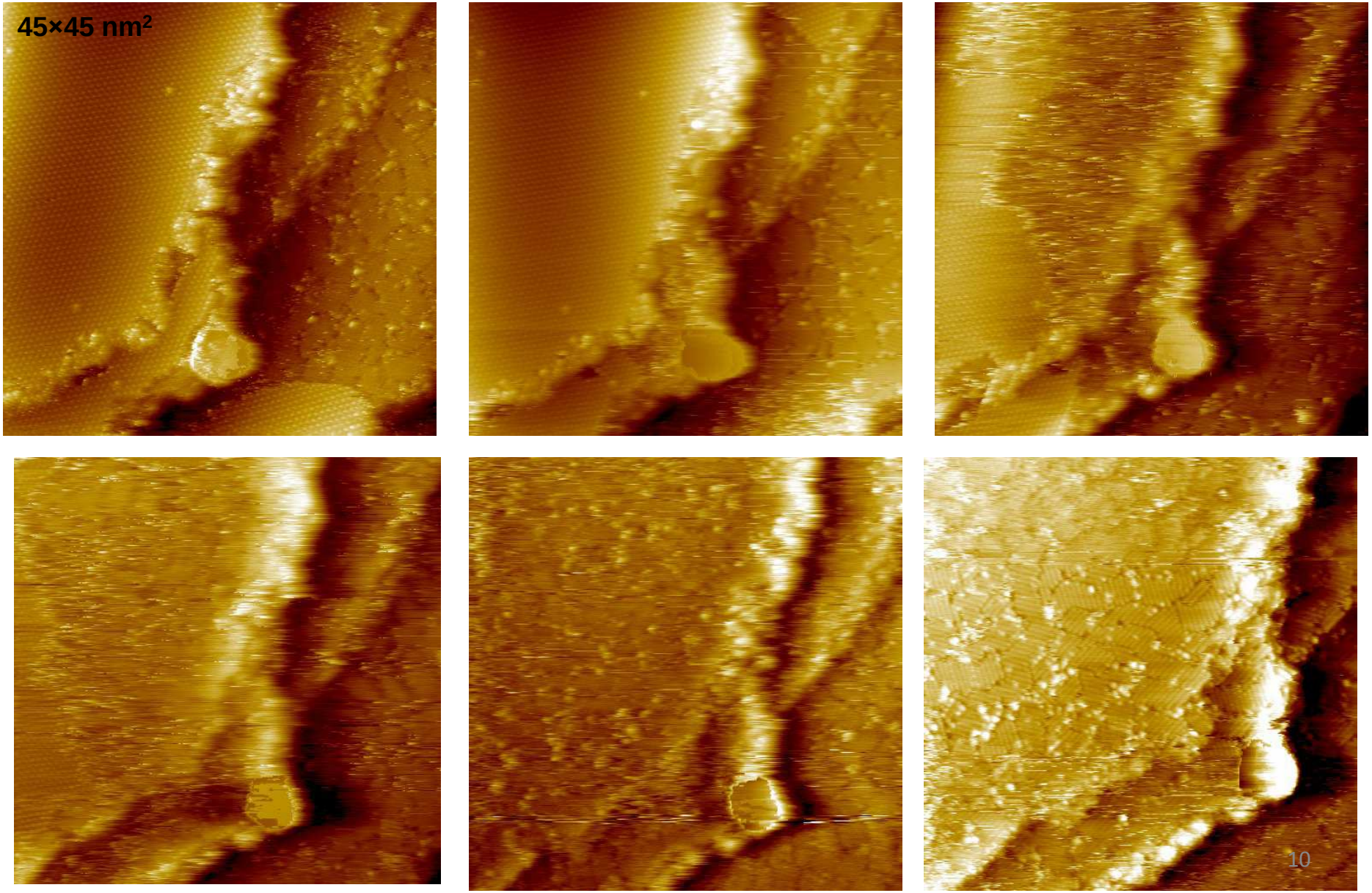


J.Chem.Phys.C 116(2012)10617

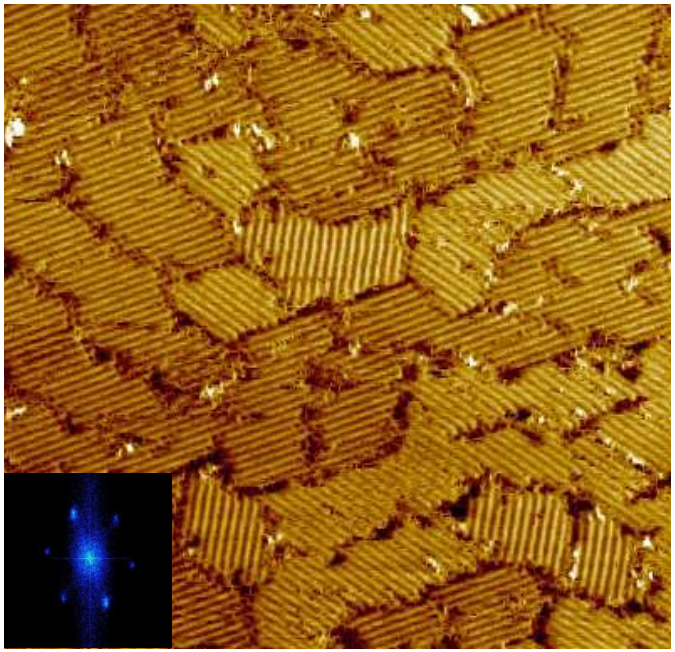
Monolayer transformation

I_t=2-10 pA; V_b = 100 mV

Surf.Sci. 617 (2013) 10



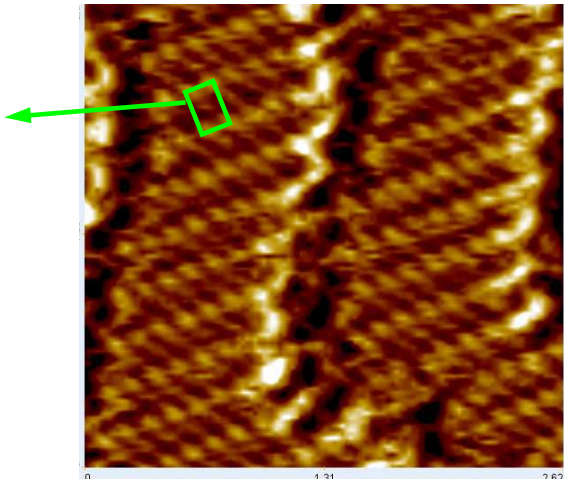
Dissociated monolayer structure on Cu(111)



25x25 nm^2; I_t= 0.1 nA; V_b= 120 mV

0.26 x 0.44 nm^2

(1x2) superstructure



5x5 nm^2; I_t= 0.12 nA; V_b= 100 mV

$Mo(CO)_x$ clusters ?

Adsorbed CO domaines ?

$$Mo(CO)_6 \xrightarrow[Cu(111)]{\text{STM tip}} Mo(CO)_x + (6\text{-}x)CO$$

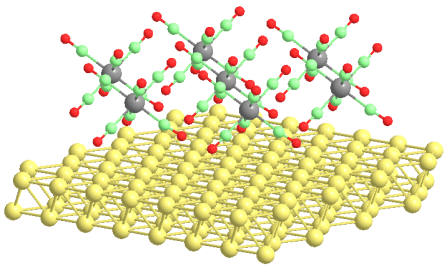
Surf.Sci. 617 (2013) 10

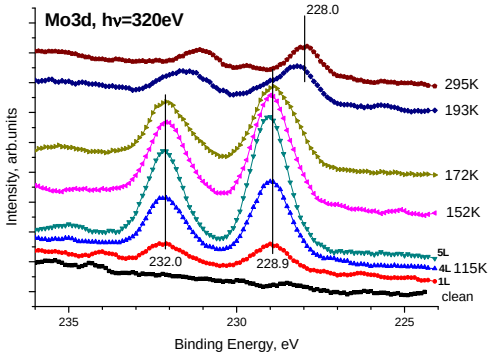
Conclusions

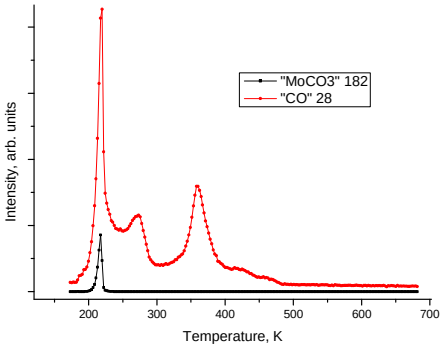
- System of introduction should be adapted for the choosen molecule
- Dissociation of carbonyls leads to elevated pressure of CO
- TPD: Choice of mass of fragments to prove adsorption of entire molecule
- XPS: Comparison of obtained specra in time because of spectra instability. Fingerprints of entire molecule.
- STM: Weak interaction with the surface. Possible decomposition under scanning

Acknowledgements

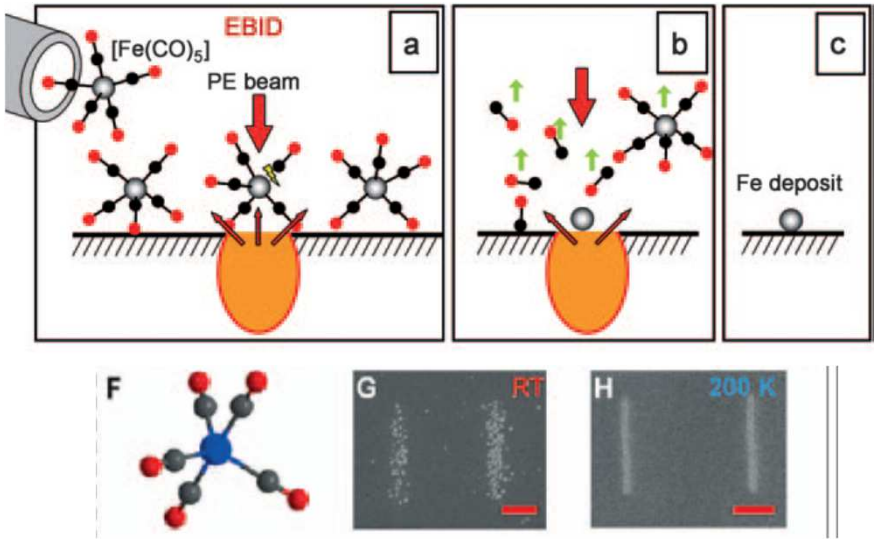
DFT	Peter Krüger (Chiba University, Japan) Celine Dupont
XPS (SR)	Bruno Domenichini, Sylvie Bourgeois
TPD	Gian-Andrea Rizzi (University of Padua, Italy) Pierre Pauffert





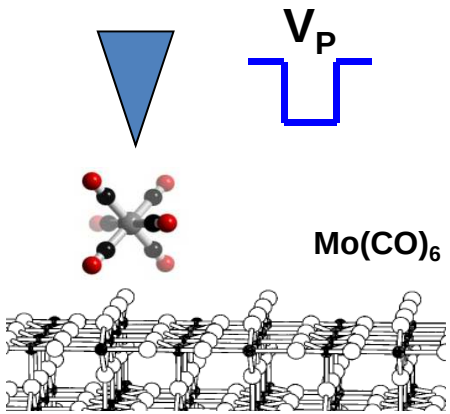


Applications



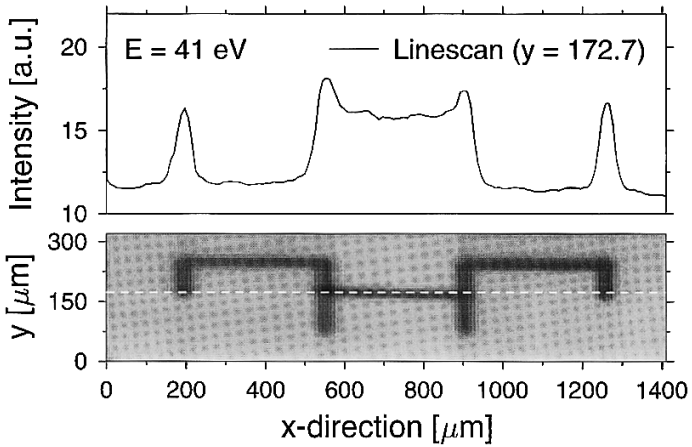
Omicron NanoTech. Newsletter, Vol. 12 No. 2, 2008;
Angew. Chem. Int. Ed. 49 (2010) 4669

STM induced decomposition

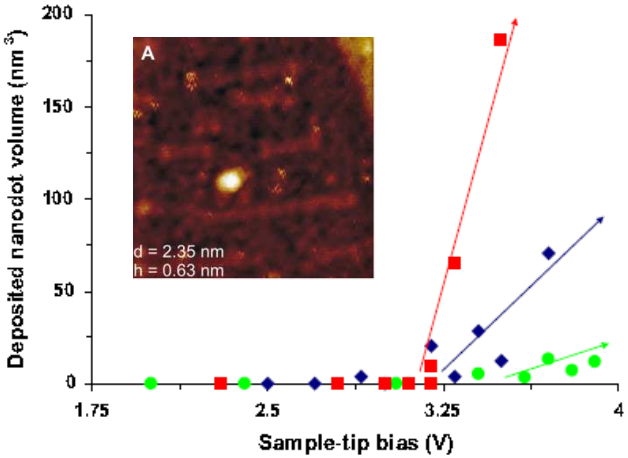


$Mo(CO)_6$ on $TiO_2(110)$

SR of $Mo(CO)_6$ on Si. Mo4d intensity map

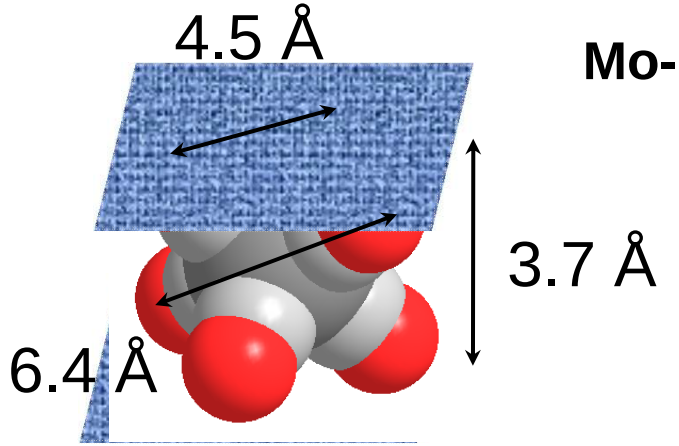


Appl. Phys. Lett. 66 (1995) 2200



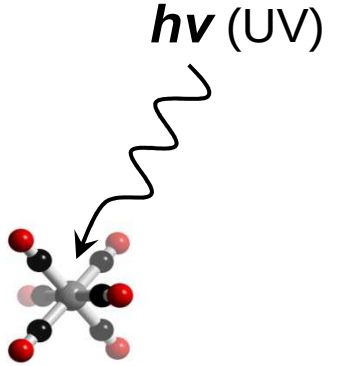
VACUUM 86 (2012) 623

$Mo(CO)_6$ single molecule



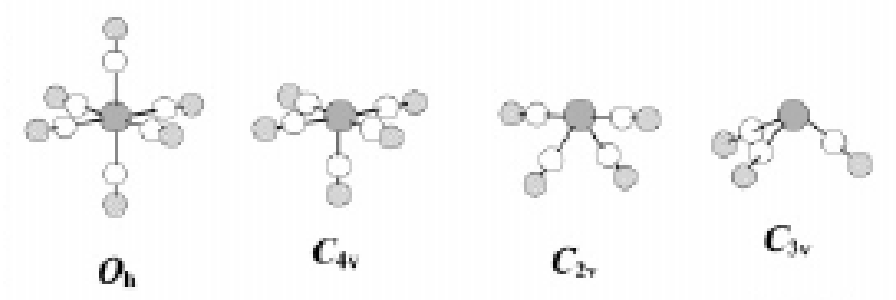
Mo-C-O 3.2Å

Photodissociation

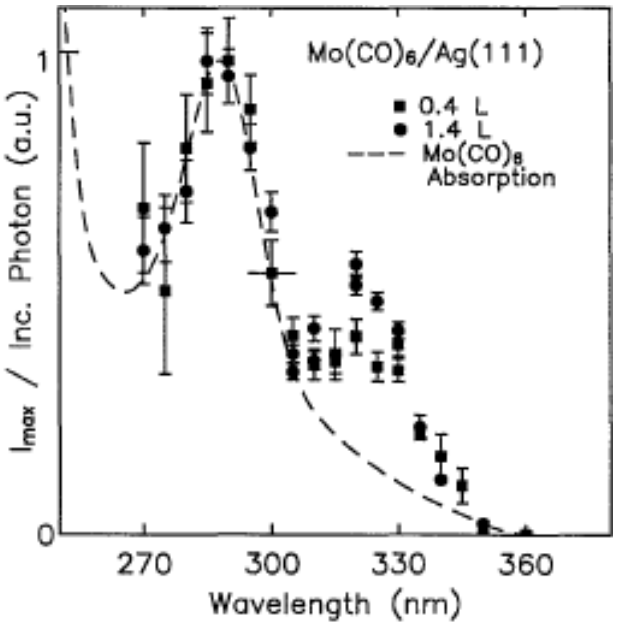


Calculated bond dissociation enthalpies on Mo(CO)*n* (*n* = 6, 5, 4, and 3) (gas phase)

≈1.4 eV/CO



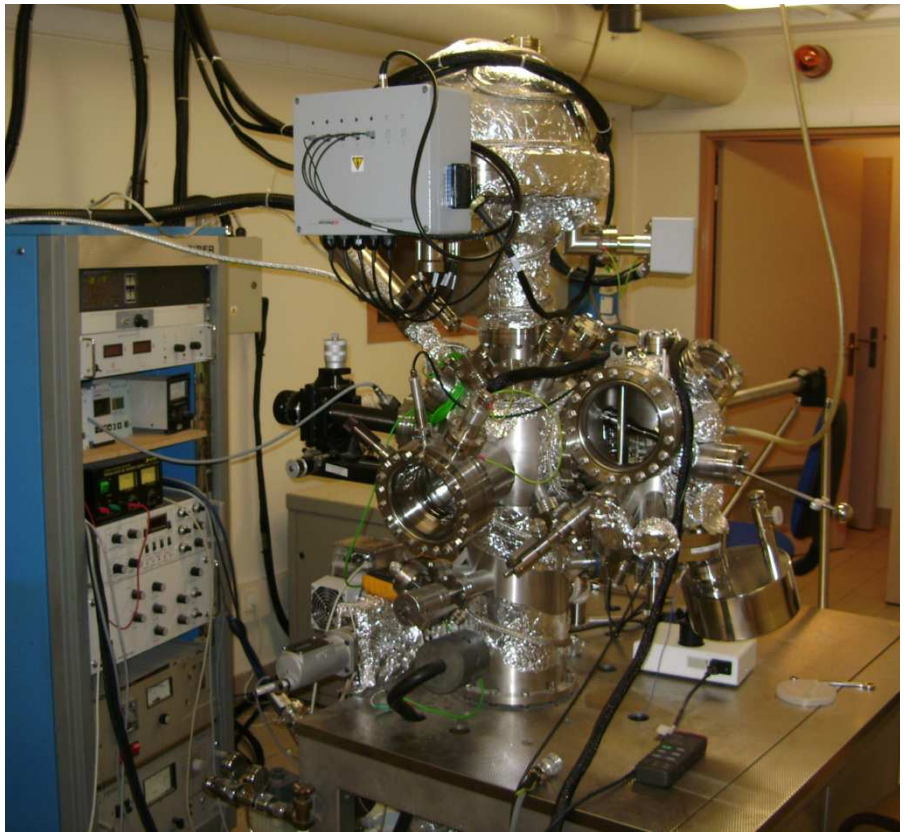
Y.Ishikawa, K.Kawakami,
J. Phys. Chem. A 111 (2007) 9940



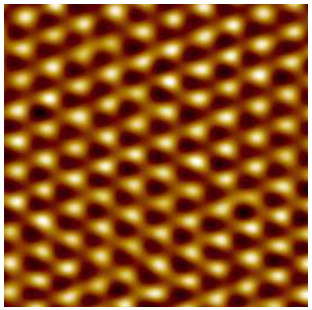
298 nm → 4.1 eV

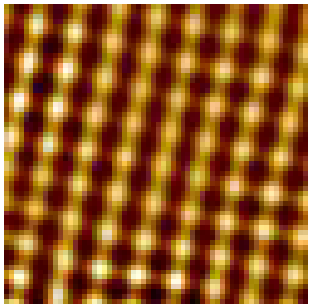
Experimental details

VT STM Omicron NT, XPS, LEED
UHV base pressure $1x10^{-10}$ mbar
LN cooling system 150÷800 K



Cu(111) **Cu(001)**



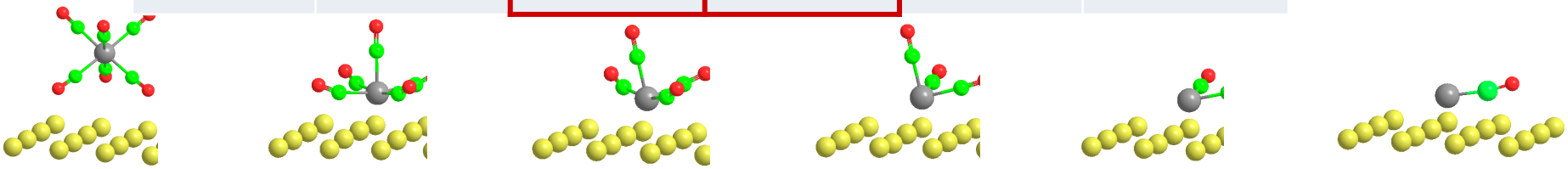


a_{Cu-Cu} **= 2.55 Å**

Dissociation energies of adsorbed (ads) and free (free) molecules by DFT

fragment	E_{dis} (free) eV	E_{dis} on Cu(111) eV	E_{dis} on Cu(001) eV	E_{ads} on Cu(111) eV	E_{ads} on Cu(001) eV
CO	-		-	-0.88	-1.06
Mo	-		-	-2.18	-2.60
MoCO	1.16	1.66	1.47	-3.56	-3.96
$Mo(CO)_2$	2.32	1.70	1.33	-3.82	-4.03
$Mo(CO)_3$	3.00	1.39	1.30	-3.08	-3.38
$Mo(CO)_4$	1.80	0.96	0.86	-3.11	-3.50
$Mo(CO)_5$	1.76	0.67	0.67	-2.90	-3.47
$Mo(CO)_6$	1.77	-1.23	-1.98	-0.78	-0.78

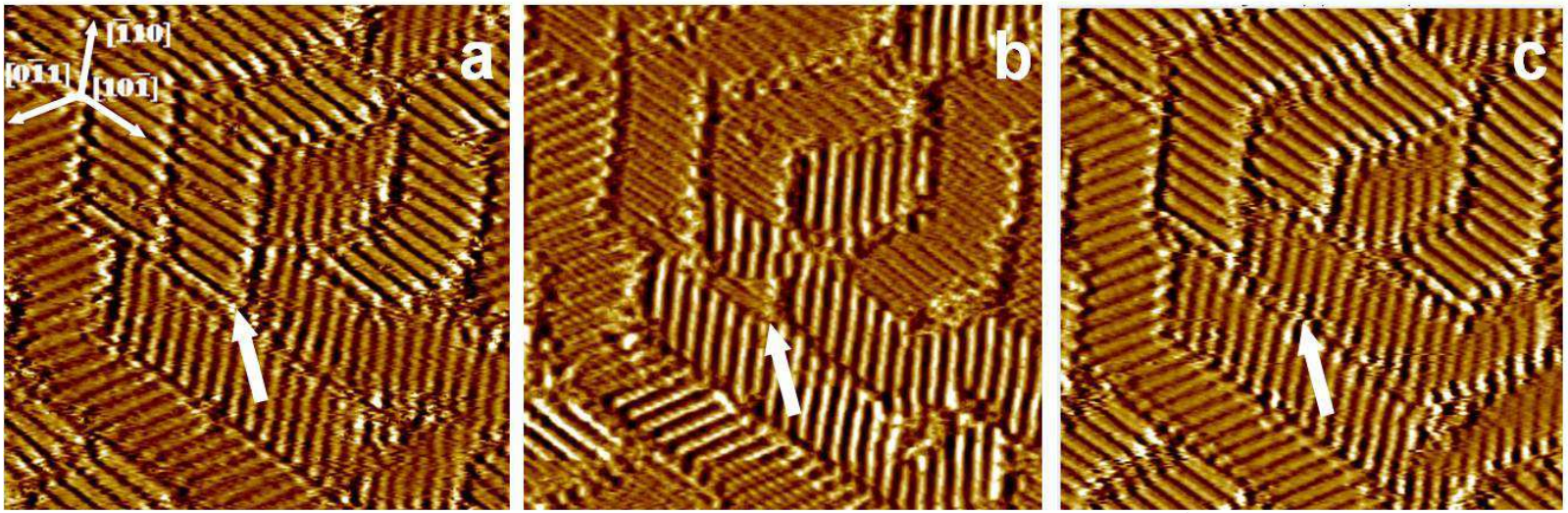
E_{coh}(Mo) = 6.82 eV/atom



XPS (SR)

Samp, Temp	BE, Mo3d	Area, Mo3d	BE, C1s	Area, C1s	BE, O1s	Area, O1s	Ratio C:O per 1Mo
1L, 115K	228.9	0.944	287.3 293.0 sat	0.86 0.382	533.8 539.3 sat	0.945 0.1	11.04:11.92
3L, 115K	229.0	2.71	287.6 293.1 sat 289.9	2.678 0.765 0.194	533.9 539.5 sat	1.739 0.39	11.3:8.43
5L, 115K	229.0	4.812	287.6 293.1 sat 290.1	3.928 1.153 0.131	533.9 539.4 sat	2.836 0.716	9.14:7.94
152K	228.9	4.166	287.5 292.9 sat 289.6 286.5	2.29 0.994 0.1337 0.764	533.7 539.3 sat	2.177 0.593	7.48:6.32
172K	228.8	3.31	287.6 292.9 sat 290.2 286.6	1.68 0.809 0.181 0.522	533.7 539.1 sat	1.497 0.36	8.4:6.23
193K	228.1 228.9	1.11 0.412	287.6 292.5 sat 286.2	0.613 0.137 0.864	532.2 533.8 539.4	0.398 0.82 0.234	8.9:10
295K	227.9	0.78	284.64 286.0	0.646 0.62	531.9	0.499	6.68:6.85
523K	228.5	0.572	284.55	0.75	-	-	

Domain reorientation



12×12 nm^2 ; I_t=20 pA; V_b = 100 mV