Size-Selected Au_n and Ag_n Nanoclusters on Rutile TiO_2(110): Cluster Shape, Binding Site and Electronic Structure Probed by UHV-STM

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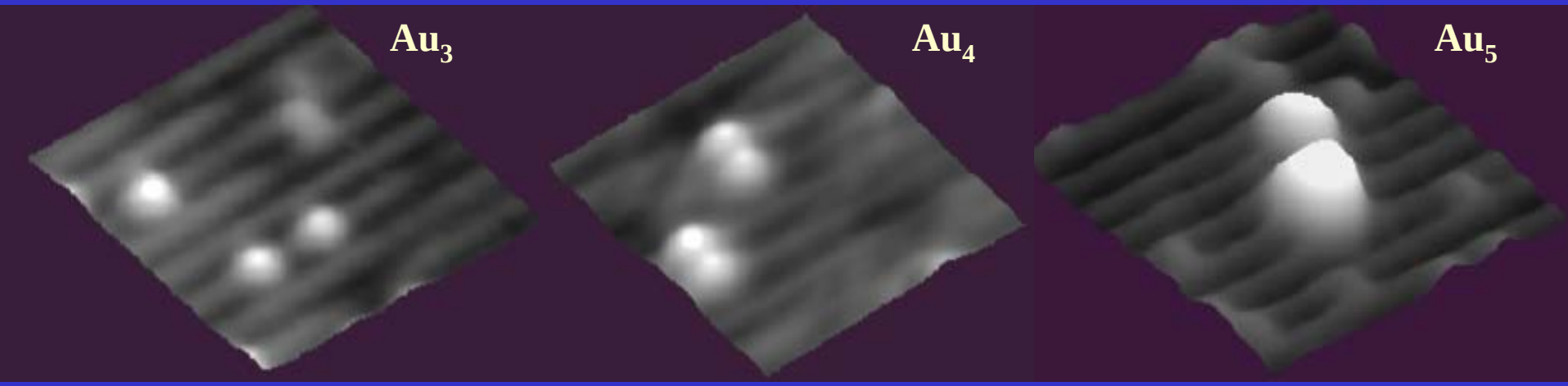
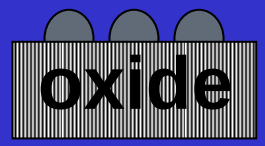
Department of Chemistry & Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106



Funding: AFOSR – DURINT Program

Motivation

Metal nanoparticles, < 10 nm diameter

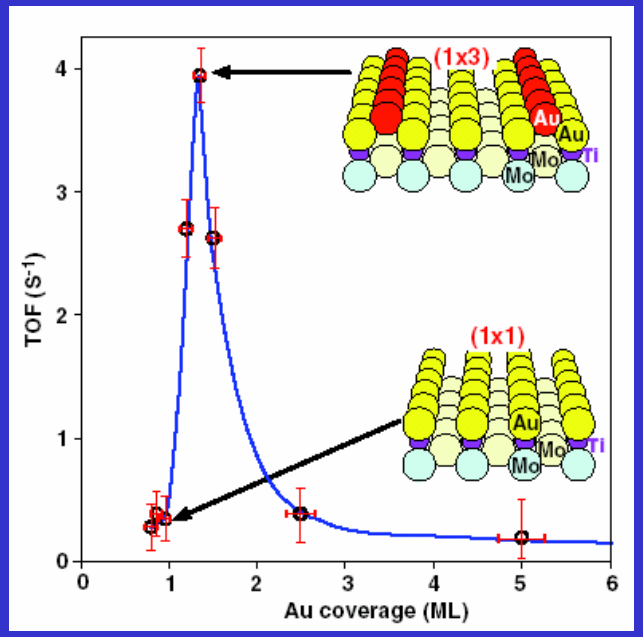


CO Oxidation

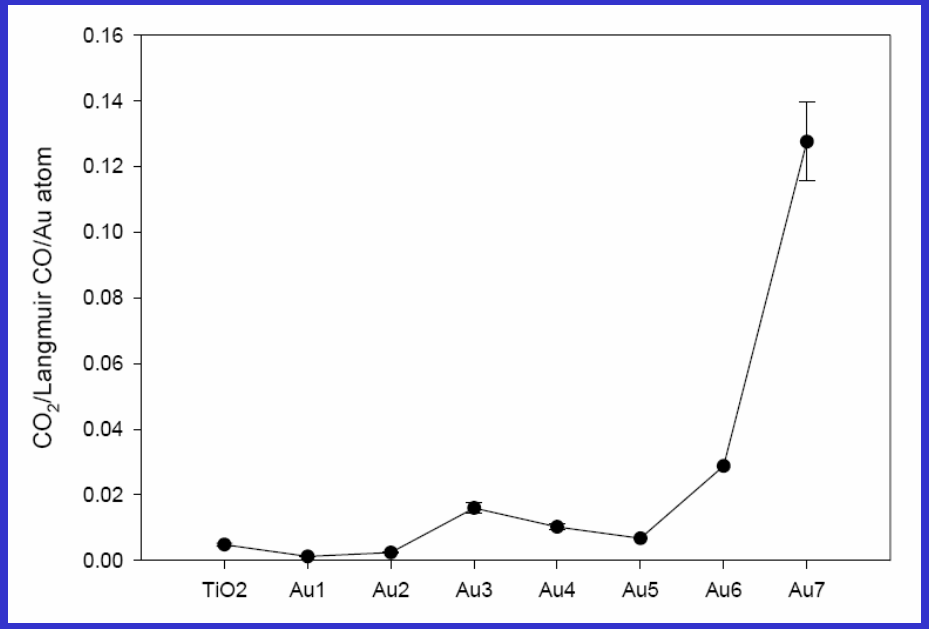
NO Reduction

Epoxidation of propylene

Haruta, M. et al. *J. Catal*. **1989**, 115, 301
Sanchez, A., Heiz, U., et. al. *JPCA* 1999, 103, 9573



Chen, M.S., Goodman, D.W. *Science*, **306**, 252 (2004)



Lee, S et al. *J.Phys.Chem.*, **123**, 124710 (2005)

Instrumental Setup

Deposition Parameters:
Flux ~ 1nA/cm^2
Coverage ~ 0.02ML
Average Energy: 0 – 2 eV/atom

Laser Entrance

Magnet

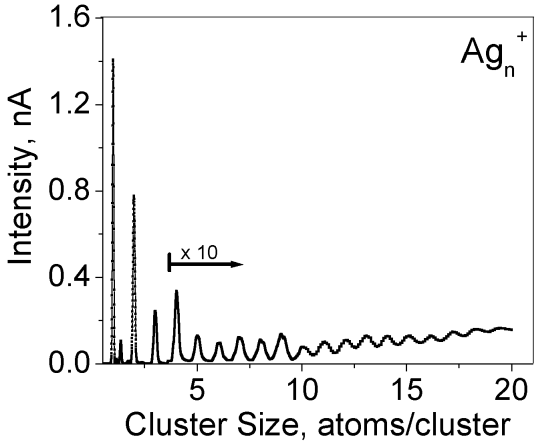
Cryogenic Manipulator

Cluster source

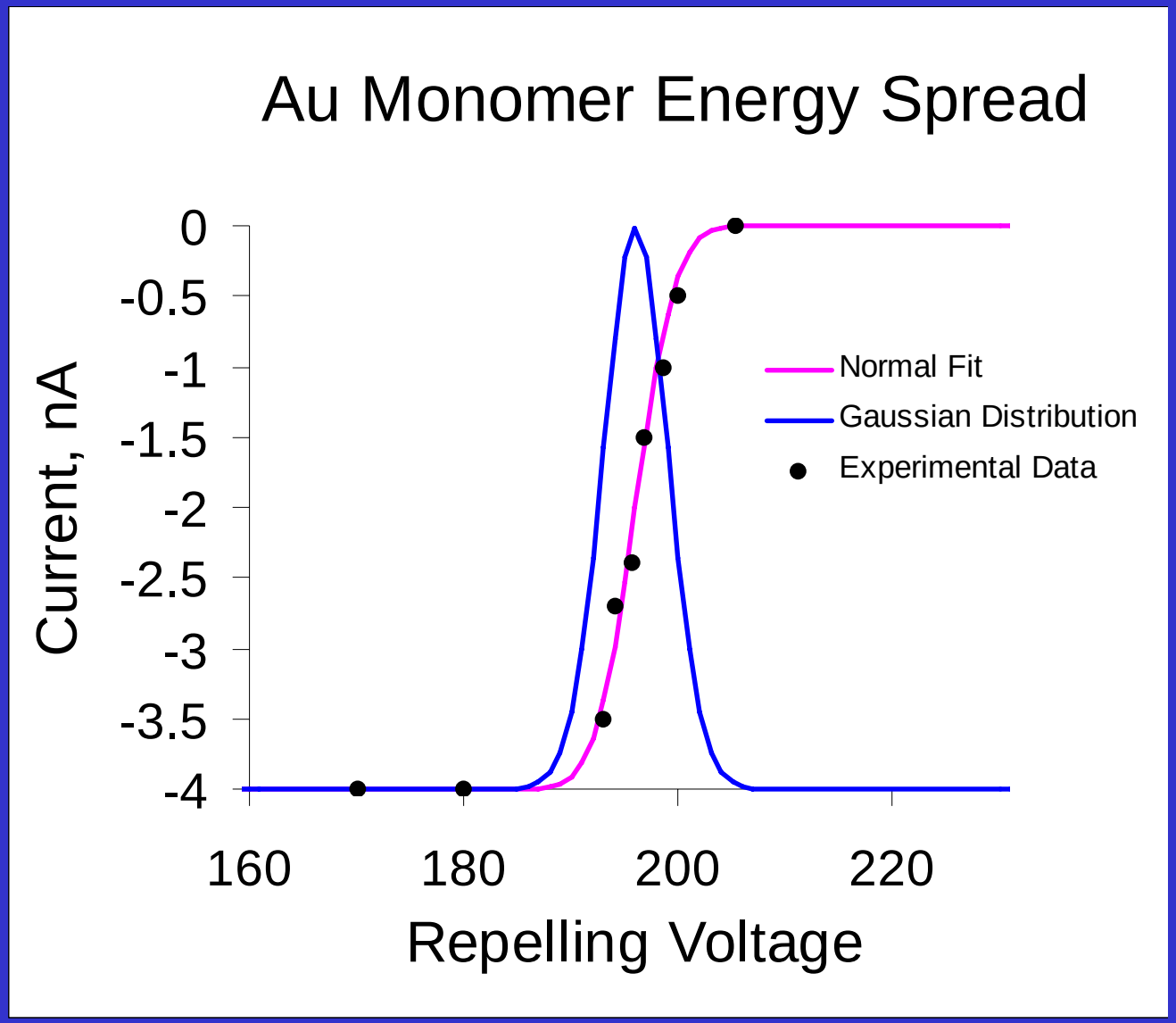
Movable Detector

Deposition Chamber
(TPD/AES/XPS)

STM Chamber



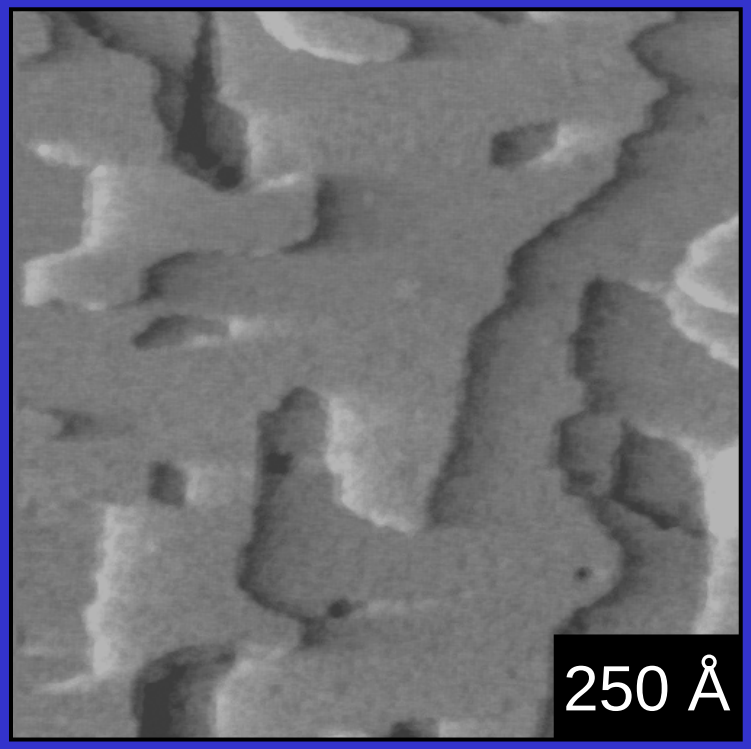
P. Kemper et al., *Int. Jour. Mass Spec.*, **254**, 202 (2006)

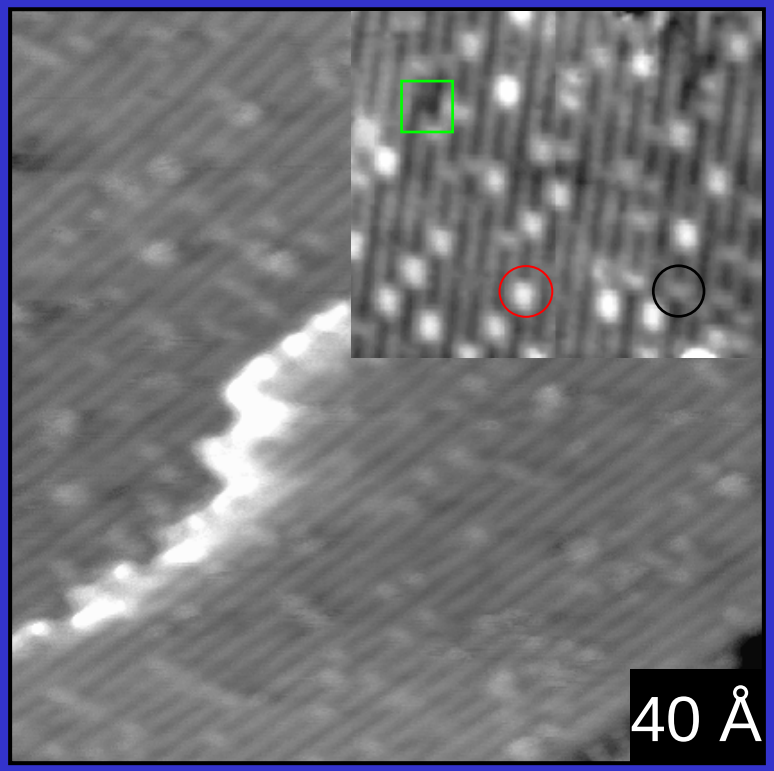


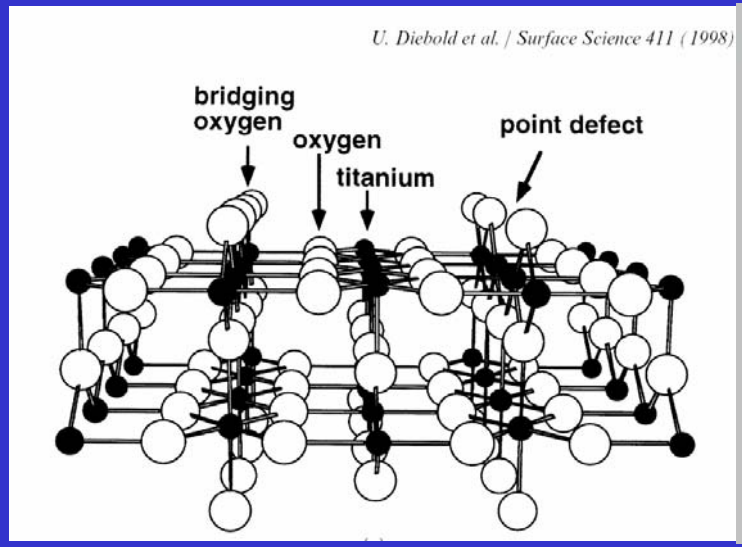
Energy Spread (eV)

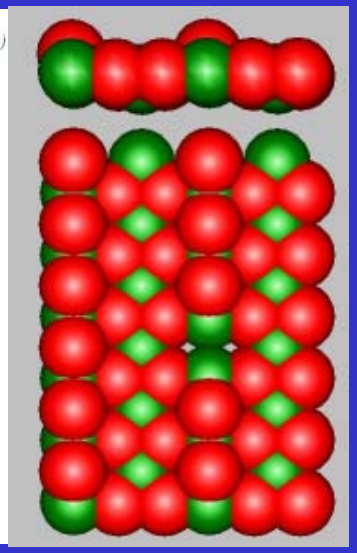
n	Au_n	Ag_n
1	3	1
2	3	2
3	3	5
4	5	-
5	6	8
6	6	-
7	6	-
8	8	-

STM of a Clean TiO_2 (110)-(1x1) Surface



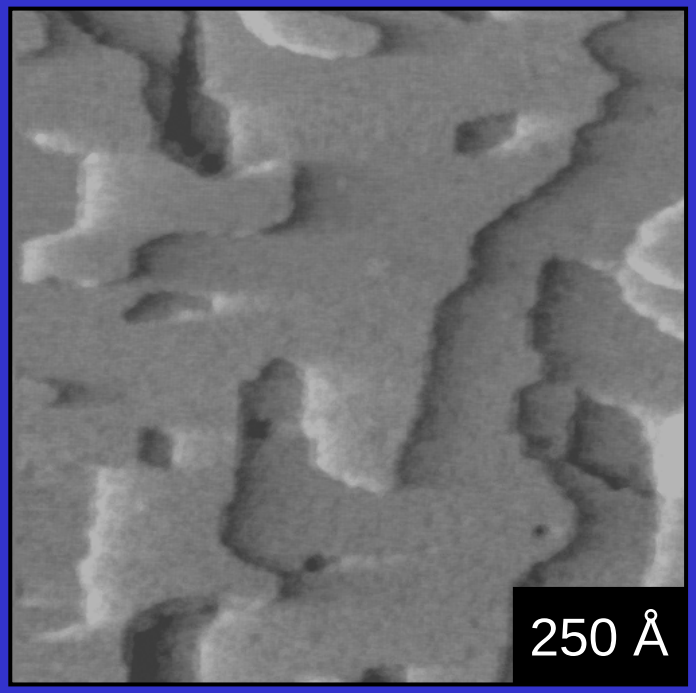


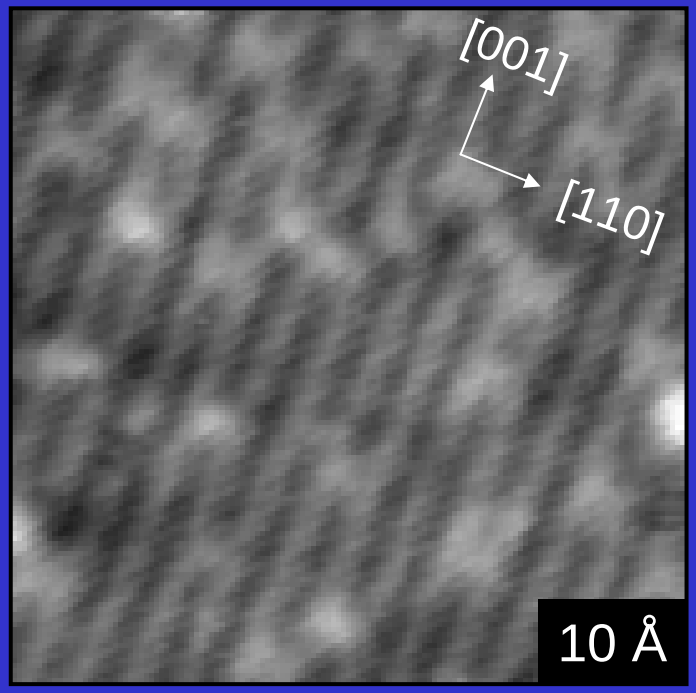


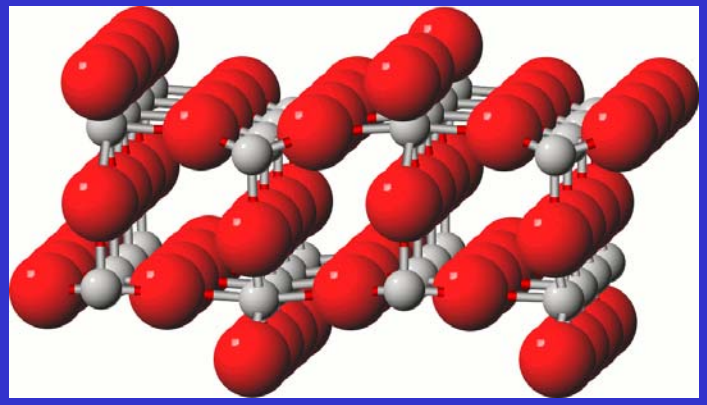


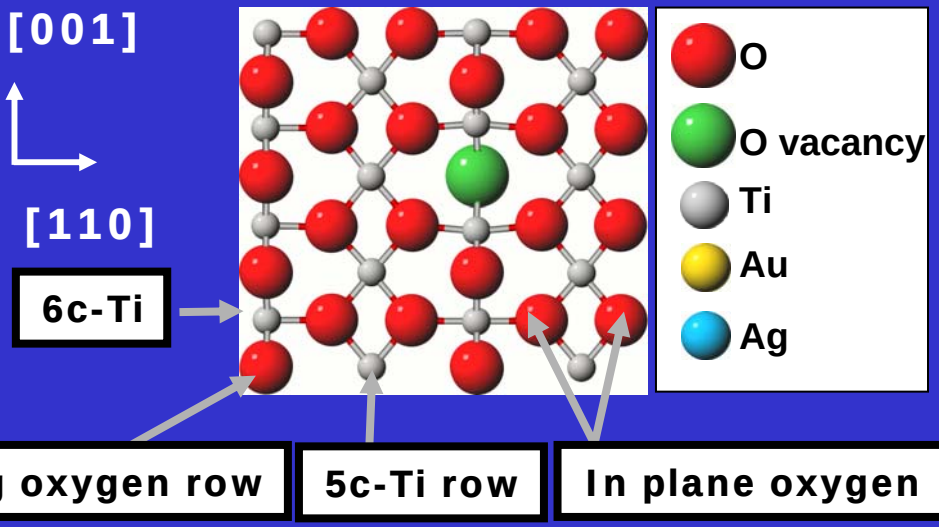
U. Diebold et al. Surf. Sci. 411 (1998) 137
S. Suzuki et al. PRL 84, (2000), 2156
R. Schaub et al. PRL 87, (2001), 266104
S. Wendt et al. PRL 96, (2006), 66107

Clean TiO_2 (110)-(1x1) Surface









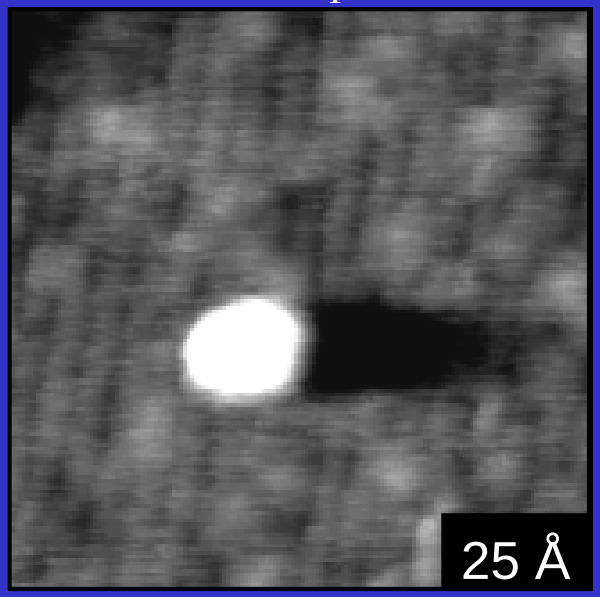
Gold Soft Landing

Au_n^+ (n = 1 – 8) clusters with average incident energies of 0 eV

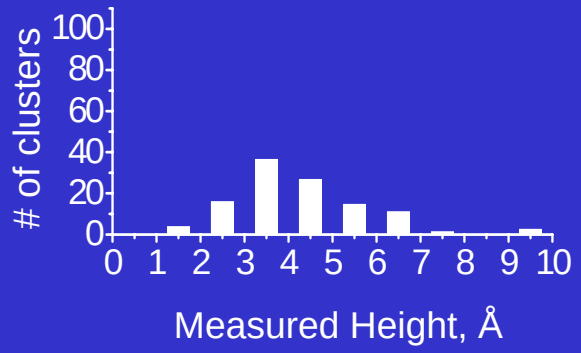
$TiO_2(110)$

Deposition of Au_1-Au_3

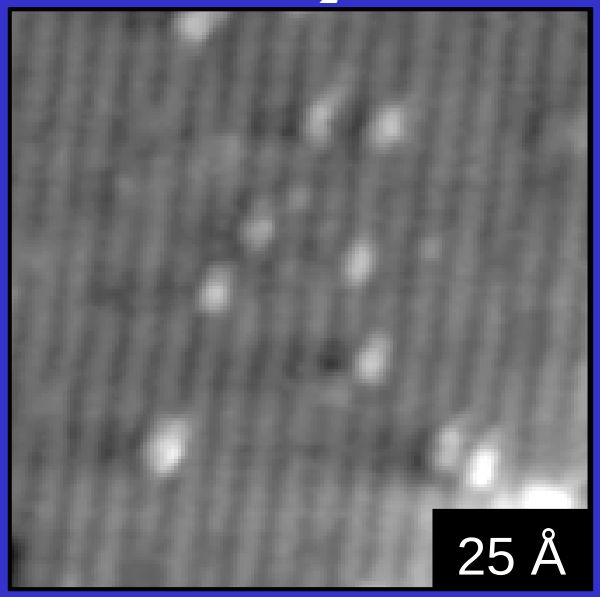
Au_1



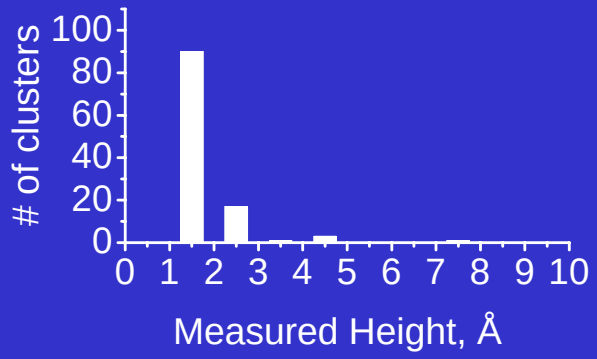
Height: 4.3 Å ± 1.7 Å



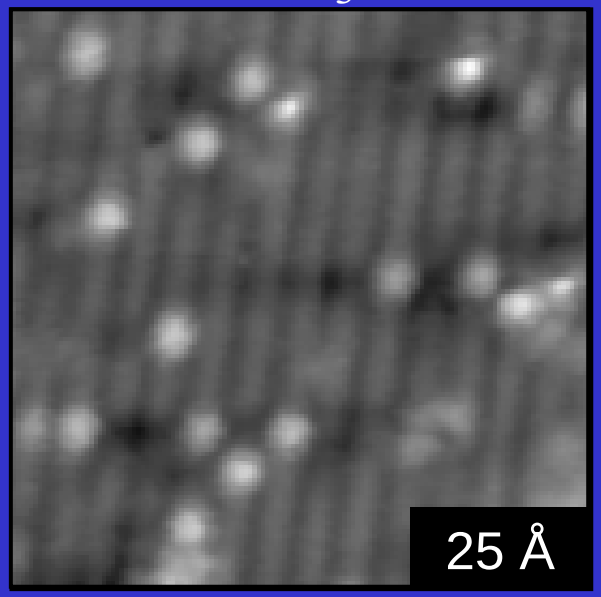
Au_2



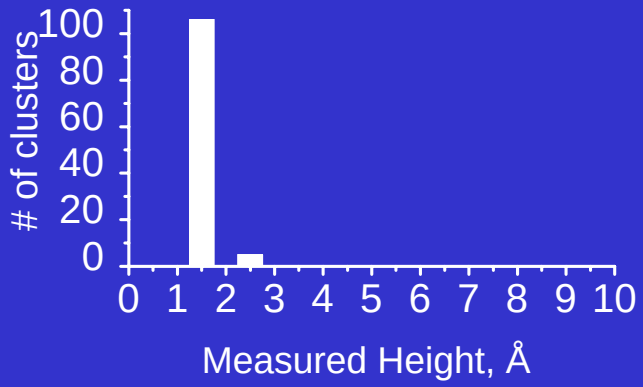
Height: 1.6 Å ± 0.5 Å



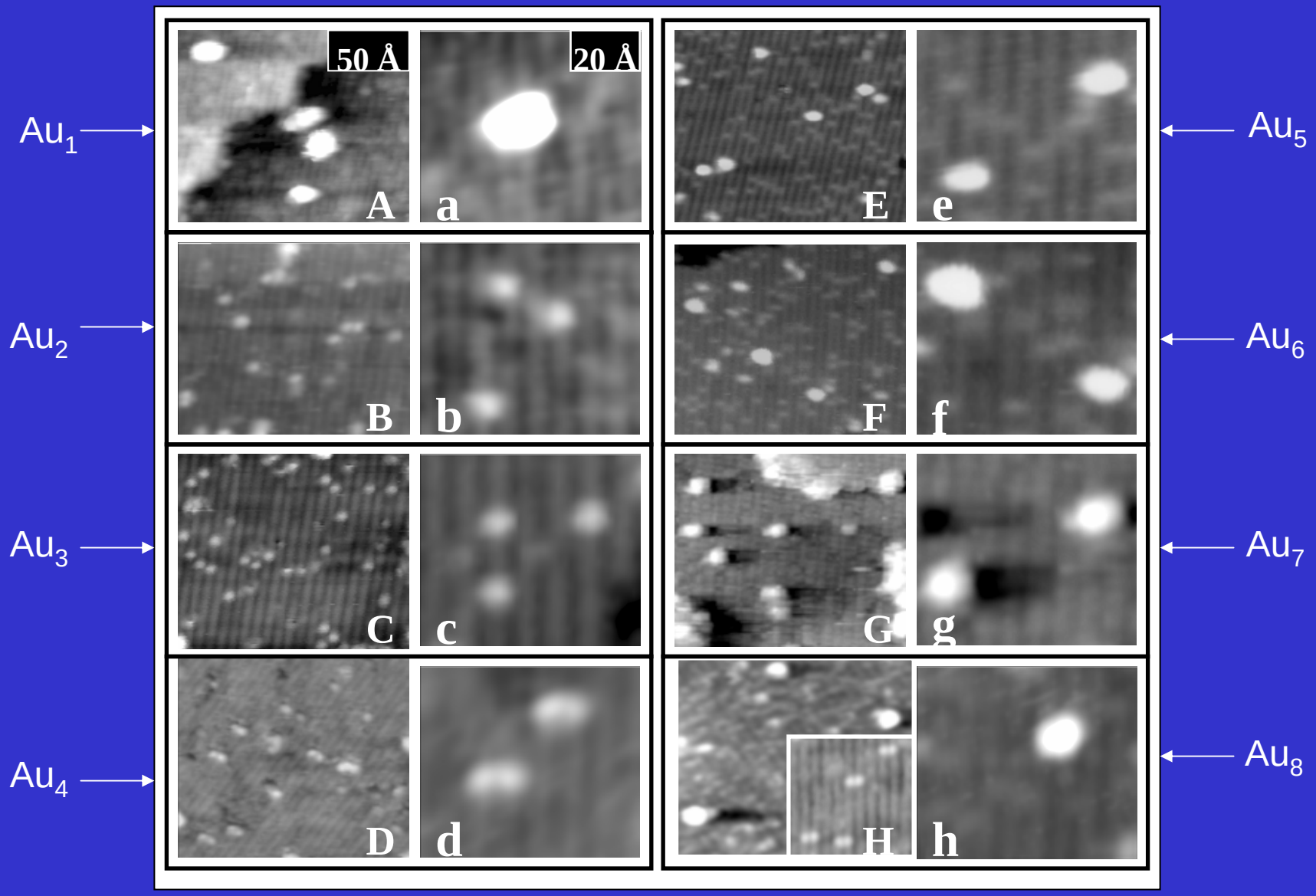
Au_3



Height: 1.5 Å ± 0.2 Å

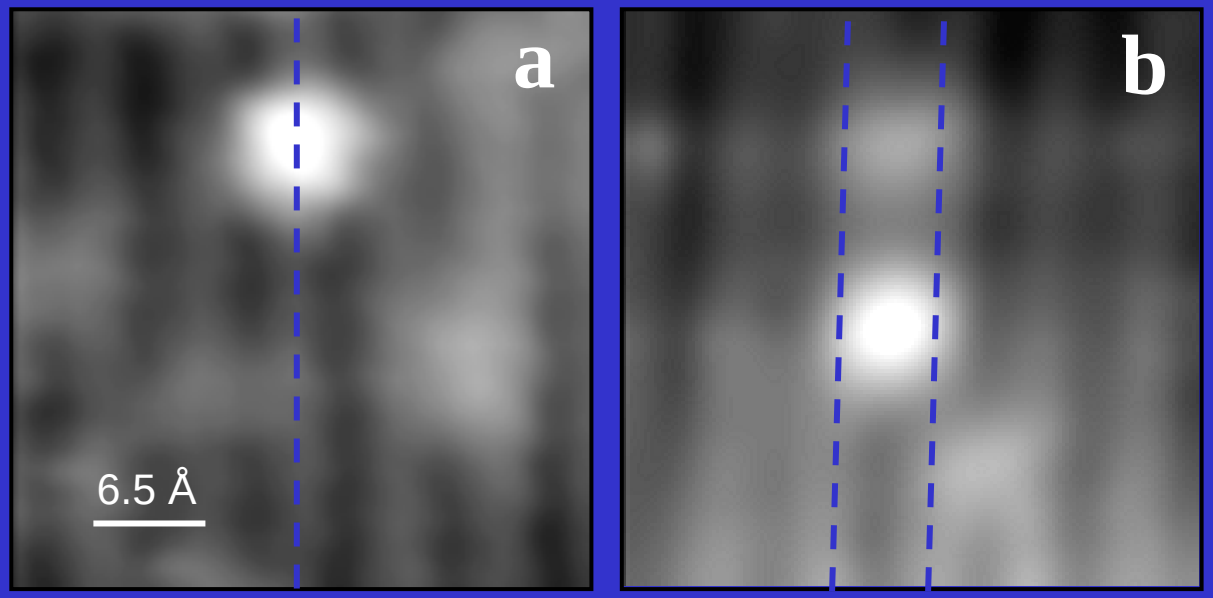


STM of Soft-landed Mass-selected Au_n^+ Clusters

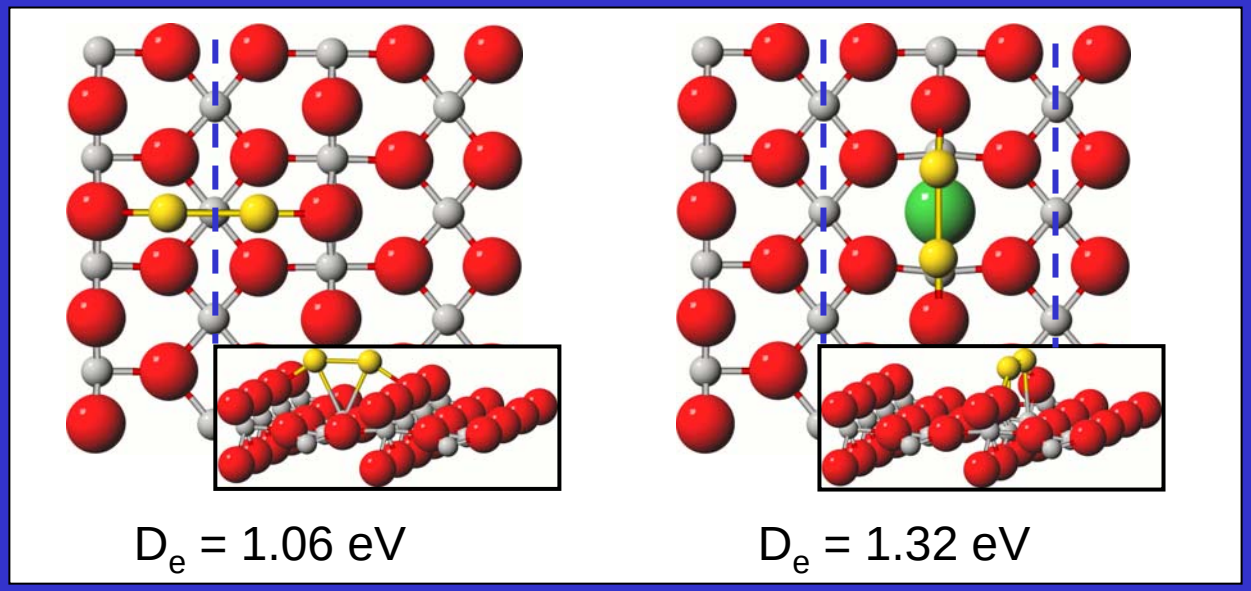


X. Tong, L. Benz, P. Kemper, H. Metiu, M.T. Bowers, and S.K. Buratto, *J. Am. Chem. Soc.* **127** 16516 (2005)

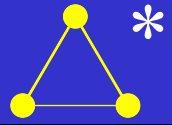
Adsorption sites of Au_2



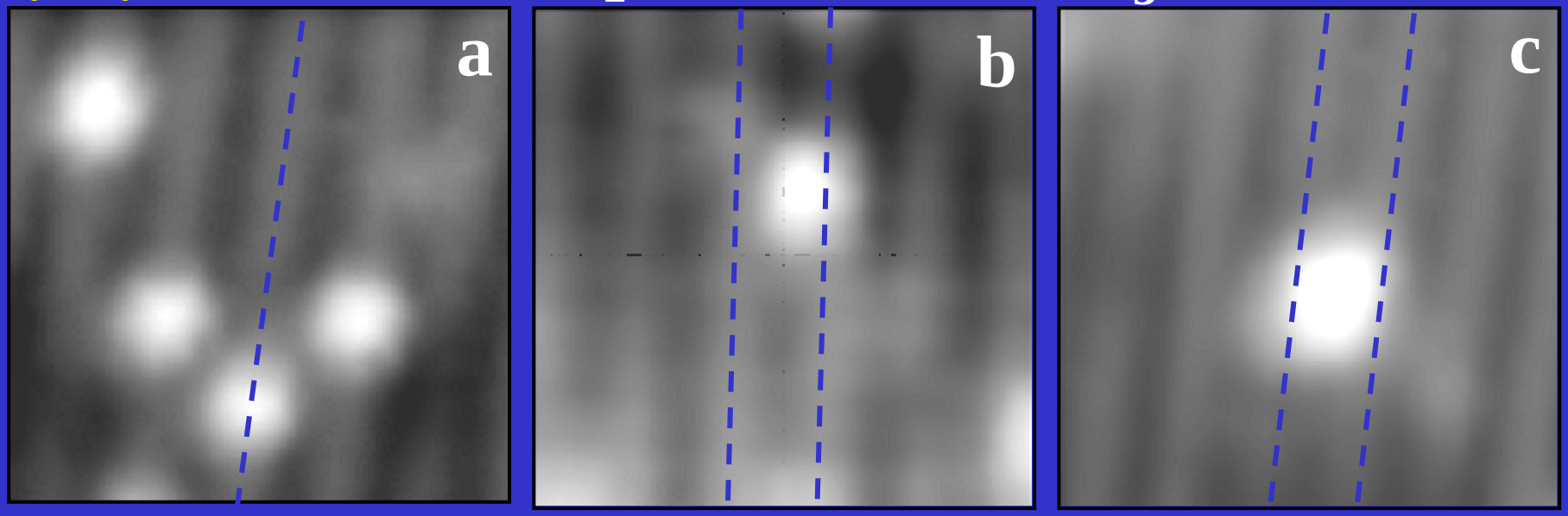
77% 23%

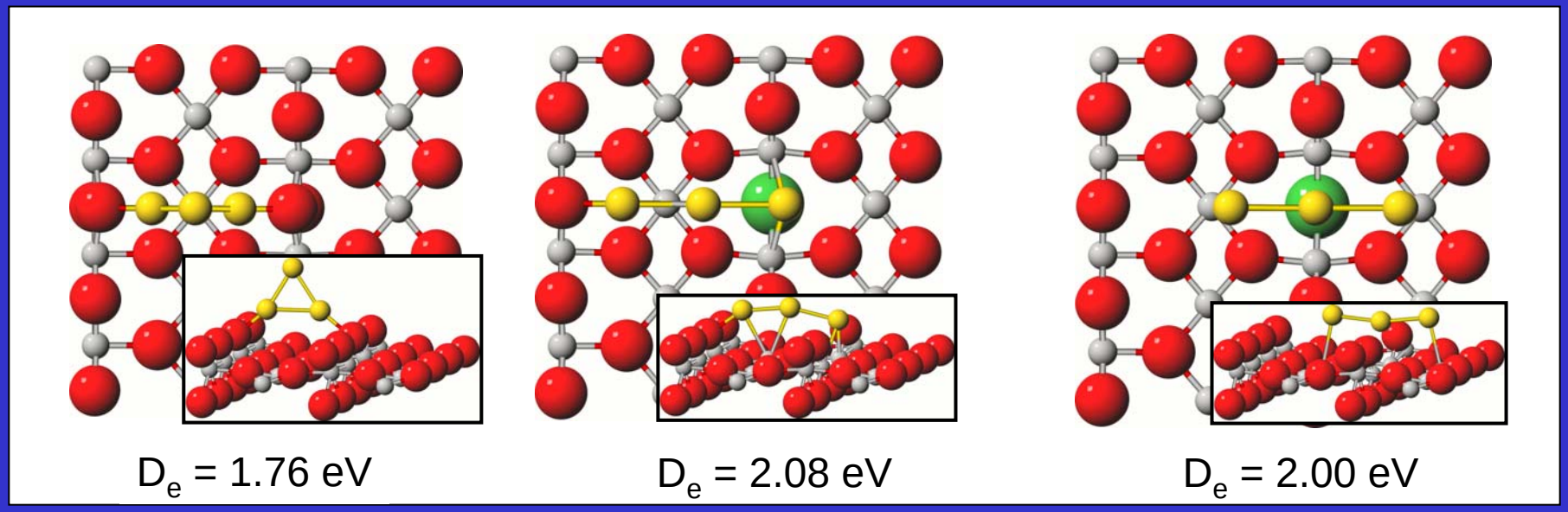


D_e = 1.06 eV D_e = 1.32 eV



Adsorption sites of Au_3*

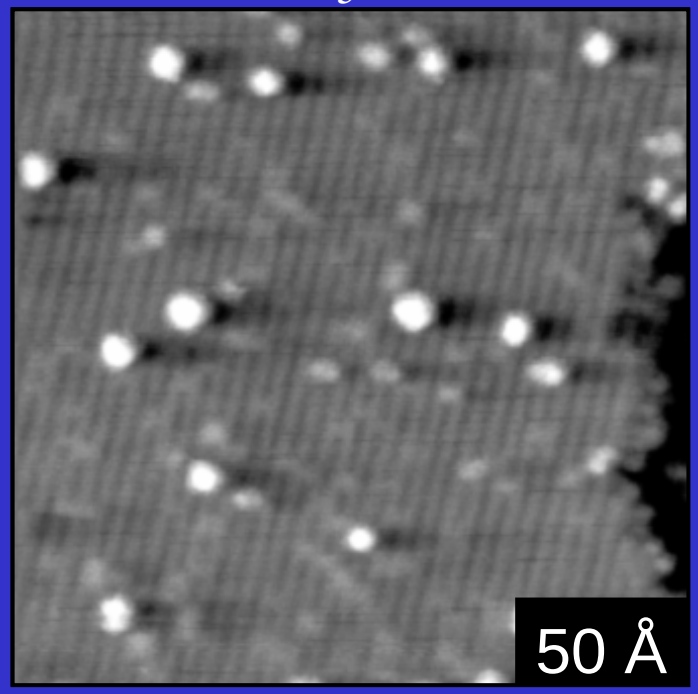




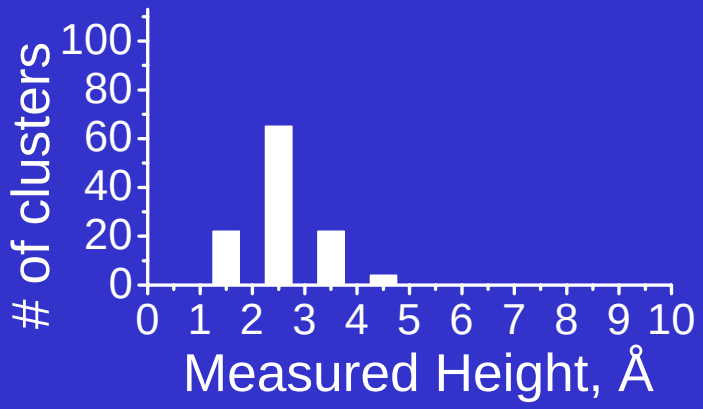
*All gas phase structures from Gilb, S. et al. JCP **116**, 4094, (2002)

Deposition of Au_5 and Au_6

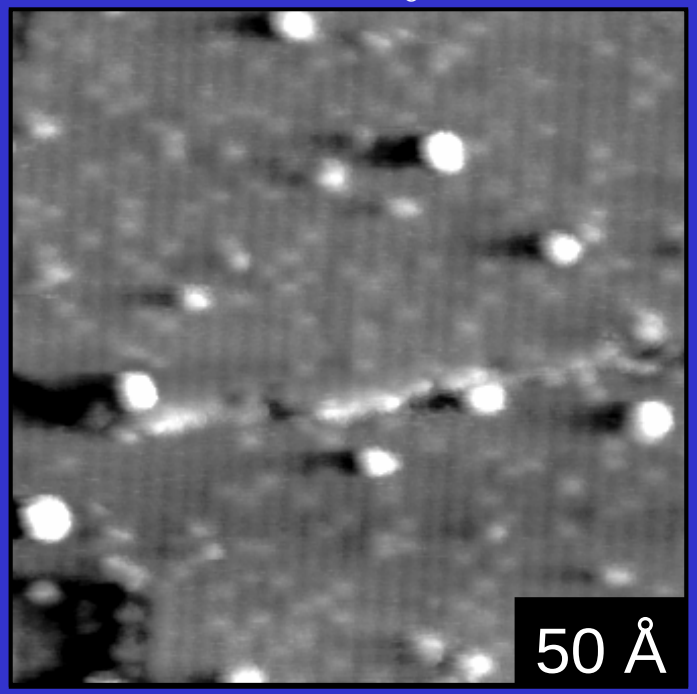
Au_5



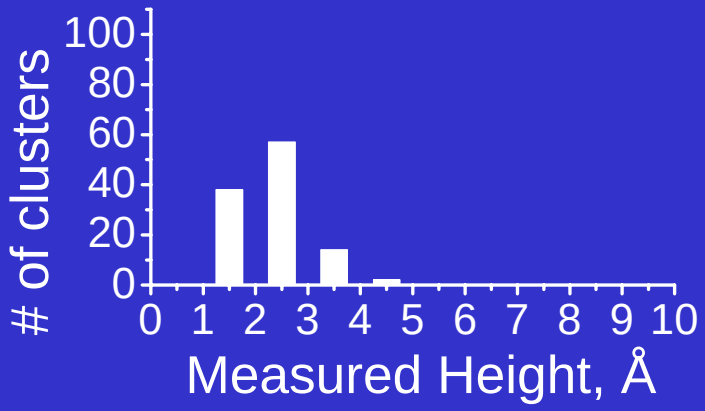
Height: 2.6 Å ± 0.6 Å



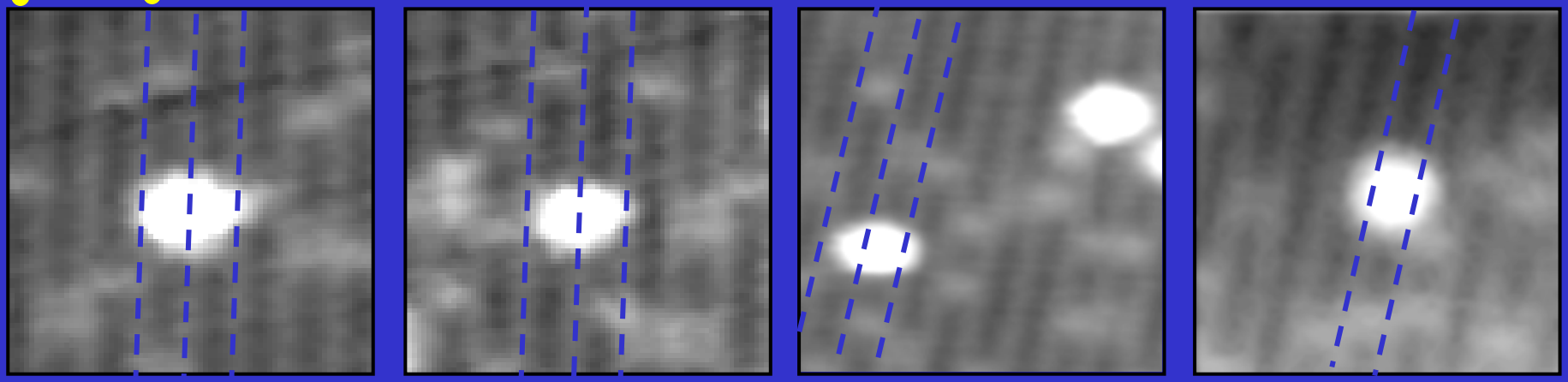
Au_6



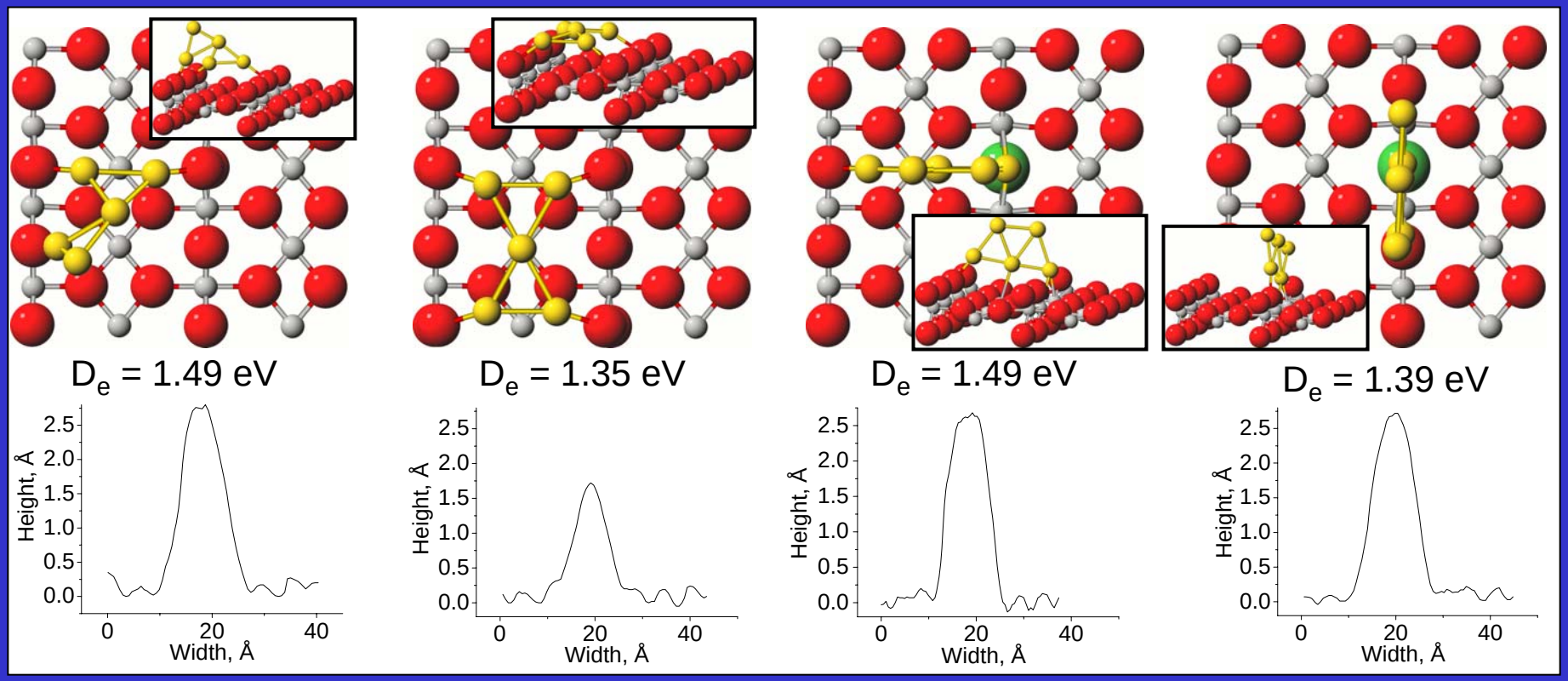
Height: 2.3 Å ± 0.7 Å

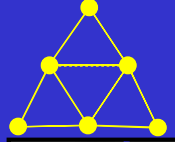


Adsorption sites of Au_5

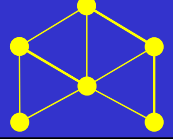


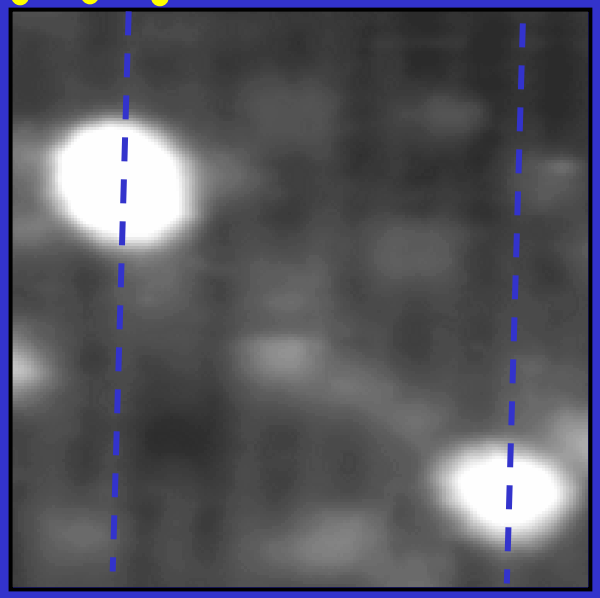
72% 16% 12%





Adsorption sites of Au_6





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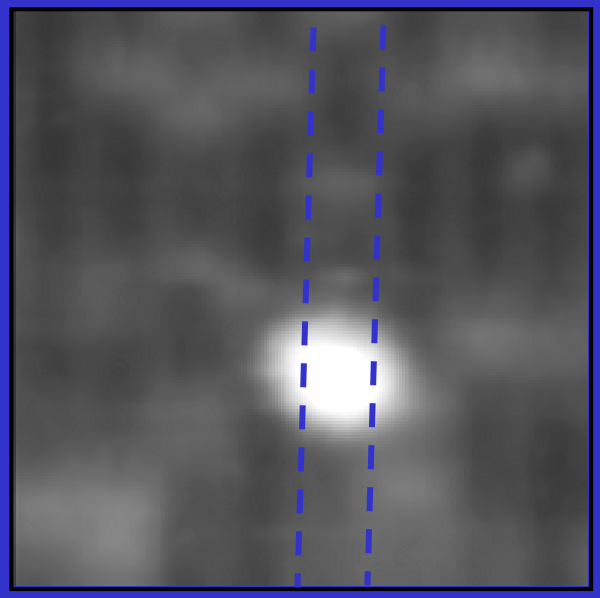

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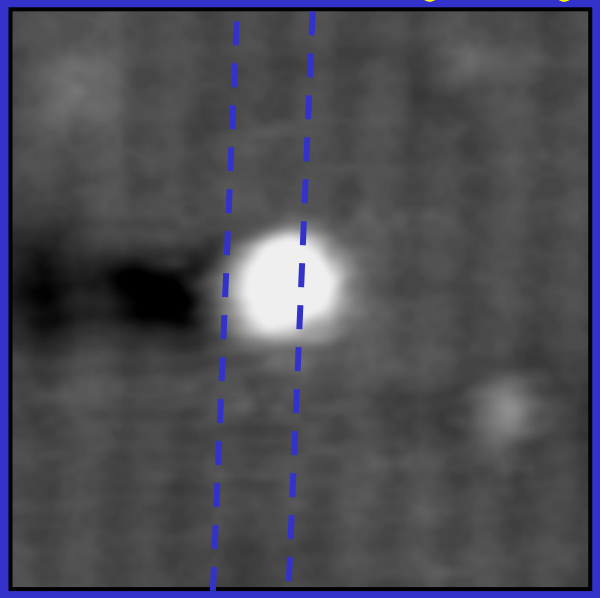

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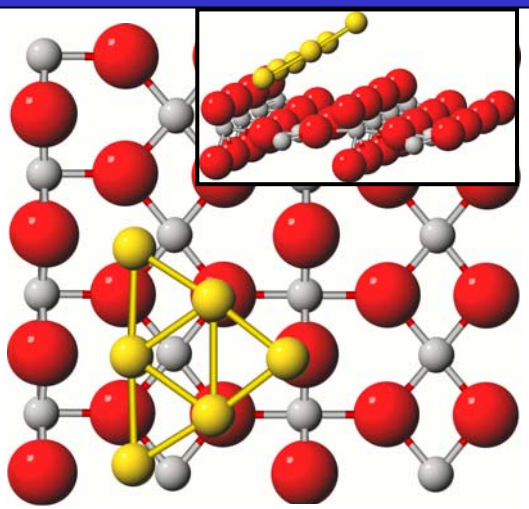
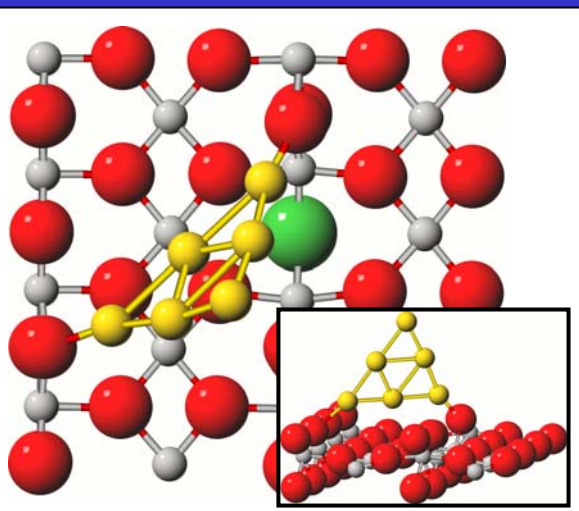
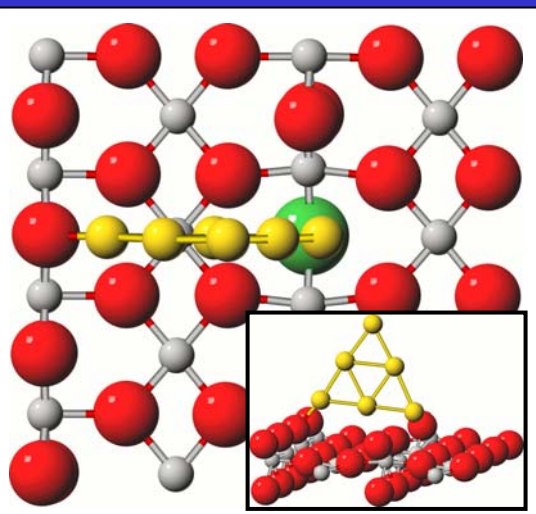


D_e = 0.71 eV

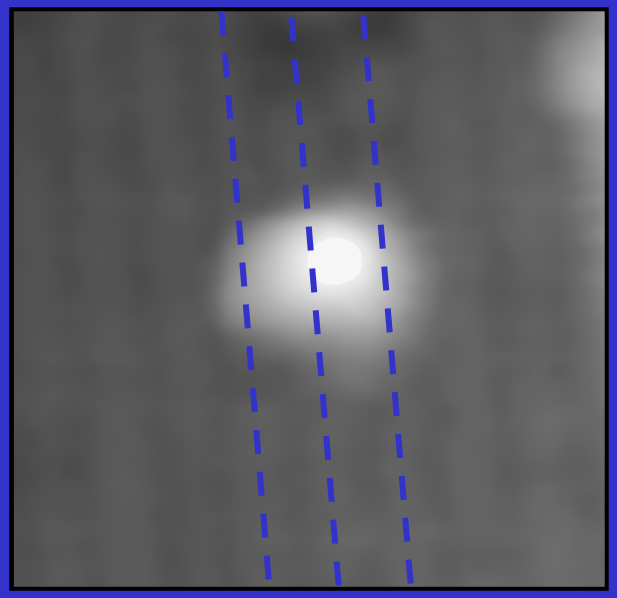


D_e = 1.00 eV



D_e = 0.88 eV

Deposition of Au_7



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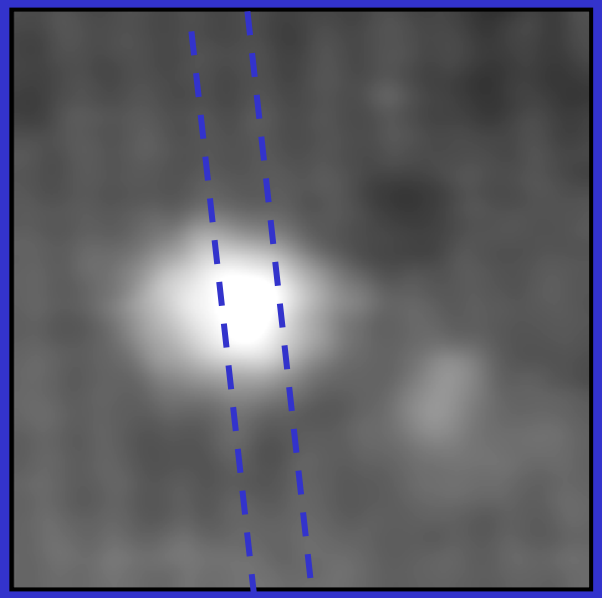

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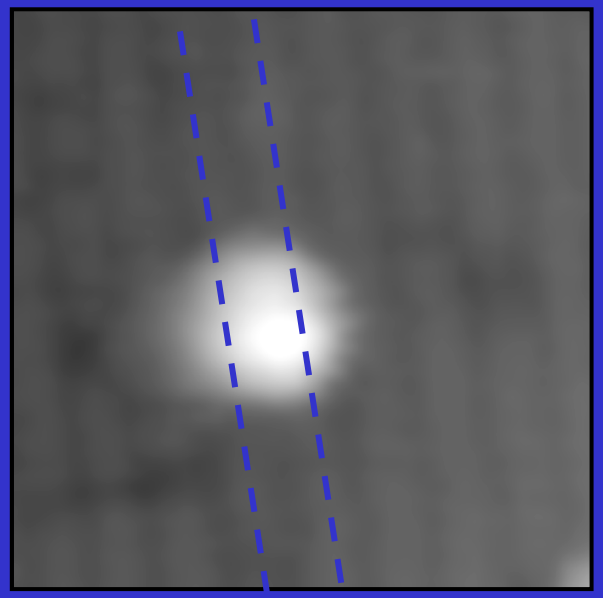

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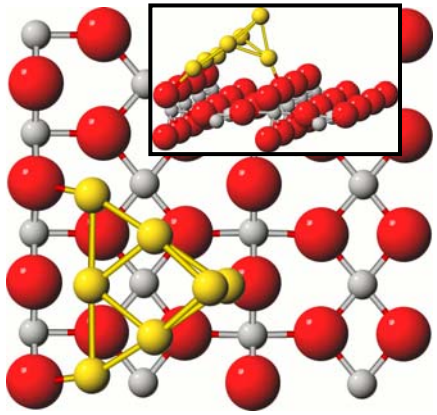
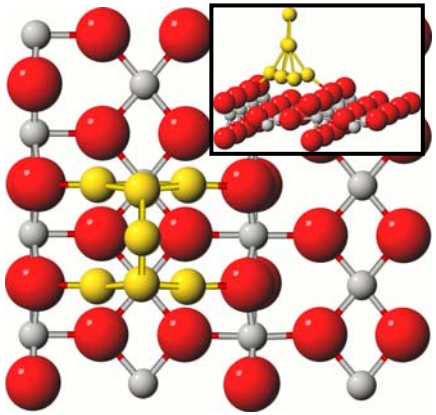
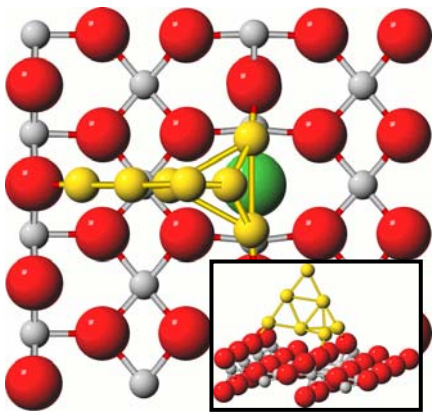


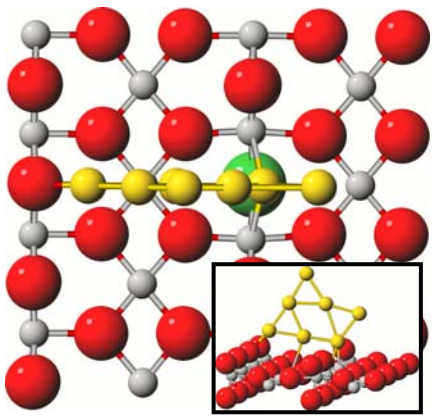
D_e = 1.52 eV



D_e = 1.41 eV

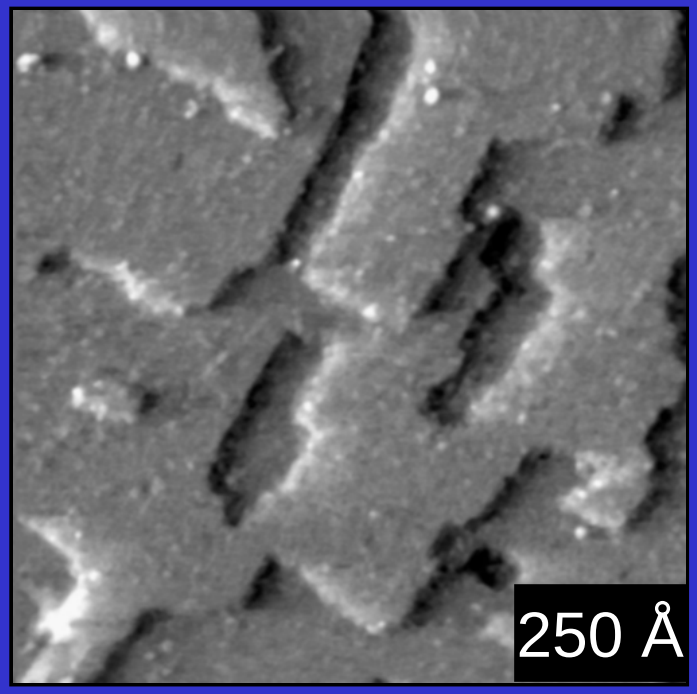


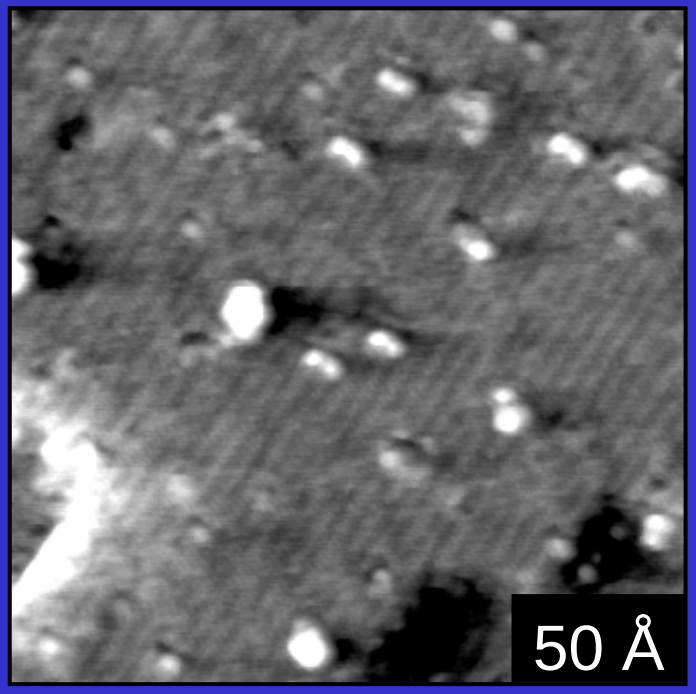
D_e = 1.72 eV

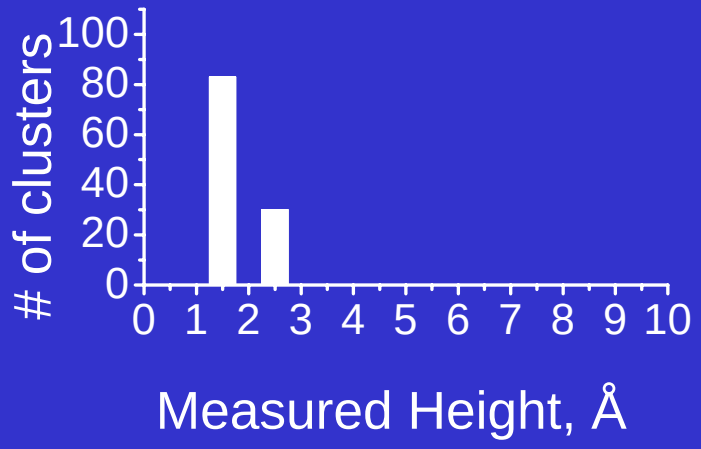


D_e = 1.56 eV

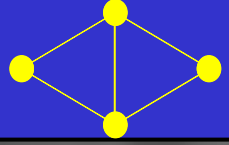
Deposition of Au_4



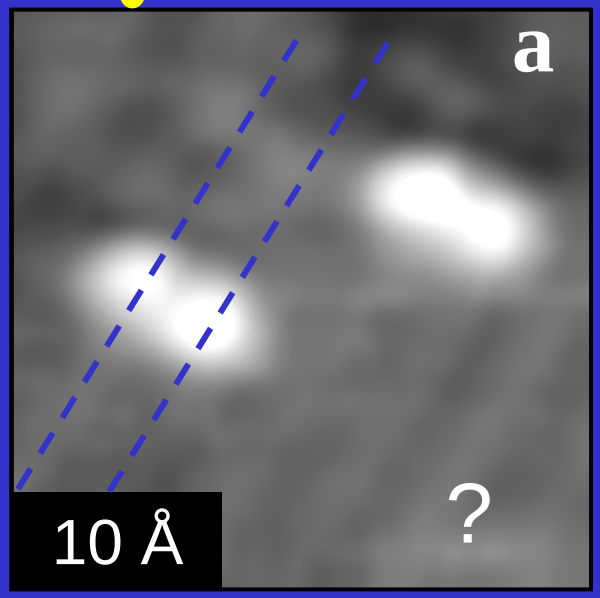




Height: 1.7 Å ± 0.2 Å



Adsorption sites of Au_4



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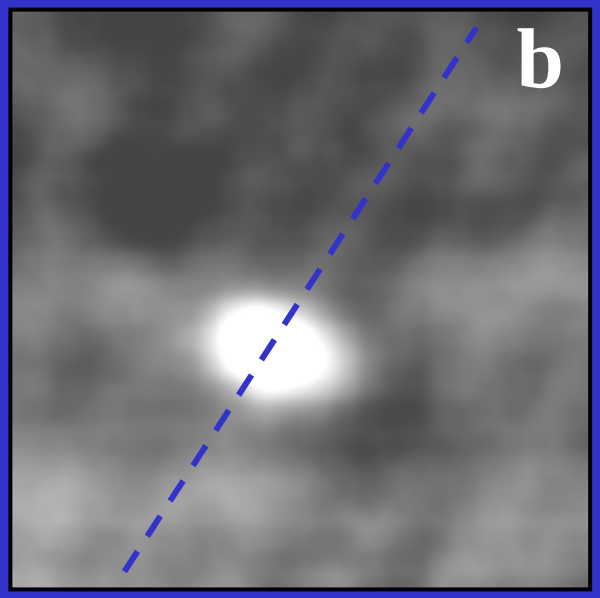

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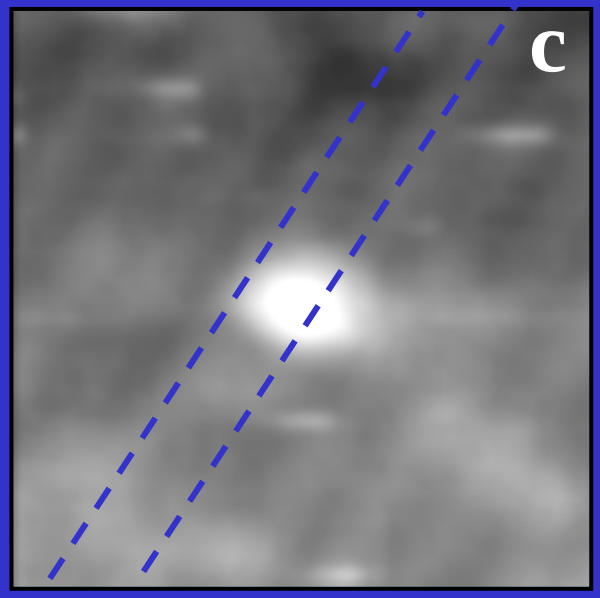

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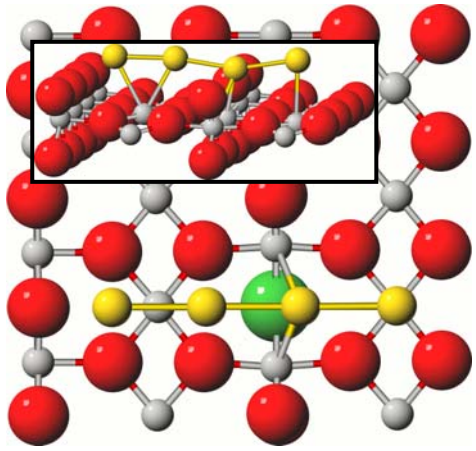
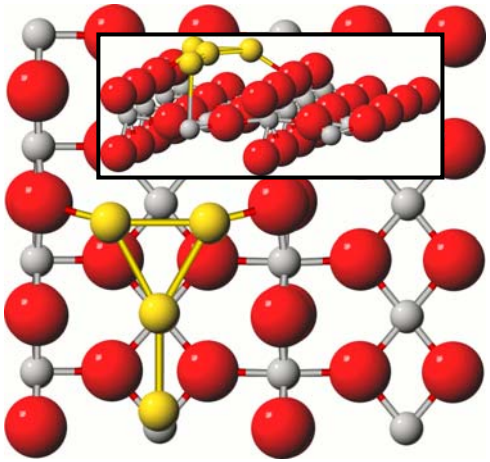
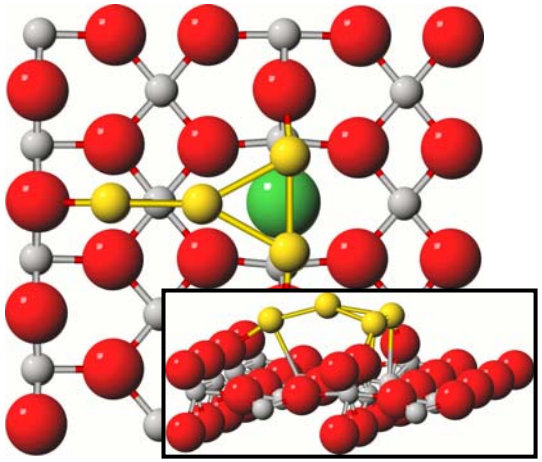


D_e = 1.37 eV

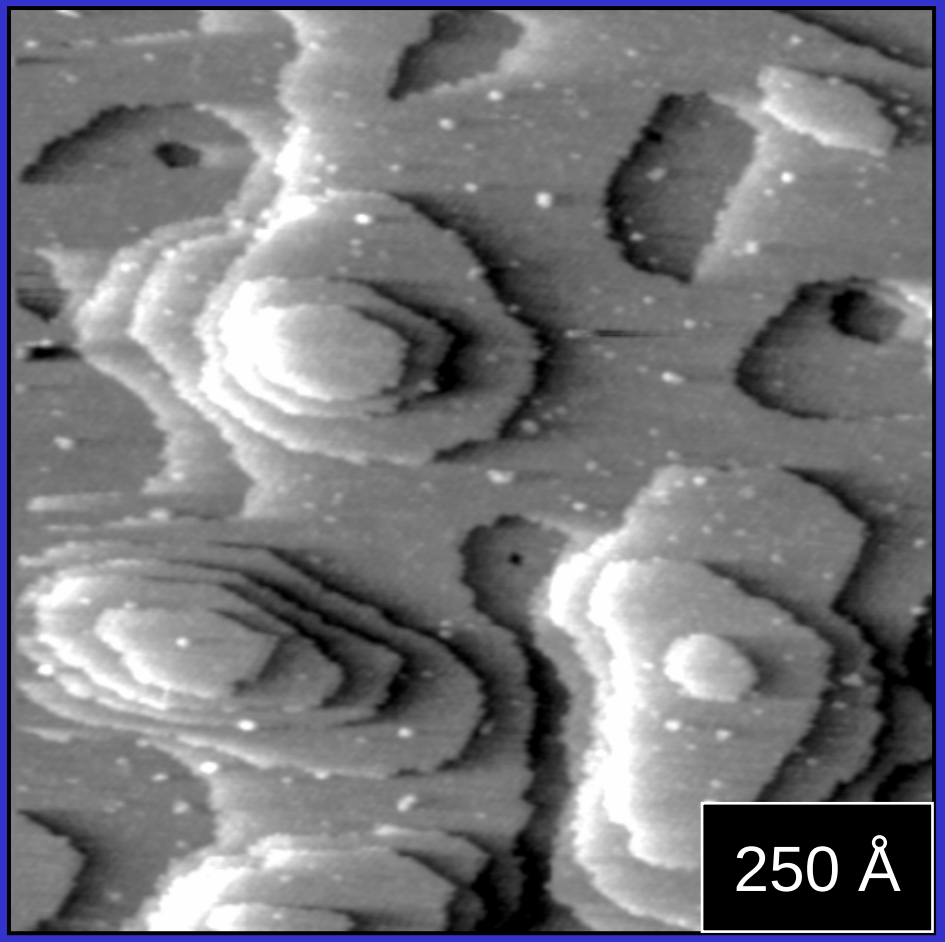


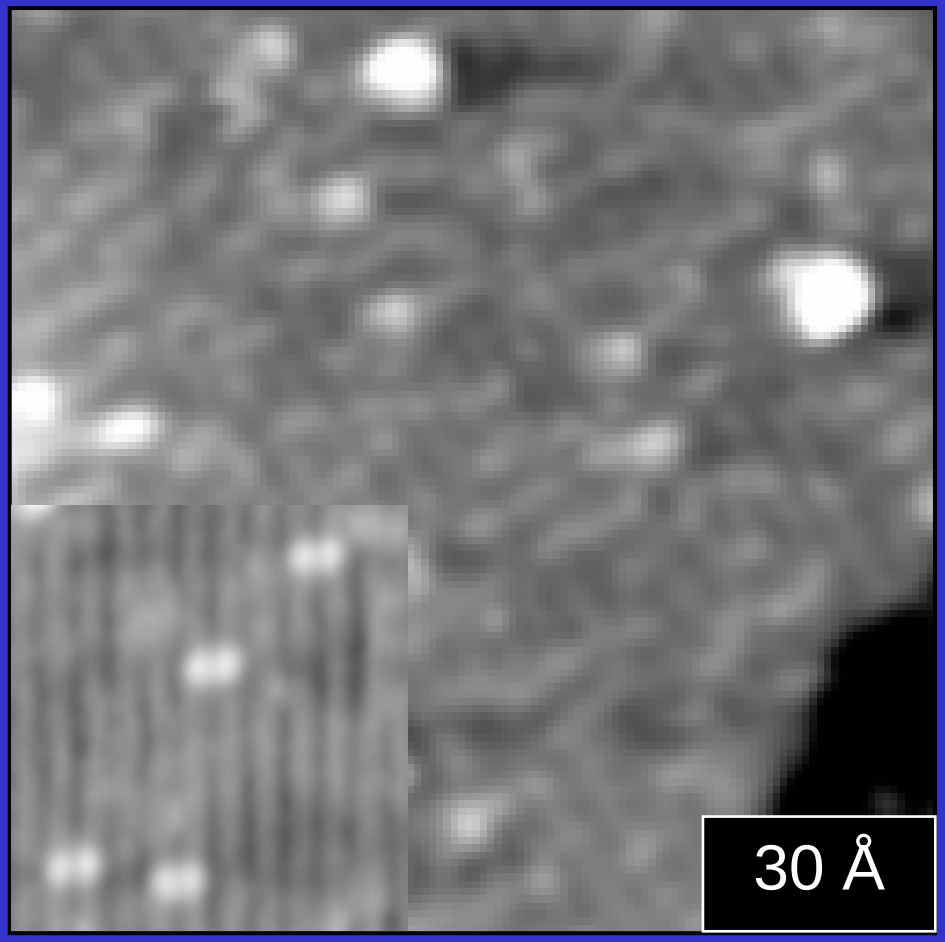
D_e = 1.37 eV



D_e = 1.64 eV

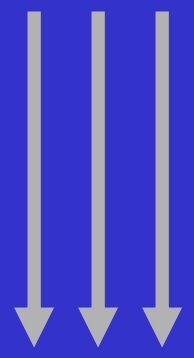
Au_8 Clusters on $TiO_2(110)$





Silver Soft Landing

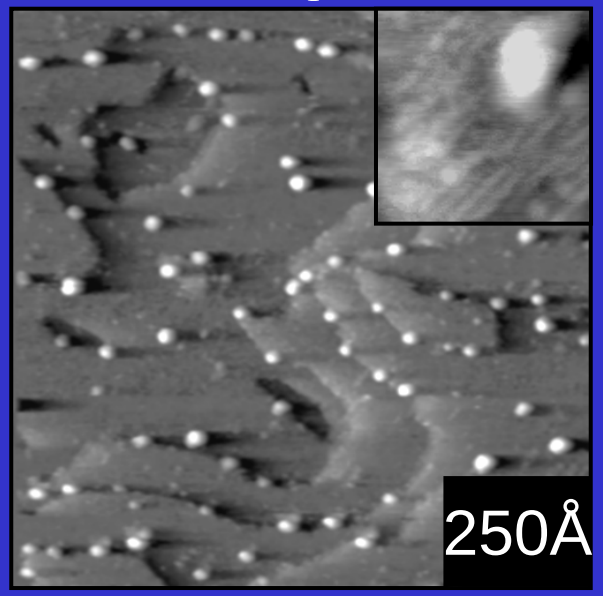
Ag_n^+ (n = 1 – 5) clusters with average incident energies of 0 eV



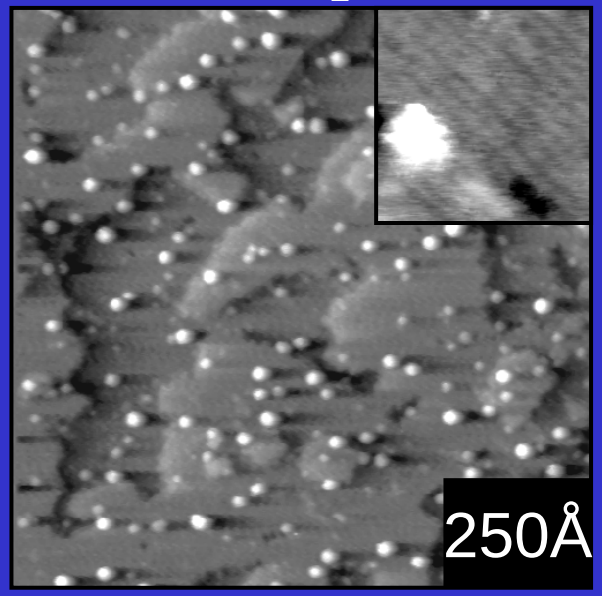
$TiO_2(110)$

Deposition of Silver

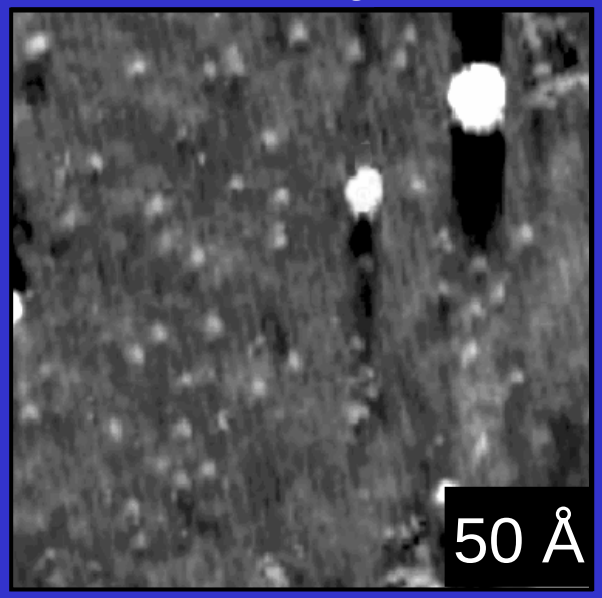
Ag_1



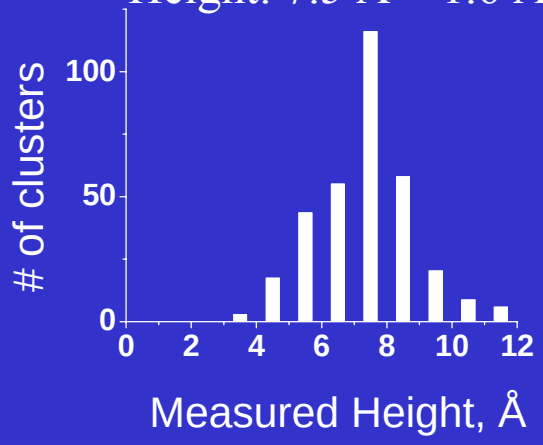
Ag_2



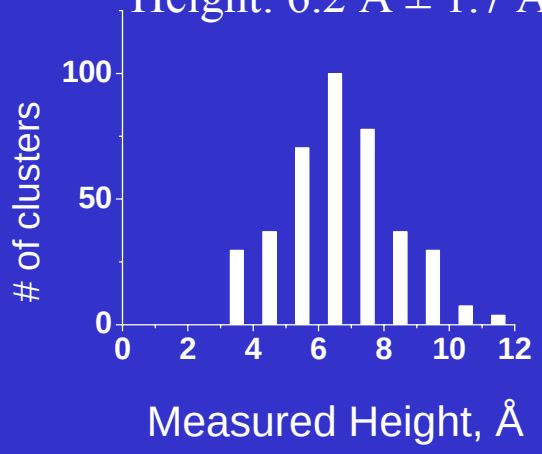
Ag_3



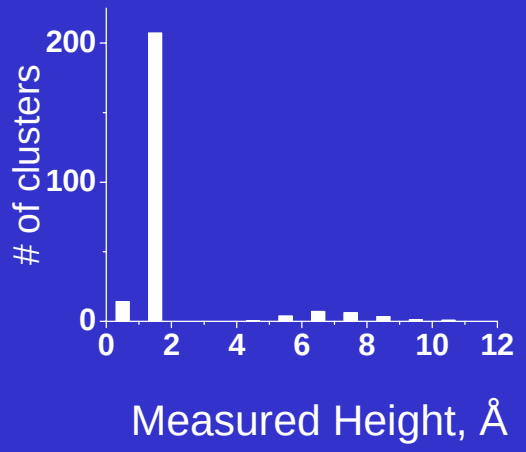
Height: 7.5 Å ± 1.6 Å



Height: 6.2 Å ± 1.7 Å

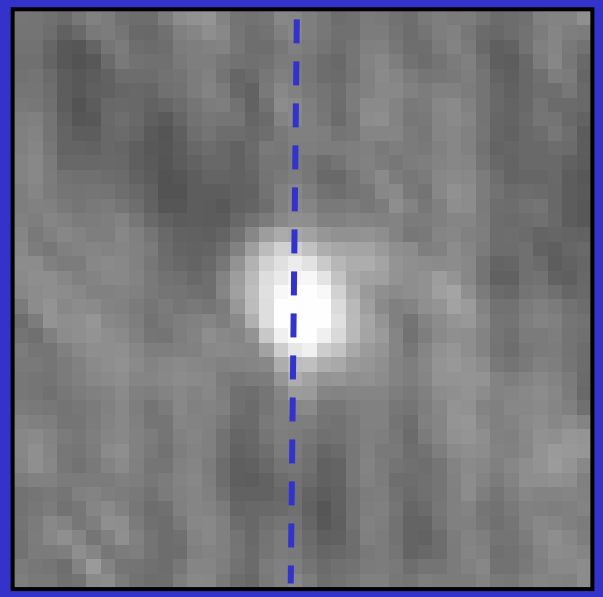


Height: 1.5 Å ± 0.3 Å

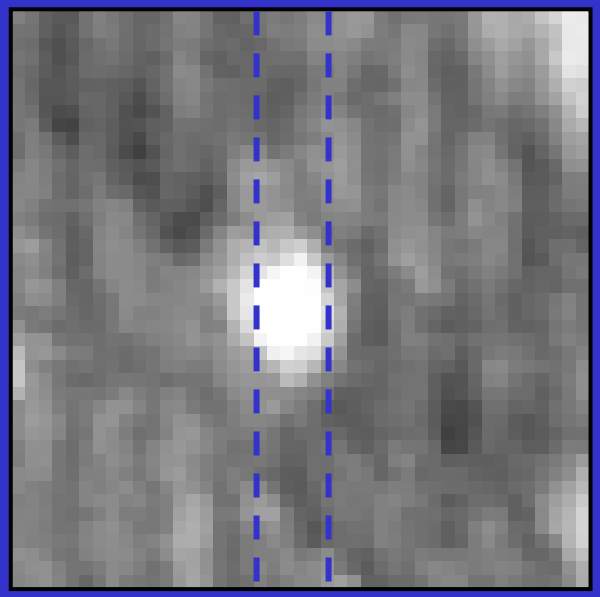


L. Benz, et al. *J. Chem. Phys.* **122** 081102 (2005)

Adsorption sites of Ag_3



94%



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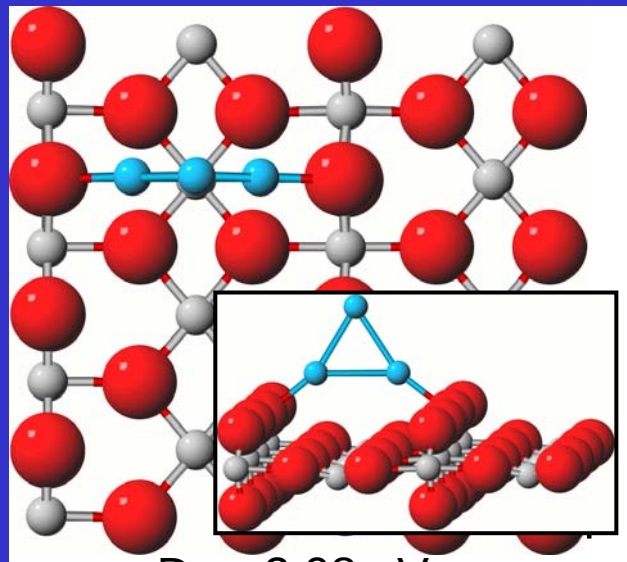
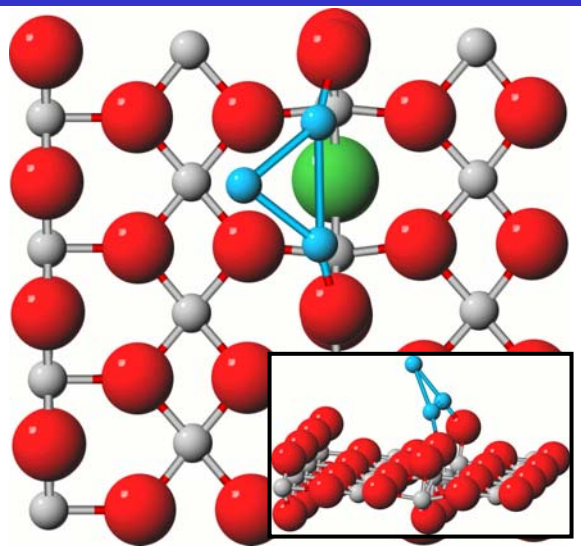
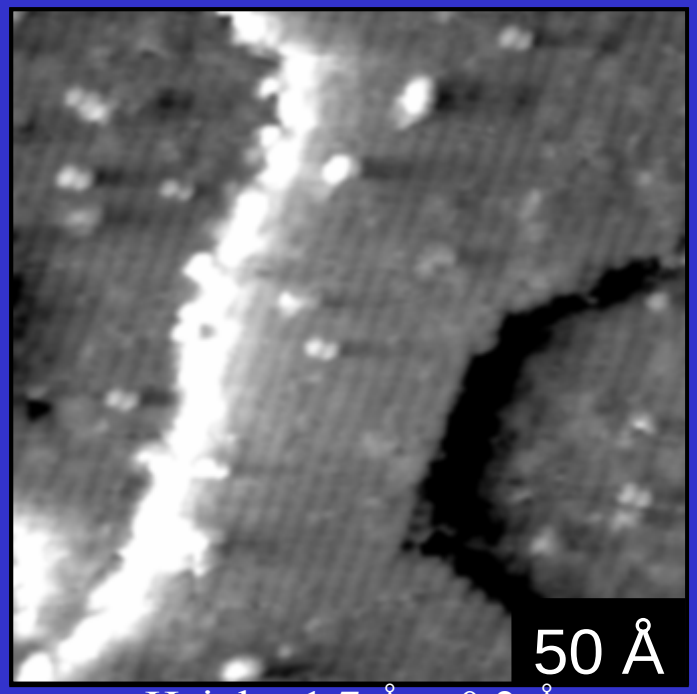


D_e = 2.08 eV

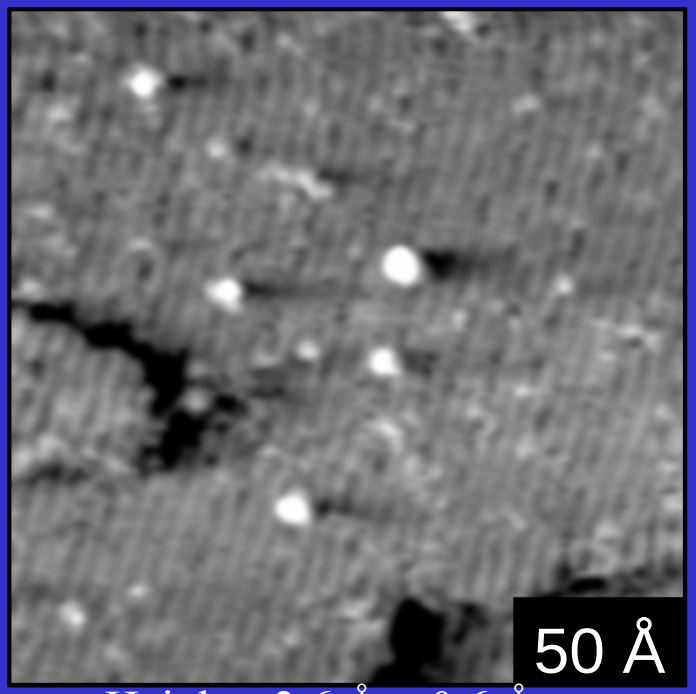


D_e = 1.80 eV

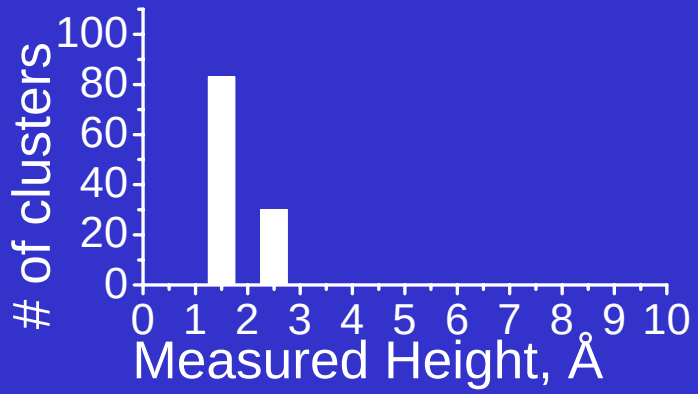
Deposition of Ag_4 and Ag_5

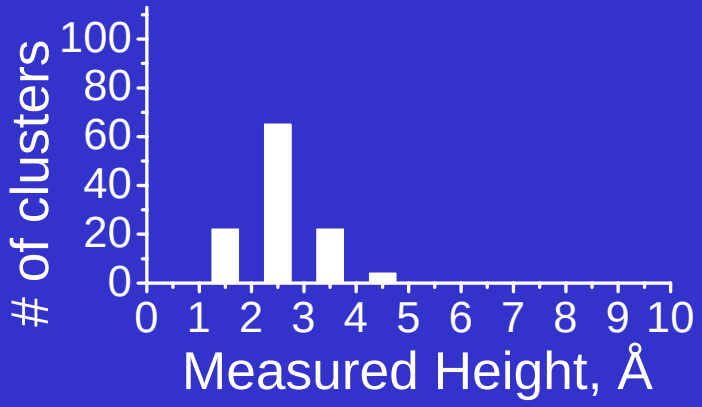


Height: 1.7 Å ± 0.2 Å

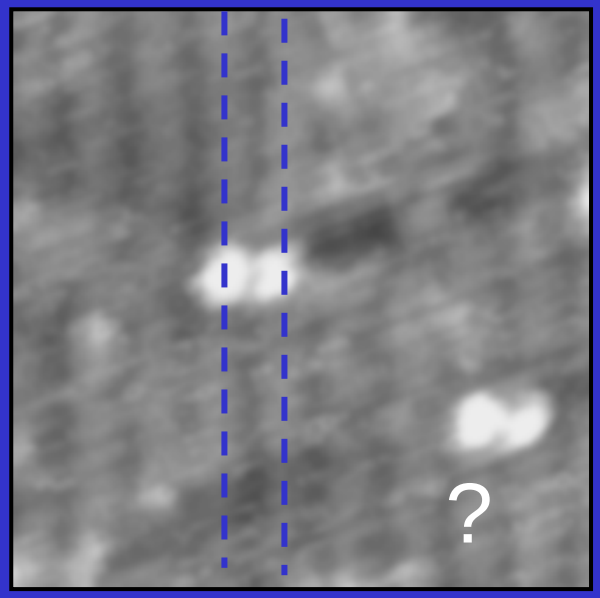


Height: 2.6 Å ± 0.6 Å





Adsorption sites of Ag_4



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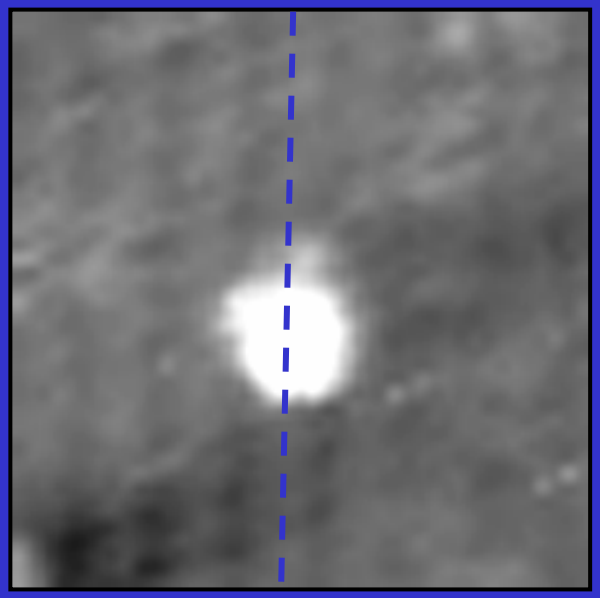

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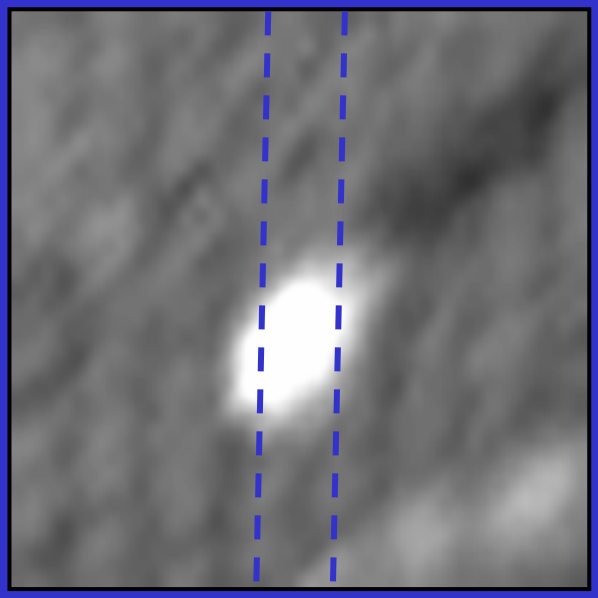

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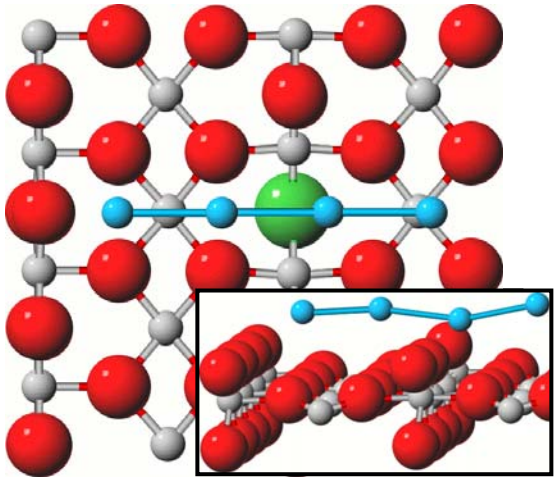
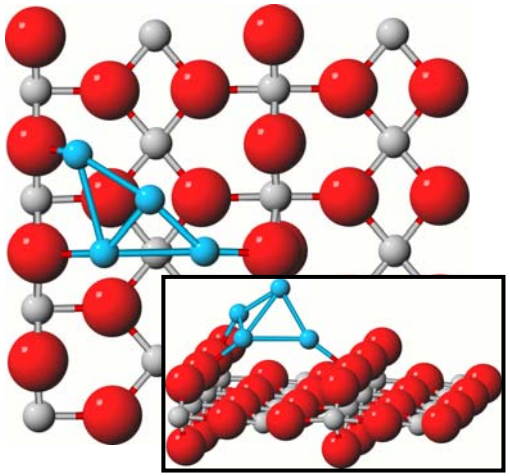
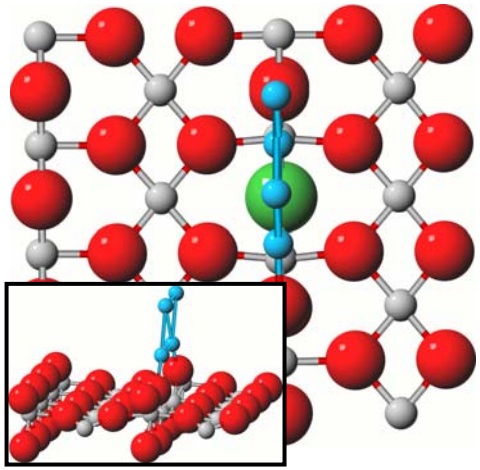


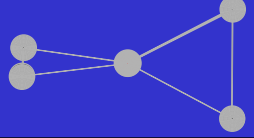
D_e = 0.85 eV



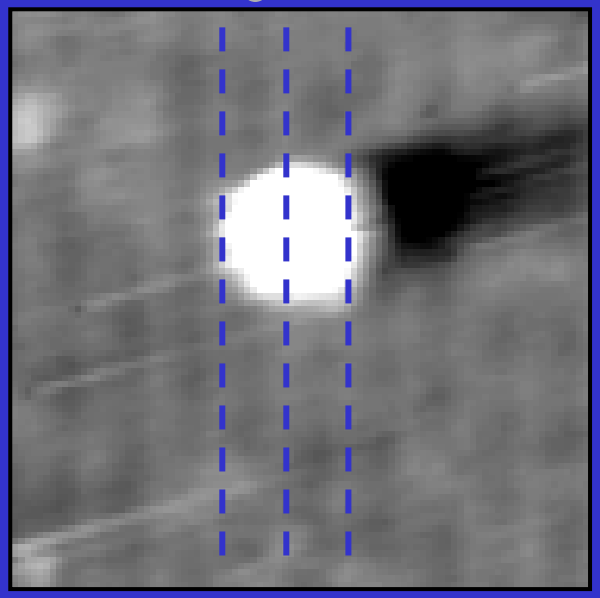
D_e = 1.16 eV



D_e = 0.99 eV



Adsorption sites of Ag_5



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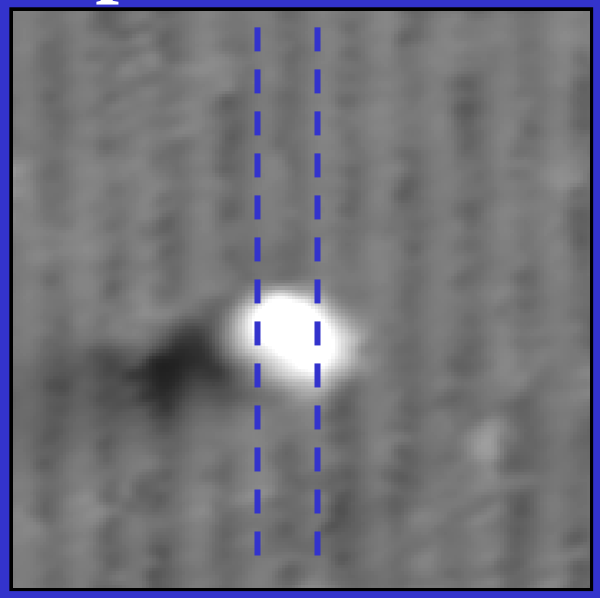

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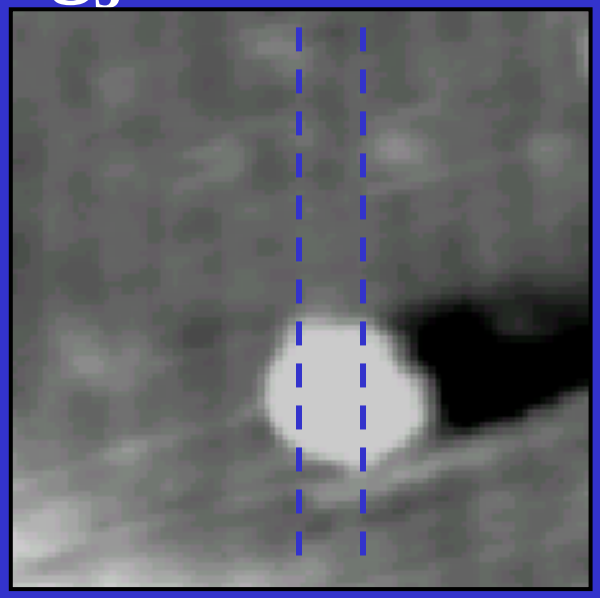
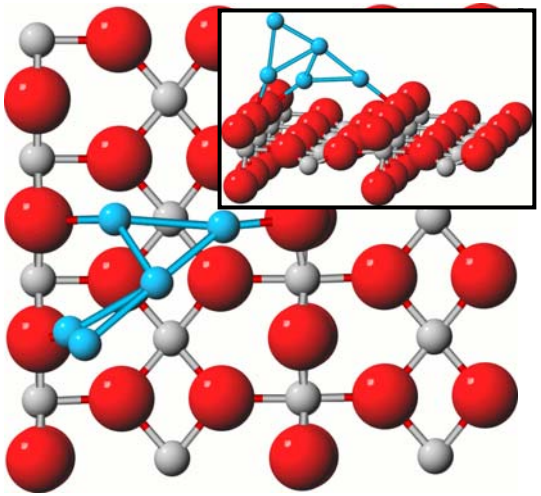
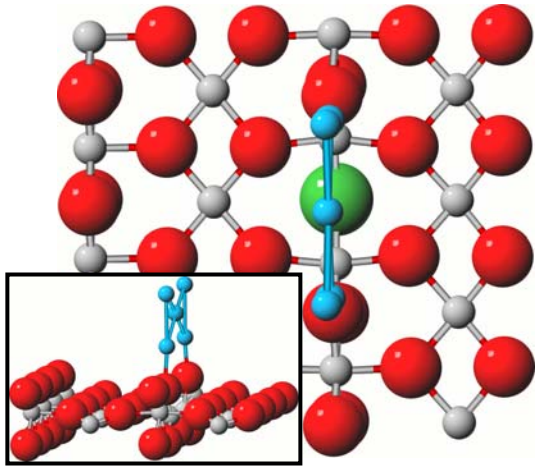


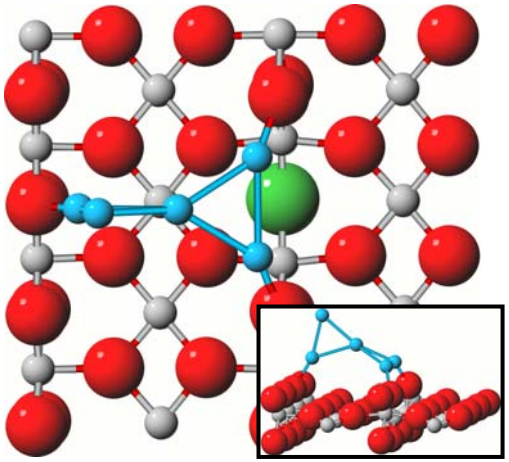
11%



D_e = 1.90 eV

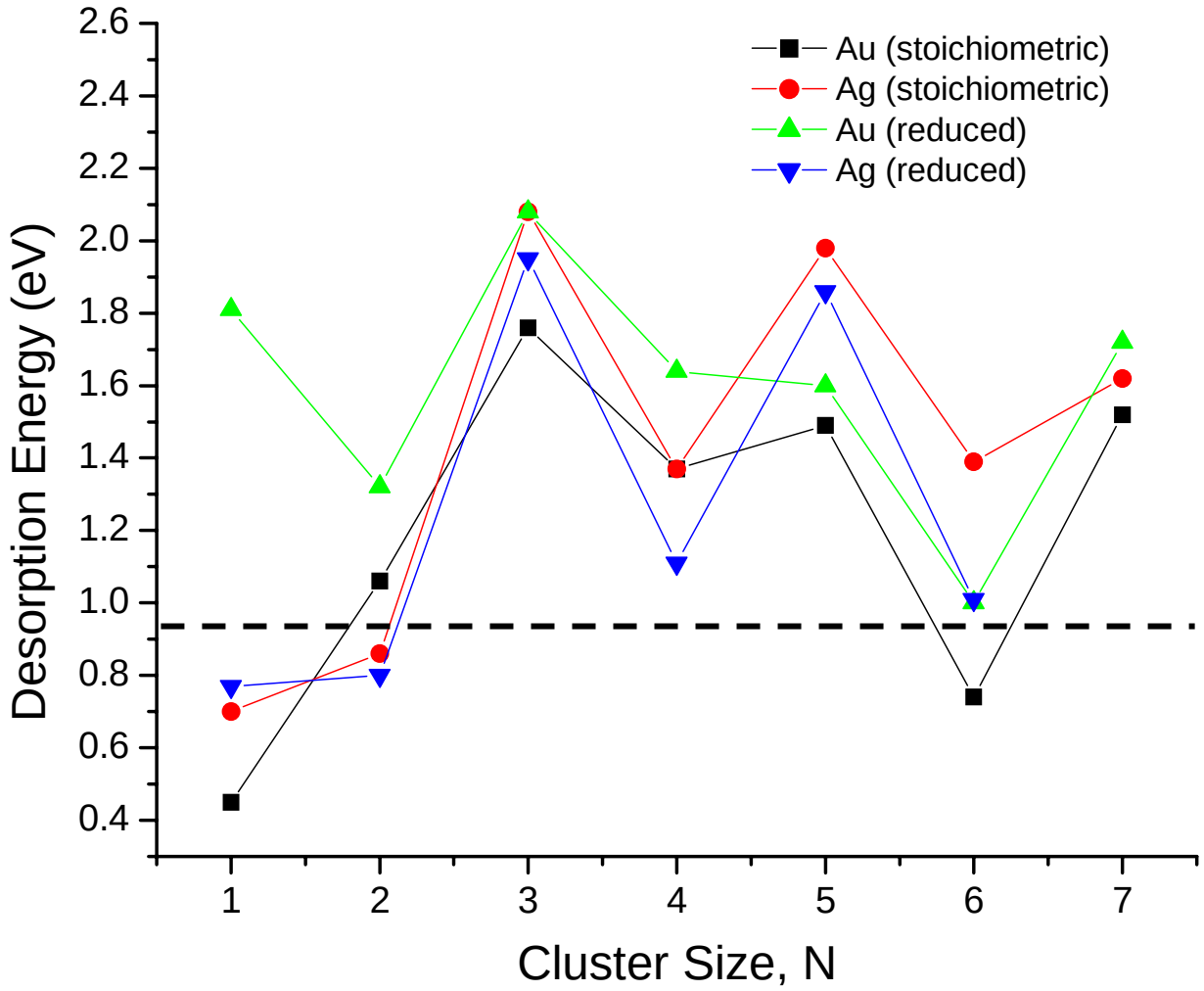


D_e = 1.33 eV



D_e = 1.77 eV

DFT Desorption Energies

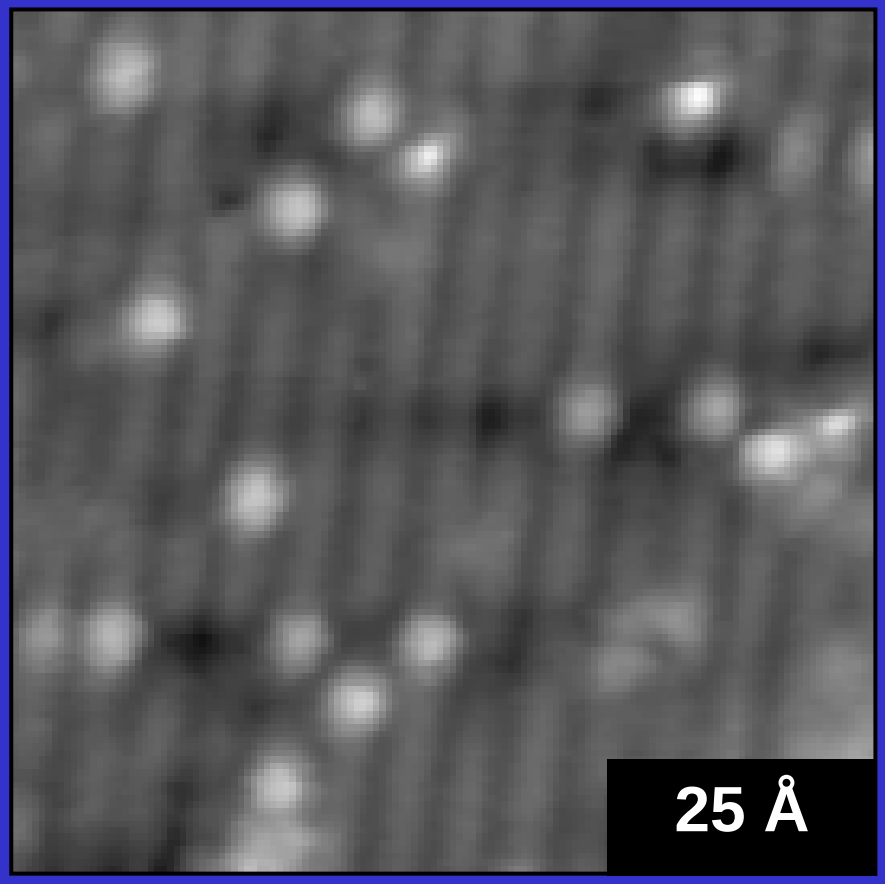


Summary (so far)

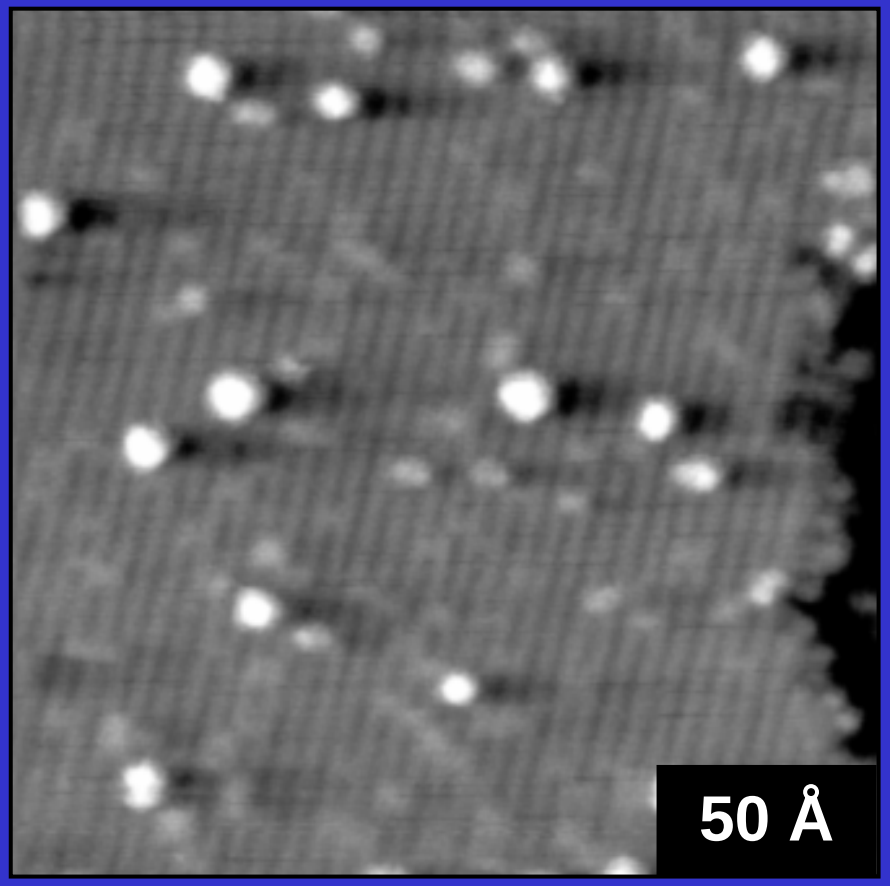
- Ag_1, Ag_2, and Au_1 are mobile on the surface of titania
- Ag_{3-5} and Au_{2-8} remain intact on the surface
- DFT suggests a binding mechanism which involves ligation of the clusters by O atoms of neighboring bridging O rows, resulting in the appearance of clusters over 5-c Ti rows, consistent with STM images
- Au_{2-4} (Ag_{3-4})form structures which appear "flatter" than structures formed from Au_{5-7} (Ag_5)

Density of vacancies between clusters depends on cluster size?!!!

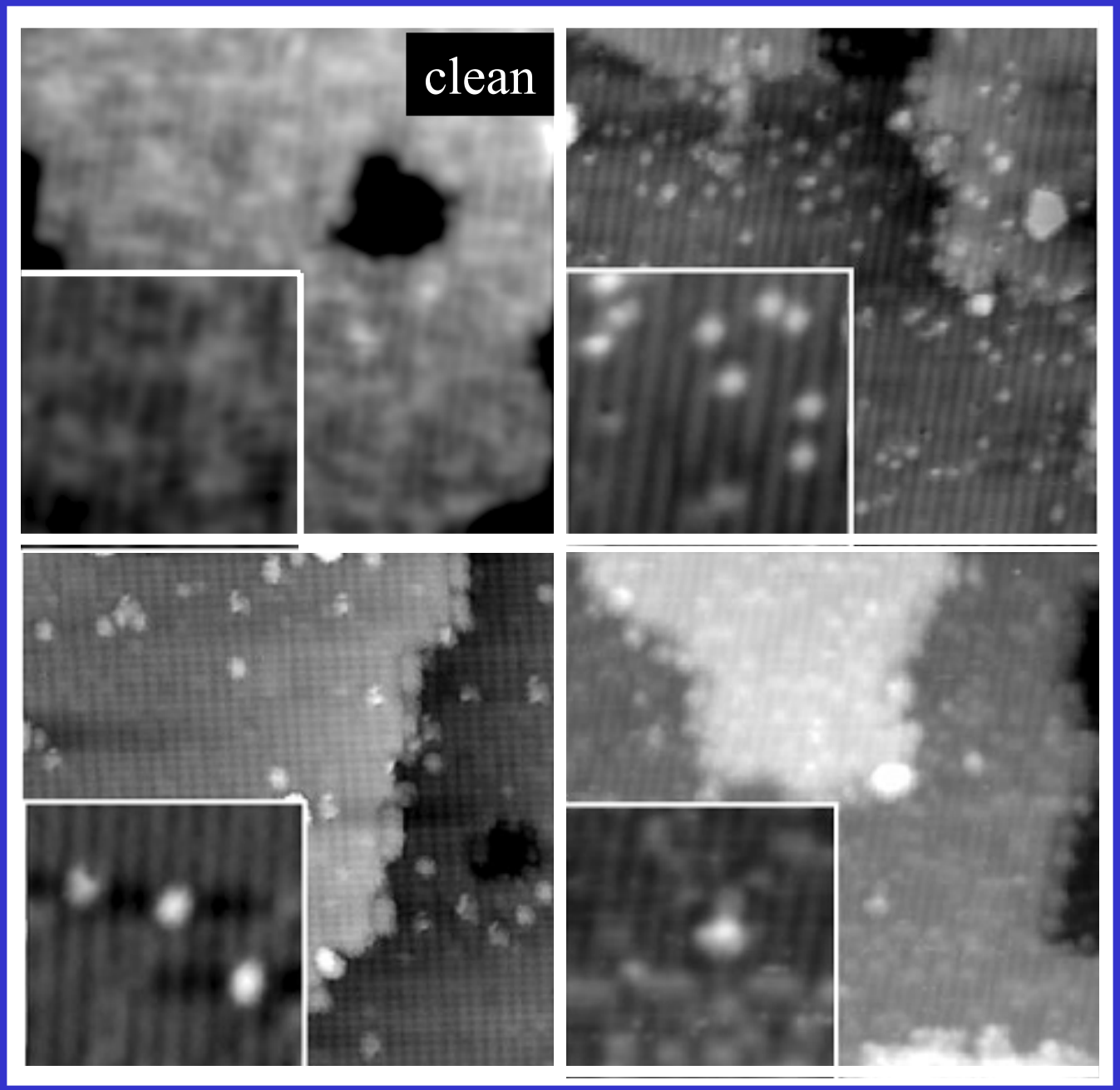
Au_3/TiO_2



Au_5/TiO_2

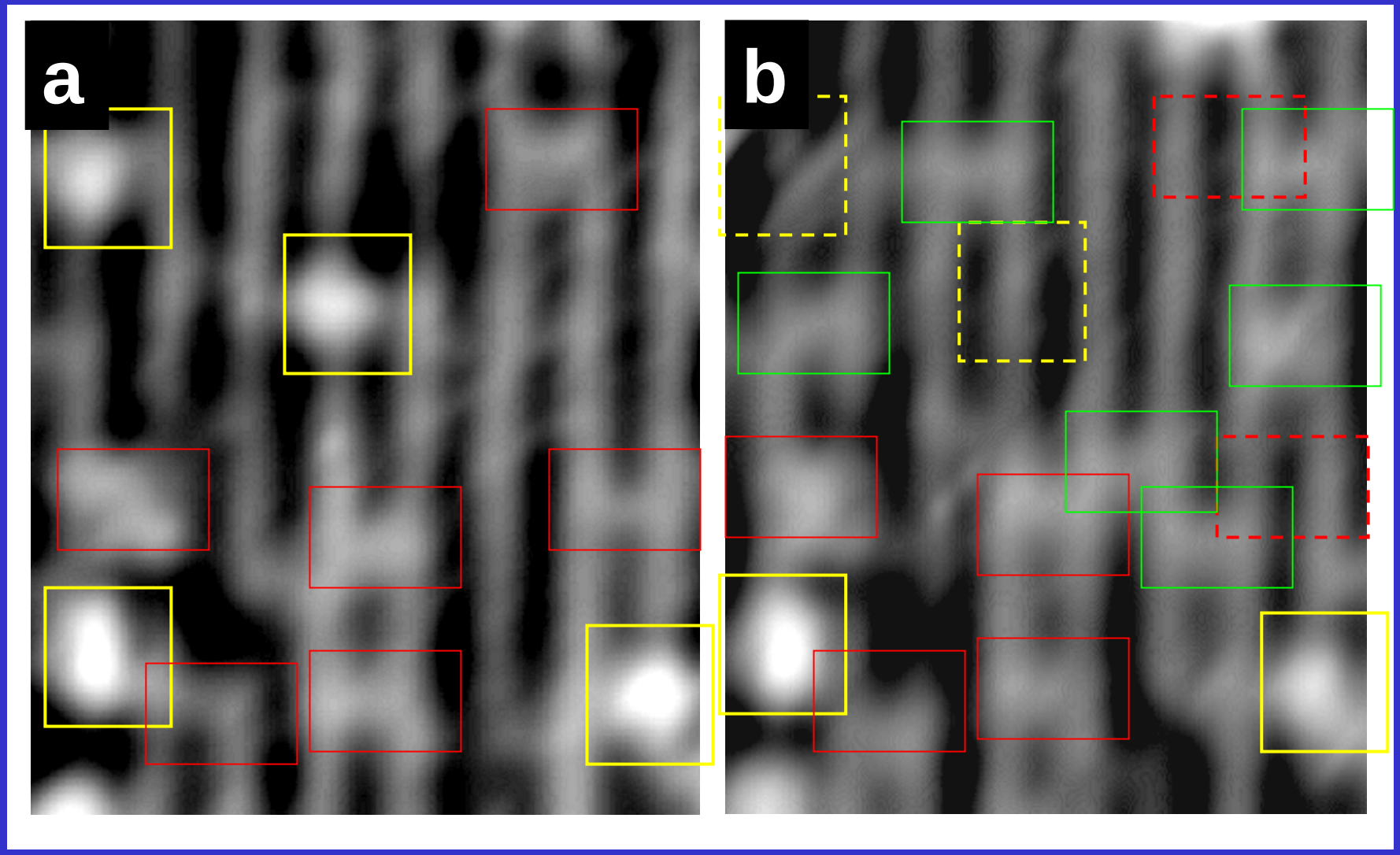


Density of vacancies increases with density of Au_3 decreases



Each Au_3 eliminated ~1.5 o-vacancies

Density of vacancies increases following the removal of Au_3



Au_3

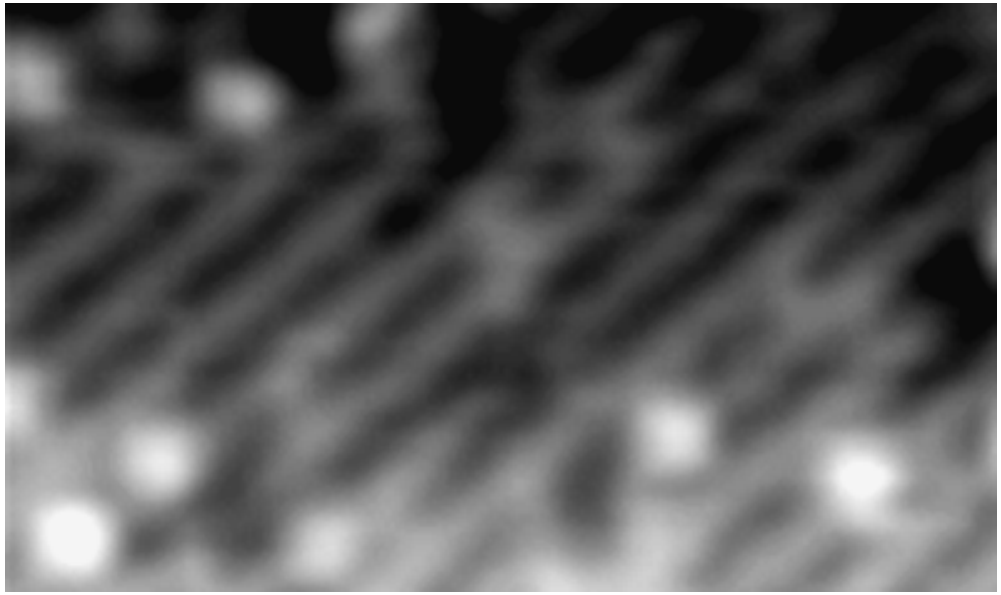
removed Au_3 due to interaction of tip with Au_3

vacancy

newly appeared vacancy

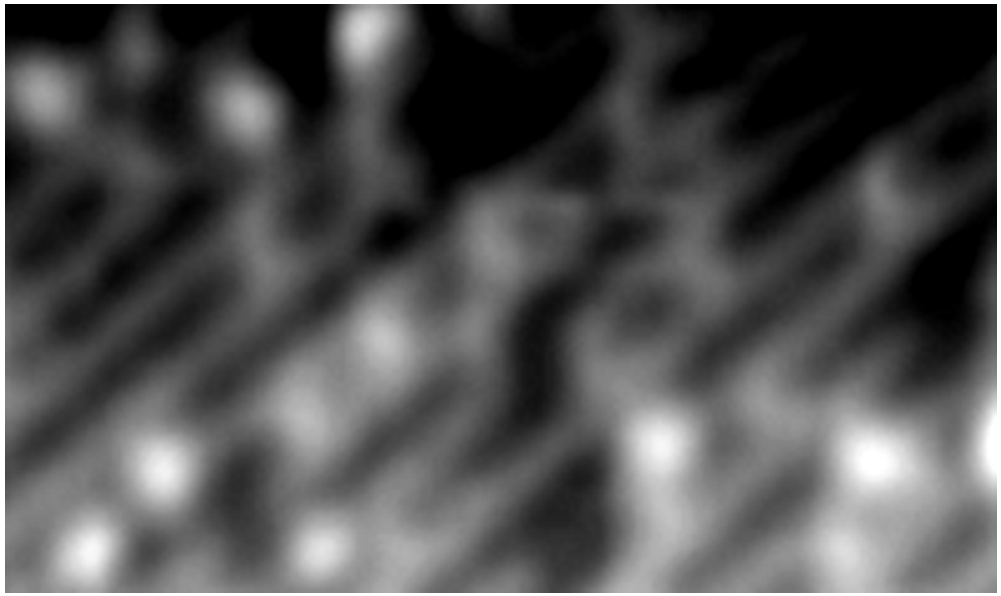
disappeared vacancy

Density of vacancies increases with tip-sample bias increase on Au_3 covered surface



Vs=1.4V,

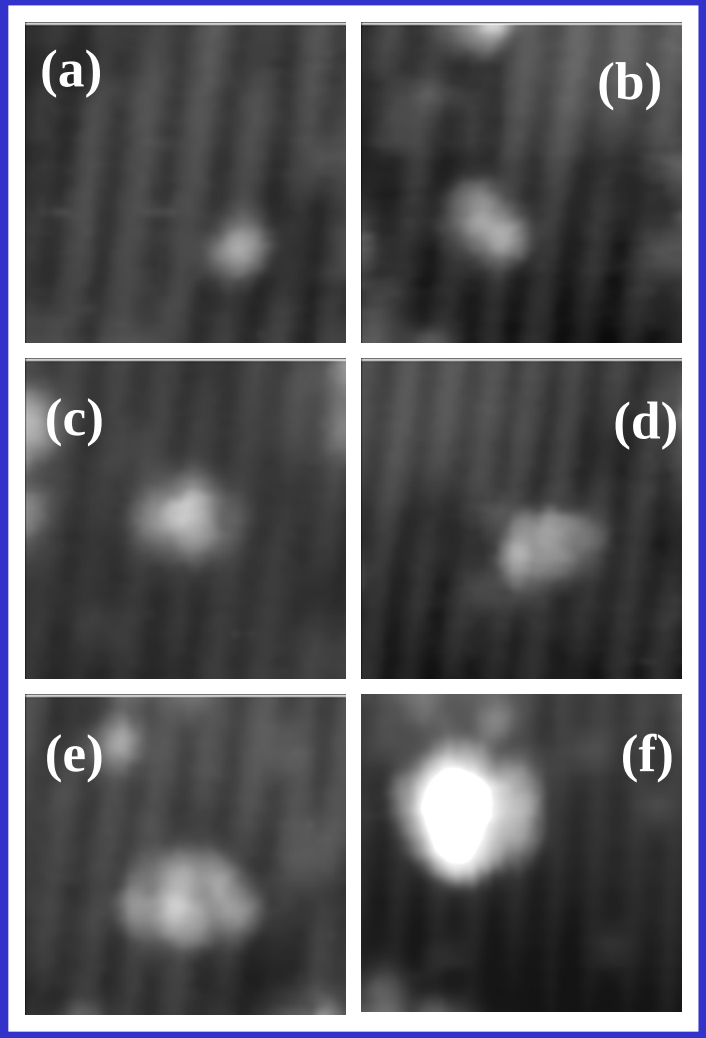
I =0.20nA



Vs=1.6V,
I=0.20nA

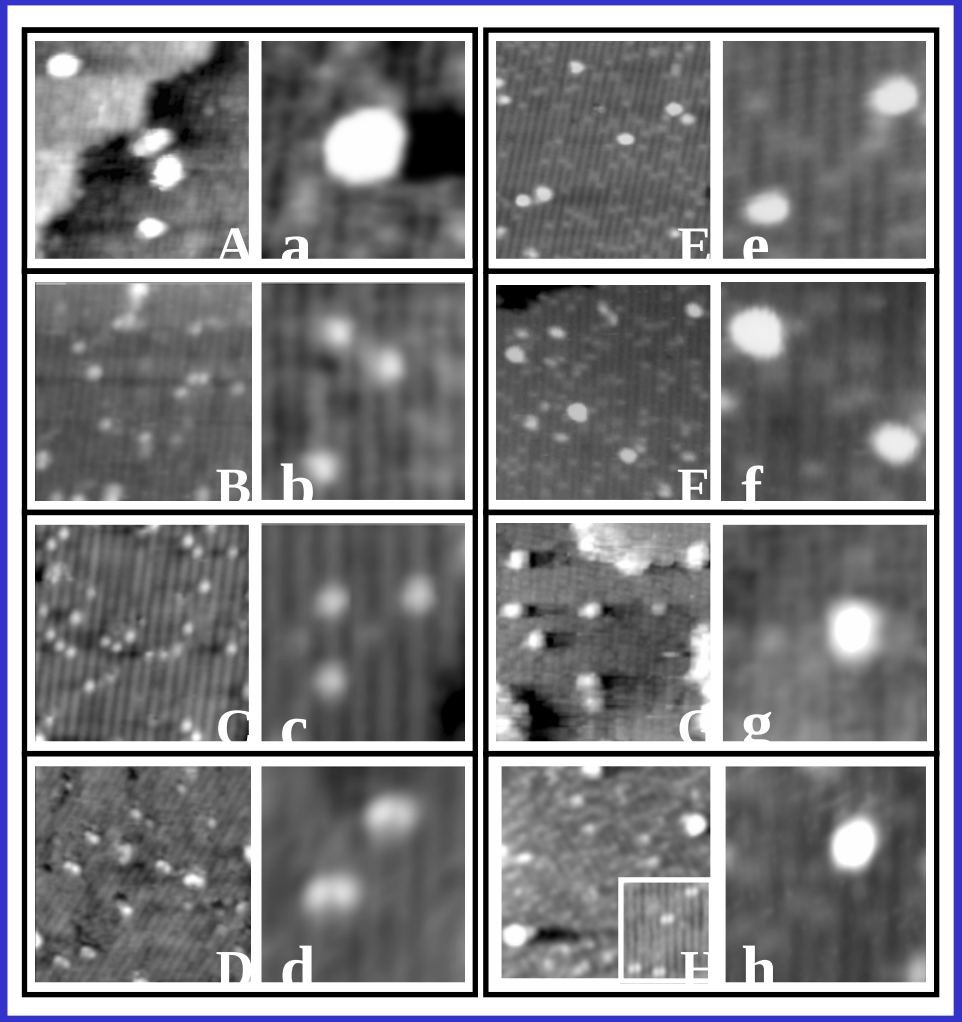
Sintering of Au_3 Clusters: Diffusion of Intact Cluster

Au_3 clusters after anneal



≠

Intact size-selected clusters



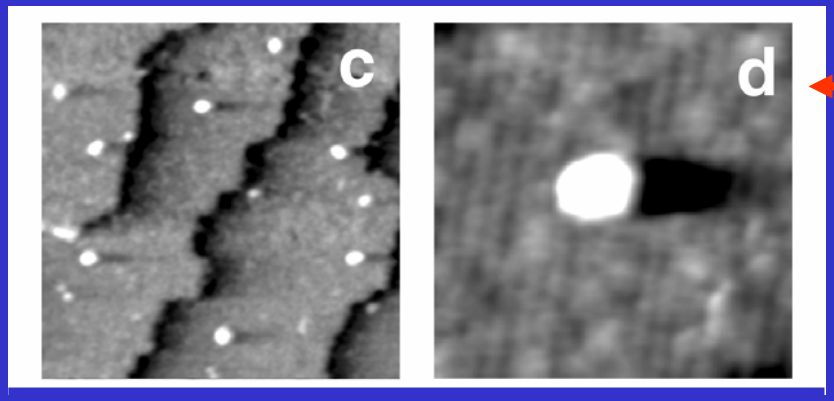
Gold Hard landing

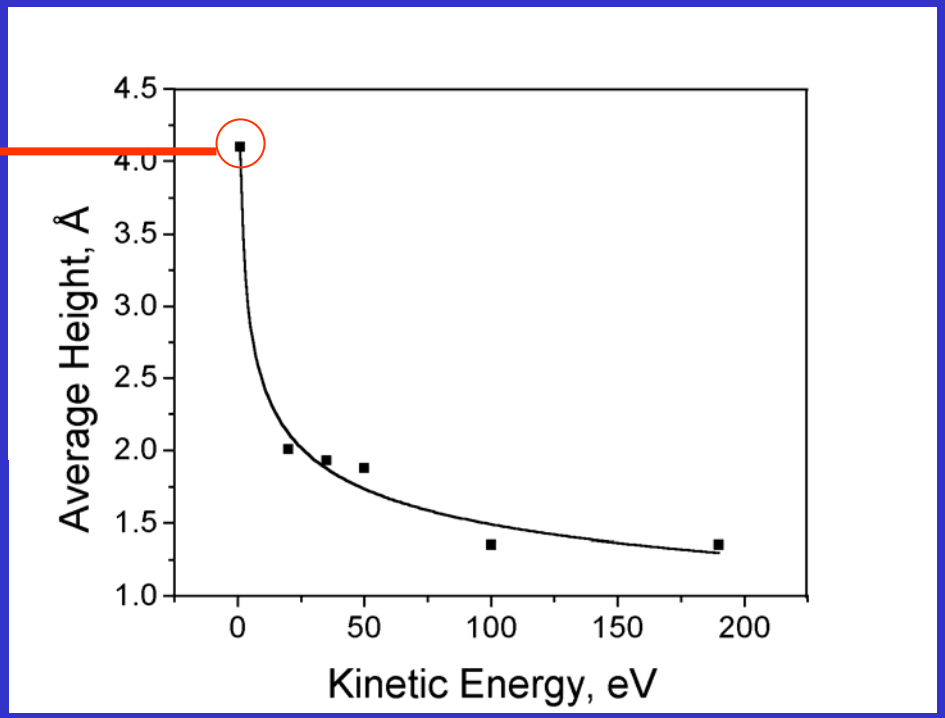
Au_1^+ clusters with incident energies of 0 - 190 eV

$TiO_2(110)$

Deposition of Au_1 with increased Kinetic Energy

500Å x 500Å 100Å x 100Å

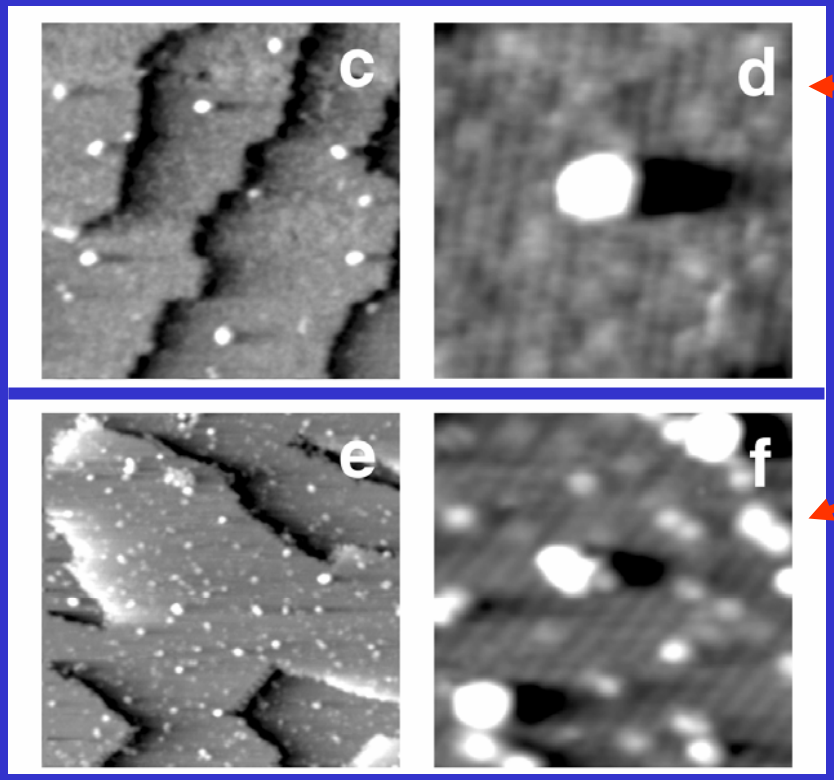


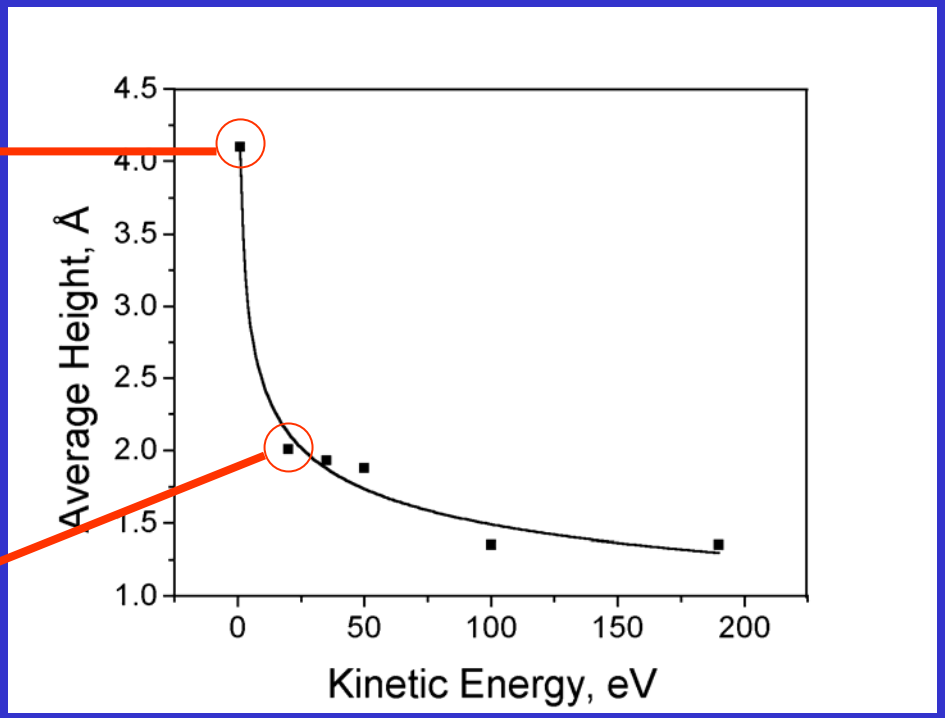


L. Benz, et al. *J. Chem. Phys.* **122** 081102 (2005)

Deposition of Au_1 with increased Kinetic Energy

500Å x 500Å 100Å x 100Å

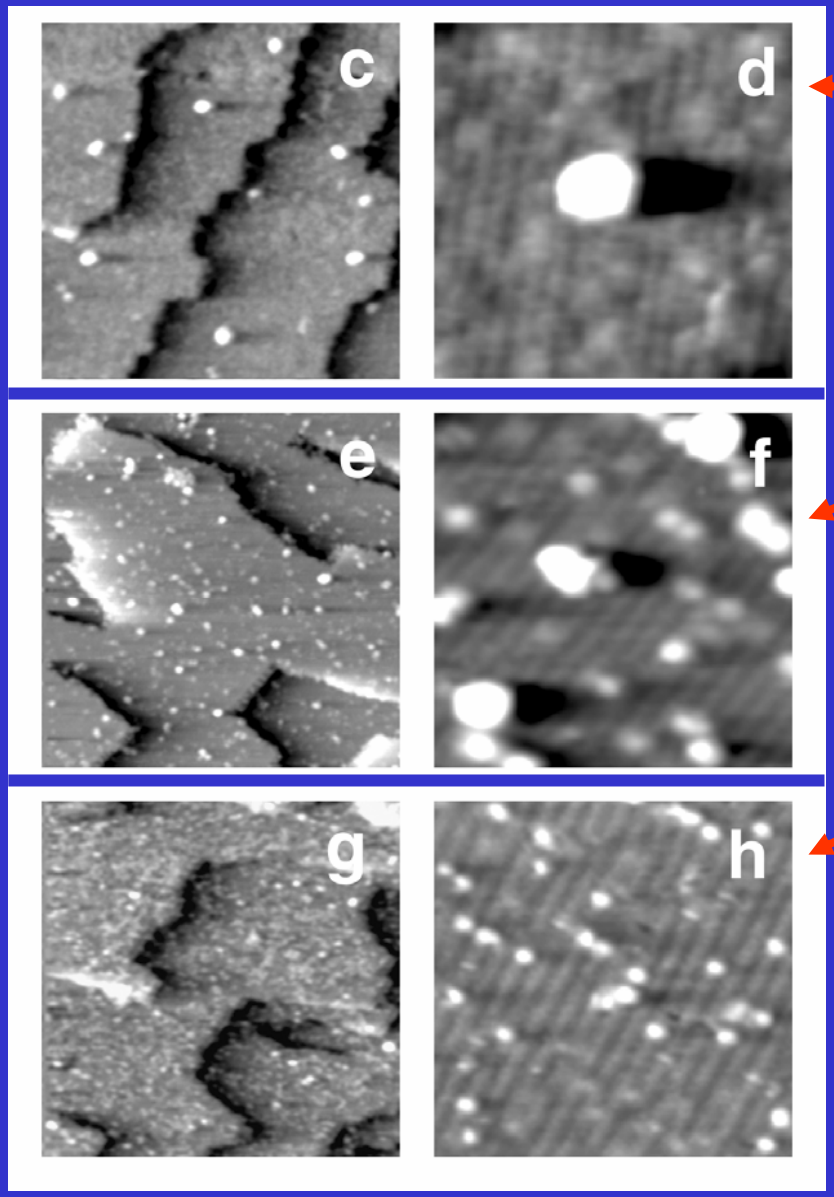


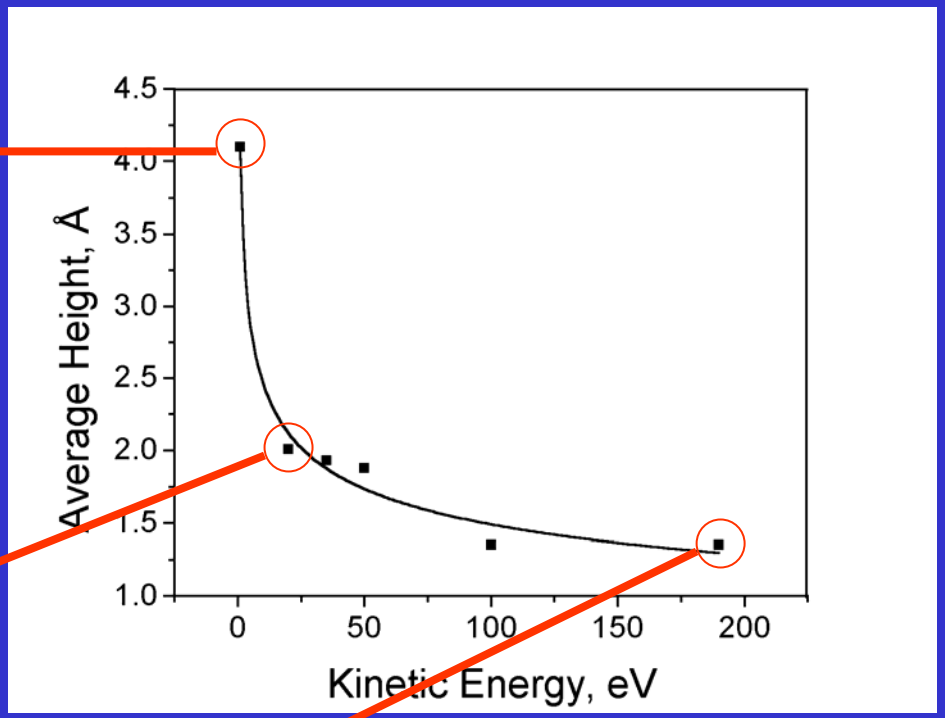


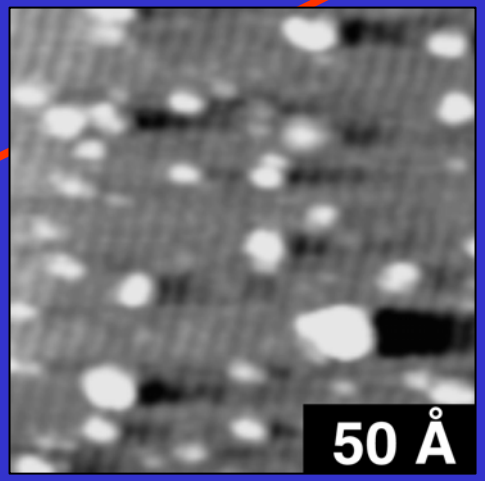
L. Benz, et al. *J. Chem. Phys.* **122** 081102 (2005)

Deposition of Au_1 with increased Kinetic Energy

500Å x 500Å 100Å x 100Å



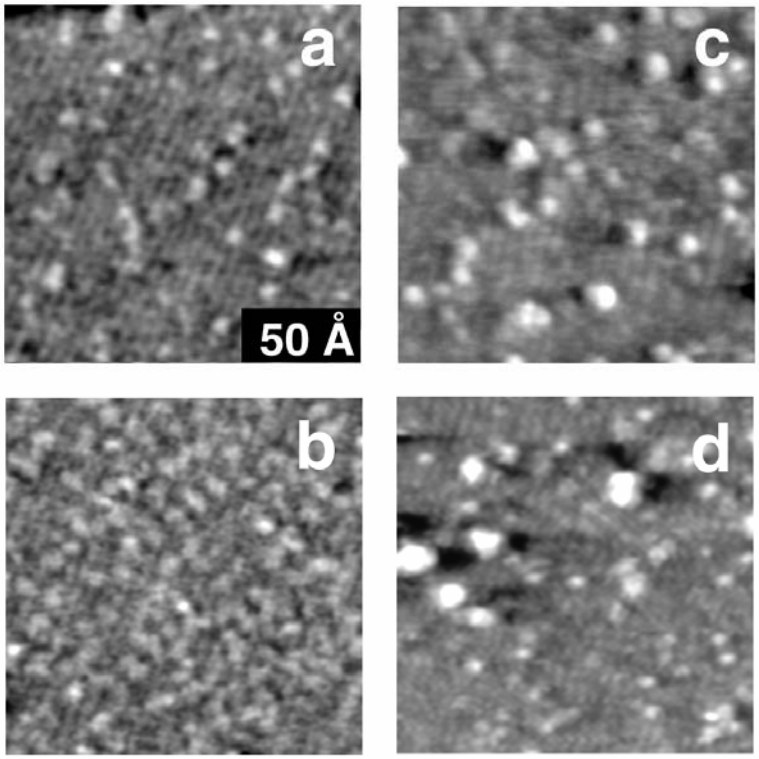


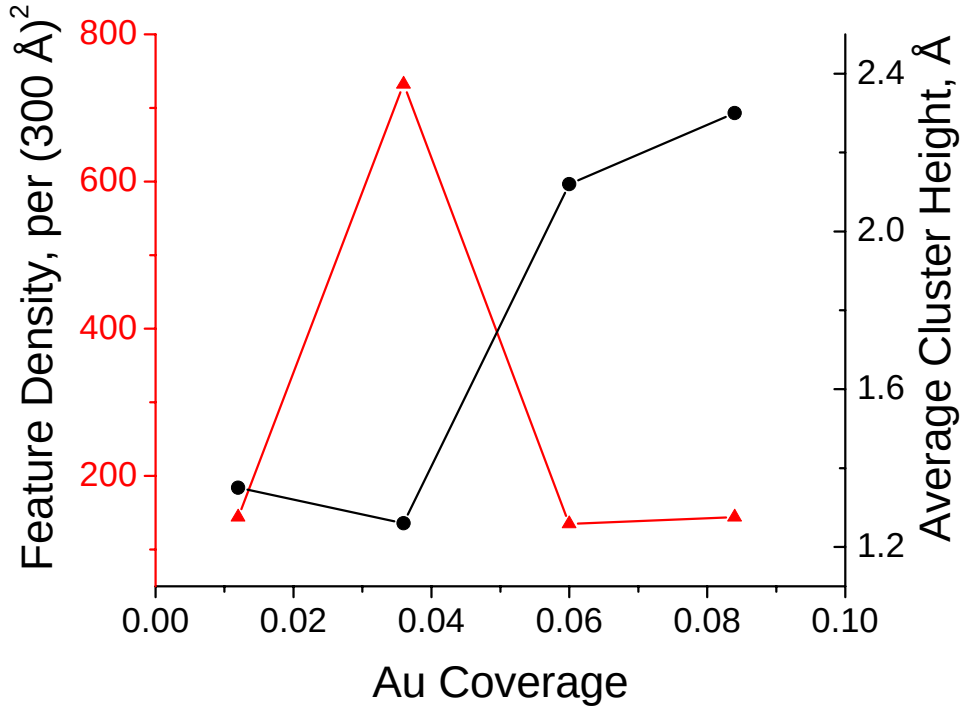


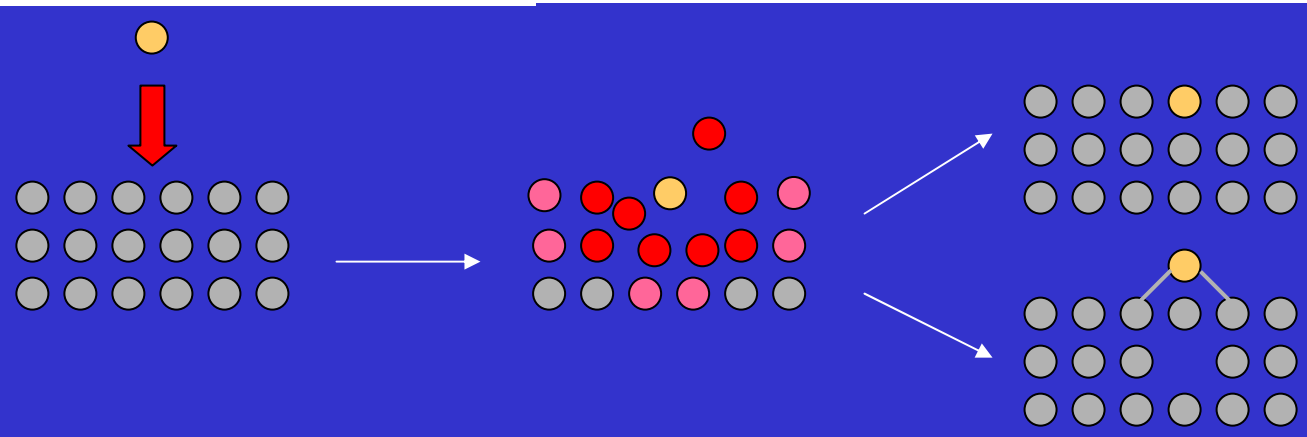
0.01 ML Au_1, KE = 190 eV
Followed by 0.01 ML KE = 0 - 2 eV

L. Benz, et al. *J. Chem. Phys.* **122** 081102 (2005)

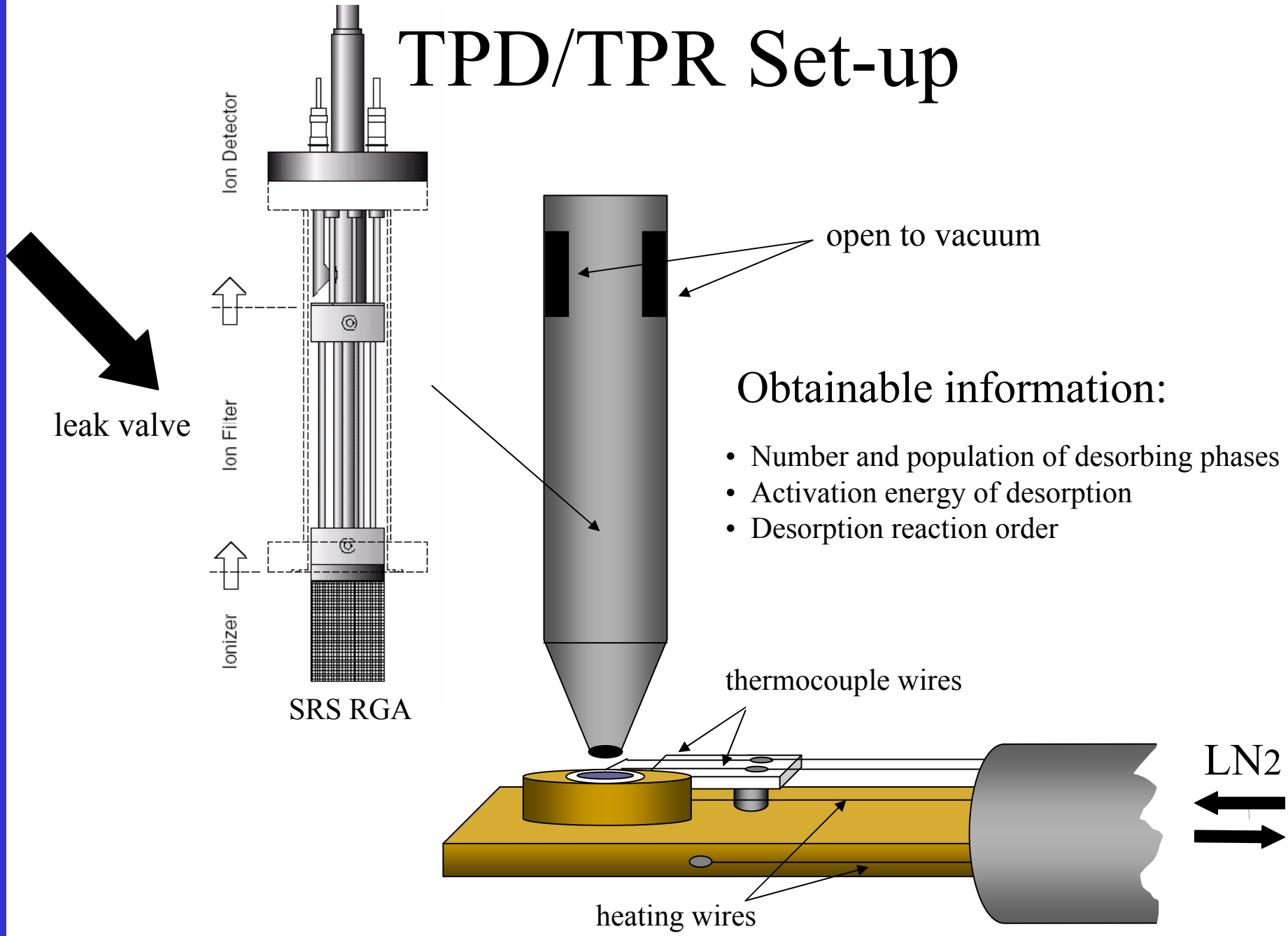
Deposition of Au_1 with increased Kinetic Energy







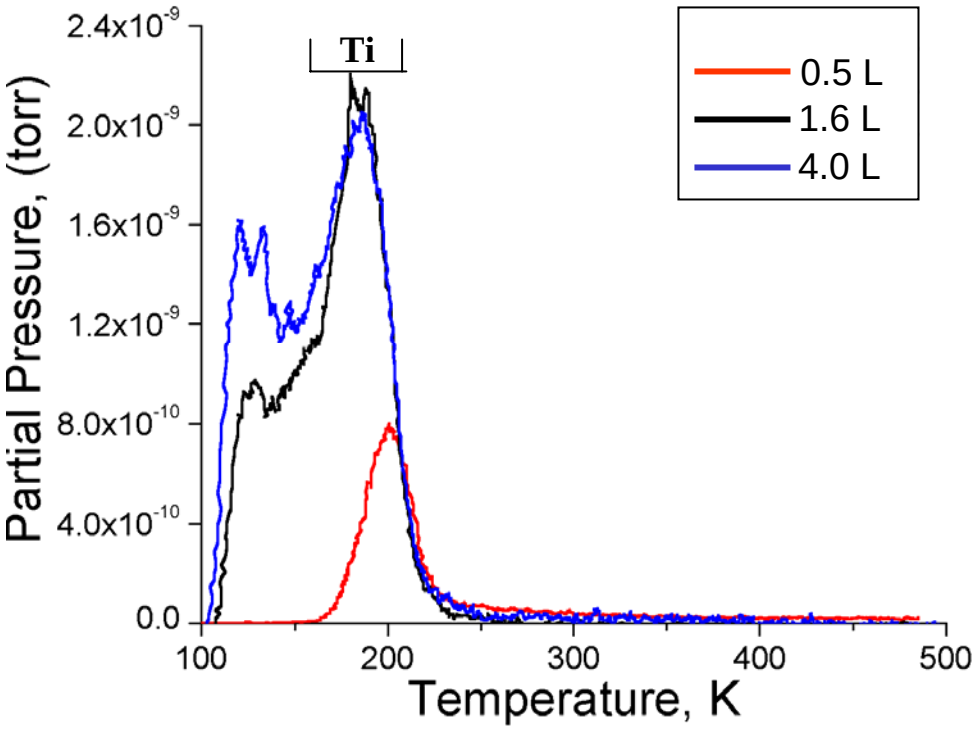
TPD/TPR Set-up

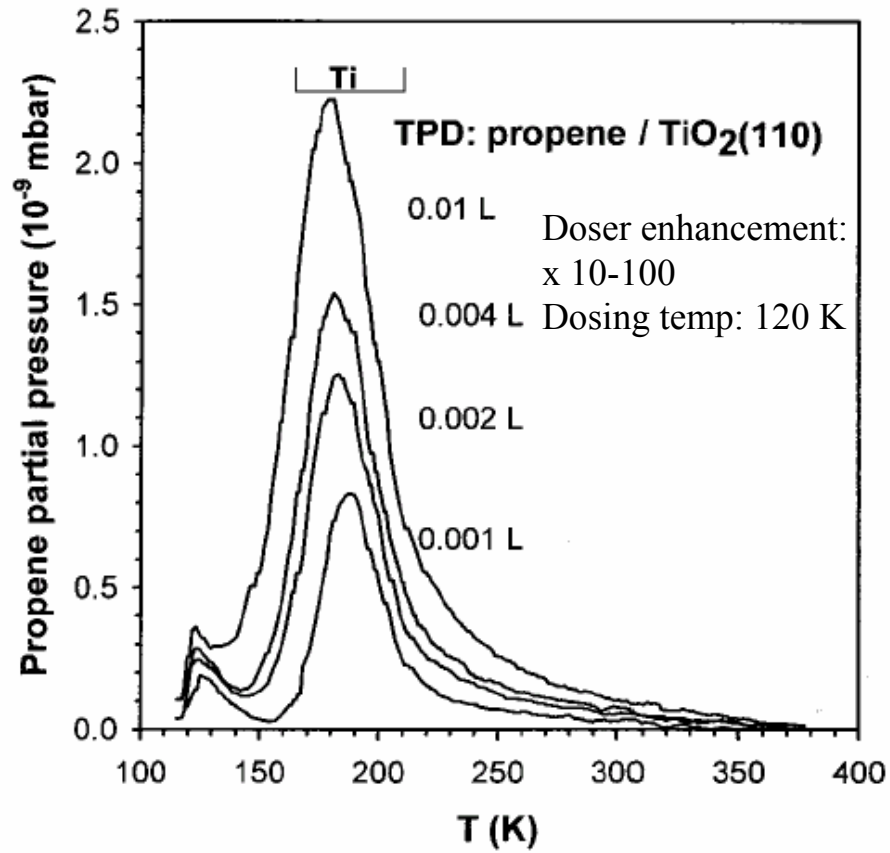


Obtainable information:

- Number and population of desorbing phases
- Activation energy of desorption
- Desorption reaction order

Propene Desorption from TiO_2





Ajo, H.M., Bondzie, V.A., and Campbell, C.T. *Cat. Let.*, **78**, (2002)

T_p~200 K, 1K/s

T_p~190 K, 5 K/s

Determination of E_{des} *

Redhead, P.A., *Vacuum*, **12**, 203 (1962)

Rate of Desorption, $N(t) = -d\sigma/dt = \sigma_n \sigma^n \exp(-E/RT)$

Where n is the order of the desorption reaction
σ is the surface coverage (molecules/cm^2)
σ is the rate constant
E is the activation energy of desorption

Assuming a linear heating rate, $T = T_o + \beta t$, where β is the rate (K/s), t is time

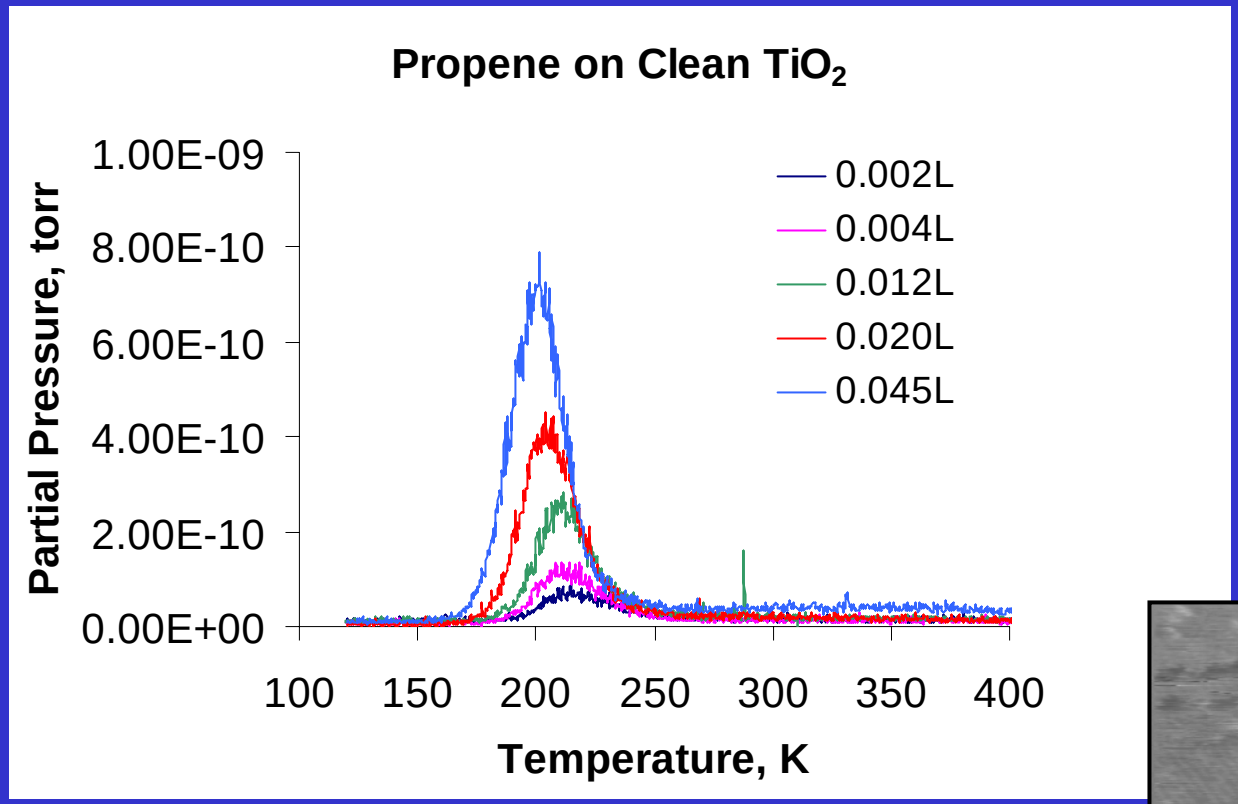
$$E/RT_p^2 = (\sigma_1/\beta)\exp(-E/RT_p) \text{ for } n = 1$$

The relation between E and Tp is nearly linear and for $10^{13} > \sigma_1/\beta > 10^8$ (K^{-1}) is given to ±1.5% by:

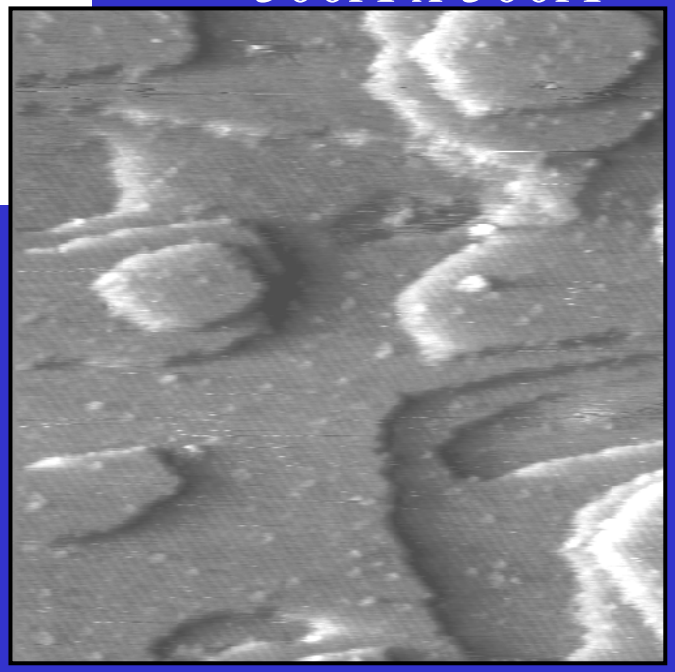
$$E/RT_p = \ln(\sigma_1 T_p/\beta) - 3.64$$

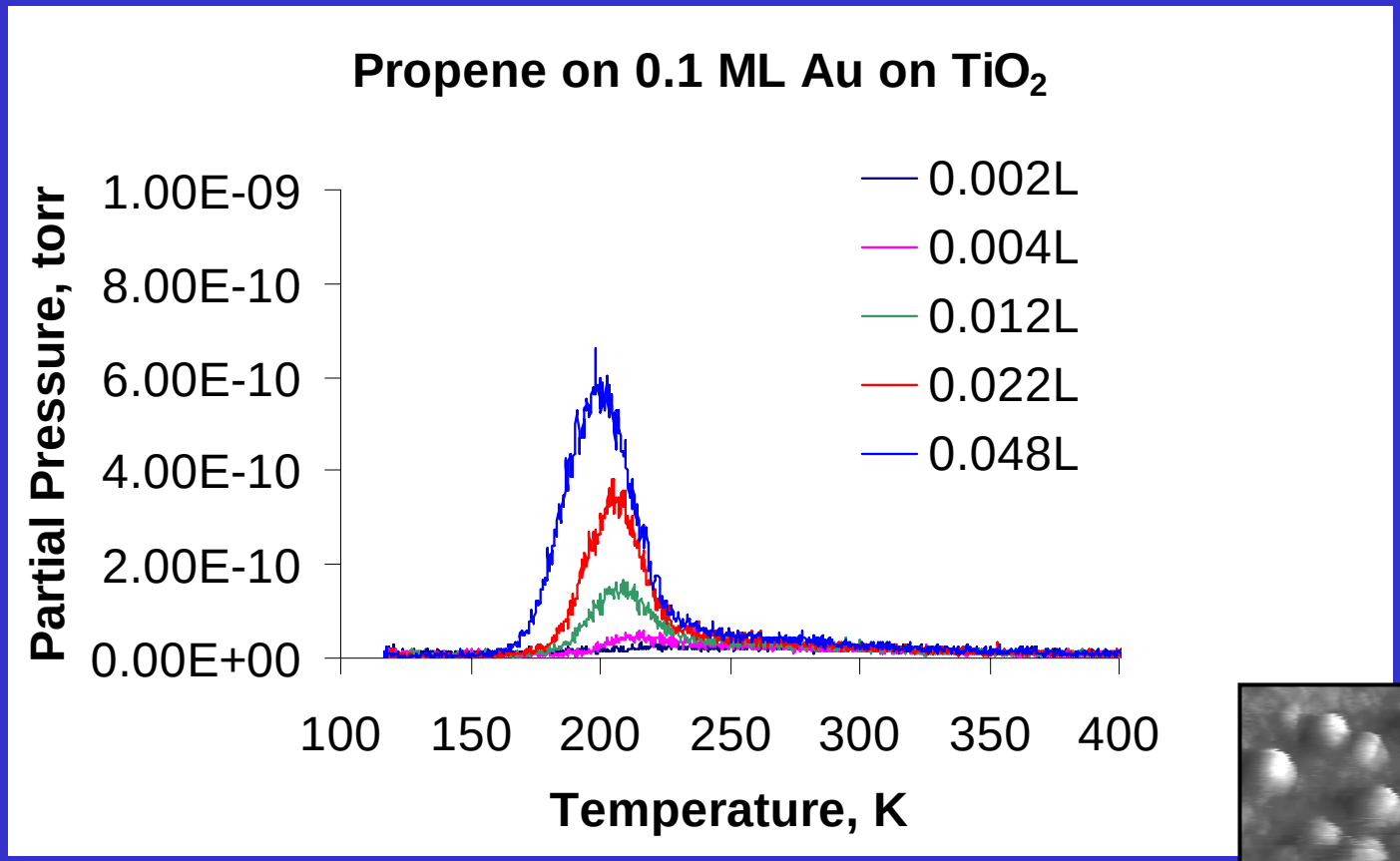
So for Tp = 190, β = 5 K/s, E=47.3 kJ/mol (Ajo)
Tp = 200, β = 1K/s, E = 52.5 kJ/mol

✓ Good agreement, within ~10%

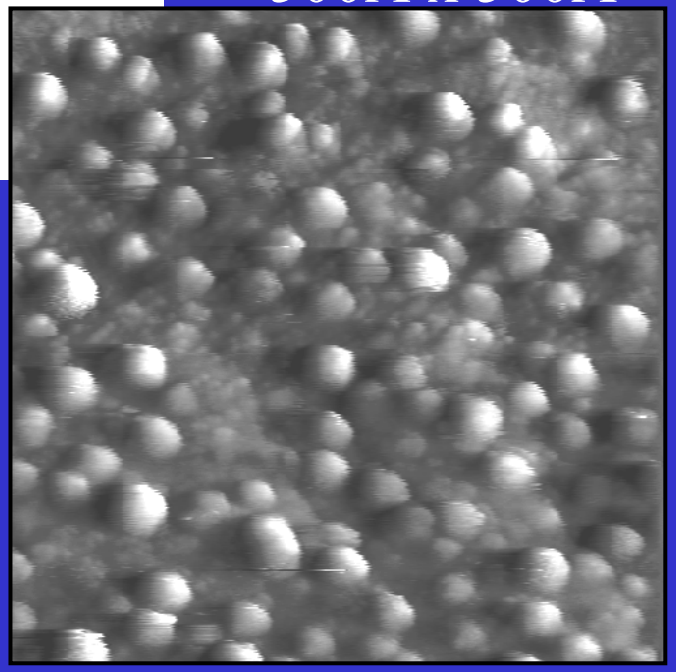

Propene on Clean TiO2
Partial Pressure, torr
1.00E-09
8.00E-10
6.00E-10
4.00E-10
2.00E-10
0.00E+00
100
150
200
250
300
350
400
Temperature, K
0.002L
0.004L
0.012L
0.020L
0.045L

500Å x 500Å

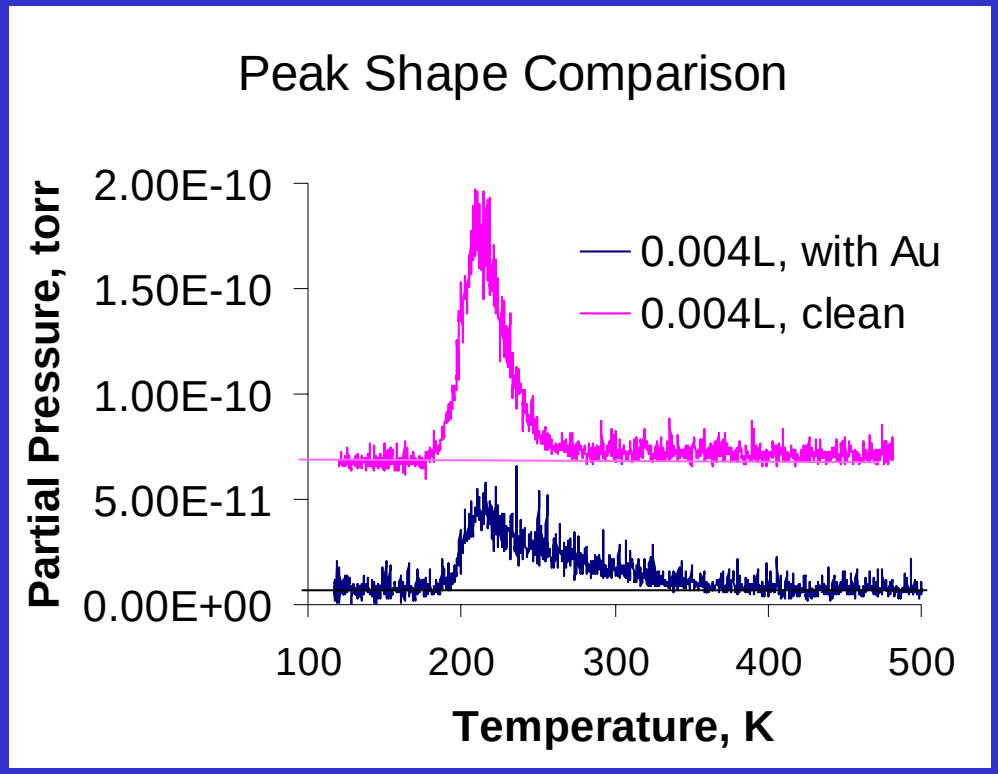


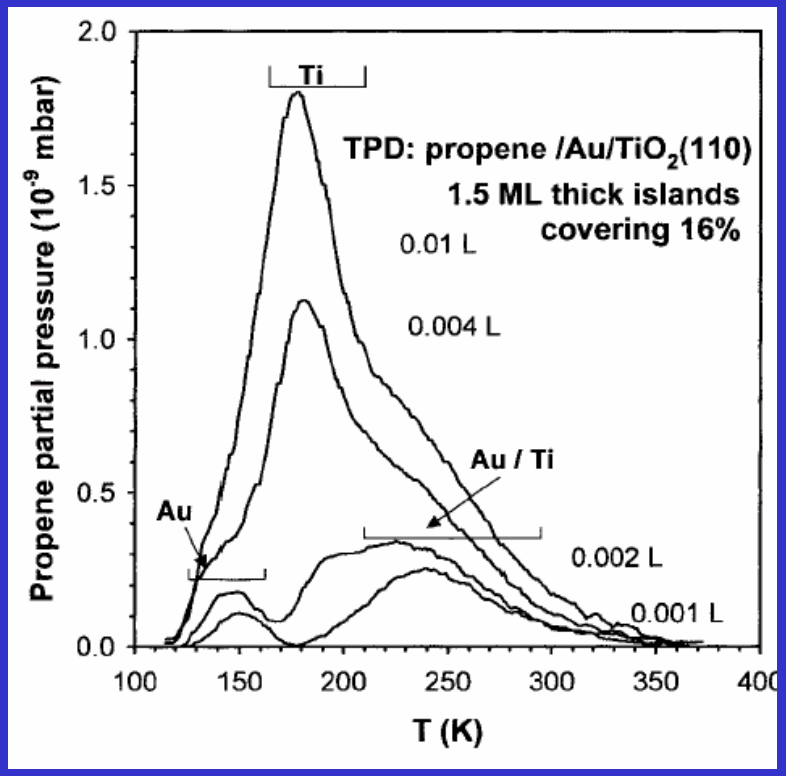

Propene on 0.1 ML Au on TiO_2
Partial Pressure, torr
1.00E-09
8.00E-10
6.00E-10
4.00E-10
2.00E-10
0.00E+00
100
150
200
250
300
350
400
Temperature, K
0.002L
0.004L
0.012L
0.022L
0.048L

500Å x 500Å



Effect of Large Au Clusters on Propene Desorption

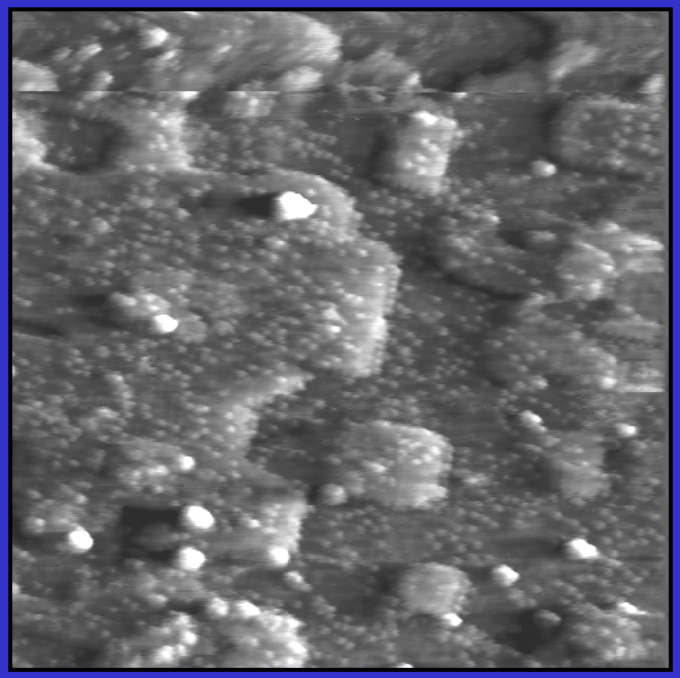




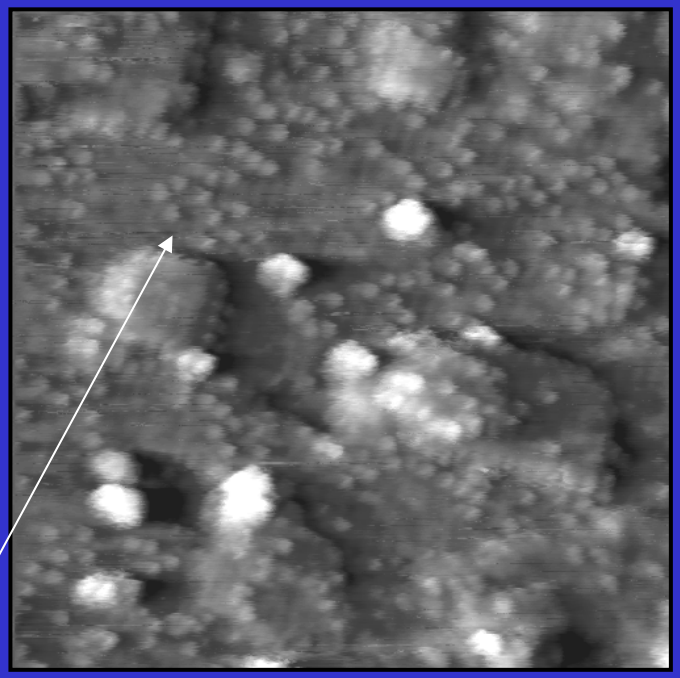
Ajo, H.M., Bondzie, V.A., and Campbell, C.T. *Cat. Let.*, **78**, (2002)

STM of Au-covered TiO_2

after sputtering and annealing



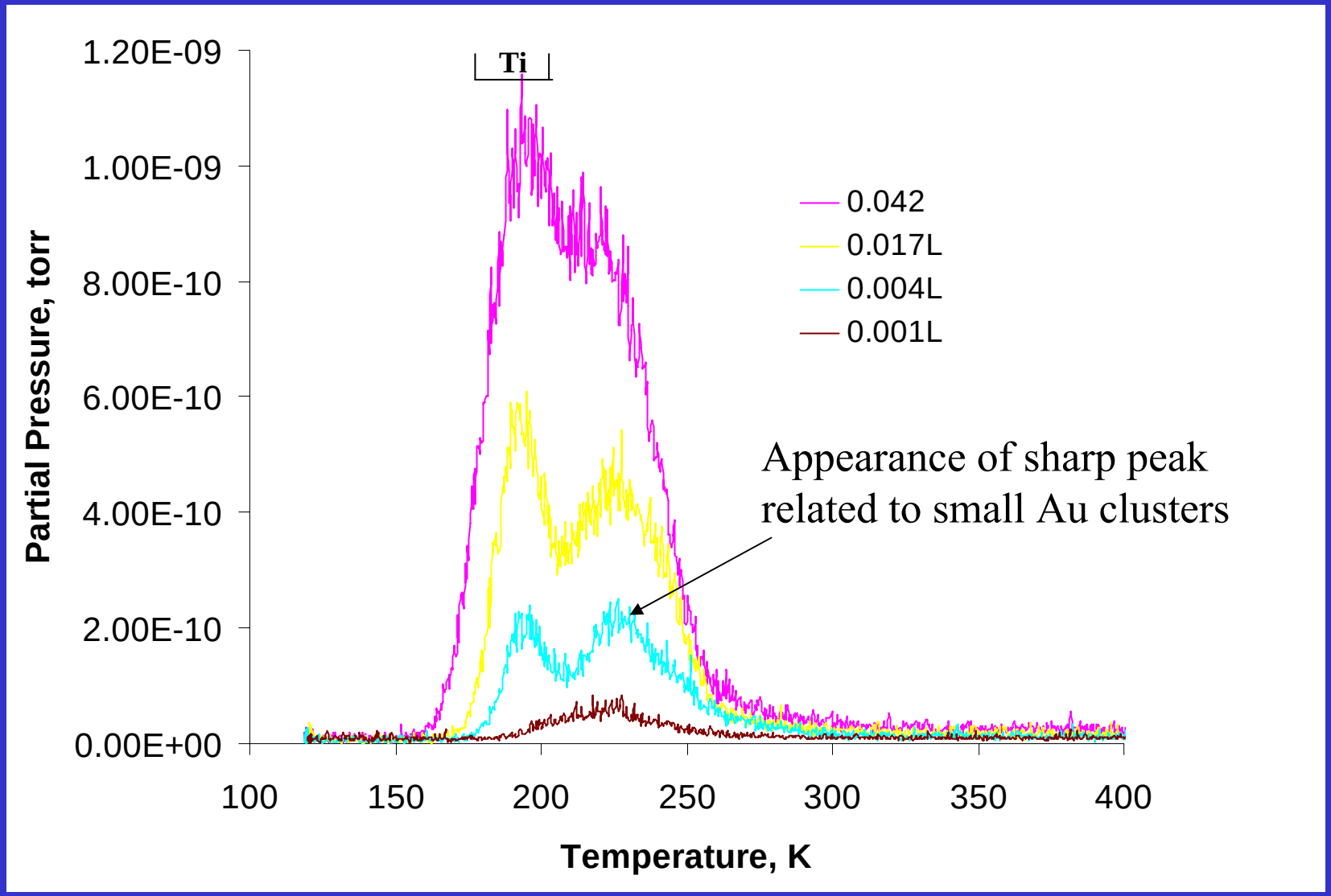
1000Å x 1000Å



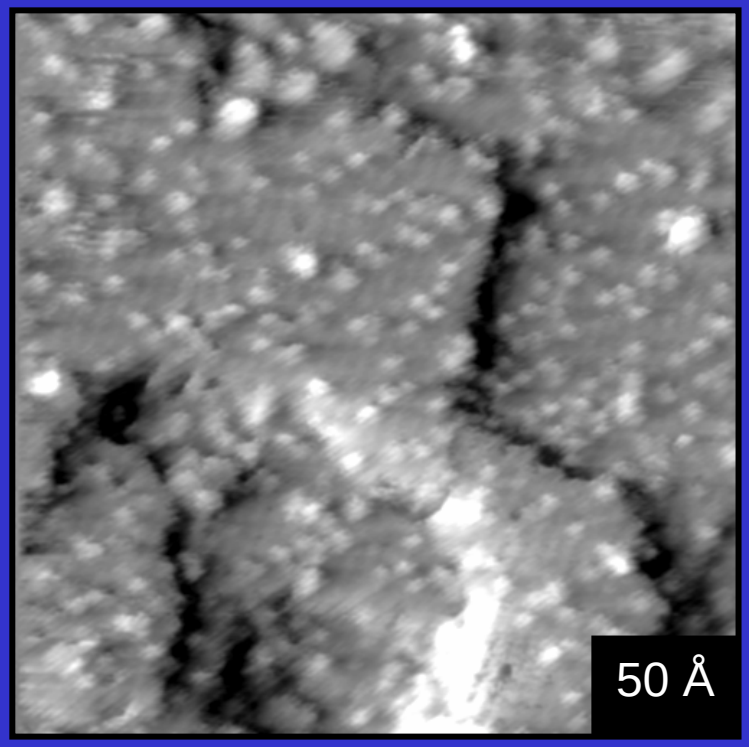
500Å x 500Å

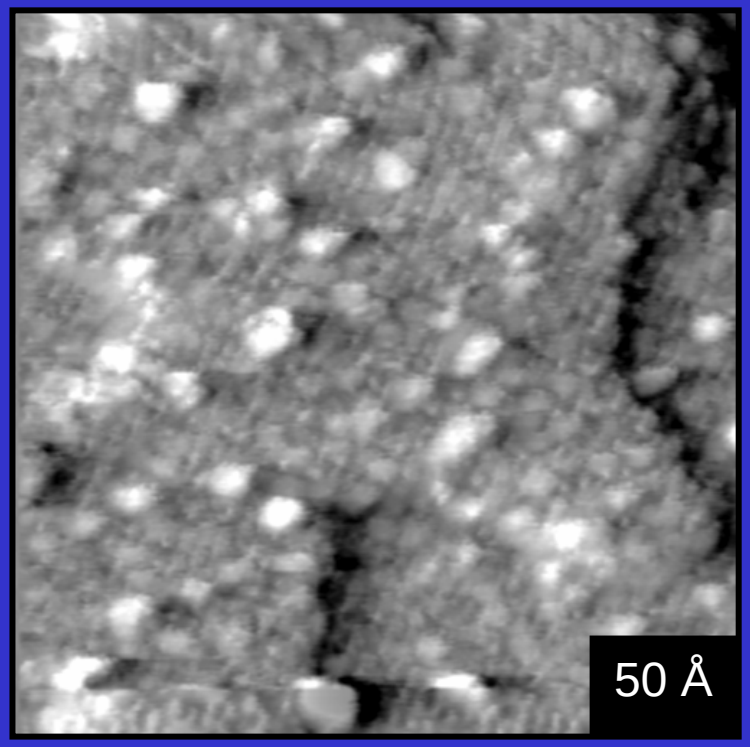
Presence of small Au centers, possibly $Au_1 - Au_3$

TPD: (after sputtering and annealing)



STM Images: Effect of TPD





After “dry run” from 100K to 600K (no O_2 present)
Au_3 features still on Ti^{4+} rows, so heat ramp does not sinter clusters

After TPD (100K – 600K)
100L O_2 total exposure

Conclusions / Future Experiments

- Au clusters (few nm) bind propene more strongly than the titania substrate
- Small Au clusters (few Å) bind propene more strongly, narrow D_e distribution
- Exposure to O_2 induces sintering of Au_3

- Perform TPD and XPS on hard-landed Au_1
- Install O source
- Pre-expose surface to O before deposition
- Perform TPR to monitor propylene epoxidation
- Image while exposing Au clusters to gas