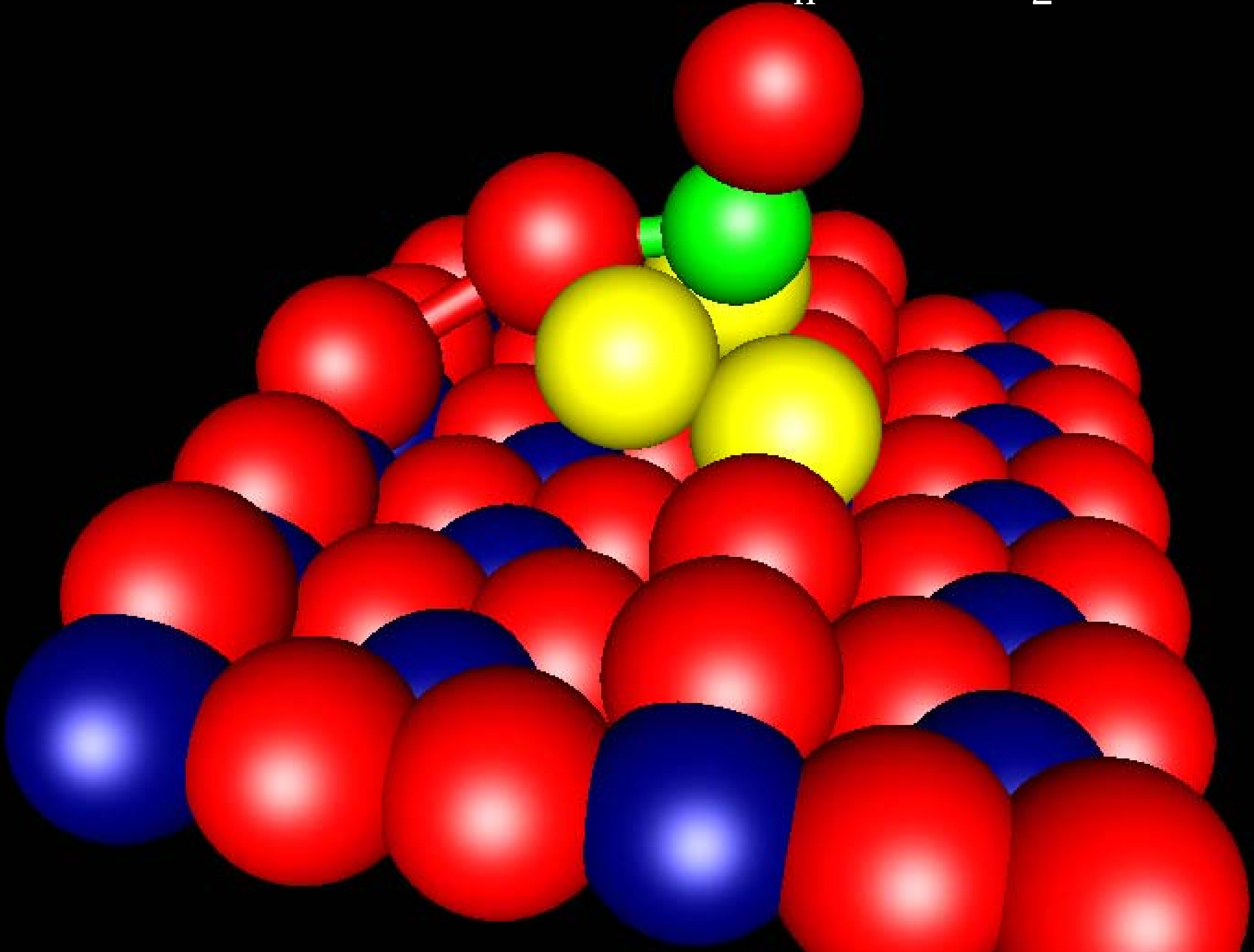
Size-selected Metal Cluster Deposition on Oxide Surfaces: Impact Dynamics and Supported Cluster Chemistry

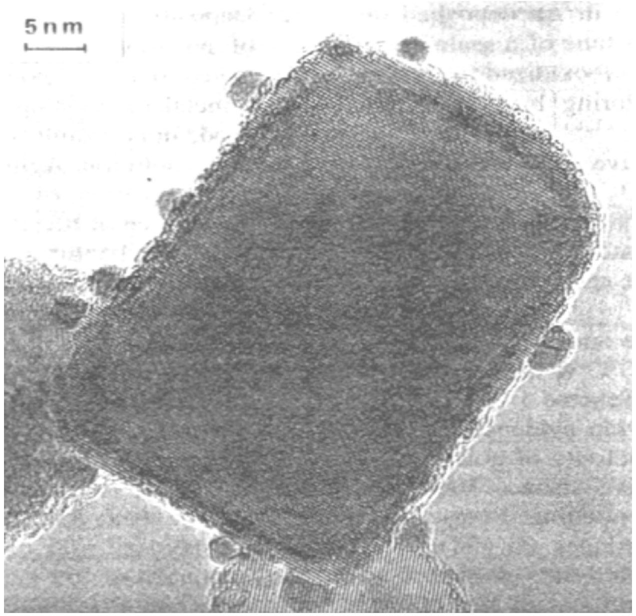
Sungsik Lee, Masato Aizawa, Chaoyang Fan, Tianpin Wu, and Scott L. Anderson

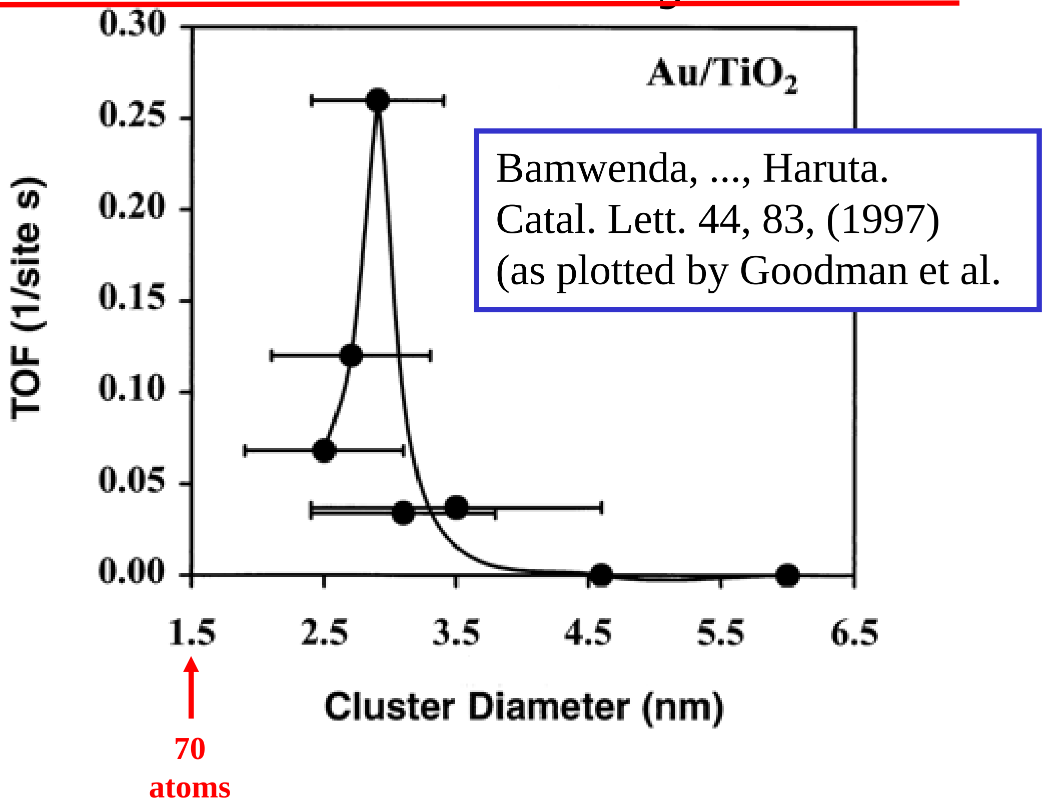
Support: AFOSR, DOE

CO oxidation on Au_n on TiO_2



Cluster Size Effects in Catalysis
CO oxidation on bulk catalyst





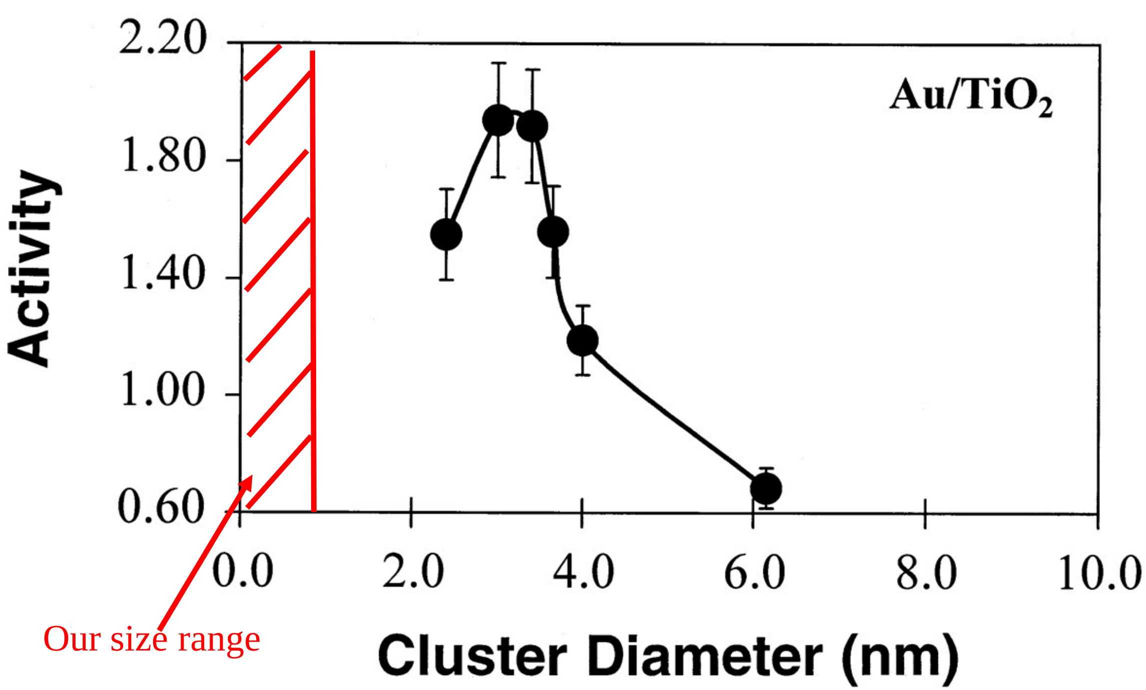
Problems:

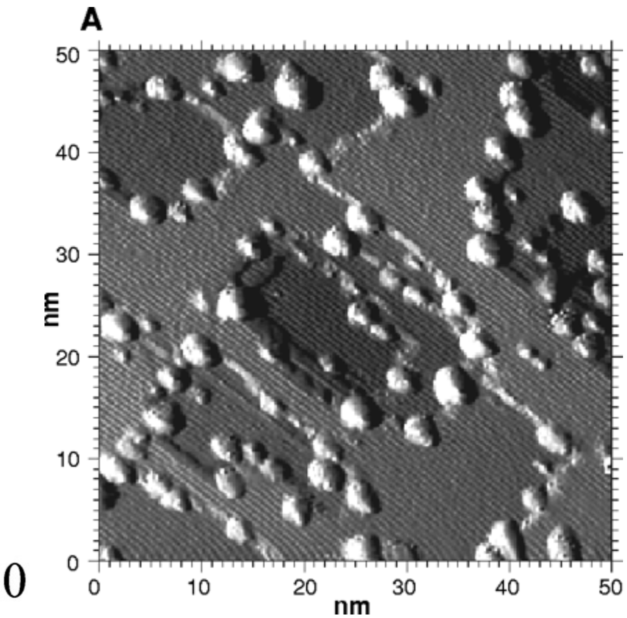
TEM characterization

Broad size distribution

Other changes together with size

Cluster Size Effects in Catalysis
CO oxidation on planar model catalyst





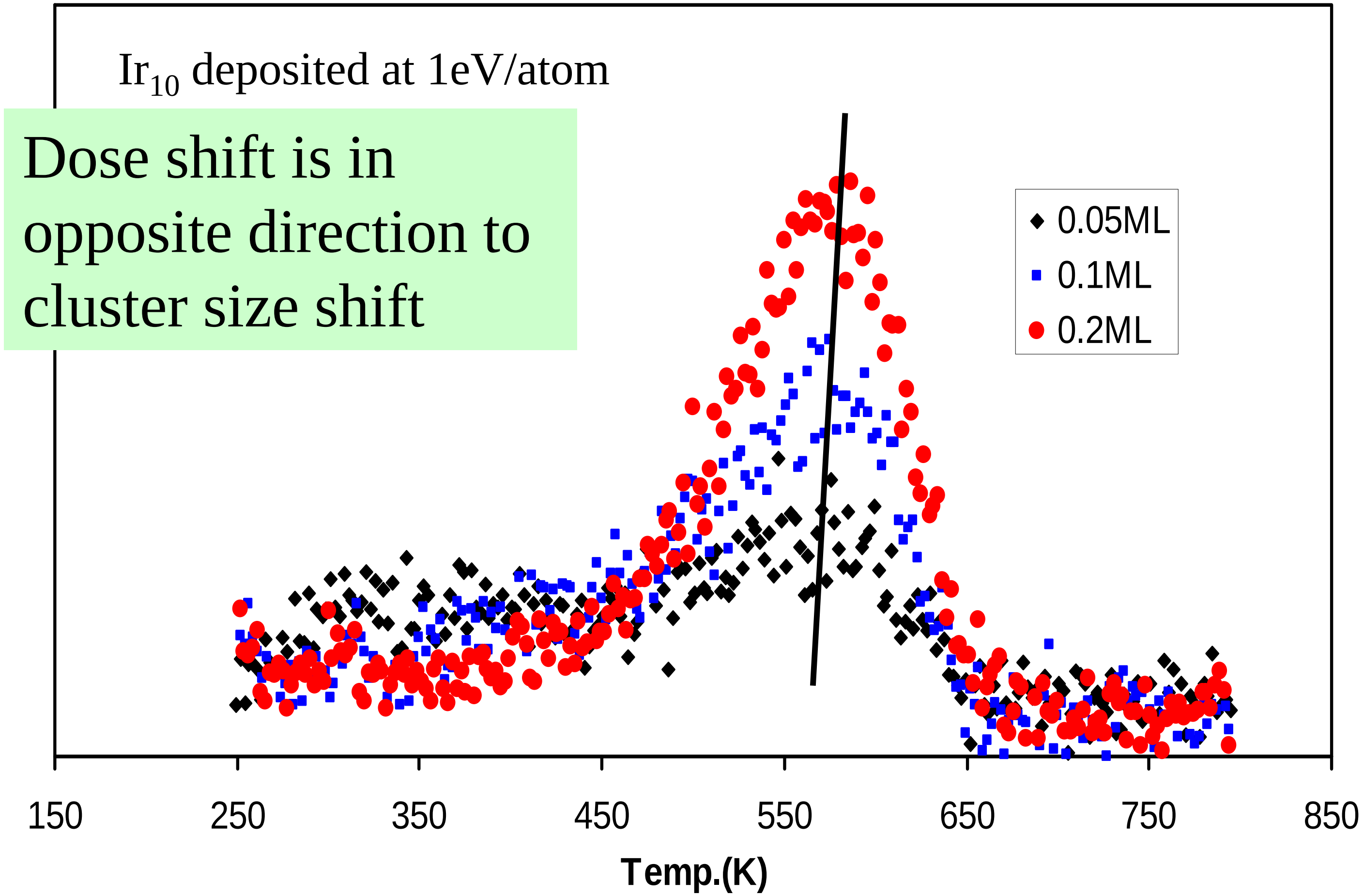
Planar model support / Cluster grown by annealing Au/TiO2

Sized by STM - Considerable size distribution, especially in the small size range.

Size proportional to metal dose

Valden, Lai, Goodman, Science 281 (1998) 1647

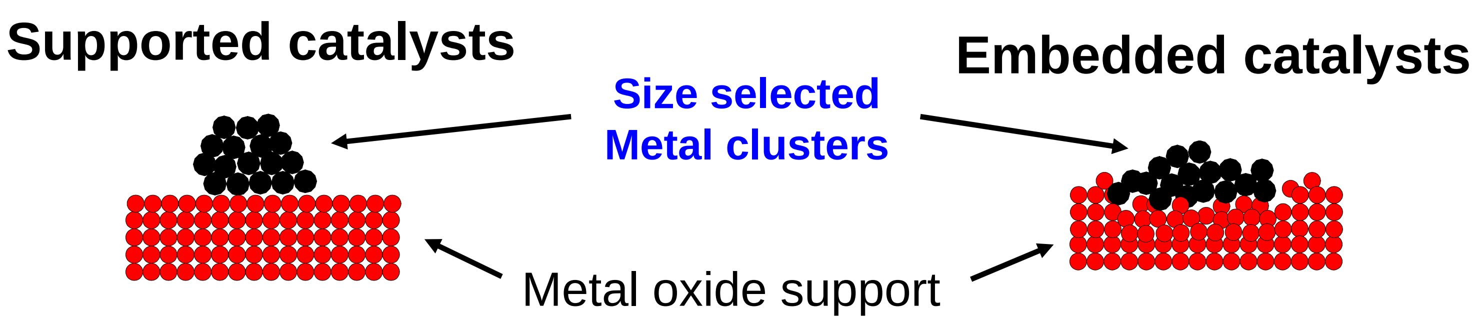
Metal dose effect on TPD



What we want to do:

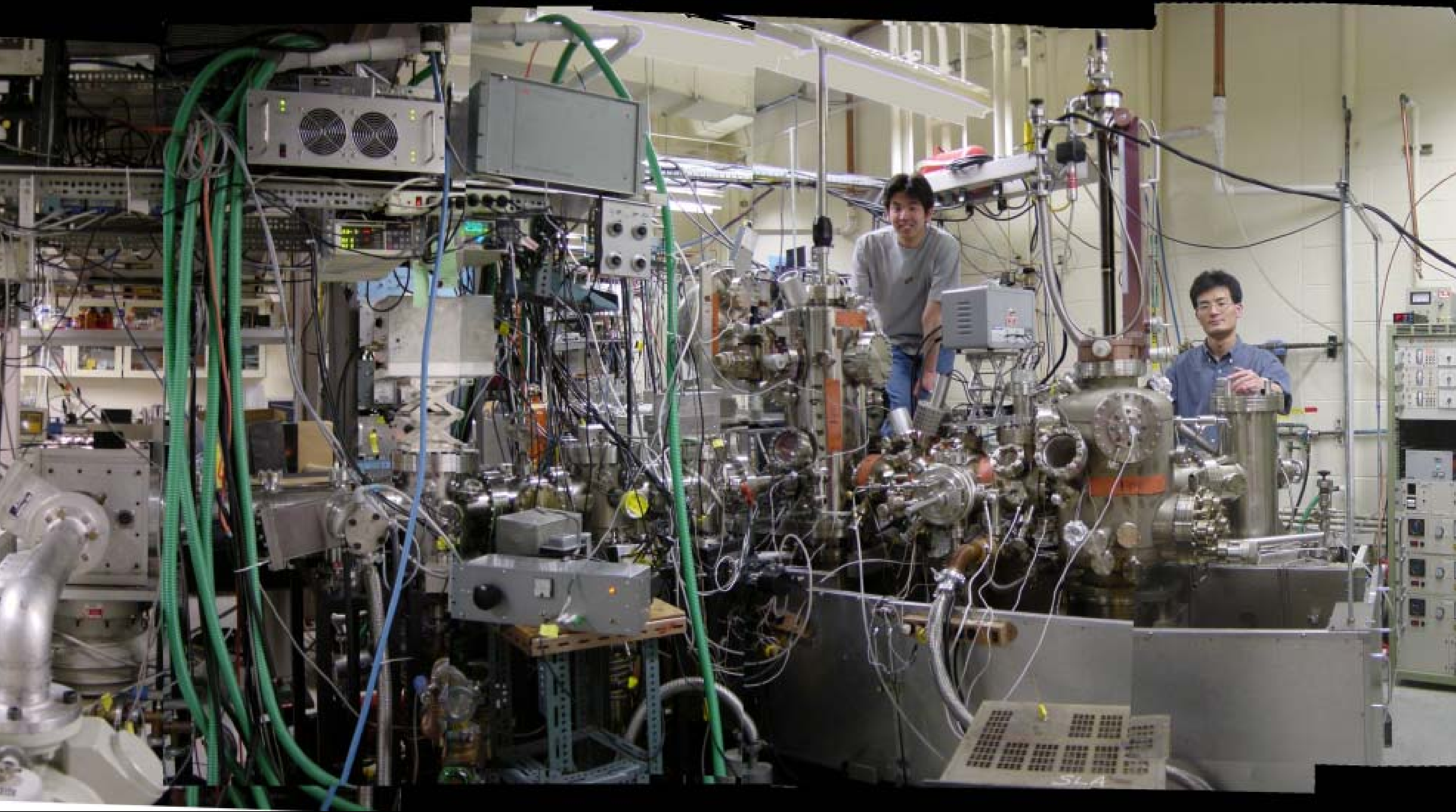
Independently vary cluster size, concentration, support structure and defects, morphology of deposit

Characterize all of the above.



Complete picture of electronic, geometry, and support effects in supported catalysts .

Utah Cluster Deposition Instrument

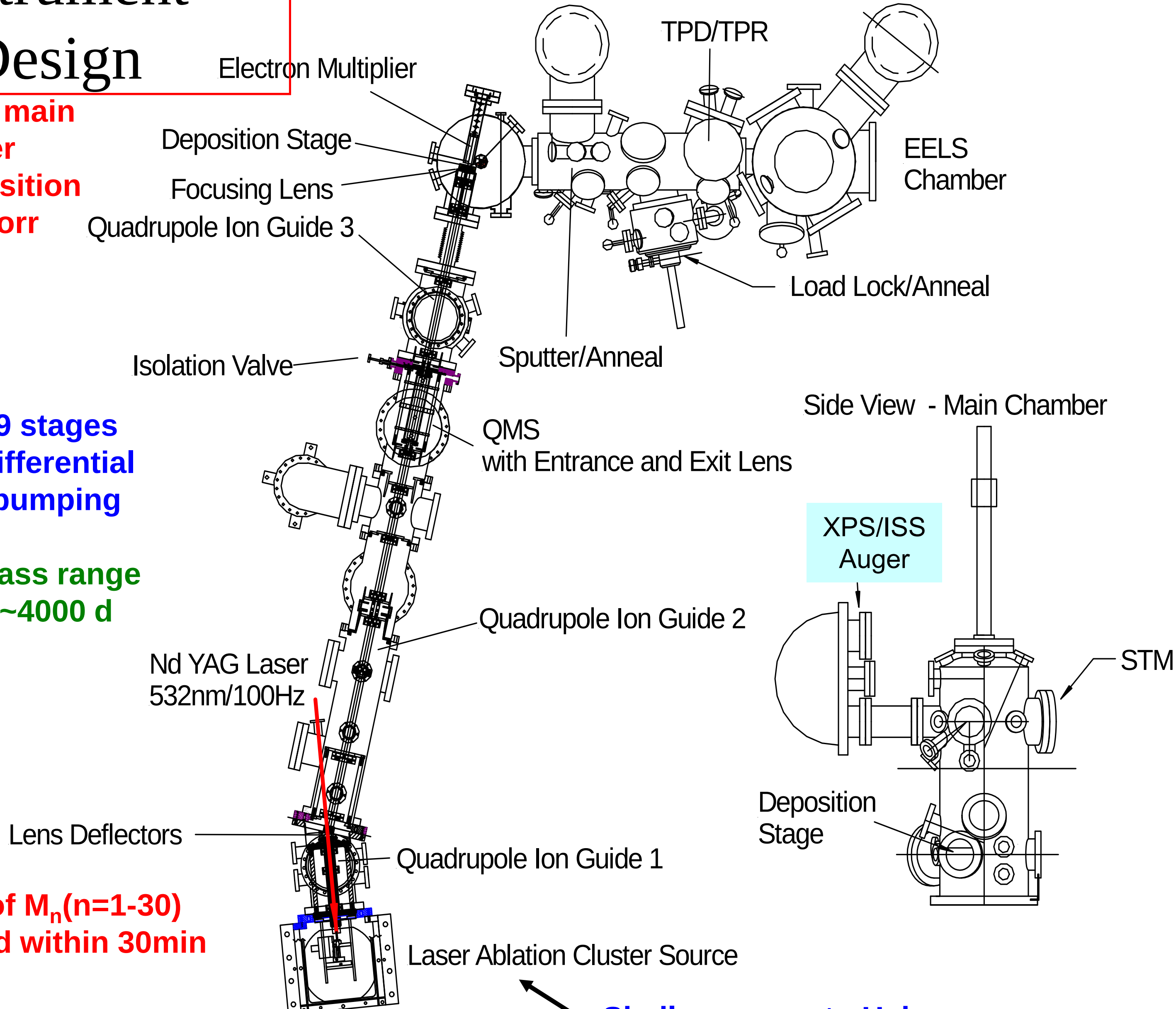


Instrument Design

Pressure in main chamber during deposition 2×10^{-9} Torr

9 stages differential pumping

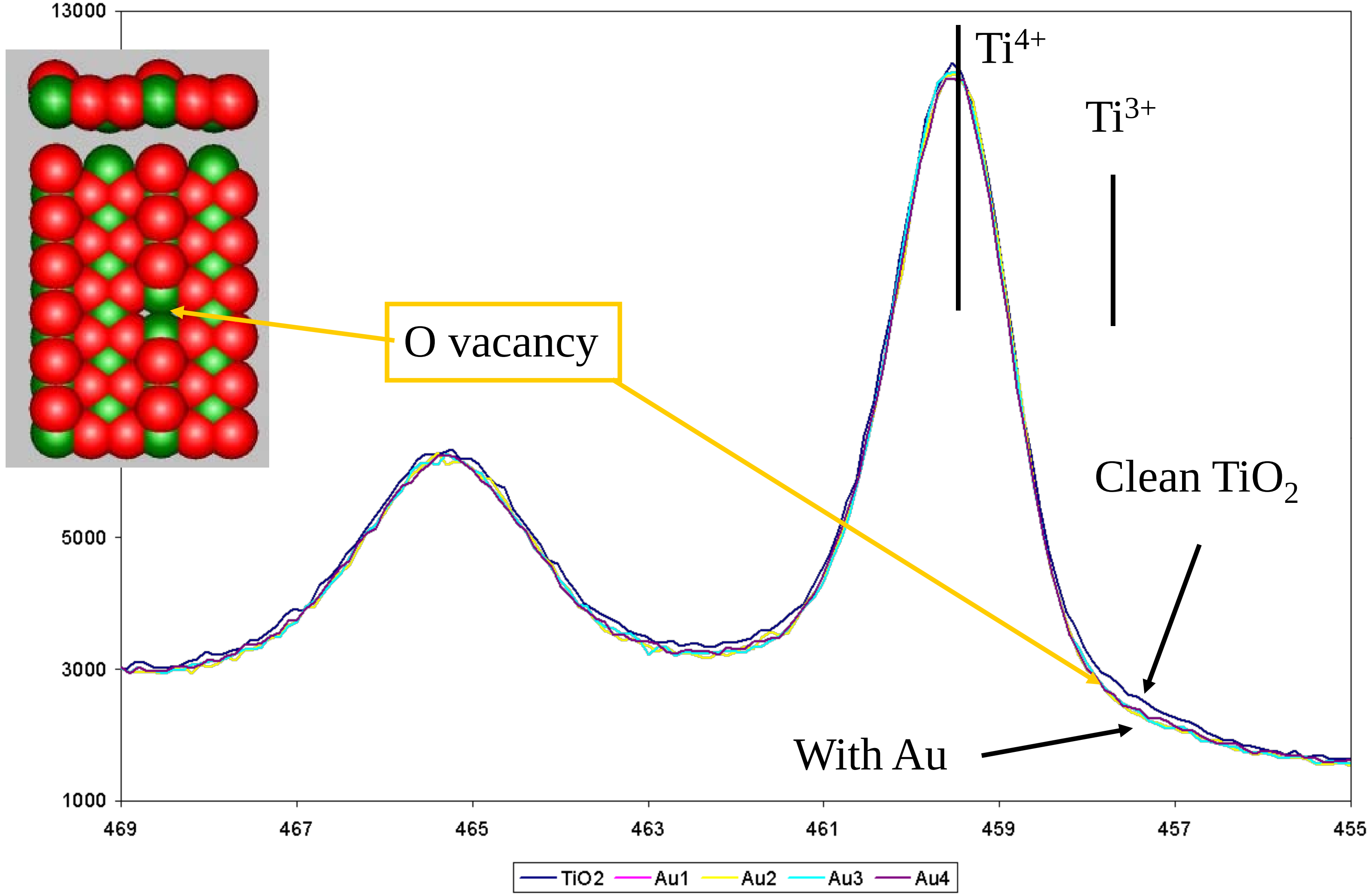
Mass range ~4000 d



0.1ML of M_n(n=1-30) deposited within 30min

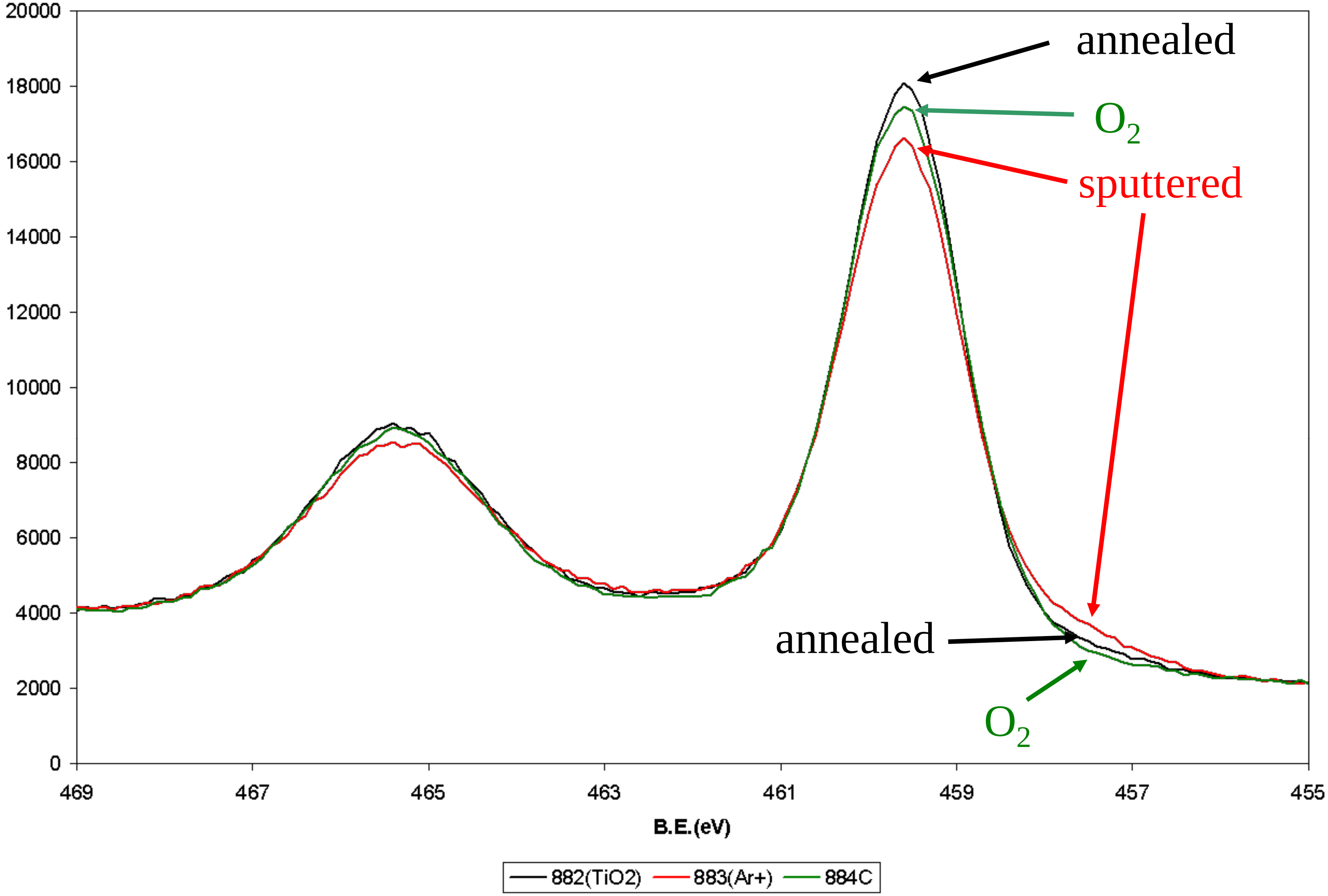
Similar source to Heiz

XPS : Ti

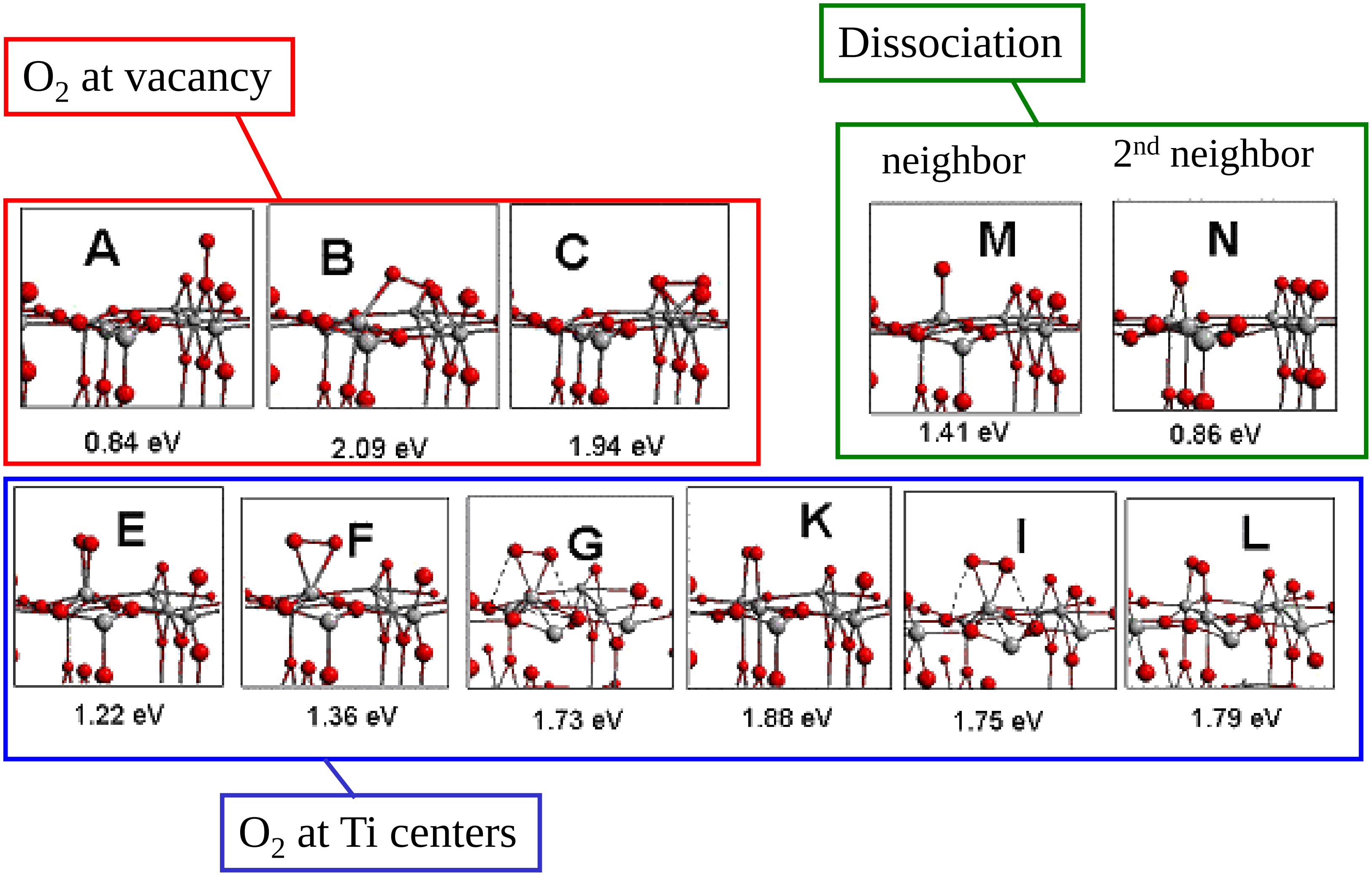


13000
5000
3000
1000
469
467
465
463
461
459
457
455
Ti4+
Ti3+
O vacancy
Clean TiO2
With Au
TiO2
Au1
Au2
Au3
Au4

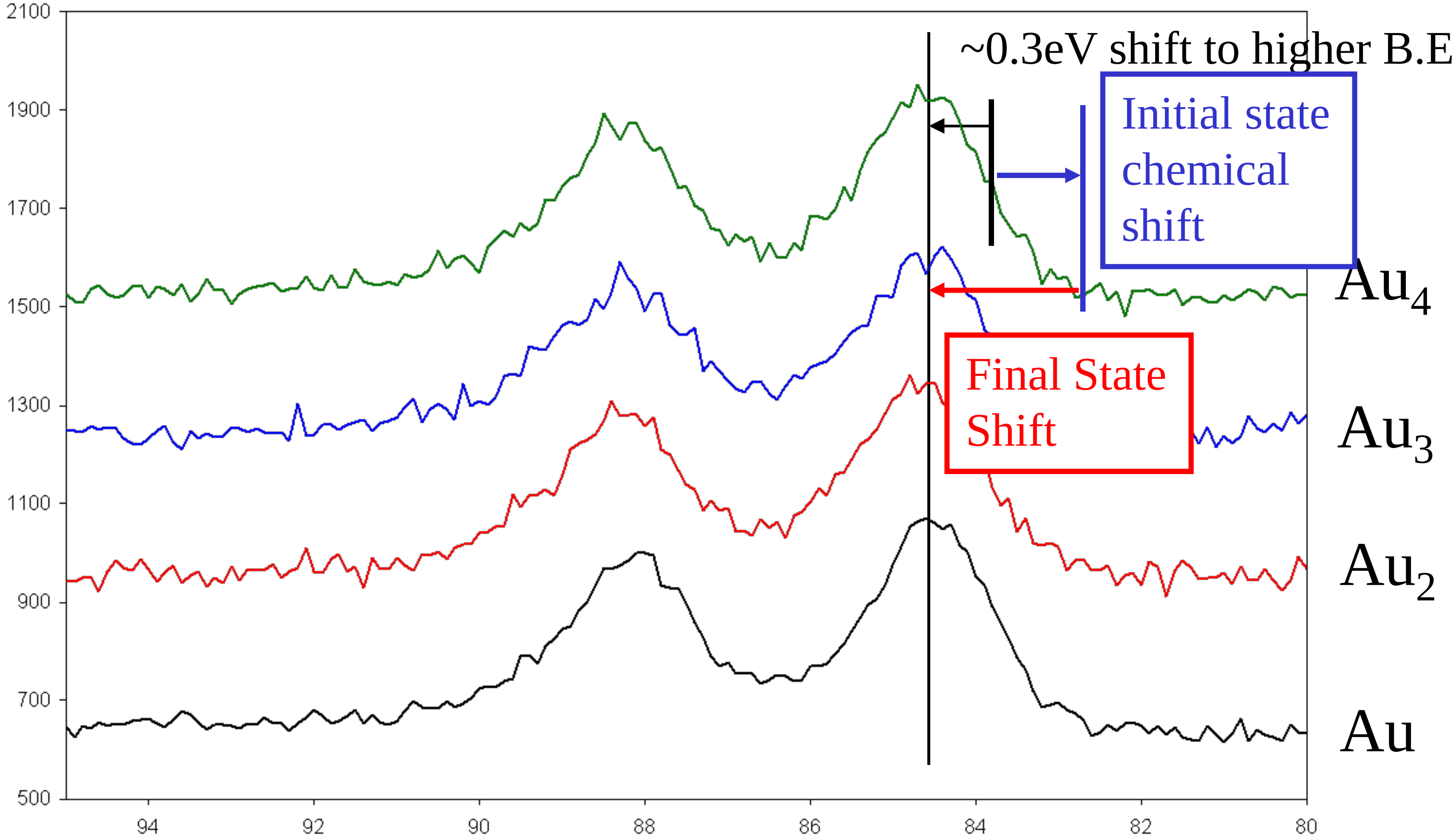
O_2 interaction with TiO_2 vacancies



O_2 at vacancies (Gyeong Hwang *et al.*)



XPS : Au 5f

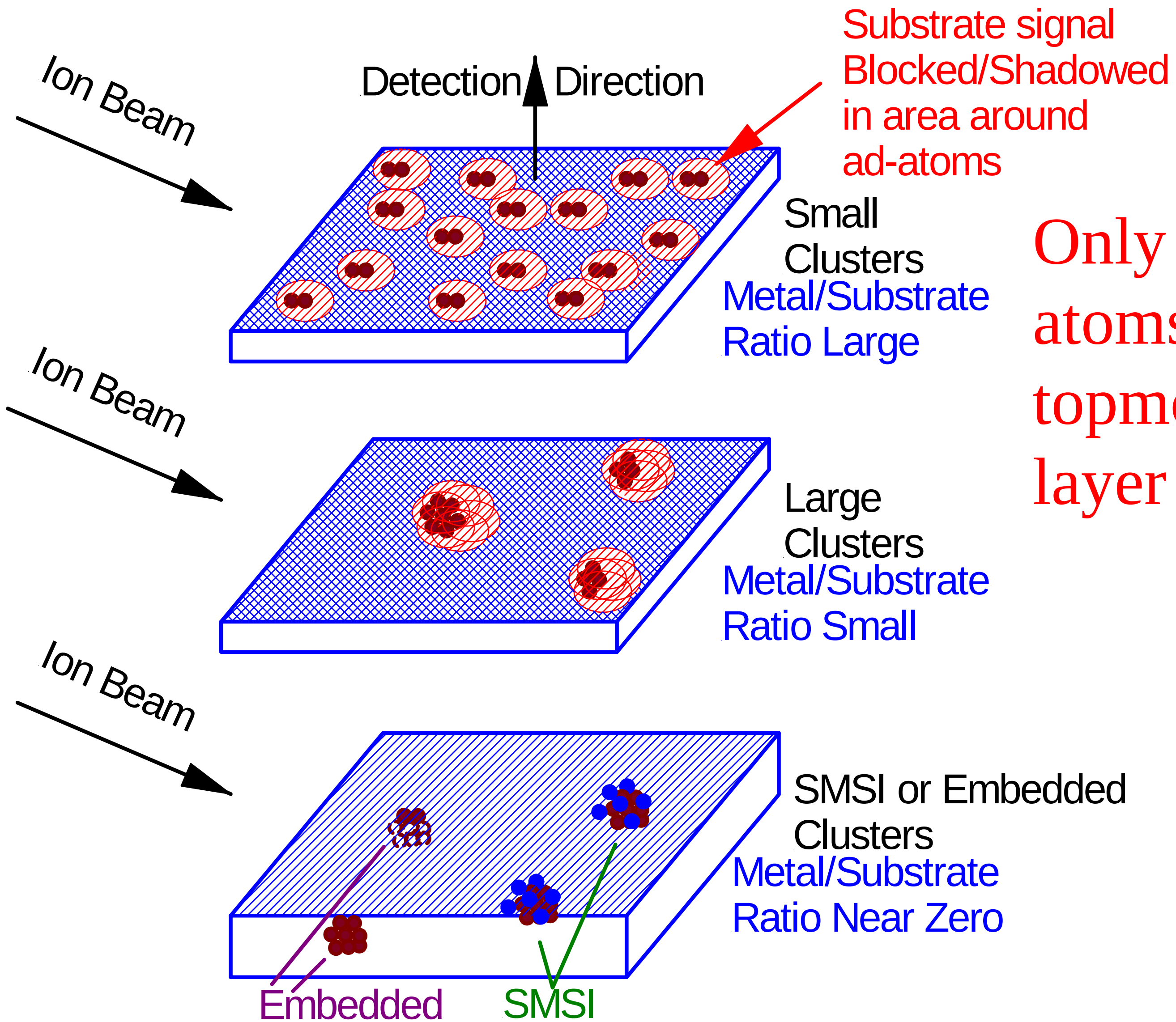


Constant signal = constant sticking coefficient ~1.0

No shifts with cluster size – not seen in any system in this size range

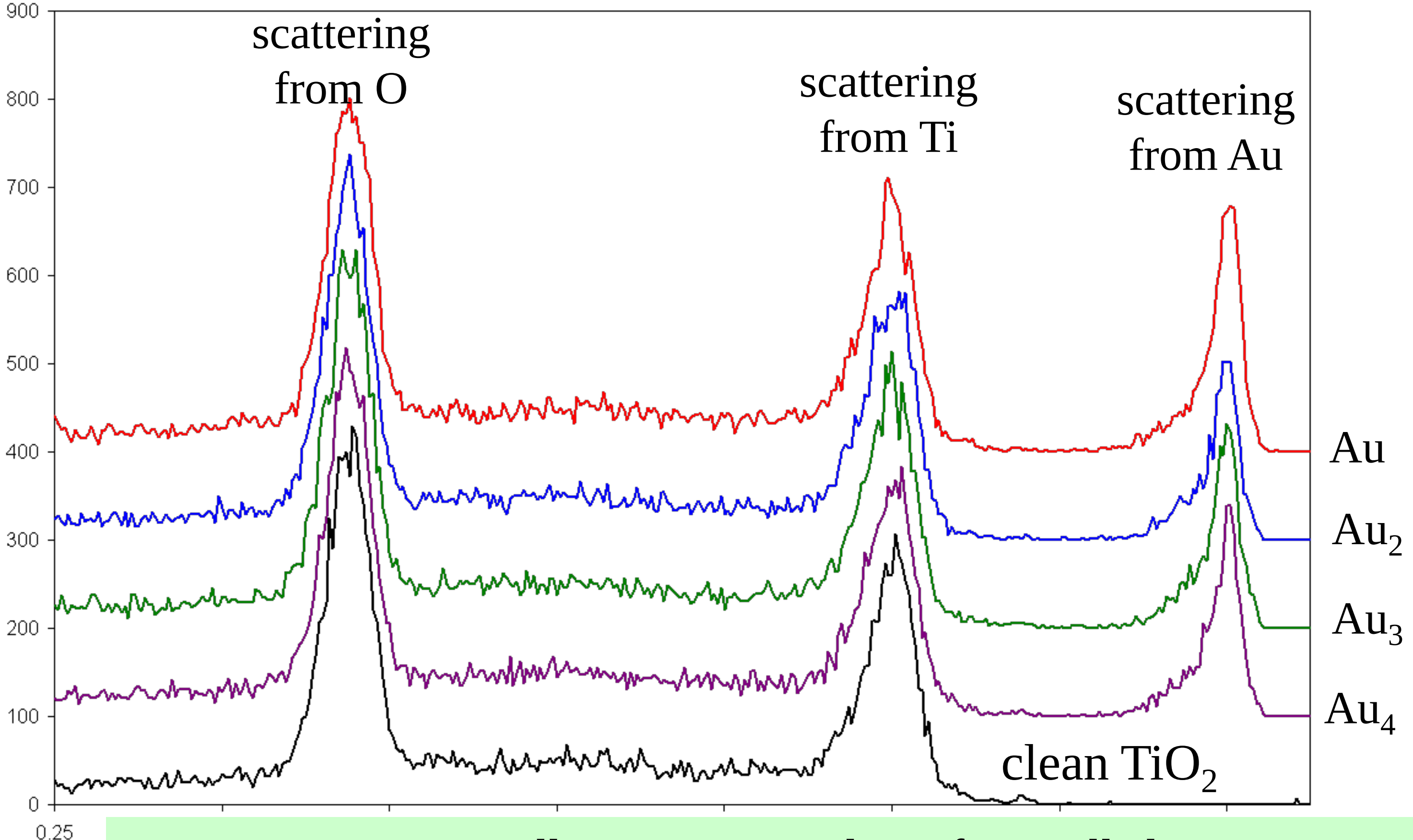
Morphology: ISS

$^4He^+$
1keV
45° incident angle



Only detect atoms in topmost layer

ISS : cluster size



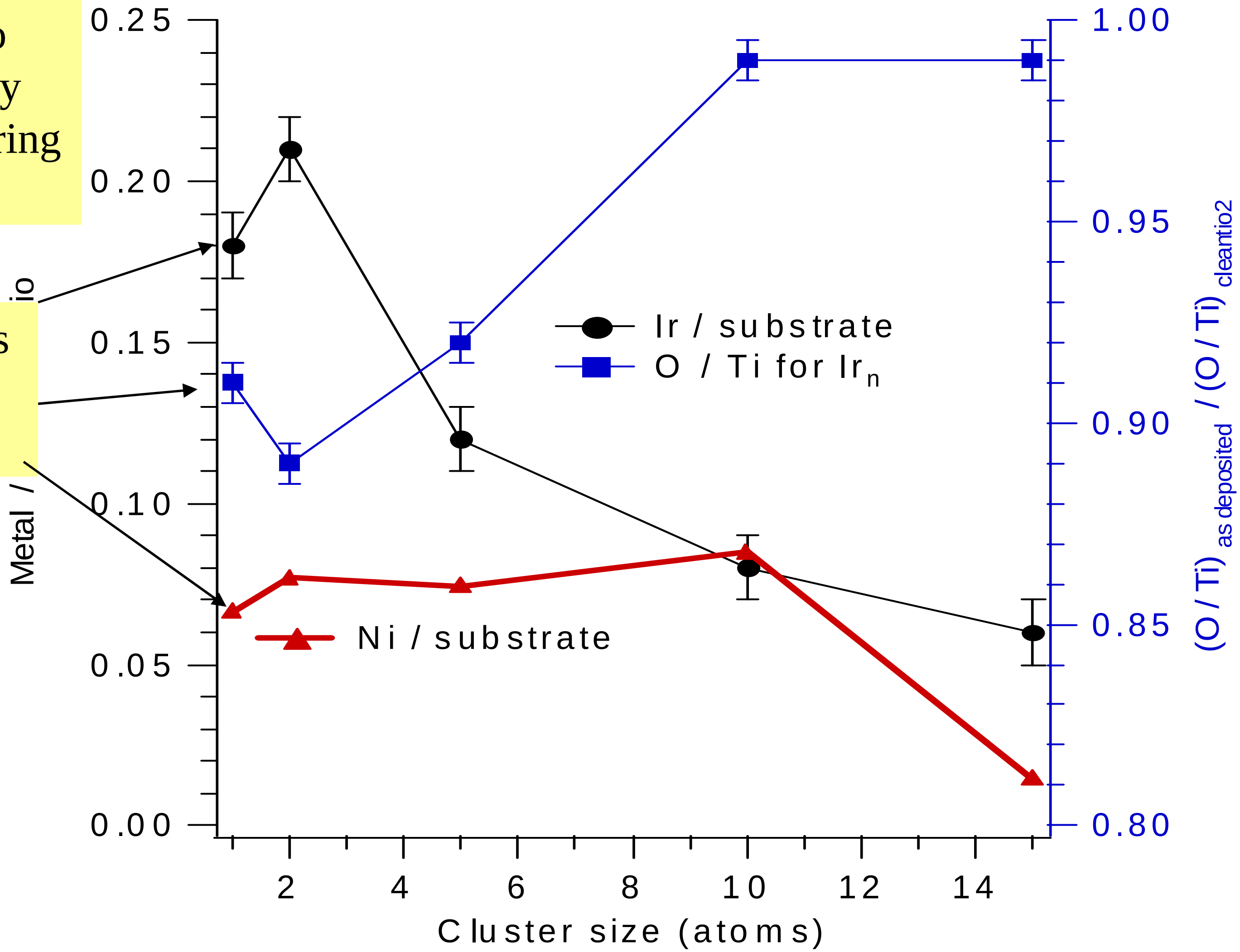
Constant intensity: All Au in topmost layer for small clusters?

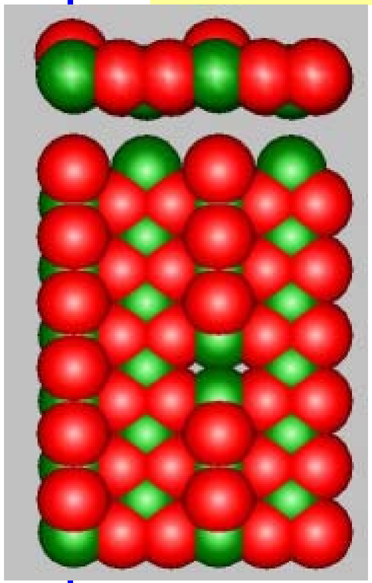
Are clusters sintering?

ISS ratios: Cluster Size Effects

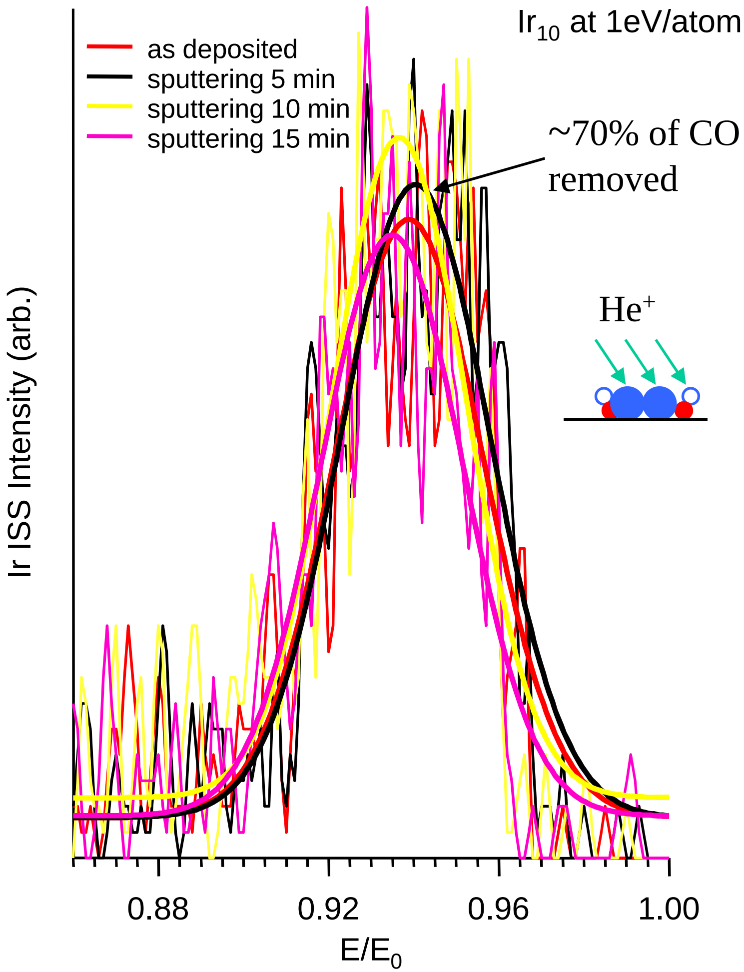
Decrease in O/Ti ratio
- Ir_n preferentially attenuates scattering from O

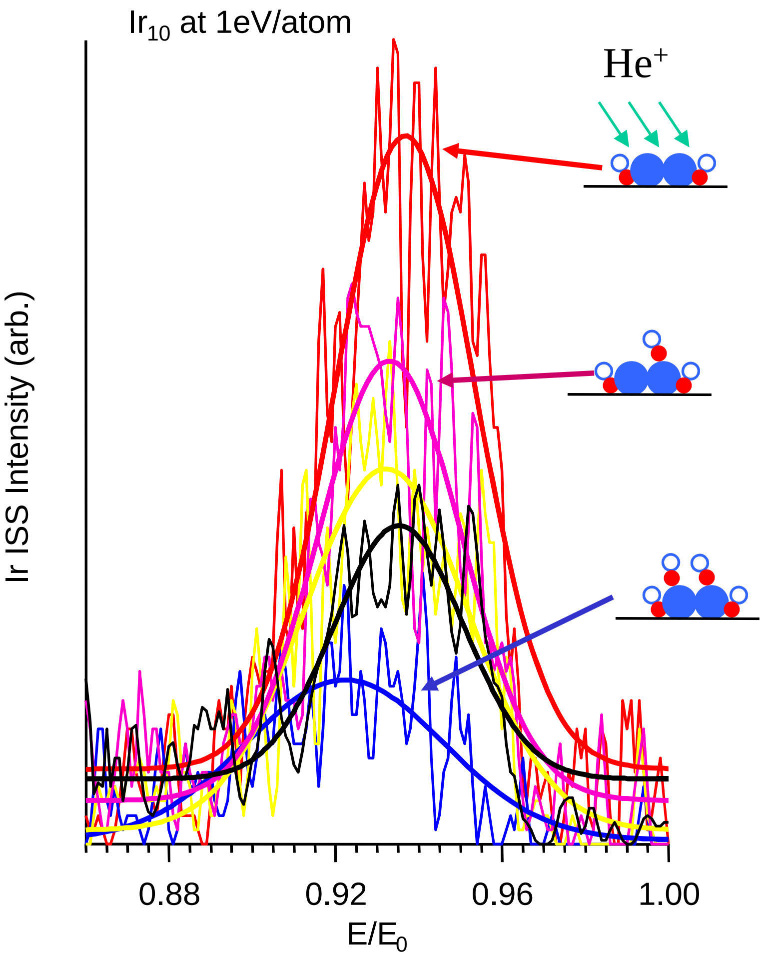
Anomalous behavior for atoms





ISS probing of CO binding sites





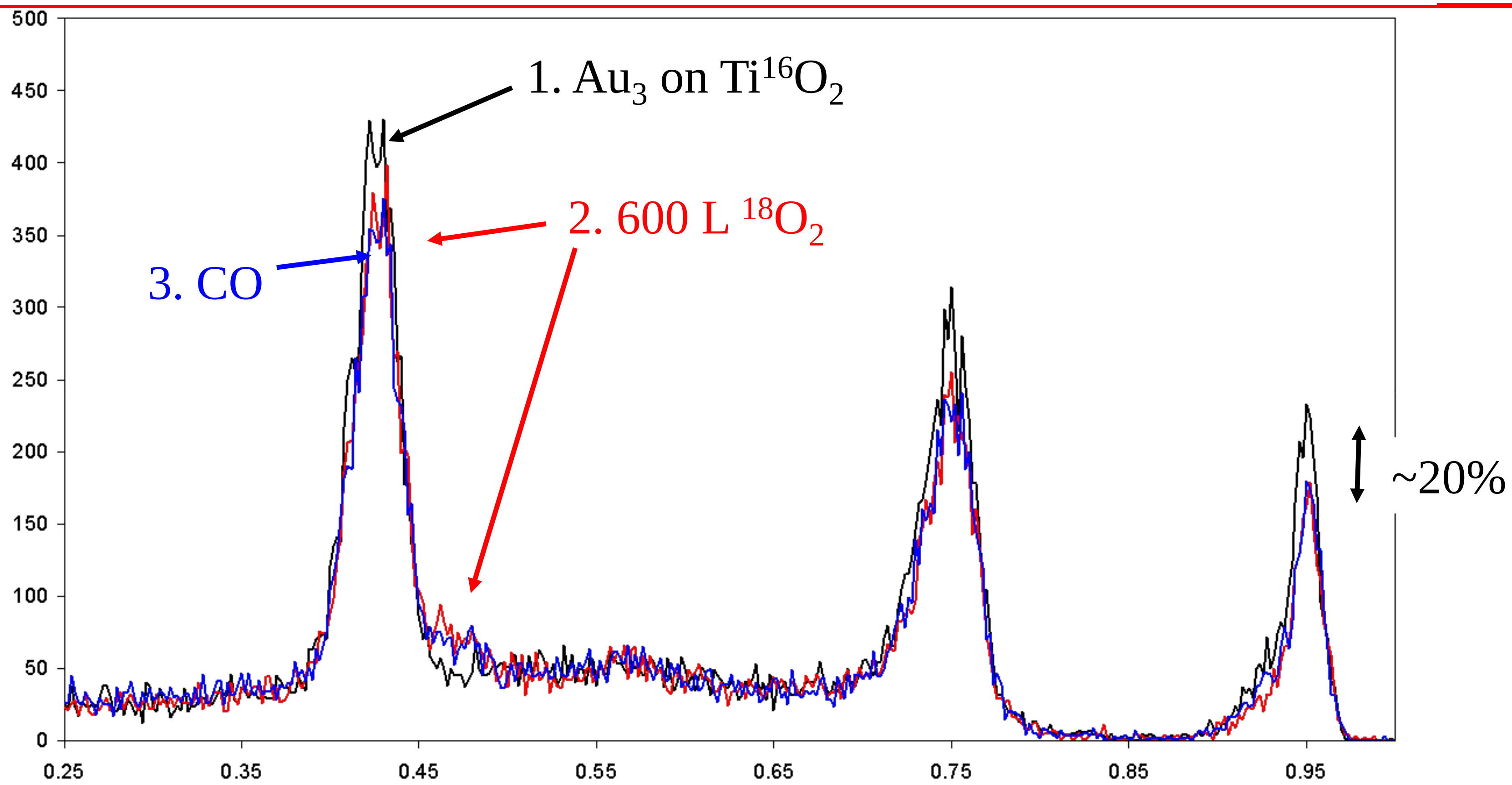
Aizawa, M.; Lee, S.; Anderson, S. L., *Surf. Sci.* 2003, *542*, 253-75.

How to study CO oxidation in UHV?

- ☑ CO sticks to small Au
- ☒ O_2 adsorbs on catalyst
- ☑ CO_2 desorbs at lower temperature than CO
  - – doesn't poison catalyst

All previous UHV studies have used atomic O

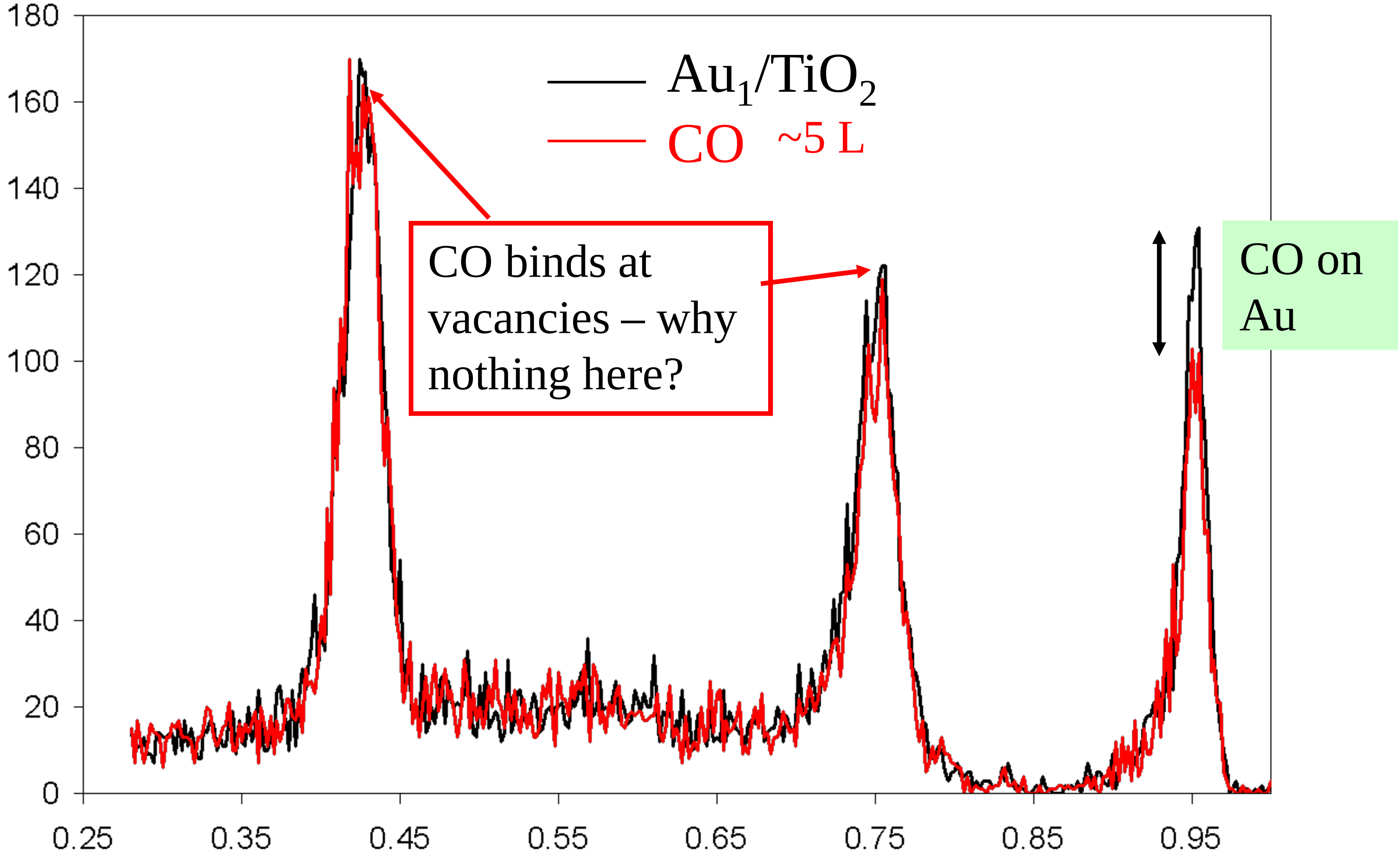
ISS : ^{16}O, ^{18}O exchange



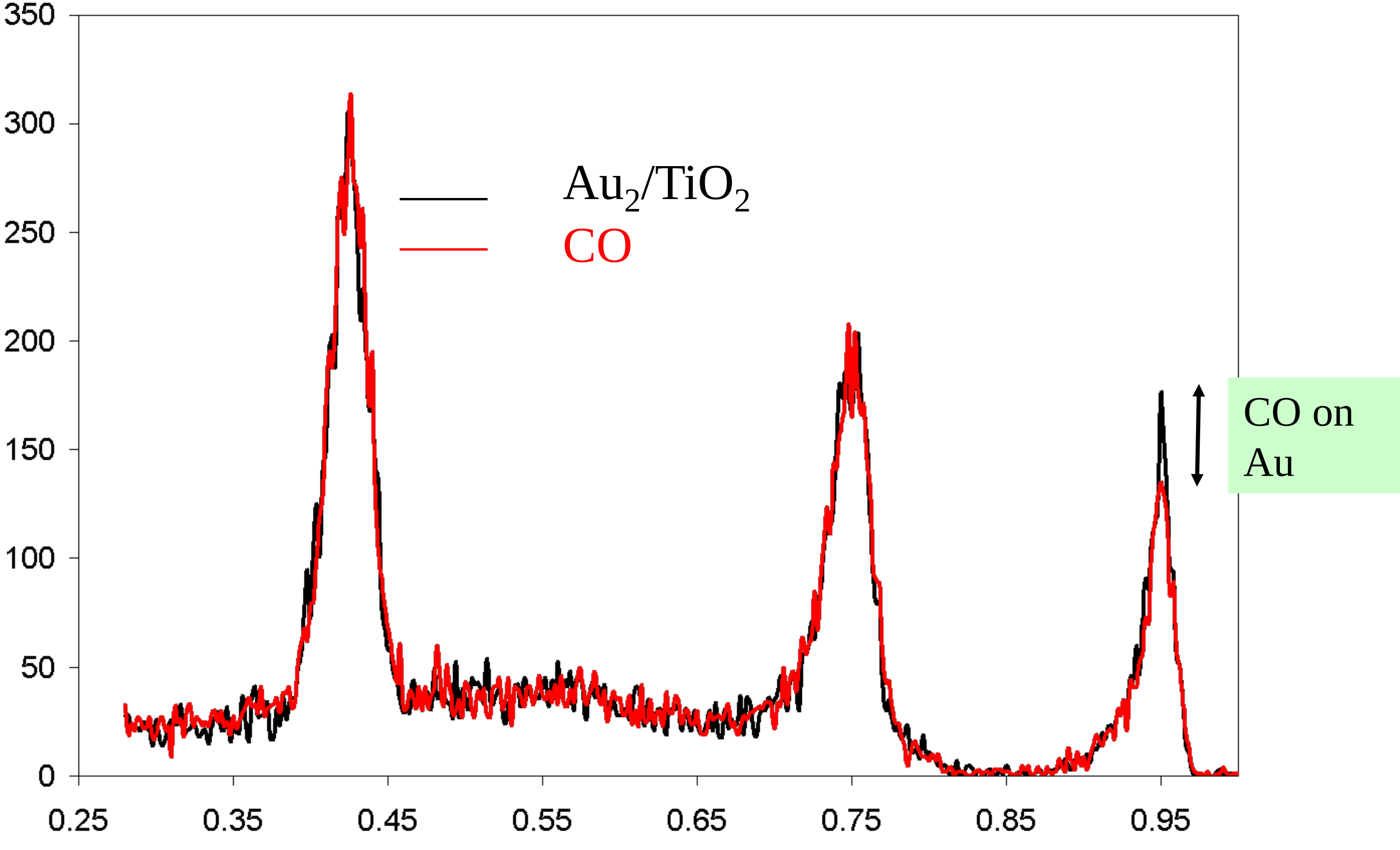
^{18}O bound at O vacancies ~9% of surface O is ^{18}O

Some O bound at Au cluster sites – attenuation too low to be atop

CO dose effect on ISS: Au_1/TiO_2

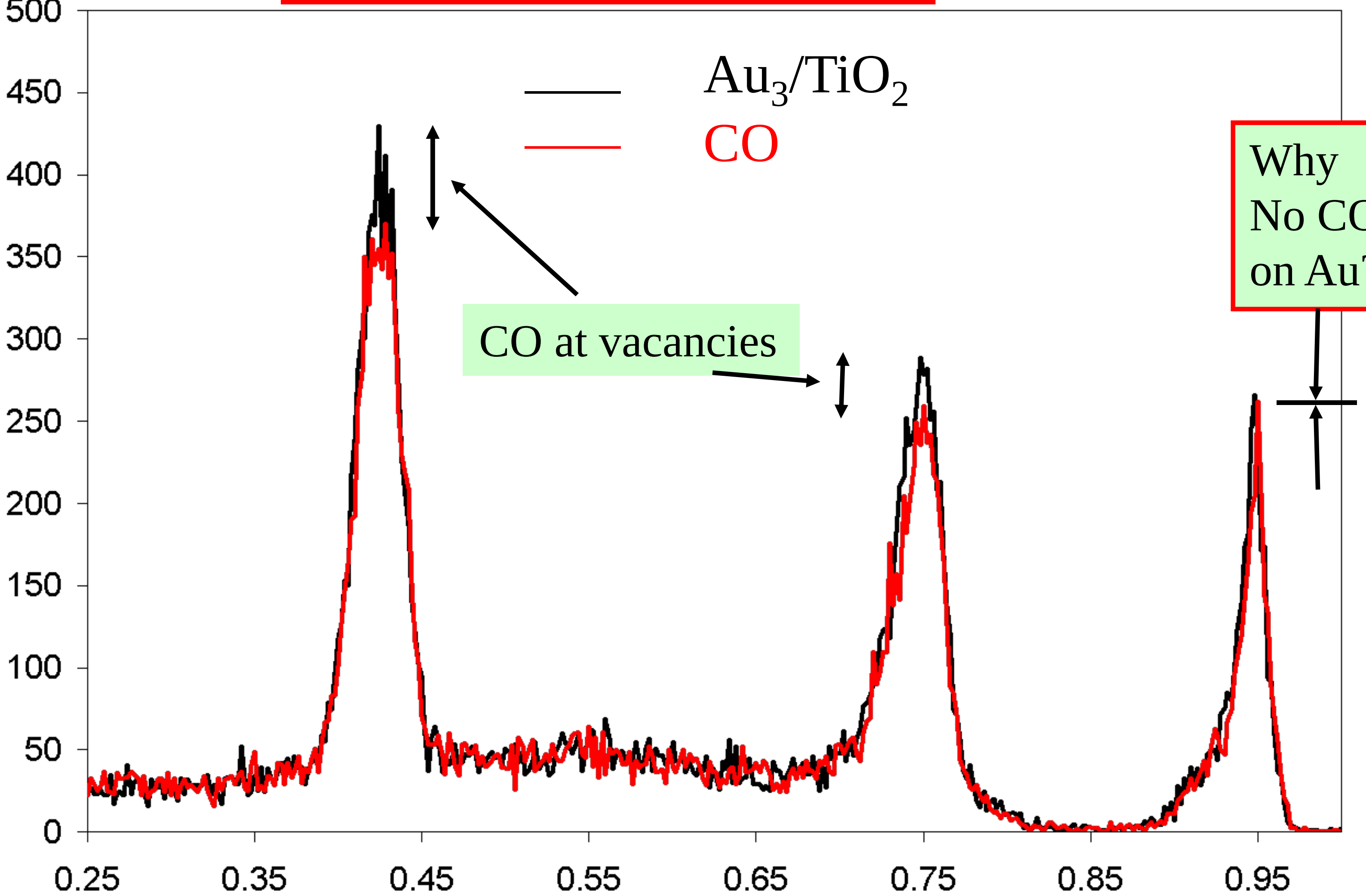


CO dose effect on ISS: Au_2/TiO_2



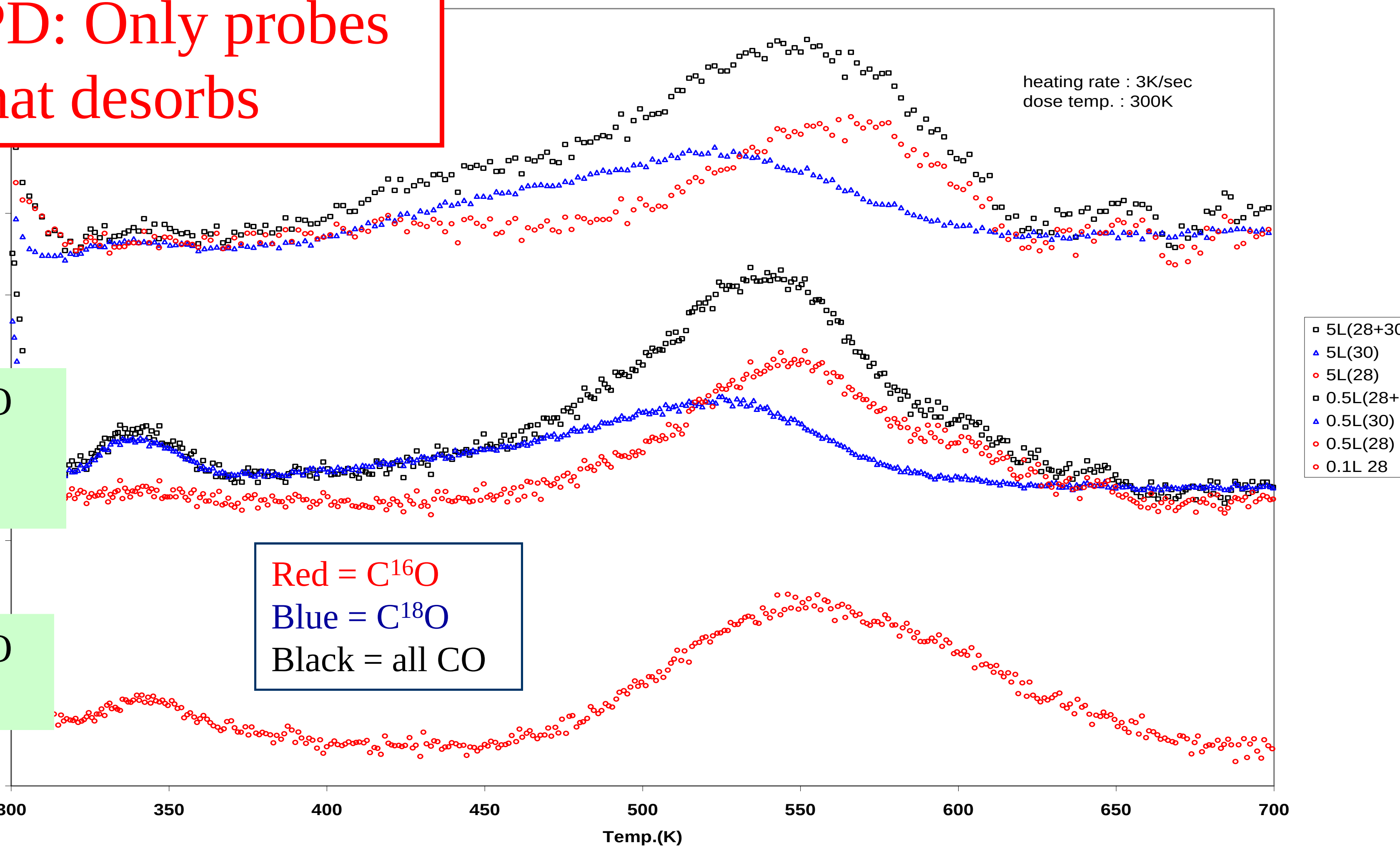
CO dose effect on ISS: Au_3/TiO_2

First sign of chemical differences



Chemical Probing - TPD (CO on Ir_2/TiO_2)

TPD: Only probes what desorbs

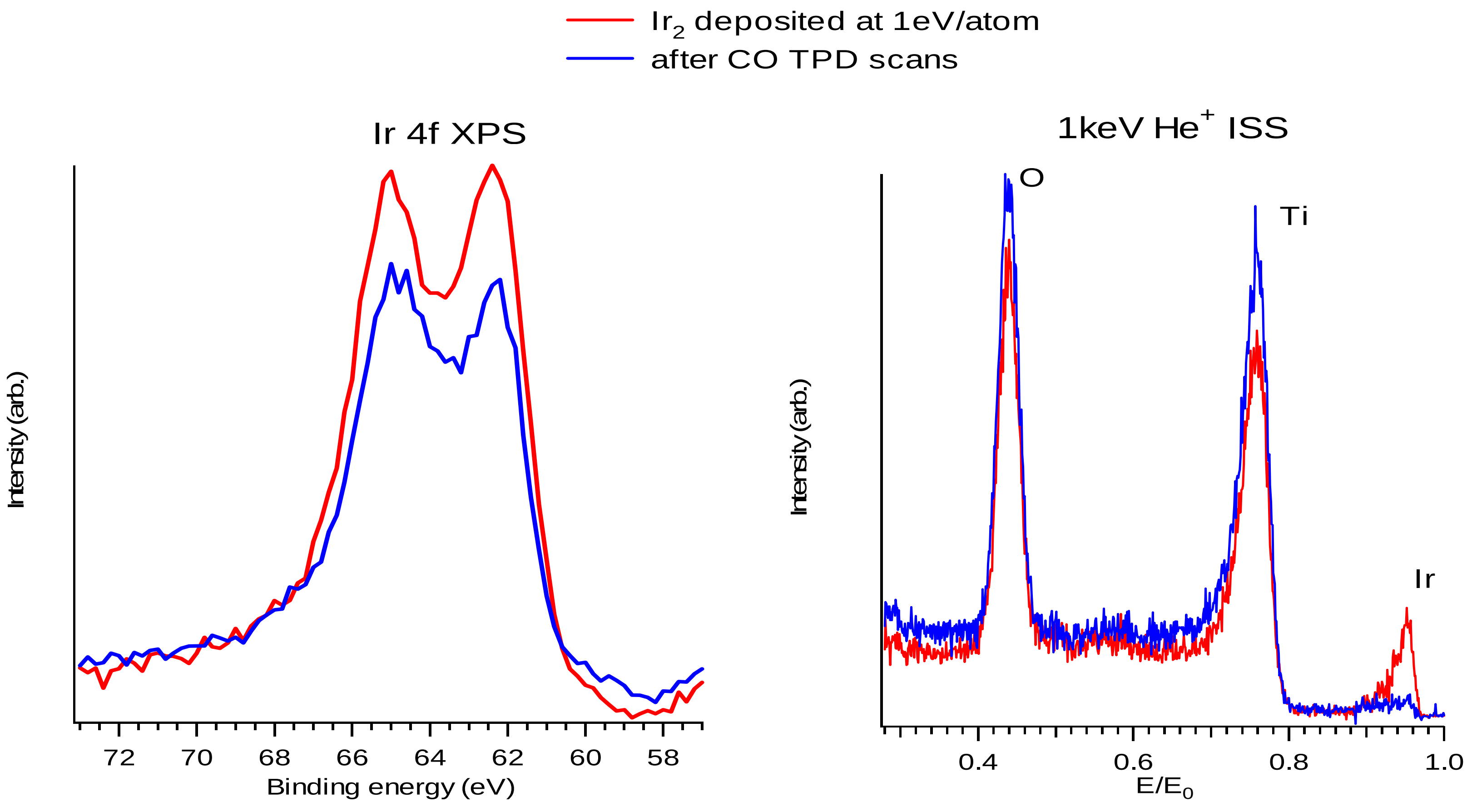


~0.1 L $C^{16}O$ plus 0.5 L $C^{18}O$

Red = $C^{16}O$
Blue = $C^{18}O$
Black = all CO

~0.1 L $C^{16}O$ exposure

Bad News



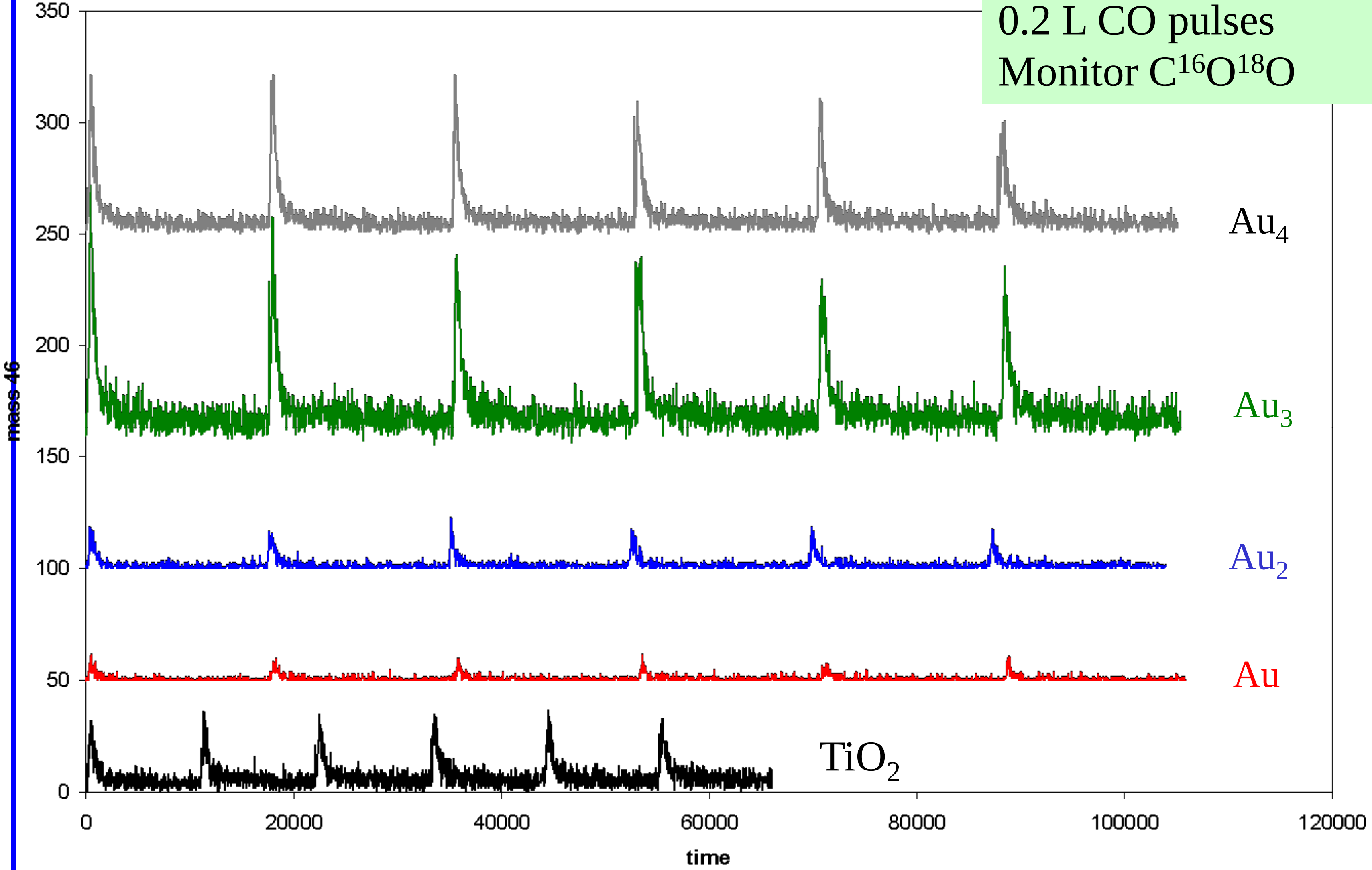
Ir2 deposited at 1eV/atom
after CO TPD scans
Ir 4f XPS
Intensity (arb.)
72
70
68
66
64
62
60
58
Binding energy (eV)
1keV He+ ISS
O
Ti
Ir
Intensity (arb.)
0.4
0.6
0.8
1.0
E/E0

Chemical Probing II

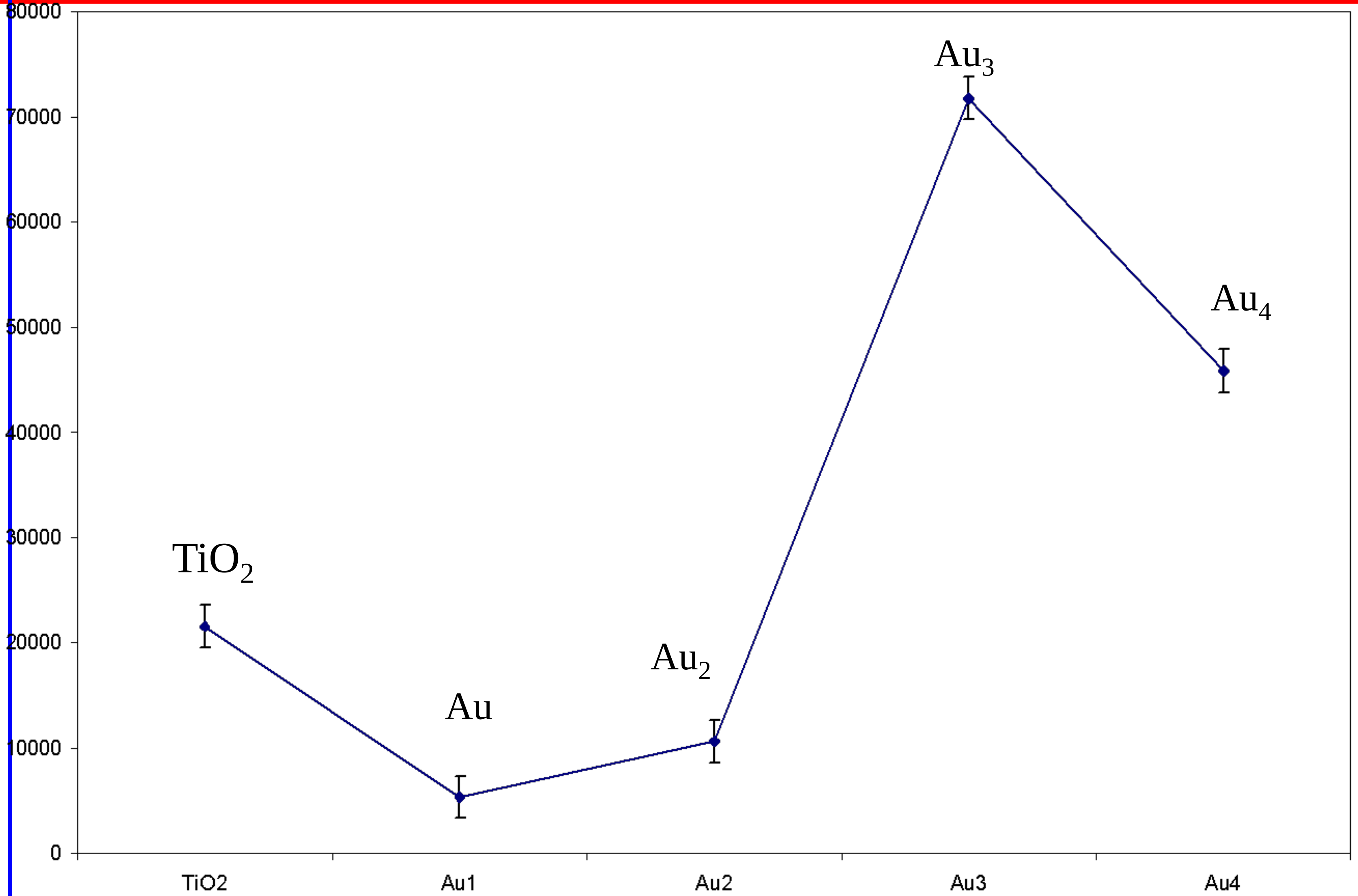
	Single Crystal	Small Clusters
TPD:	Only probe what desorbs	Destructive – 1 shot expt
Pulsed dosing	Only probe what desorbs	Less destructive if low T?

CO oxidation reaction I : size

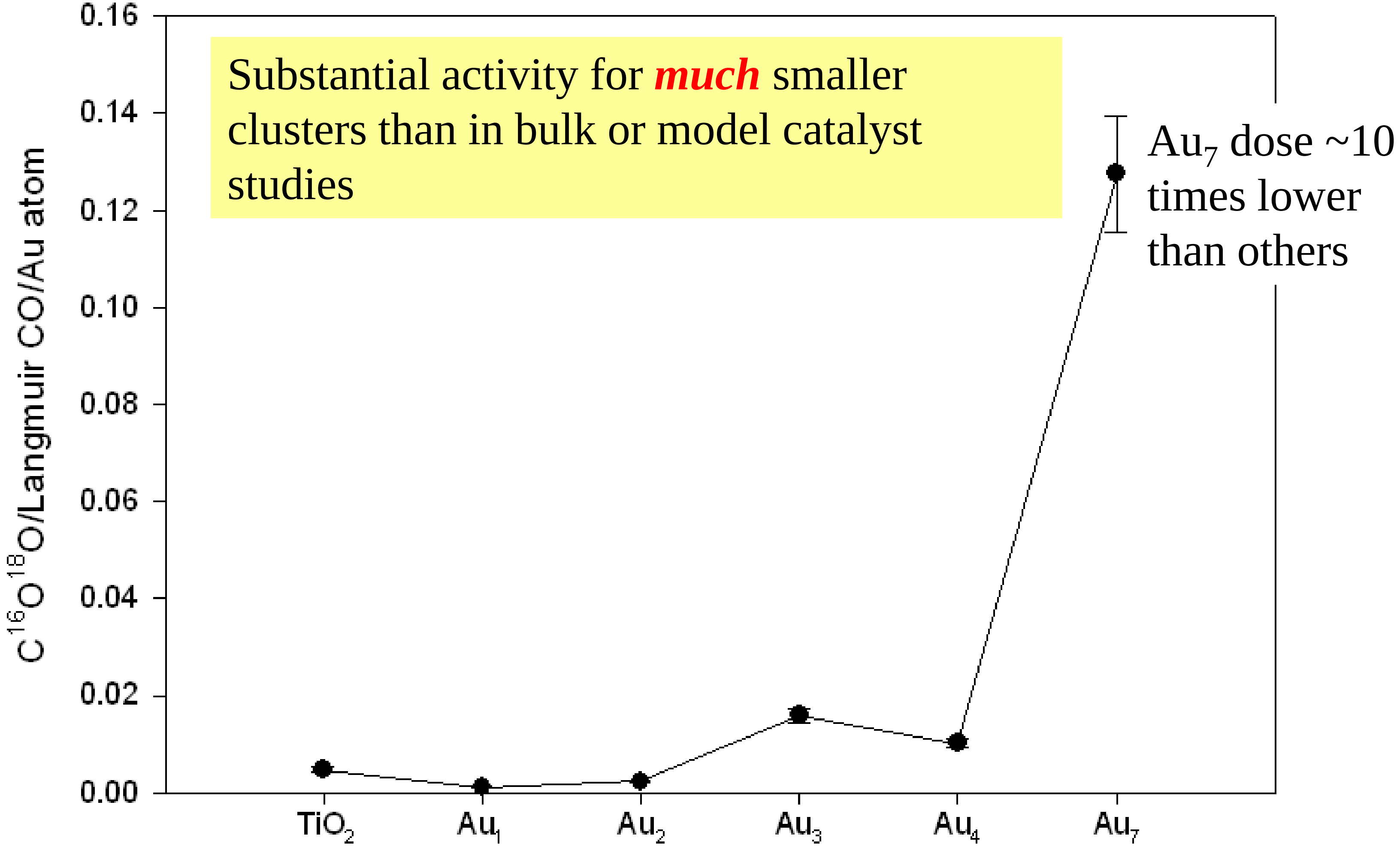
600L pre-dose of $^{18}O_2$
0.2 L CO pulses
Monitor $C^{16}O^{18}O$



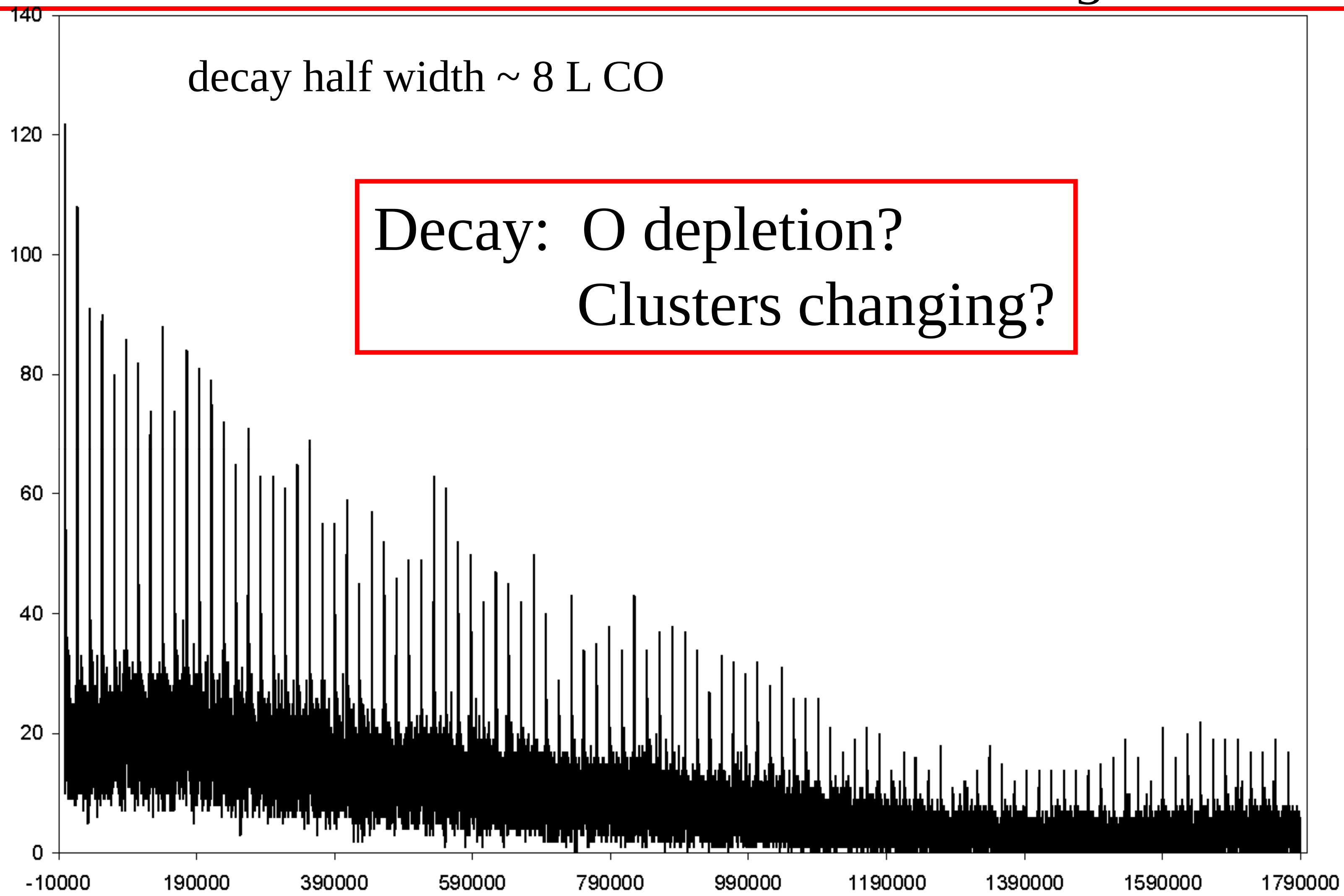
CO oxidation – size effect



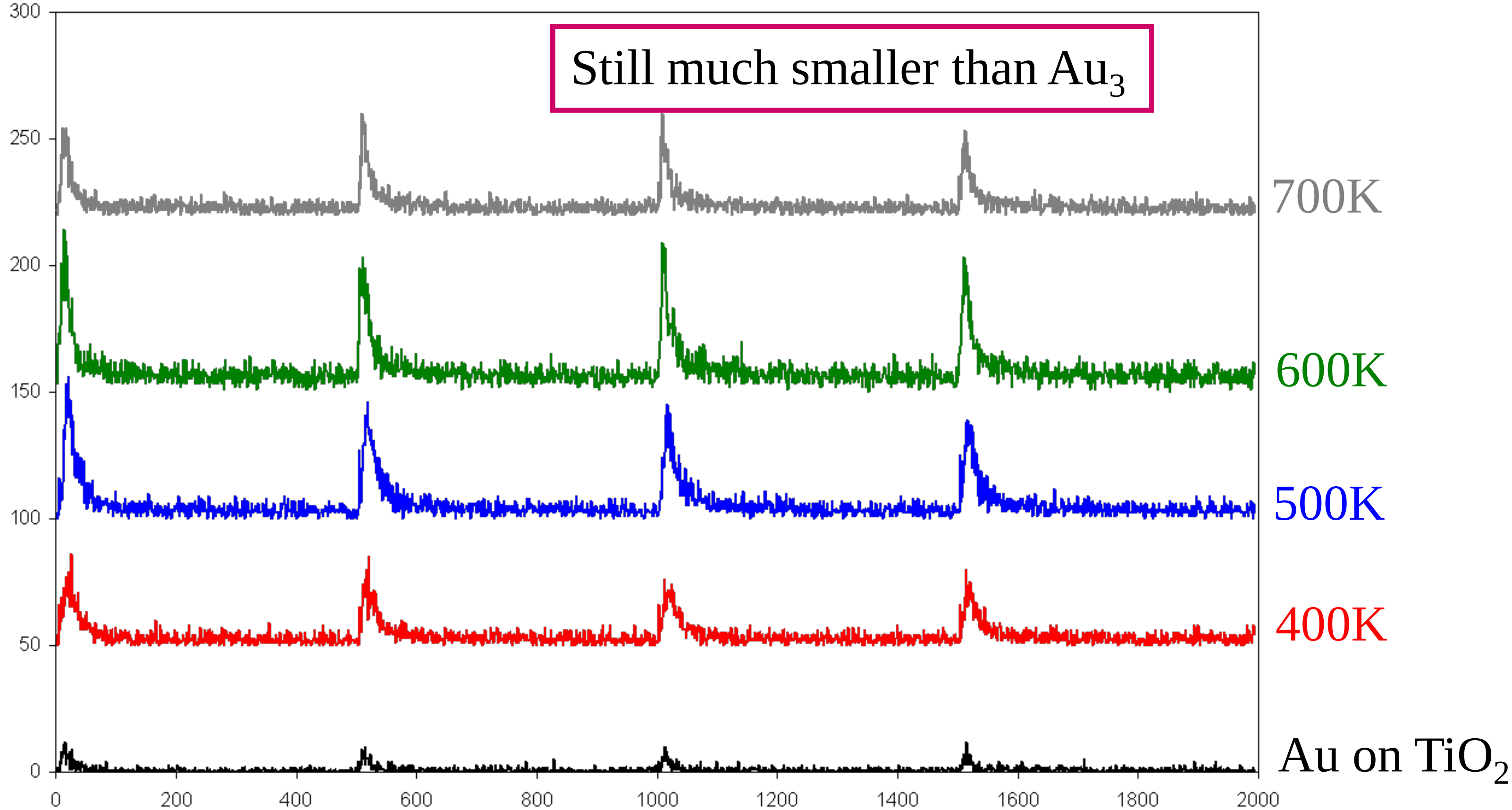
CO oxidation – size effect



CO oxidation reaction : Au_3

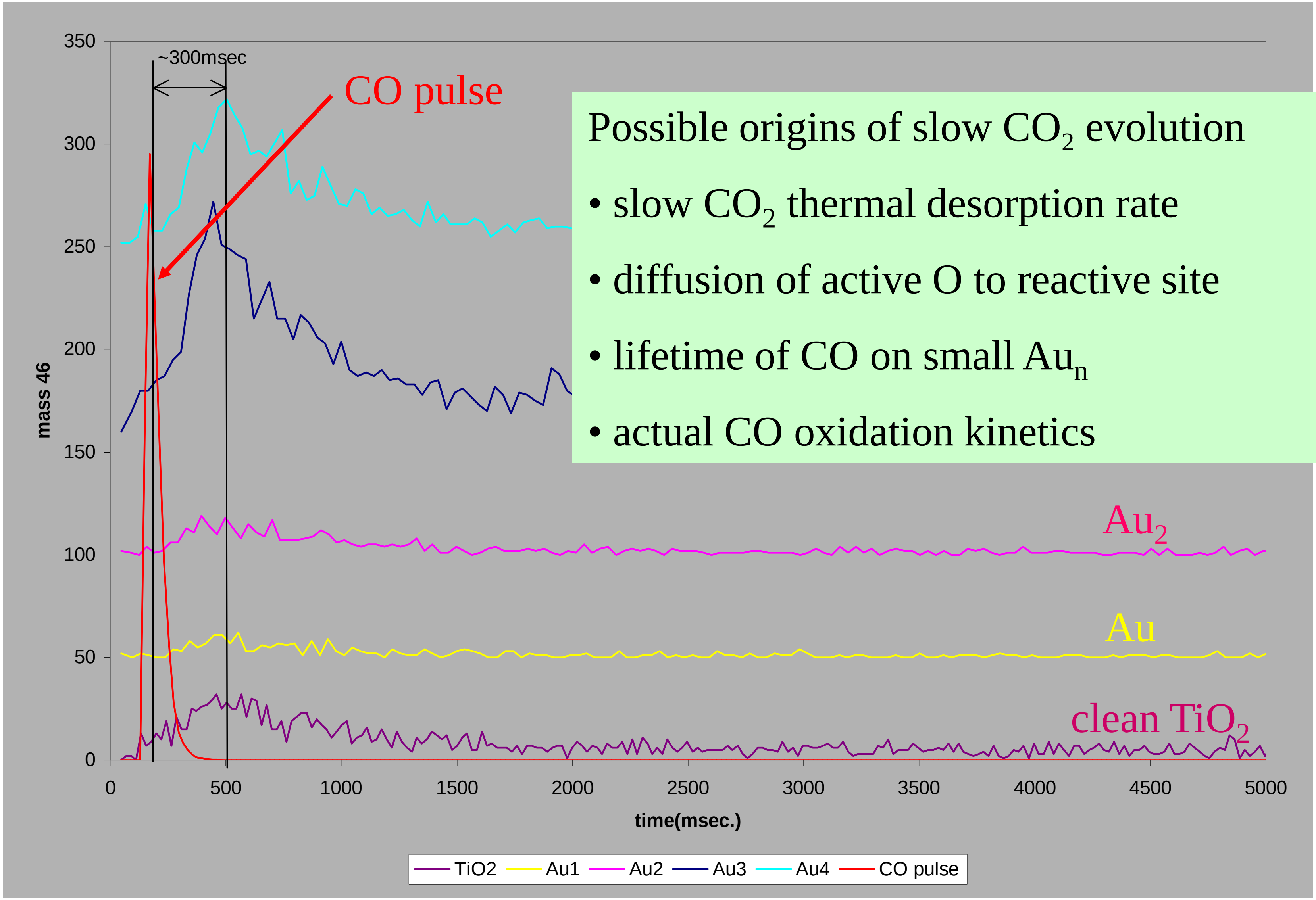


CO pulse reaction II : atom annealing



Growing larger clusters? Unblocking defects?

CO pulse reaction III : pulse shape



Possible origins of slow CO_2 evolution

- slow CO_2 thermal desorption rate
- diffusion of active O to reactive site
- lifetime of CO on small Au_n
- actual CO oxidation kinetics

What happens with Au_n^+ are deposited

Expts of Wahlström *et al.*

→ Should have Au_n, n ~ 20 for all samples

CO oxidation … rongly dependent on deposited si…

WHY?

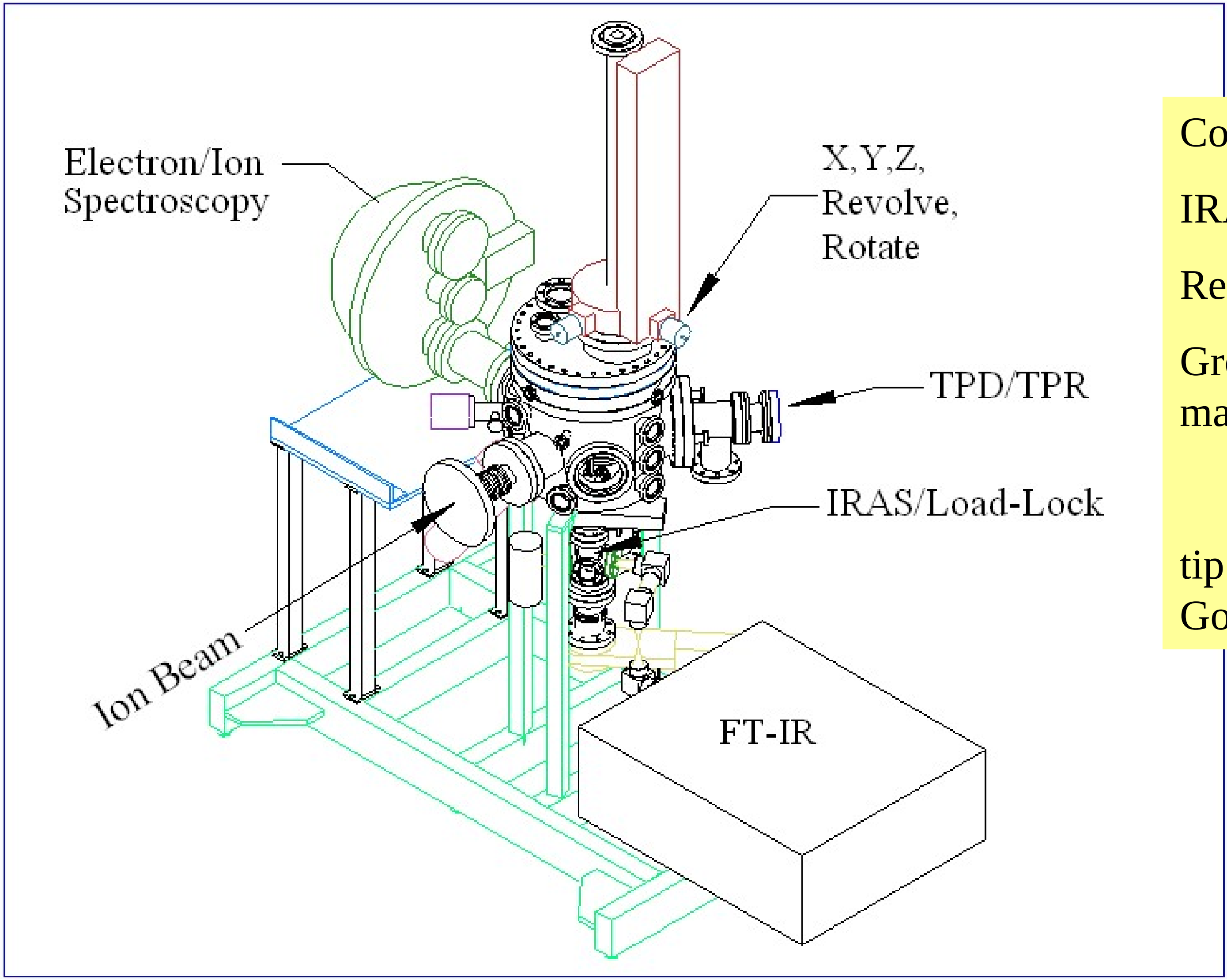
Catalysts are … few hour timescale for many cycles of O_2 / CO

→ Samples do not reach an equilibrium state.

Needed

- $^{13}CO + ^{18}O_2$ to allow measurement of both $C^{16}O_2$ and $C^{16}O^{18}O$
  - Only seeing the tip of the iceberg?
- Low temperature deposition and analysis to reduce/change sintering
- Probe steady state species on surface – not just species desorbing

New Endstation



Continuous T control

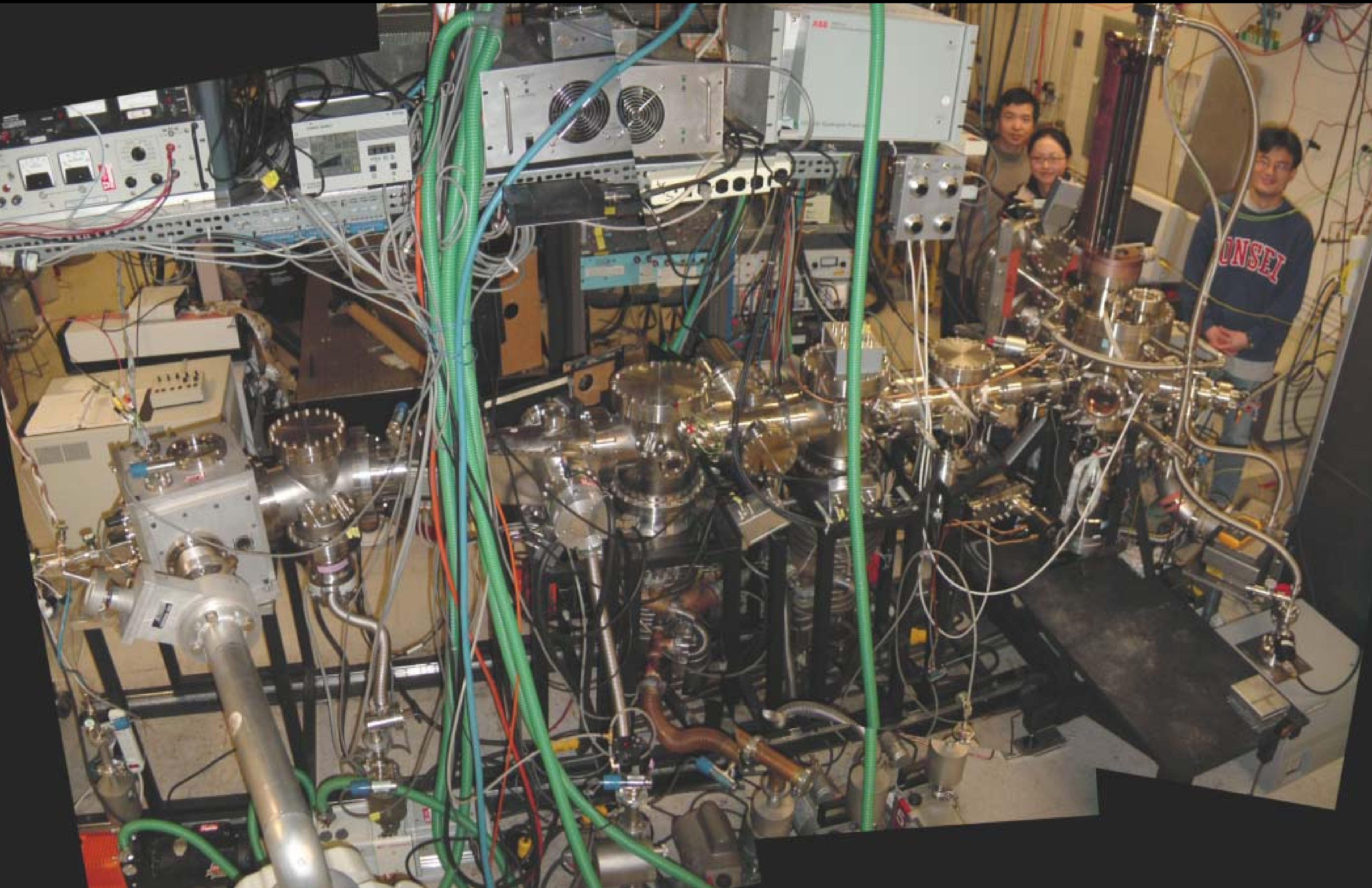
IRAS capability

Retain load/lock

Greatly simplified manipulations

tip ‘o the hat - Wayne Goodman

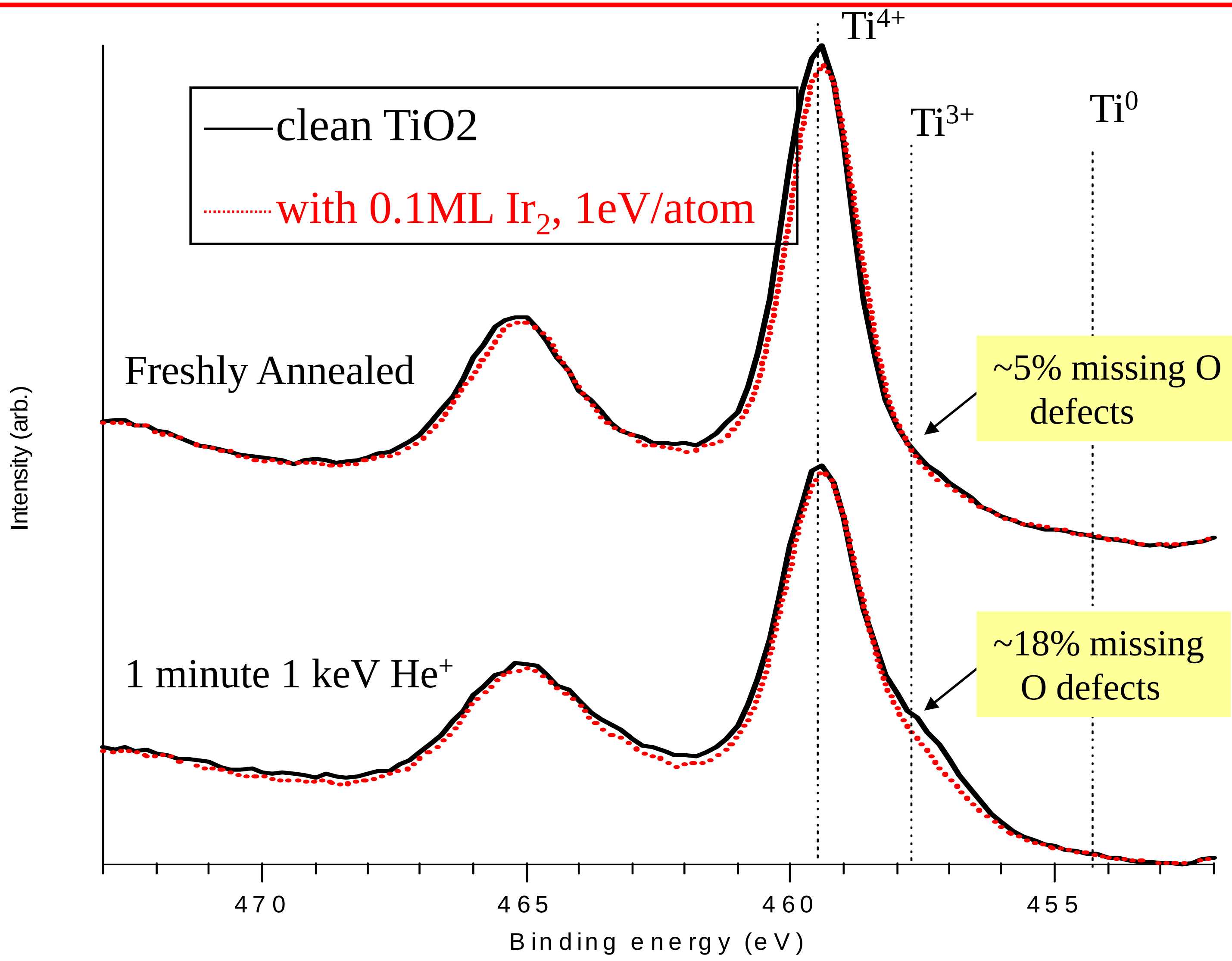
Utah Cluster Deposition Instrument

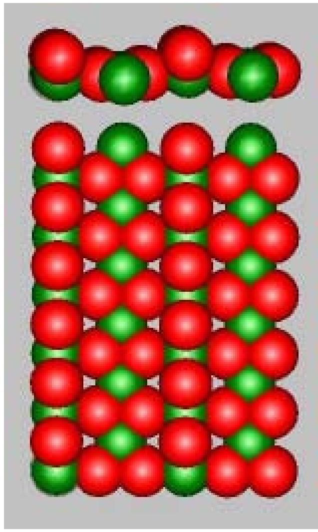


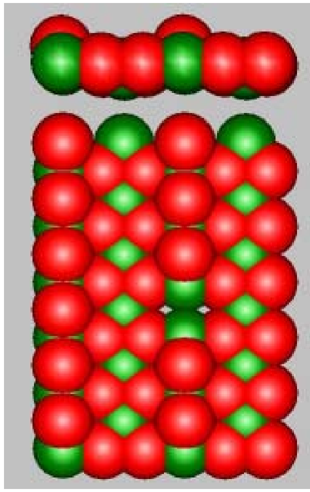
Ti XPS

Mg Kα

1253.6 eV







ISS cluster size effect

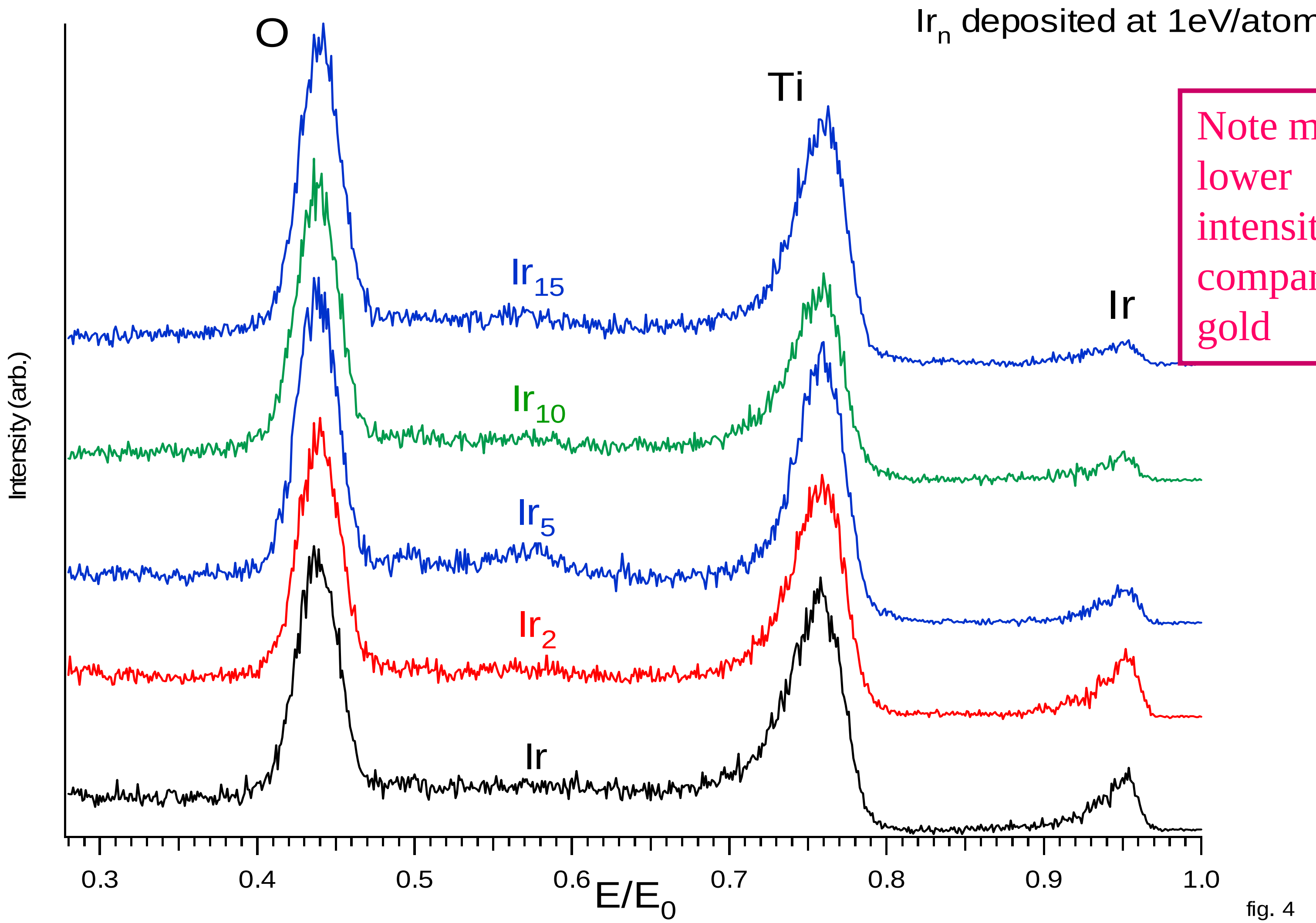
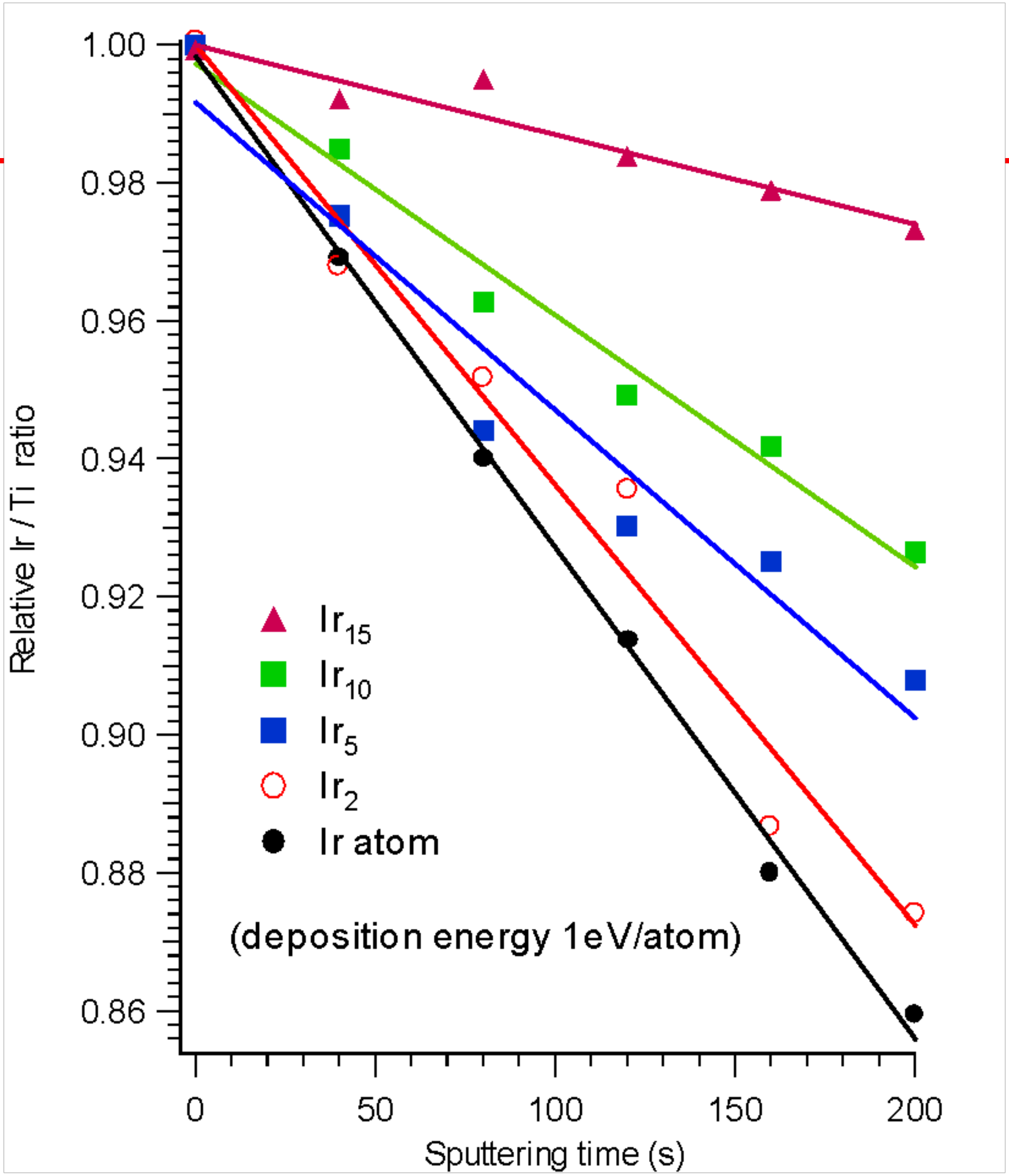


fig. 4

Note much lower intensity compared to gold

Ir ISS v.s. Sputter Time

Slow sputtering for large n
--Multilayer clusters
--Stronger Ir-Ir binding

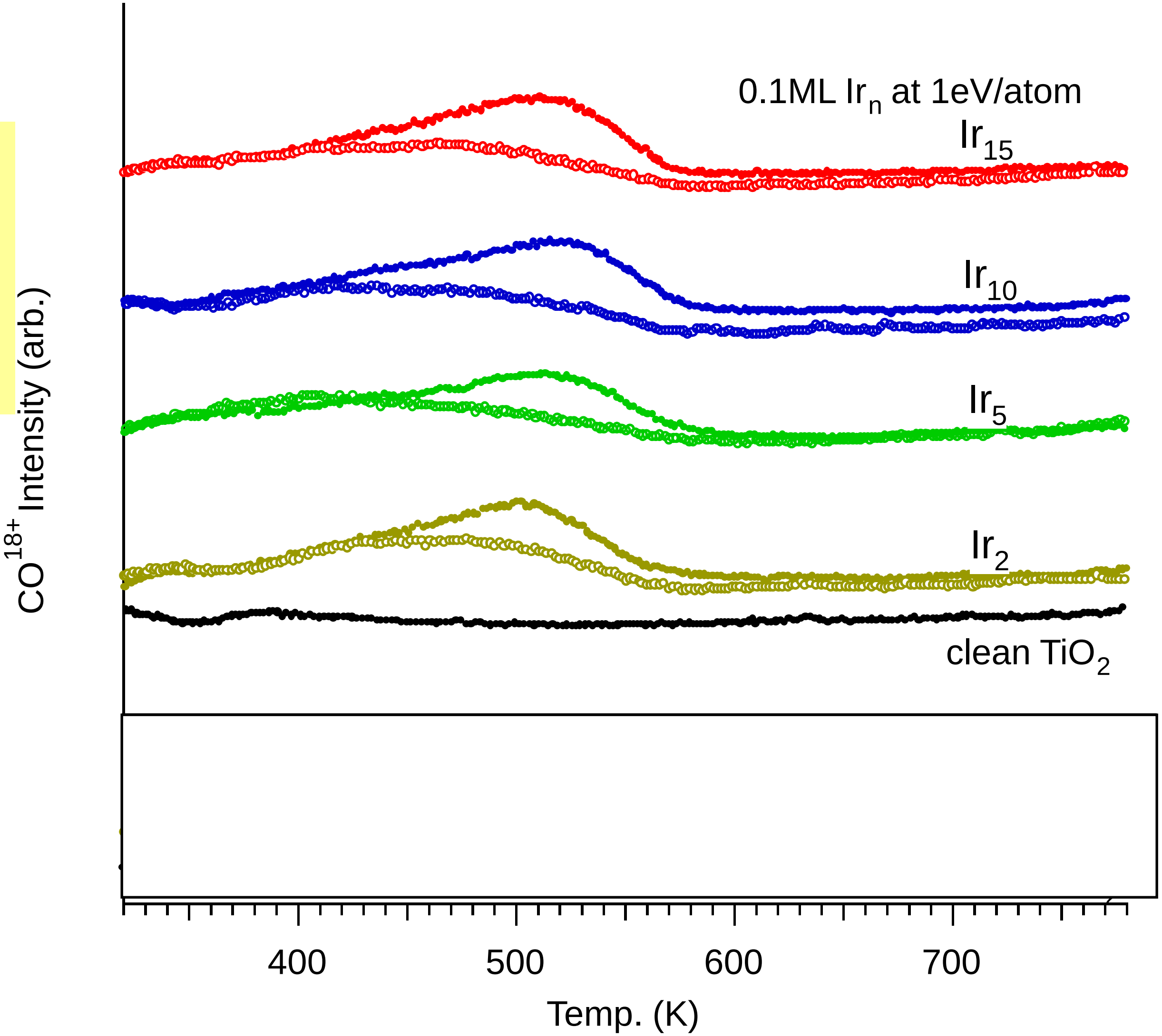


Effects of TPD on the sample

5 L dose of $C^{18}O$ at room temperature

Solid = 1st TPD run

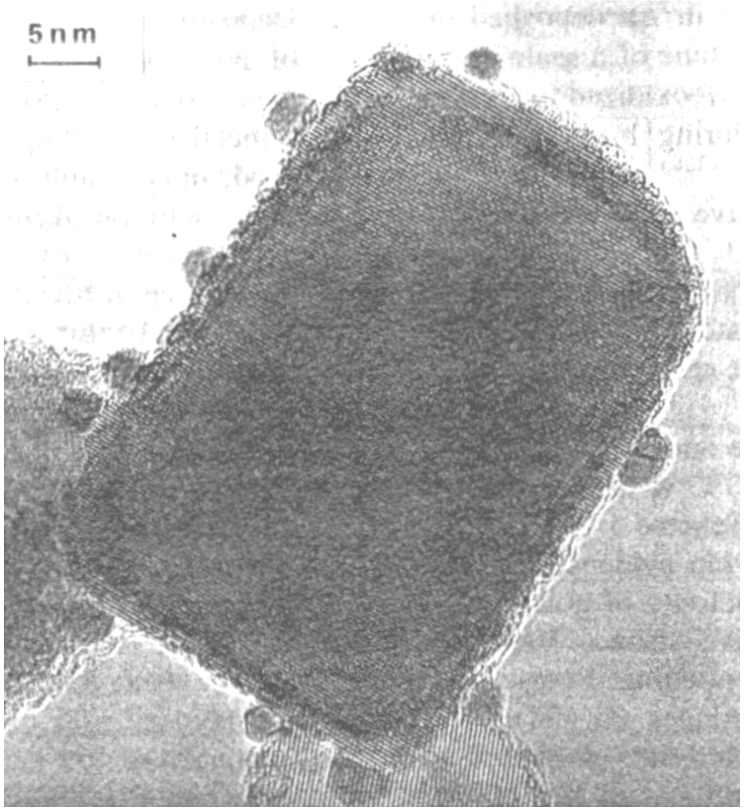
Open = 2nd TPD run

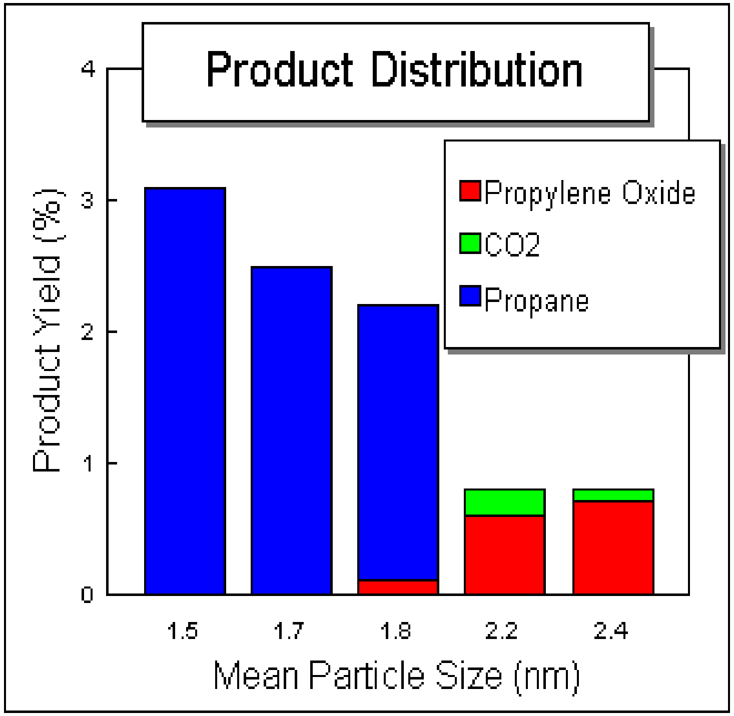


Cluster Size Effects in Catalysis (background)

Example:

Gold cluster catalyst, from Haruta, 1997.
2 - 3 nm gold clusters on TiO_2





Variation in product yield with cluster size.

Propene/O_2/H_2 mixture over Au/TiO_2 catalyst (from Haruta 1997)