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Chemistry of free transition metal clusters

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FHI Berlin, Molecular Physics

How can free clusters help the understanding of heterogeneous catalysts?

nano-disperse gold catalysts

Literature

R. L. Johnston: **Atomic and Molecular Clusters**, 2002, (Taylor & Francis, London)

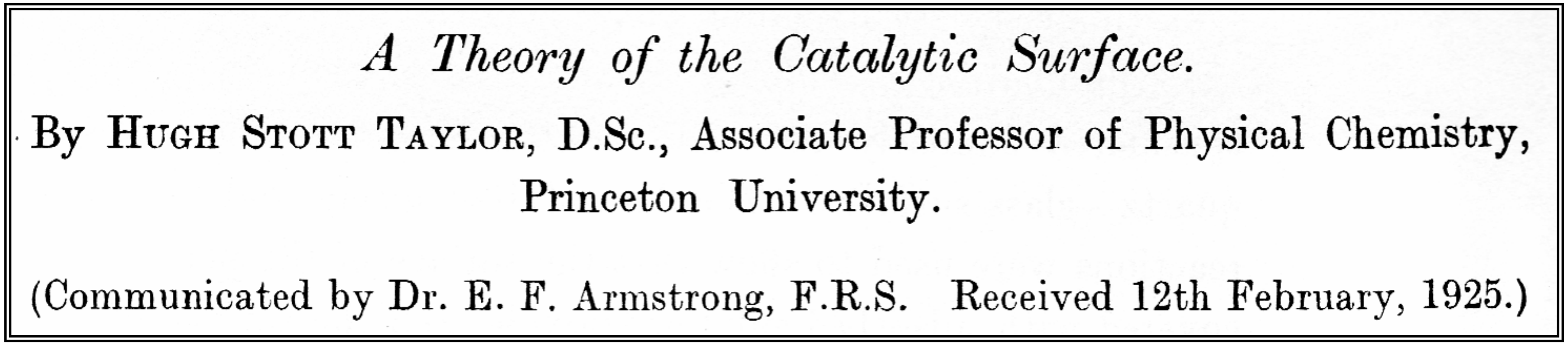
M. B. Knickelbein, **Reactions of Transition Metal Clusters with Small Molecules**, Ann. Rev. Phys. Chem. 50, 79 (1999).

T. M. Bernhardt, **Gas-phase kinetics and catalytic reactions of small silver and gold clusters**, Int. J. Mass Spectr. 243, 1 (2005).

Y. D. Kim, **Chemical properties of mass-selected coinage metal cluster anions: towards obtaining molecular-level understanding of nanocatalysis**, Int. J. Mass Spectr. 238, 17 (2004).

B. Yoon et al., **Charging Effects on Bonding and Catalyzed Oxidation of CO on Au8 Clusters on MgO,** Science, 307, 403 (2005).

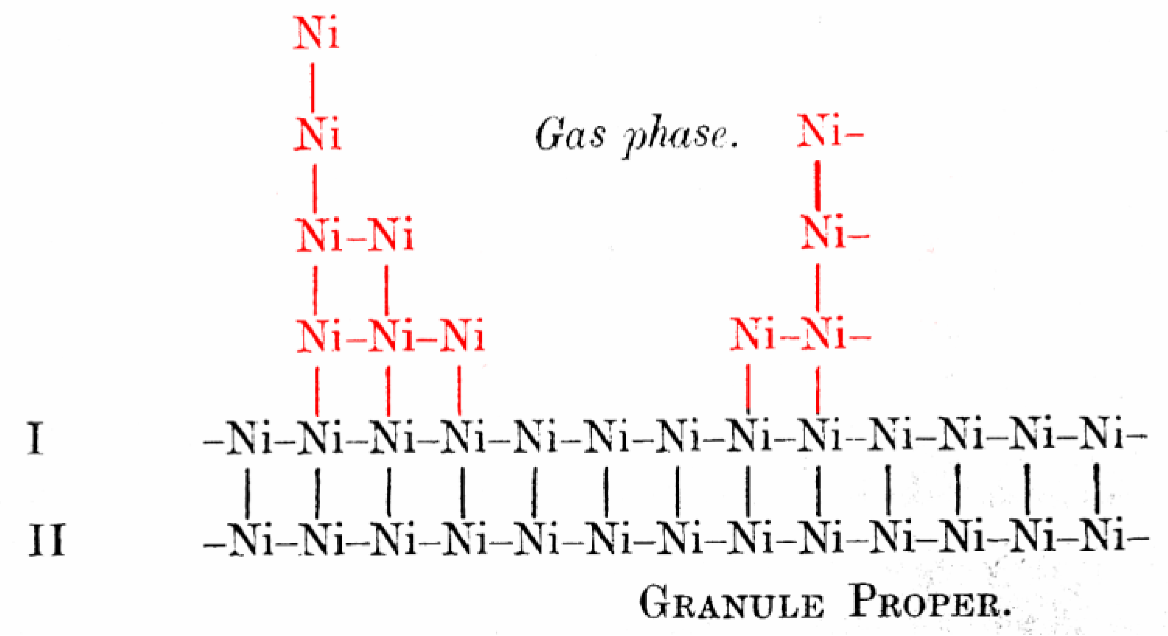
The Concept of “Active Sites”



A Theory of the Catalytic Surface.

By Hugh Stott Taylor, D.Sc., Associate Professor of Physical Chemistry, Princeton University.

(Communicated by Dr. E. F. Armstrong, F.R.S. Received 12th February, 1925.)

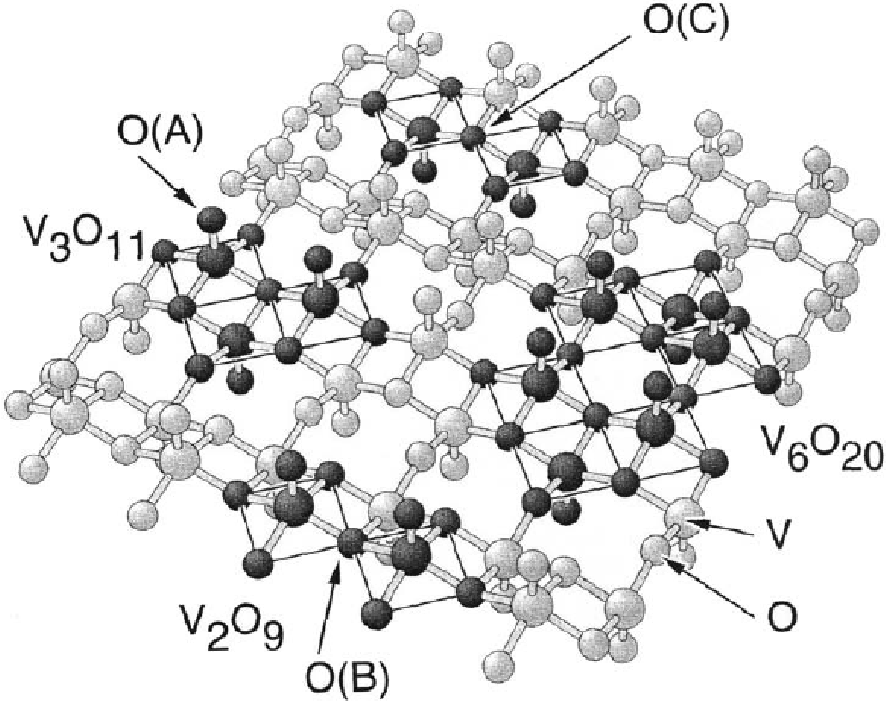


CO hydrogenation on Ni

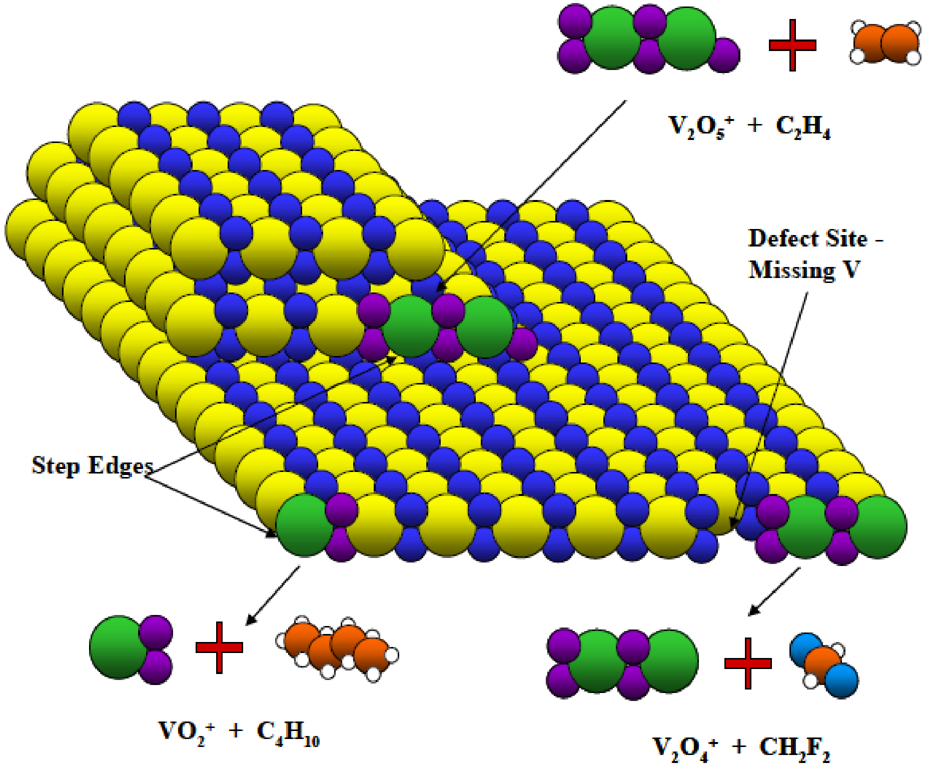
Observation: Catalyst can be deactivated by very small amounts of a poison

Proc. Roy. Soc. [London] A 108 (1925) 105

Clusters as subunits of surfaces?



M. Witko, M.; Hermann, K.; Tokarz, R., *J. Electron. Spec. Rel. Phenom.*, **69** (1994) 89.



Justes, D.R., Phd Thesis, Pennstate U (2004).

Neglects binding within the surface

Free clusters often may rearrange and can have very different electronic and geometric structures

Motivations for the study of free metal clusters

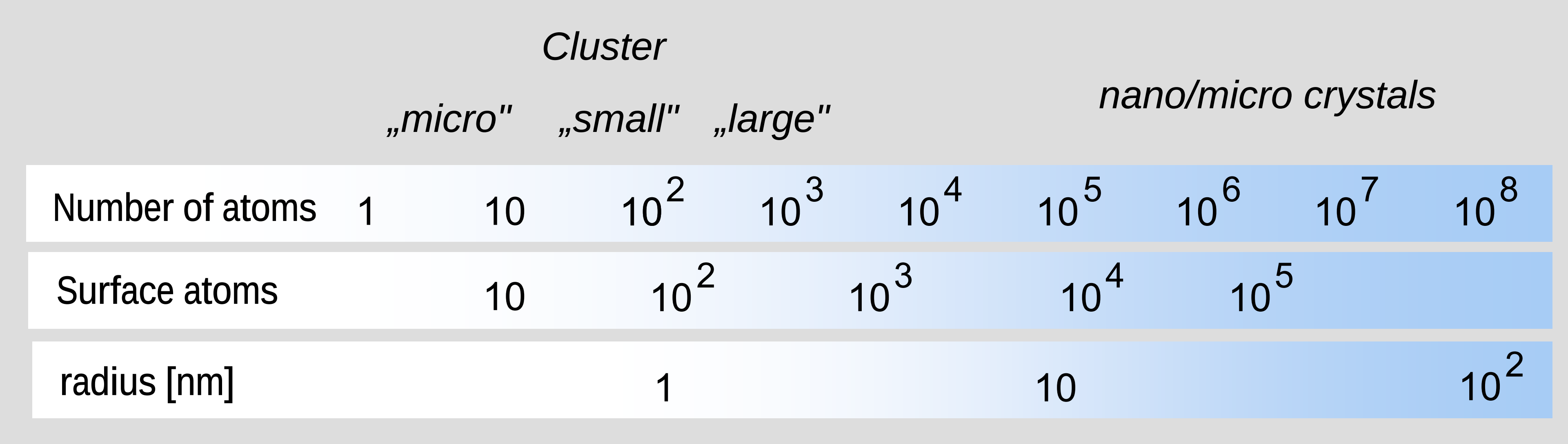
- *Fundamental aspect*
  How are properties emerging when going from the atom to the bulk?

- *Model systems*
  i) (Defect-) Sites of a bulk surface
  ii) Deposited nano-particles on a substrate

- *Reference systems*
  Test and further development of theoretical methods

Clusters of atoms and molecules

- multiples of a simple subunit, e.g. C_n, Ar_n, or $(H_2O)_n$
- The cluster size *n* can vary and determines the properties



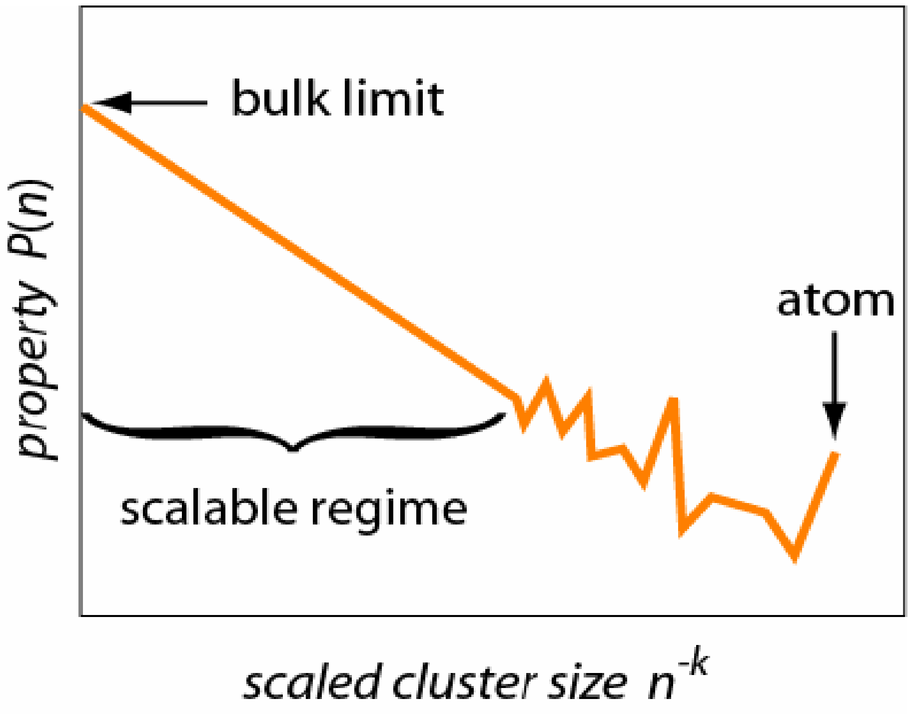
			Cluster						
		„micro"	*„small"*	*„large"*			*nano/micro crystals*		
Number of atoms	1	10	10^2	10^3	10^4	10^5	10^6	10^7	10^8
Surface atoms		10	10^2	10^3	10^4	10^5			
radius [nm]			1			10			10^2

- Small clusters have (nearly) all atoms on the surface

Experiments on free clusters

- Clusters in different charge states can be prepared and characterized, (including neutrals)
- Characterization is often performed in molecular beams or on trapped cluster ions (gas-phase)
- Most experiments use mass spectrometric detection
- Neutrals can be detected spectroscopically or after ionization via MS
- Effect of charge, size and composition can be studied.

Properties of clusters are changing with size



Scale:

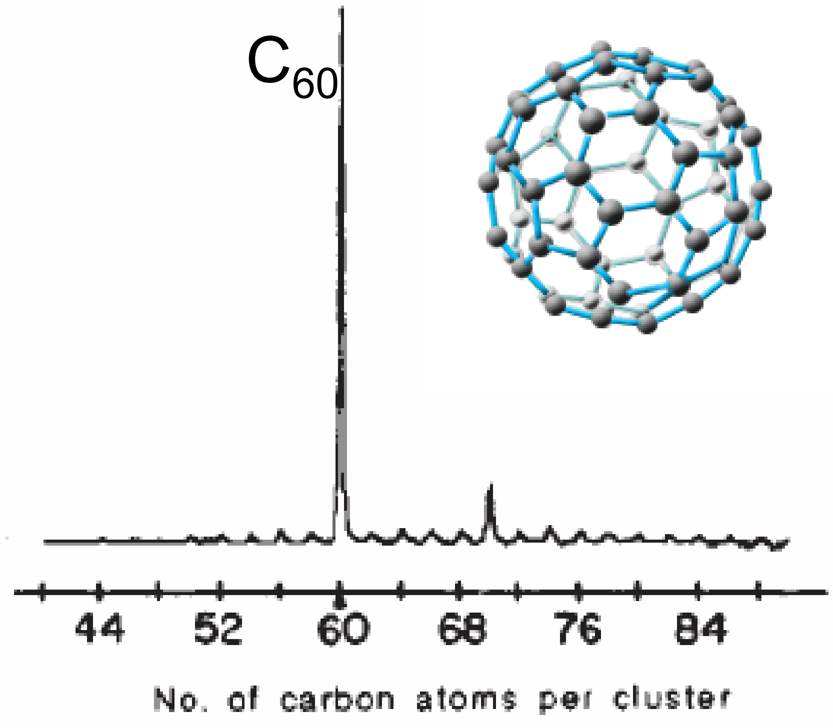
Volume	n^{-1}
Radius	$n^{-1/3}$
Surface	$n^{-2/3}$

Properties:

Binding energies
Ionization energies
Reactivity
Magnetism

Examples for non-scalable properties

Stability

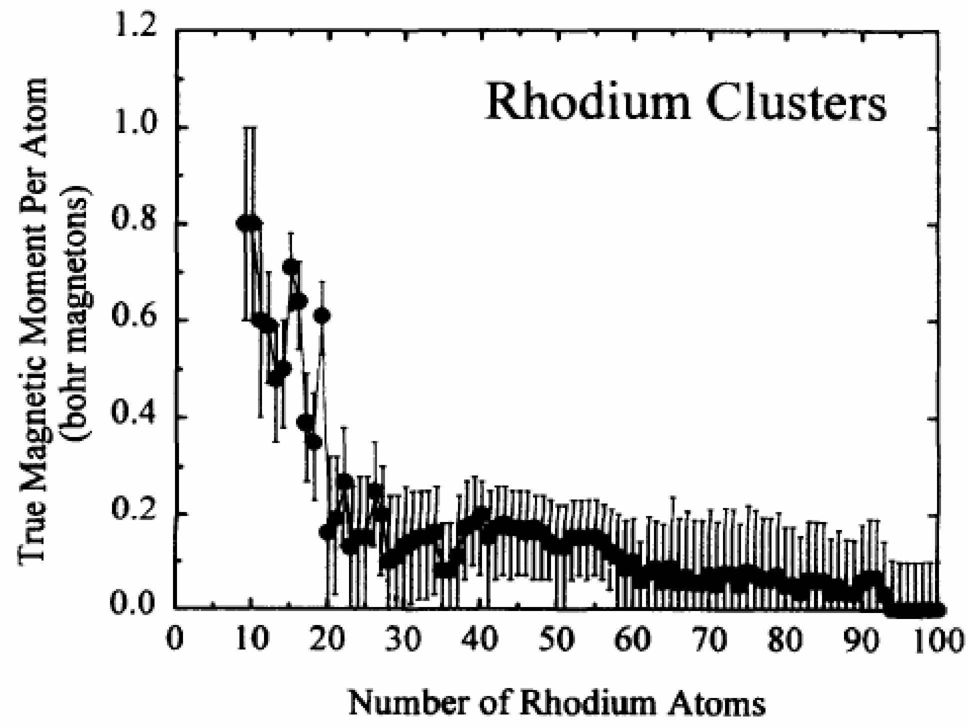


H.W. Kroto, et al. Nature **318** (1985) 162.

Examples for non-scalable properties

Stability

Magnetism



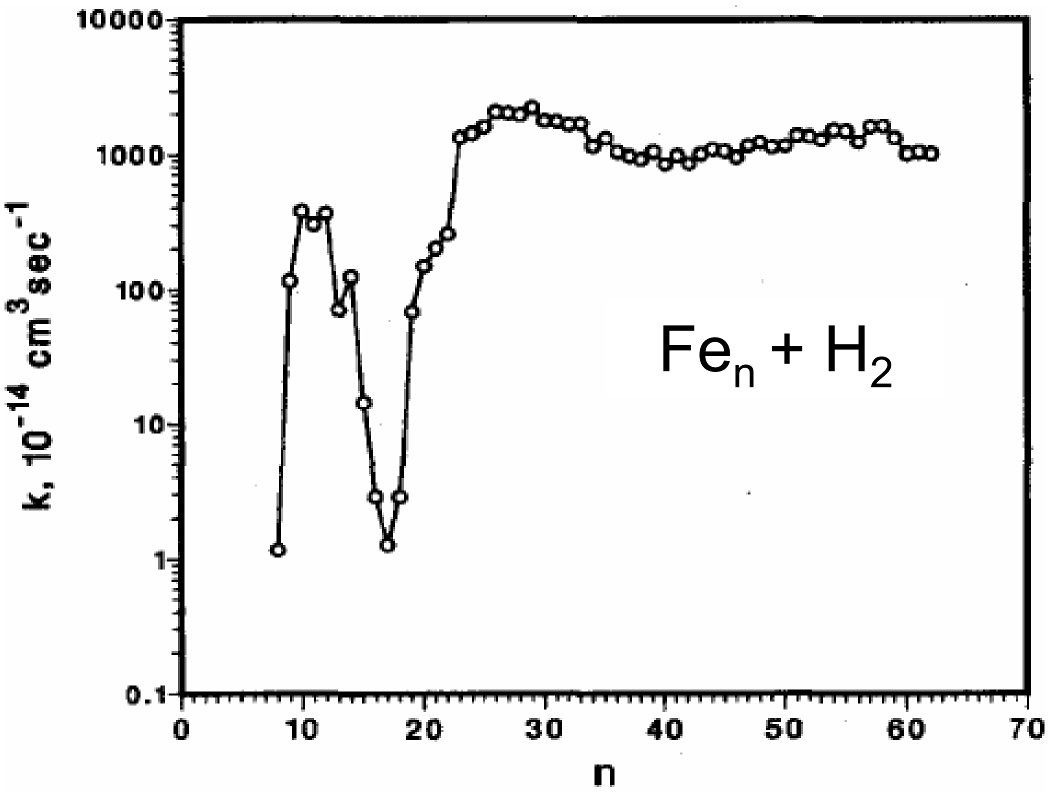
A.J. Cox et al. Phys. Rev. B **49** (1994) 12295.

Examples for non-scalable properties

Stability

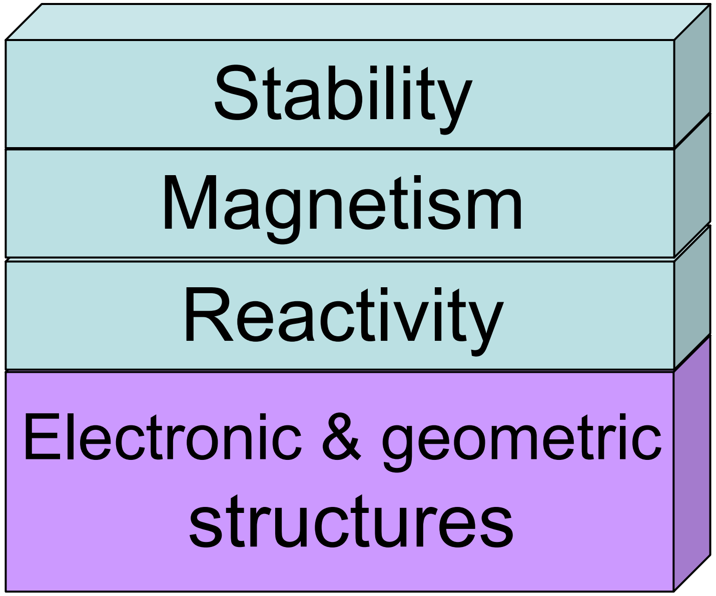
Magnetism

Reactivity



S.C. Richtsmeier et al. J. Chem. Phys. **82** (1985) 3659.

Examples for non-scalable properties



Stability

Magnetism

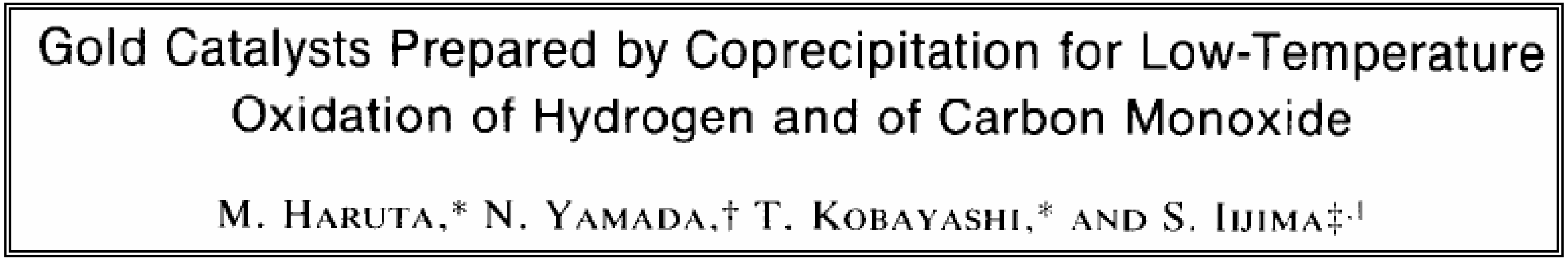
Reactivity

Electronic & geometric structures

How does the structure change with size?

Catalysis by gold clusters

The starting point

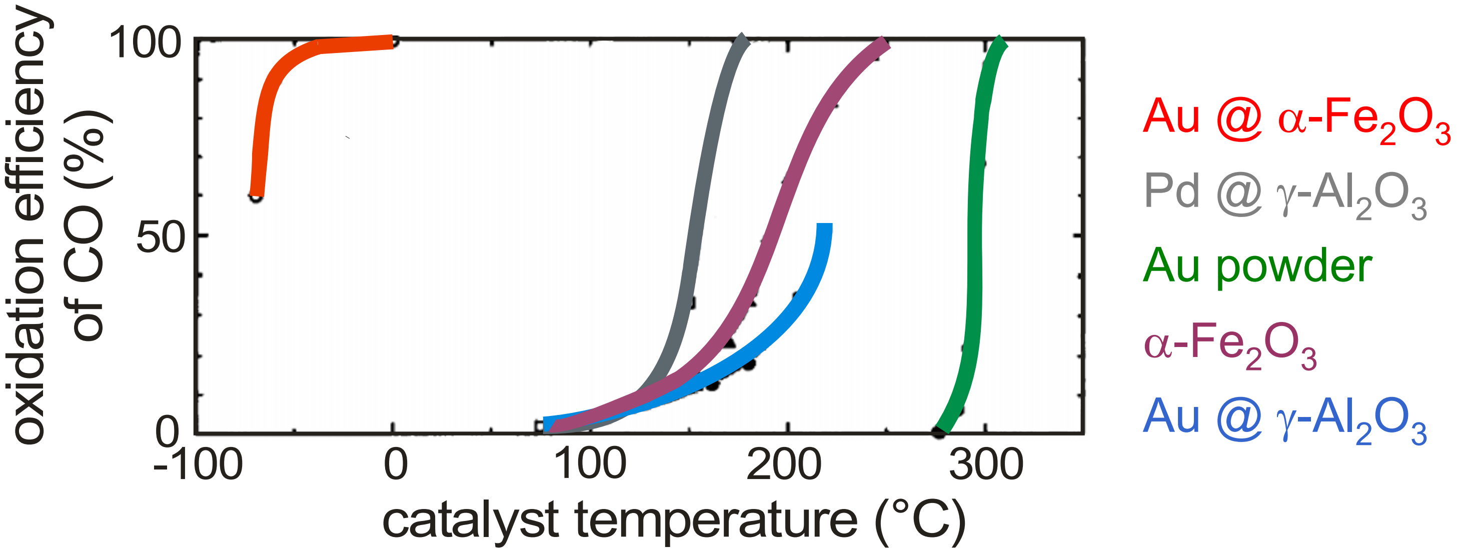


Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide

M. Haruta,* N. Yamada,† T. Kobayashi,* and S. Iijima‡,[1]

Gold nano-particles @ α-Fe_2O_3, Co_3O_4, and NiO prepared by co-precipitation

Catalytic oxidation of H_2 and CO with air as oxidant



→ Interaction of the gold with the oxide support induces activity

Haruta et al. *J. Catal.* **115** (1989) 301

Catalytic activity of gold nanoparticles

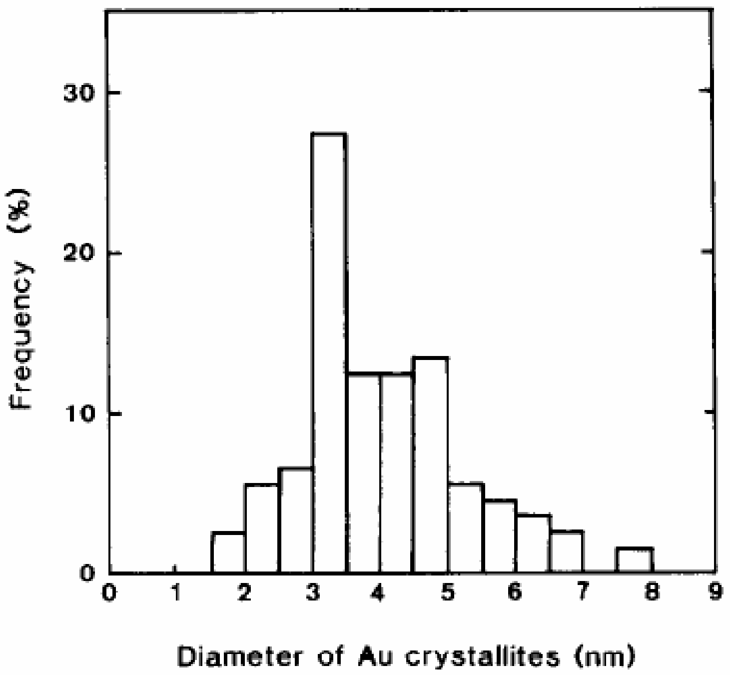
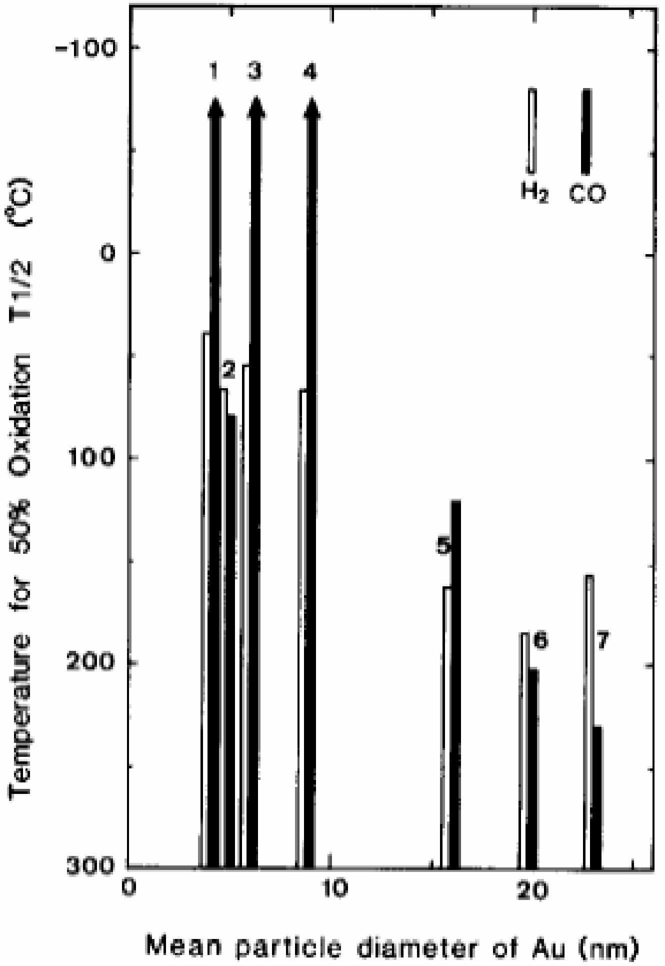


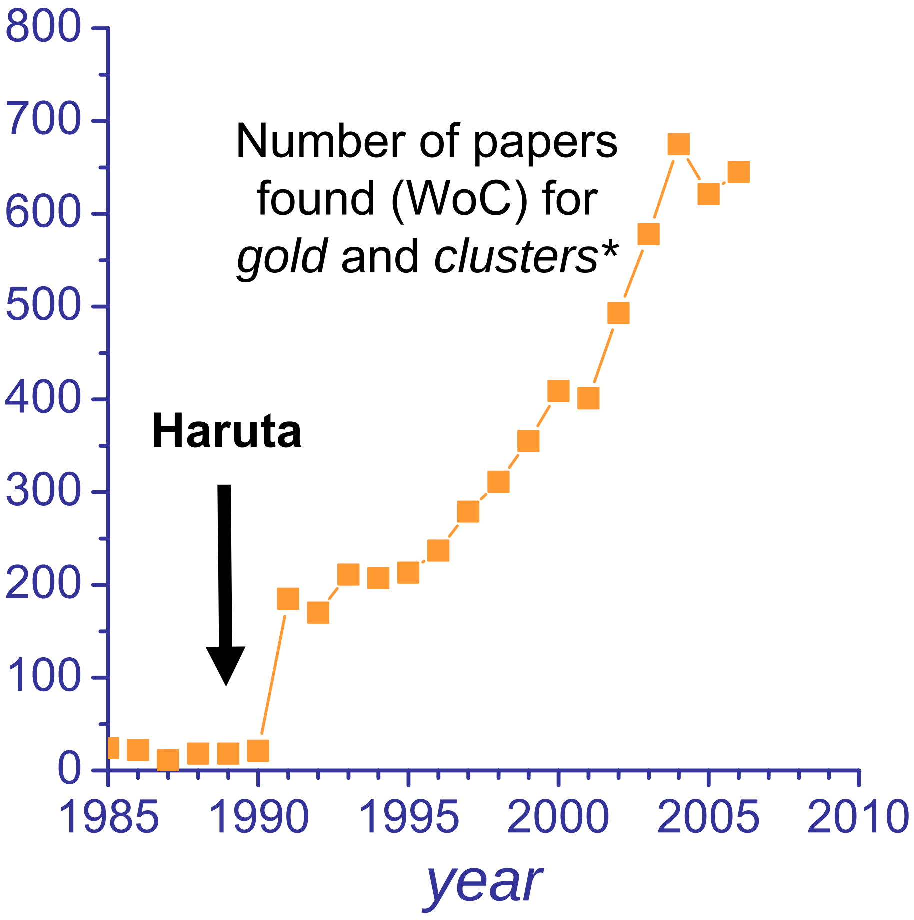
FIG. 6. Histogram of gold crystallites in Au/α-Fe_2O_3 (Au/Fe = 1/19) prepared by coprecipitation and calcination at 400°C.



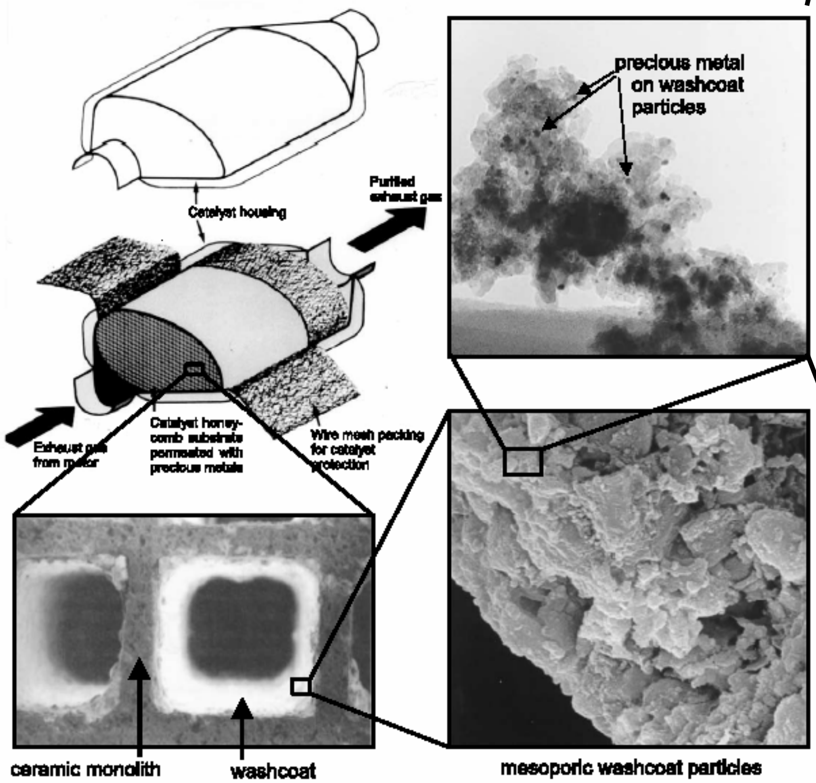
- Activity increases with decreasing size
- Most active particles are a few nm in diameter

Haruta et al. *J. Catal.* **115** (1989) 301

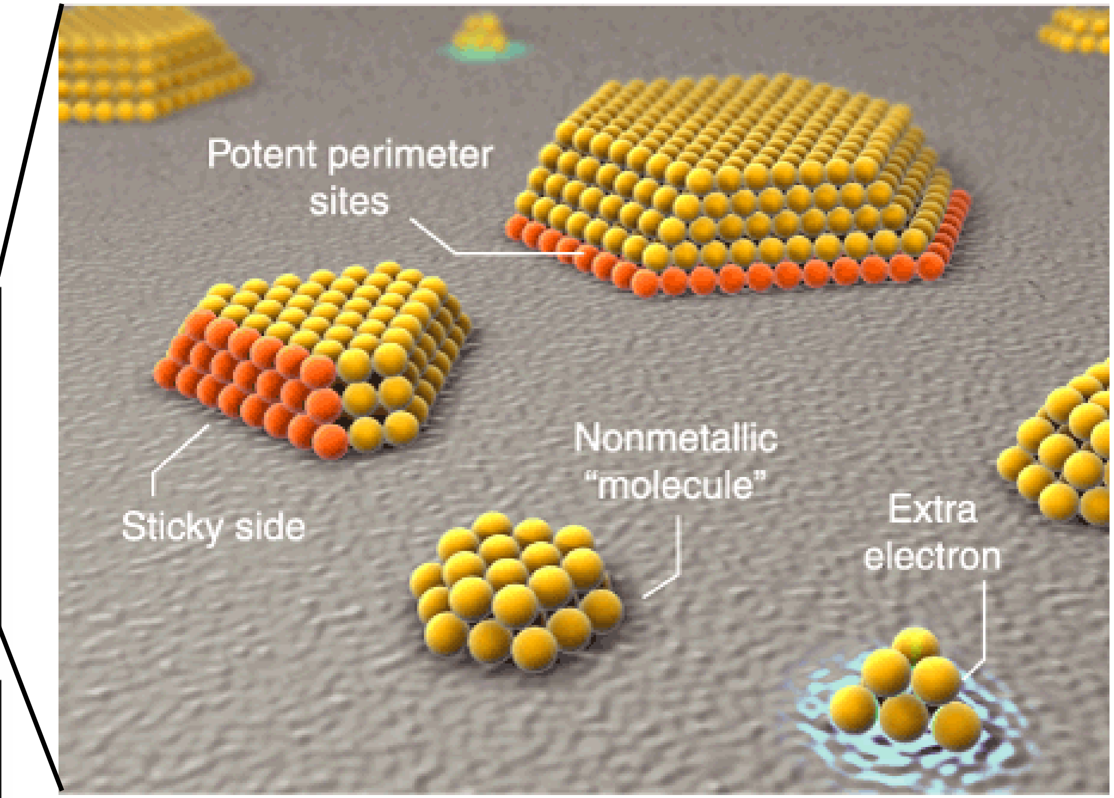
Catalytic activity of gold nanoparticles



Nano-dispersed metal catalysts



Freund: *Surf. Sci.* **500** (2002) 271



Cho: *Science* **299** (2003) 1684

What is the active site ?

Model systems:
clusters on a substrate
adsorbates on metal clusters

Model reaction $CO + O_2 \rightarrow CO_2$

On a Pt surface: Langmuir-Hinshelwood mechanism

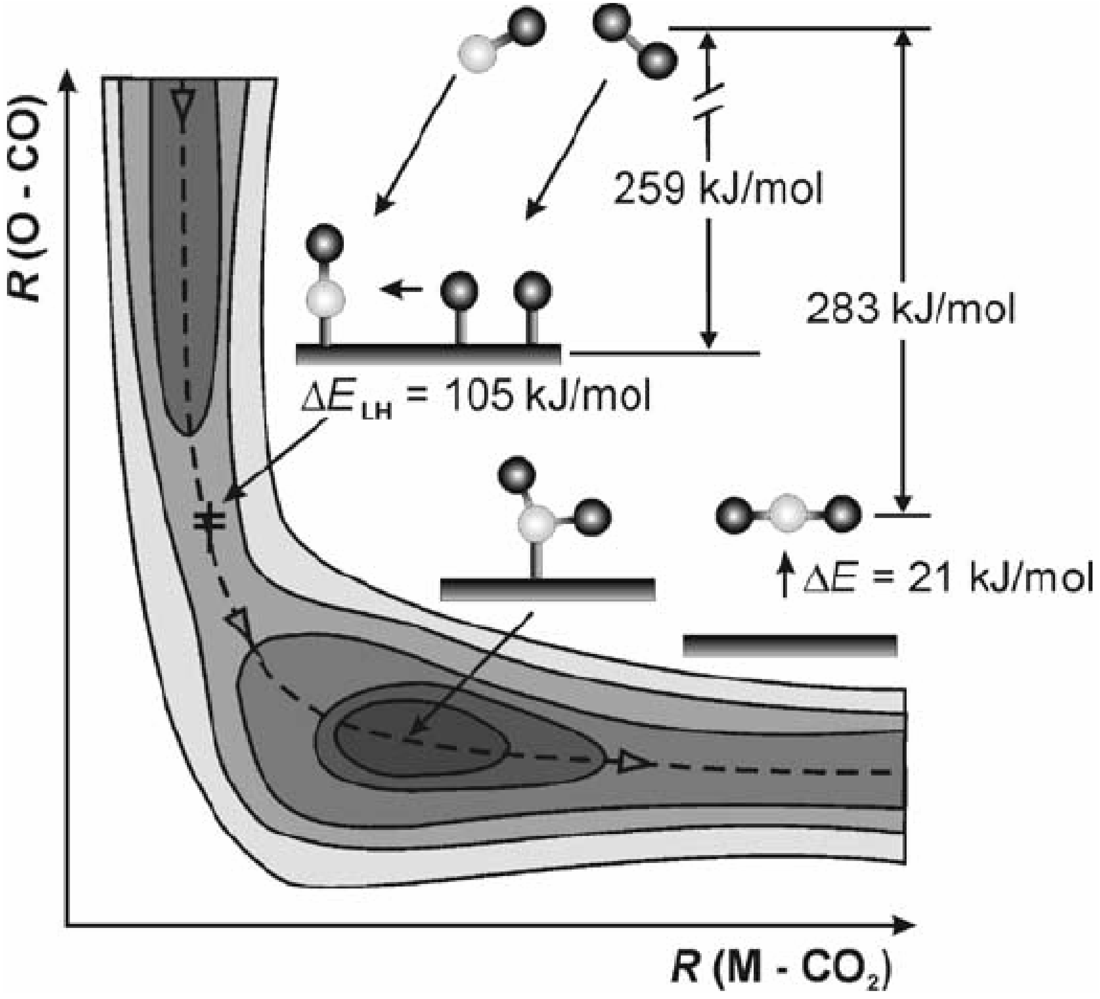
$$CO_{gas} \rightleftarrows CO_{ads}$$

$$O_{2,gas} \rightleftarrows 2\,O_{ads}$$

$$CO_{ads} + O_{ads} \xrightarrow{\text{rds}} CO_{2,ads}$$

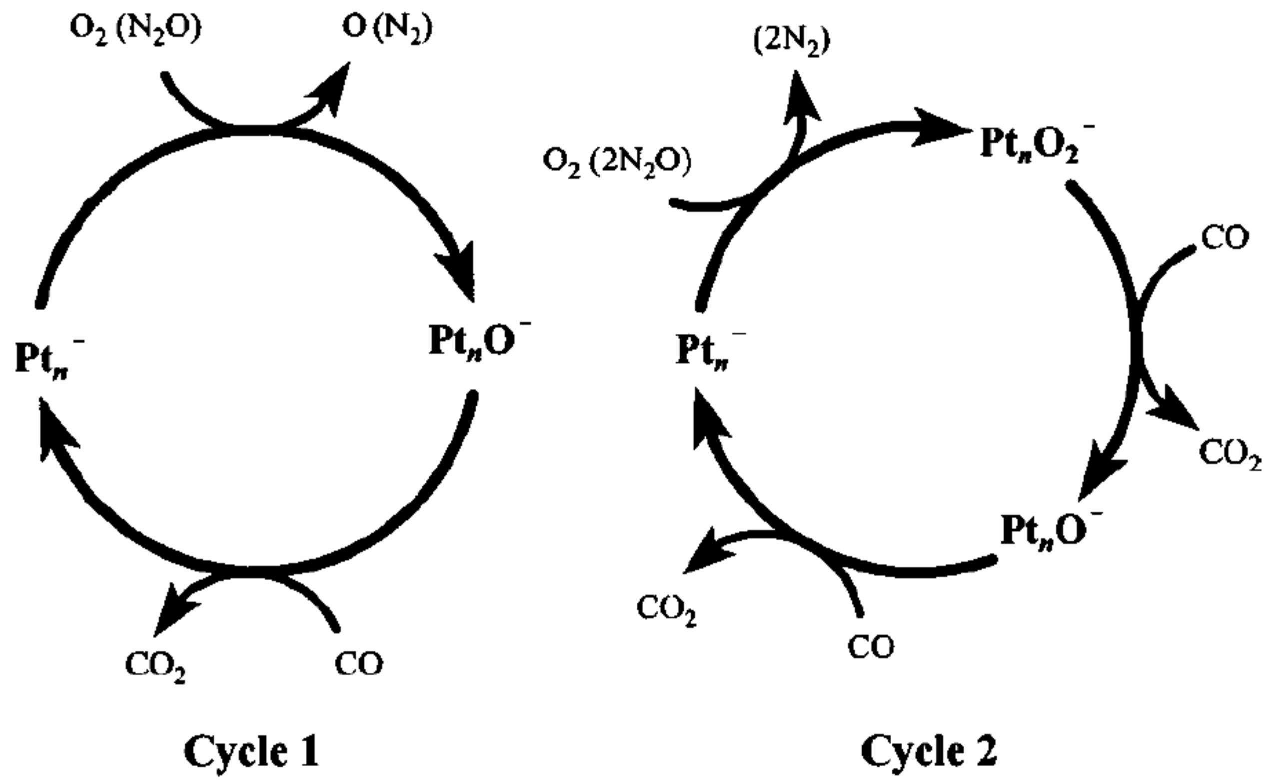
$$\downarrow \text{fast}$$

$$CO_{2,gas}$$



T. M. Bernhardt, *Int. J. Mass Spectr.* **243** (2005) 1.

Model reaction $CO + O_2 \rightarrow CO_2$

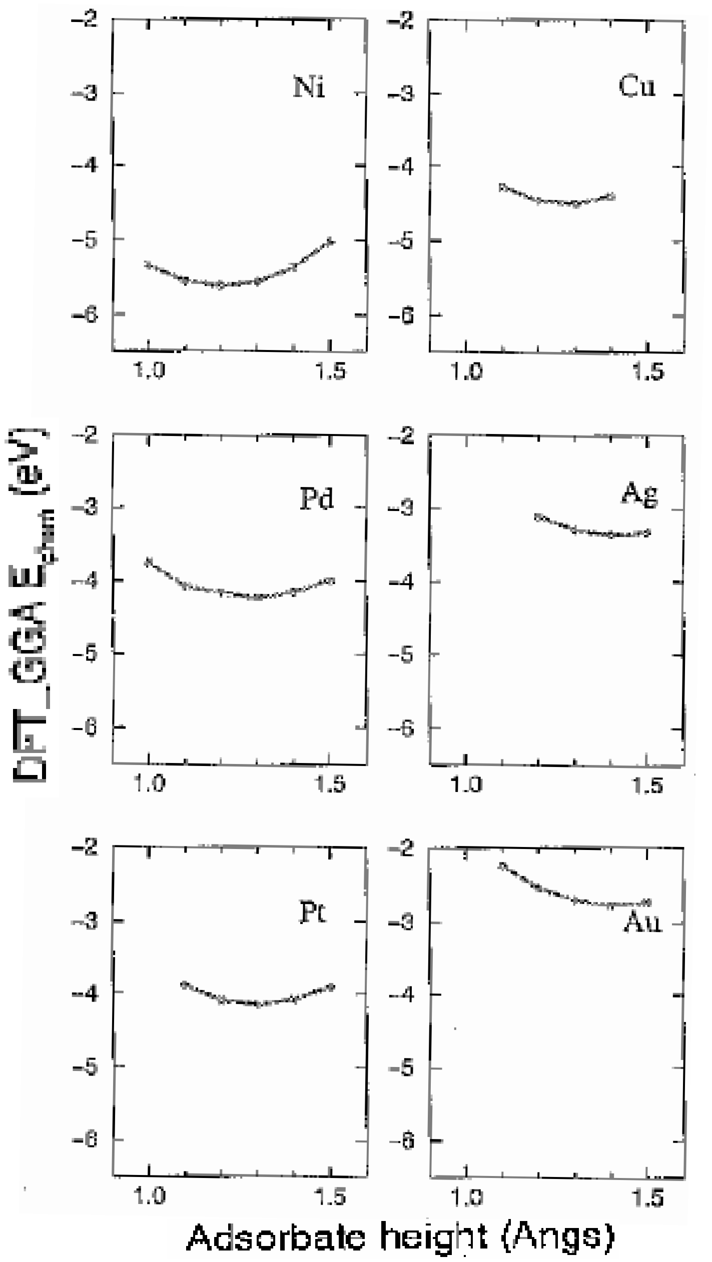


Catalytic cycles for the oxidation of CO on platinum cluster anions (*n*=3-6)

→Langmuir-Hinshelwood like mechanism

Y. Shi and K.M. Ervin, *J. Chem. Phys.* 108 (1998) 1757.

Interaction of oxygen with gold



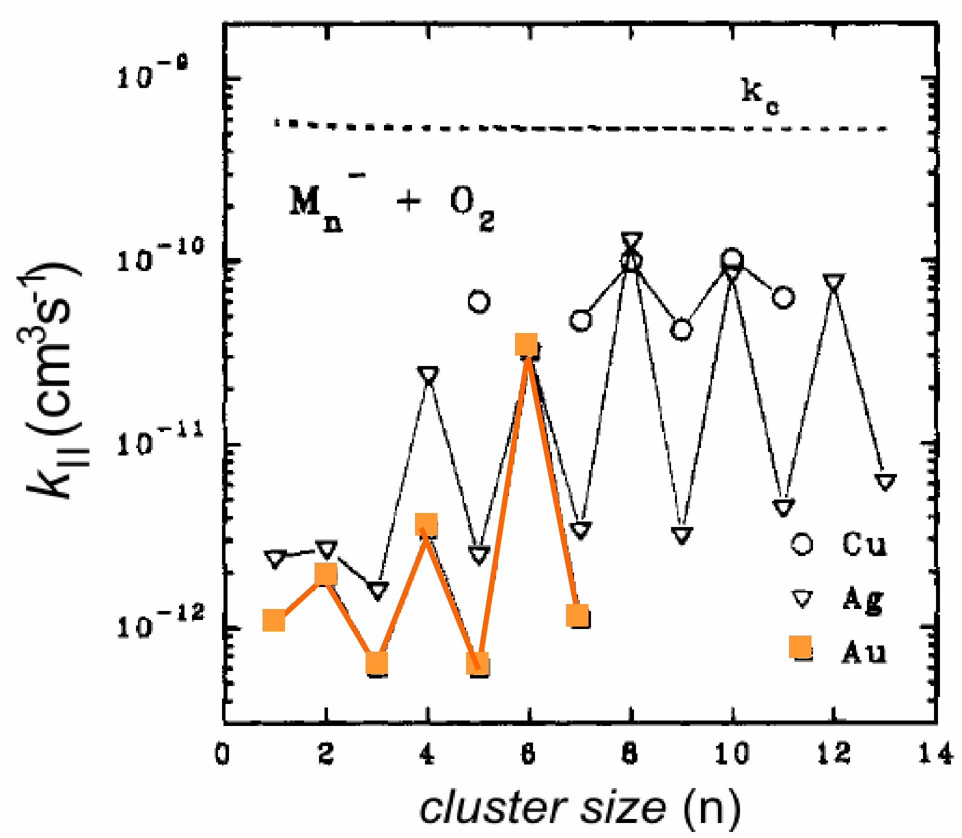
Chemisorption energy of O on fcc (111) surfaces from DFT calculations (PW91)

- Au-O bond is too weak compared to O-O
- O_2 does not dissociate on gold surfaces
- **How oxidations with O_2 are taking place?**

B. Hammer and J. K. Norskov, *Adv. Catal.*, **45**, 71 (2000).

Reactivity of gold clusters with molecular oxygen

- No reaction of *cationic* or *neutral* gold clusters with O_2
- High rate constants for gold *anions* containing an even number of Au atoms

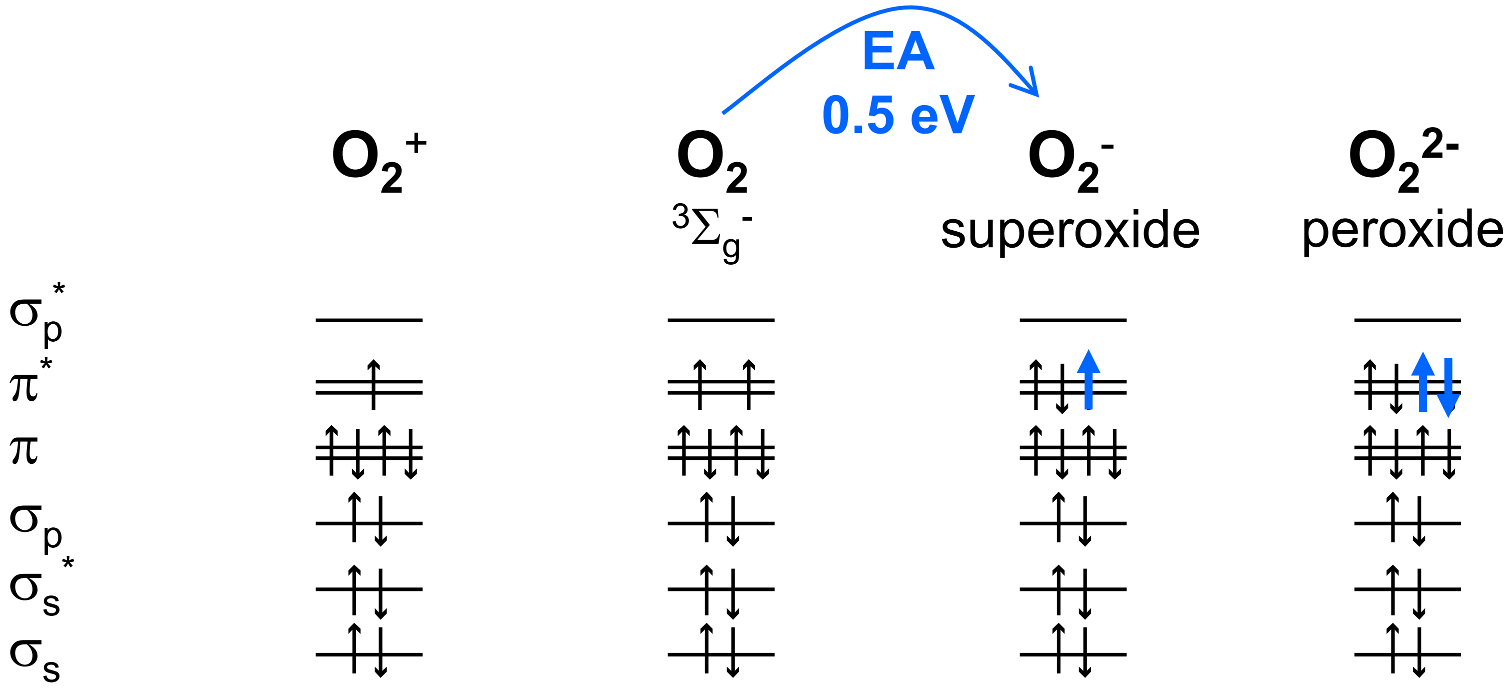


Reactivity with O_2 is related to the electron binding energy of the gold cluster

Low binding energy → High reactivity

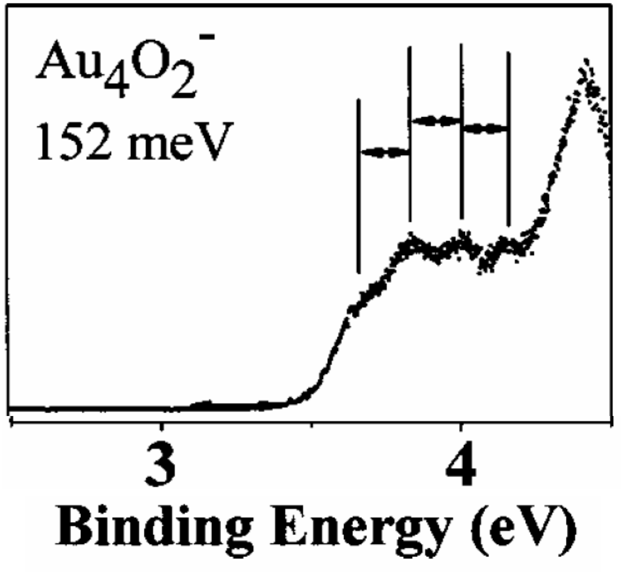
Lee & Ervin *J. Phys. Chem.* **98** (1994) 10023

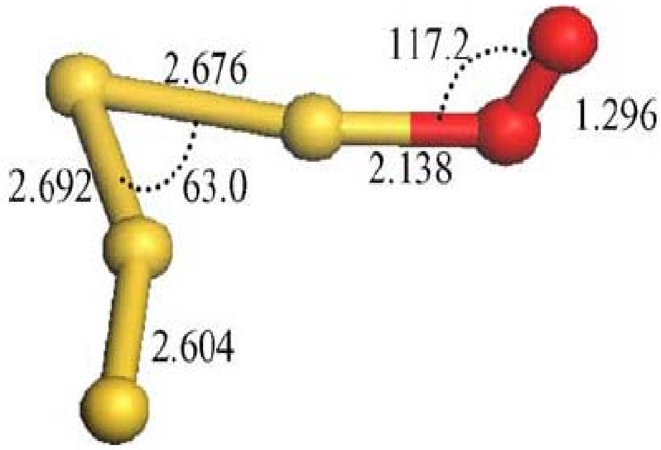
Properties of di-oxo species



BO	2.5	2.0	1.5	1.0
d(O-O) [Å]	1.12	1.21	1.33	1.50
ν [cm^{-1}]	770	1555	≈ 1150	800-900
E_{Diss} [kJ/mol]	628	499	398	126

The structure of the Au_n-O_2^- complexes

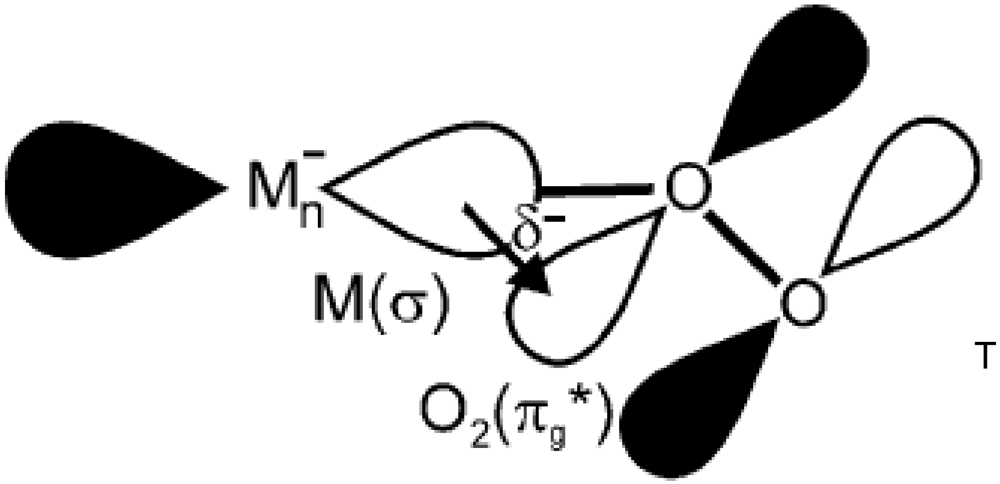




- O_2 species can be identified from vibrational structure in photoelectron spectra
- Vibrational frequency of 1200 cm^{-1}
  → corresponds to ν(O-O) of a superoxide ligand (O_2^-)

Q. Sun, P. Jena, Y. D. Kim, M. Fischer, G. Ganteför, *J. Chem. Phys.* **2004**, *120*, 6510.

The binding of superoxide (O_2^-) to gold



T. M. Bernhardt, *Int. J. Mass Spectr.* **2005**, *243*, 1.

The possibility to transfer an electron from the metal into the anti-bonding π_g^* orbital of the O_2 is related to the electron binding energy of the metal cluster, i.e. its ionization energy.

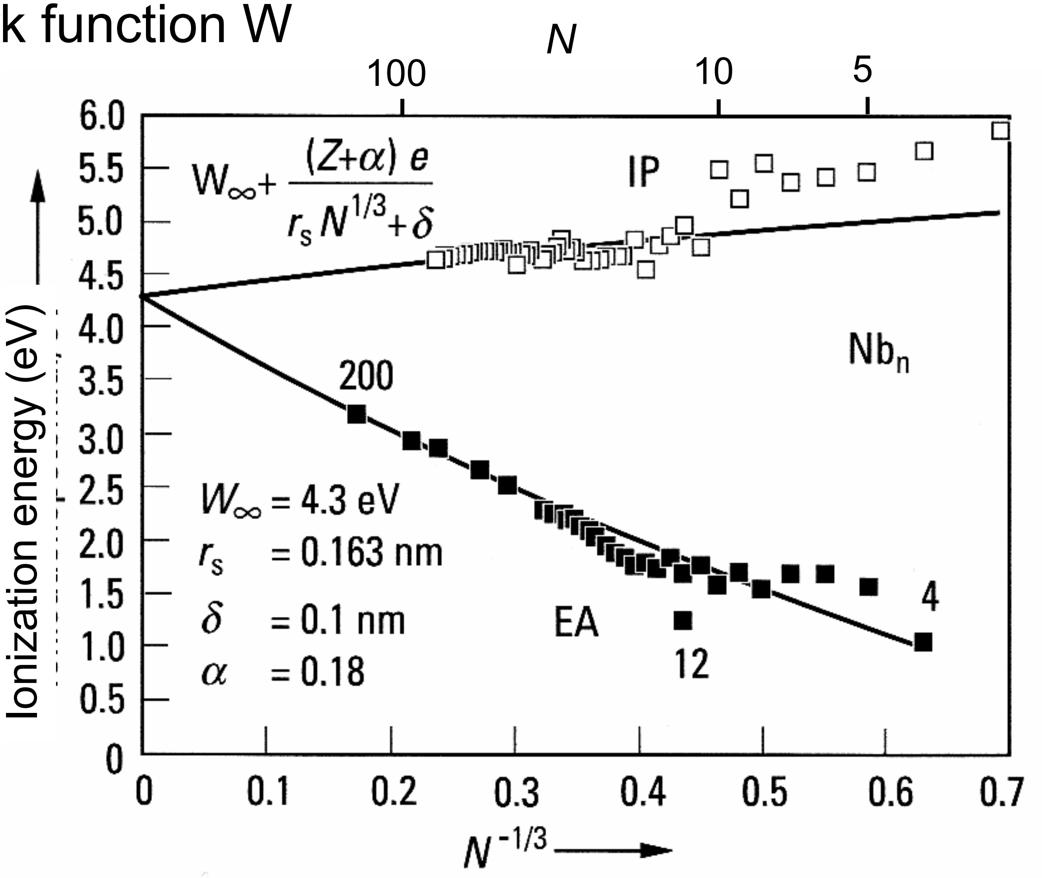
Ionization energies of metal clusters

Ionization of a metal sphere

$h\nu + A_N \rightarrow A_N^+ + e(E_{kin})$

Ionization energy of the bulk: work function W

$$IE_{N,Z} = W_\infty + (Z+\alpha)\frac{e^2}{r_s N^{1/3} + \delta}$$

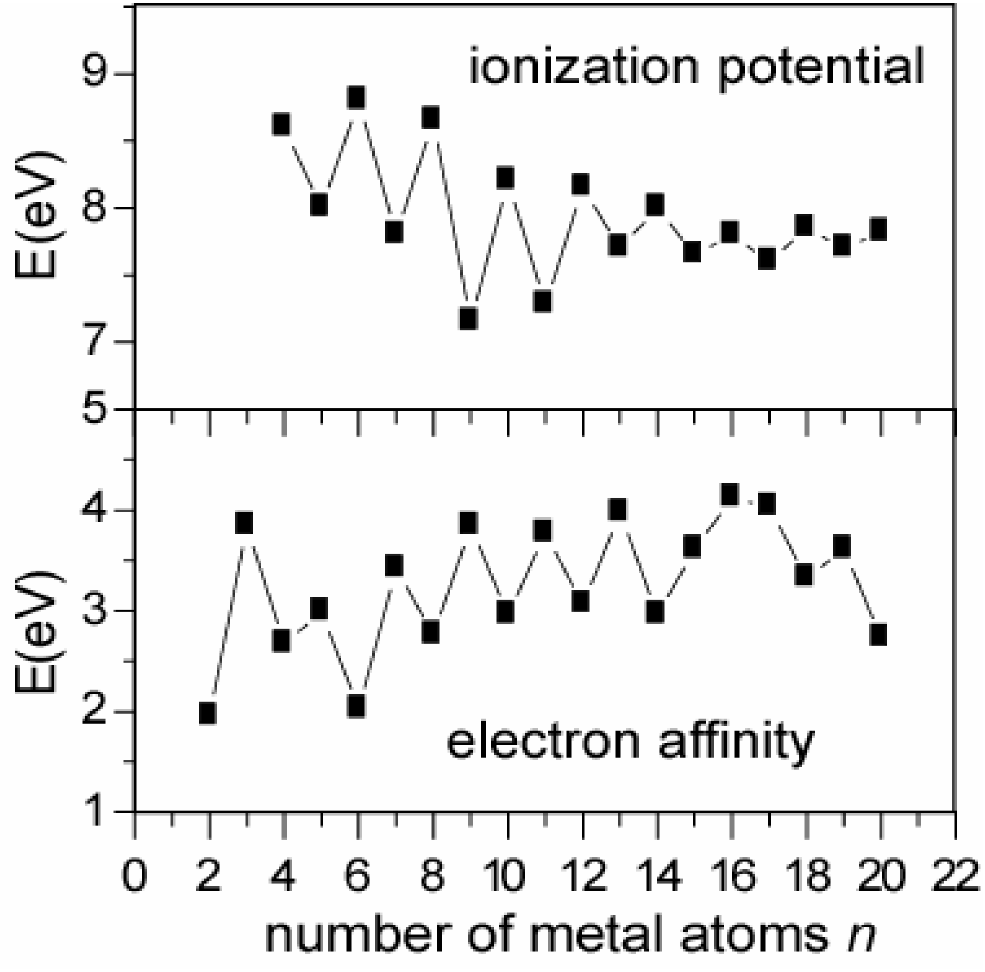


Neutral → Cation (*Z*=0)
"Ionization potential" IP

Anion → Neutral (*Z*=-1)
"Electron affinity" EA

IP and EA are approaching for $N \rightarrow \infty$ the bulk value
Deviations from the scaling law for small *N*

Ionization energies of gold clusters



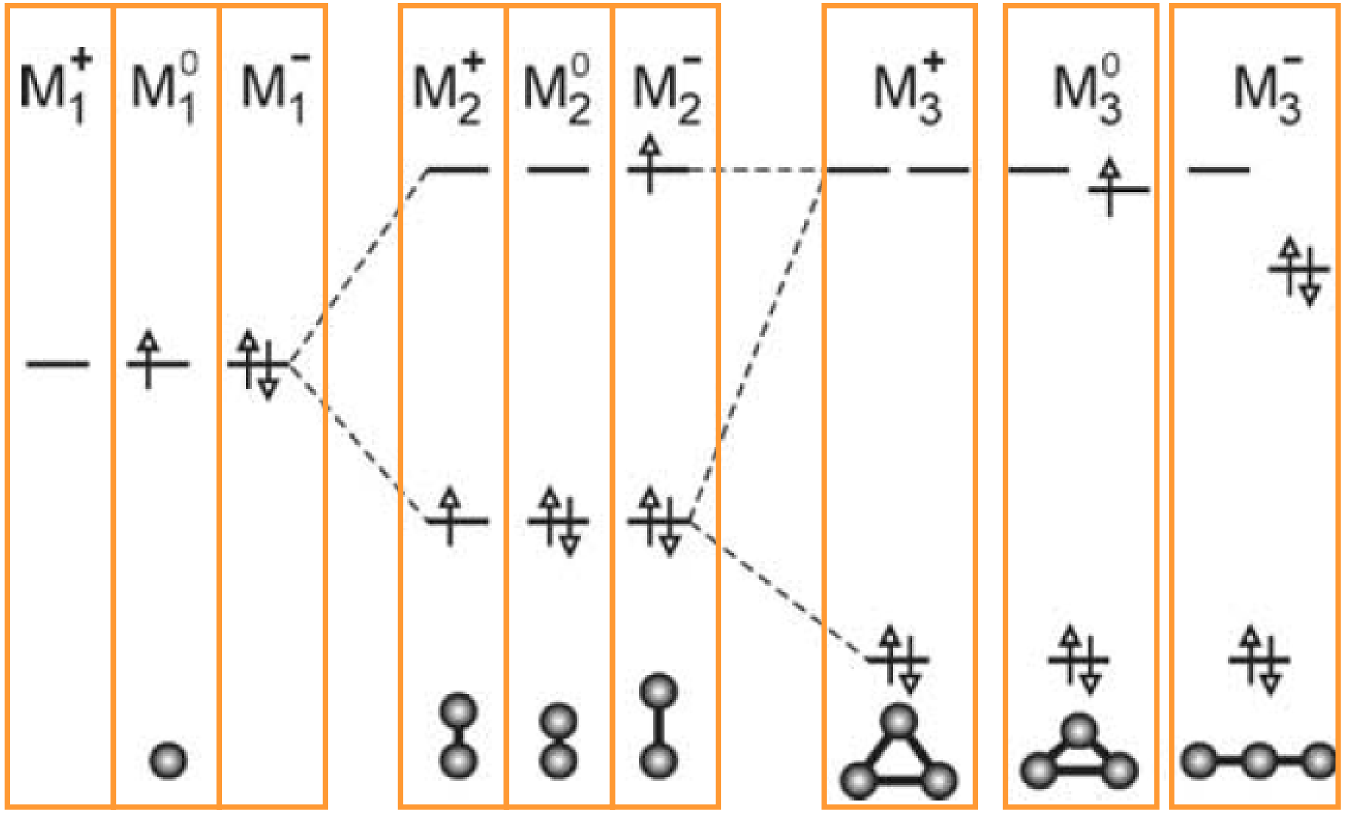
Au configuration:

[Xe]$4f^{14}5d^{10}6s^{1}$

Open shell / closed shell oscillation with *n*

Jackschath et al. *Ber. Bunsenges. Phys. Chem.* **96** (1992) 1200
Taylor et al. *J. Chem. Phys.* **96** (1992) 3319

The electronic structure of gold clusters

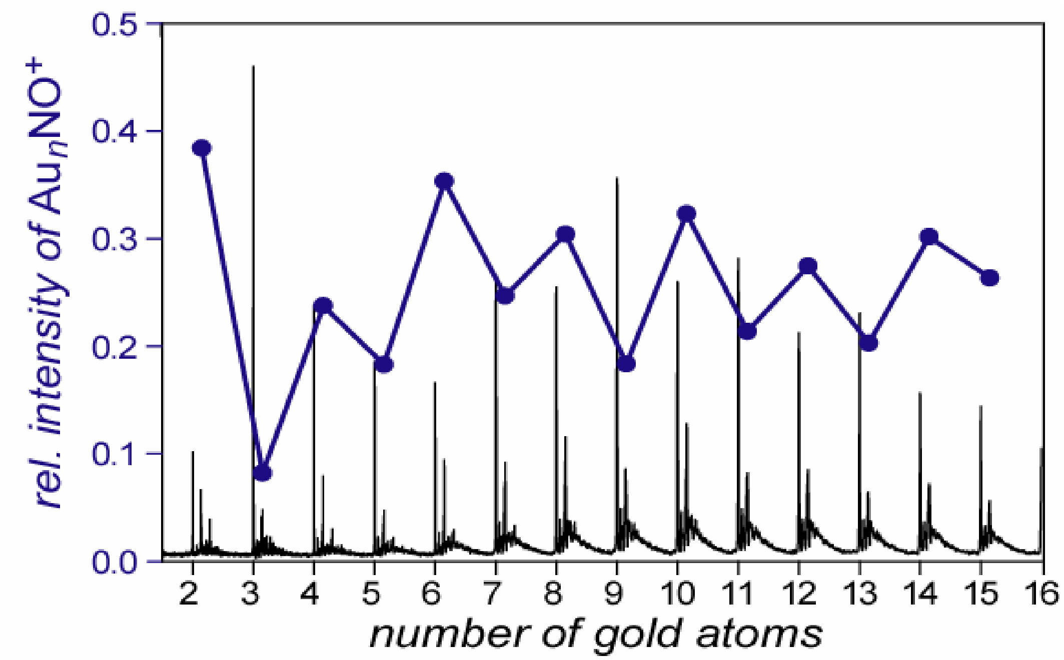


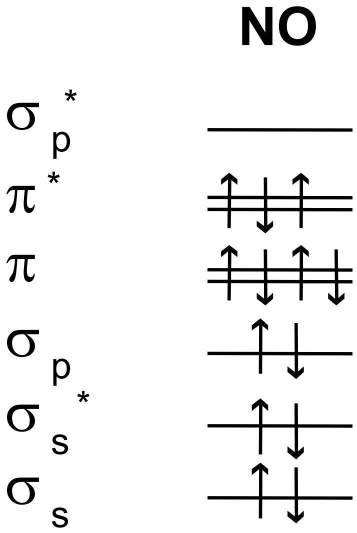
Evolution of molecular *s* orbital energies and electron occupations with cluster size and charge state up to the trimer.

T. M. Bernhardt, *Int. J. Mass Spectr.* **243** (2005) 1.

Odd/even size effects can be seen for other ligands where electron transfer is relevant in the bonding

NO adsorbed on gold cluster cations





NO

σ_p^*

π^*

π

σ_p

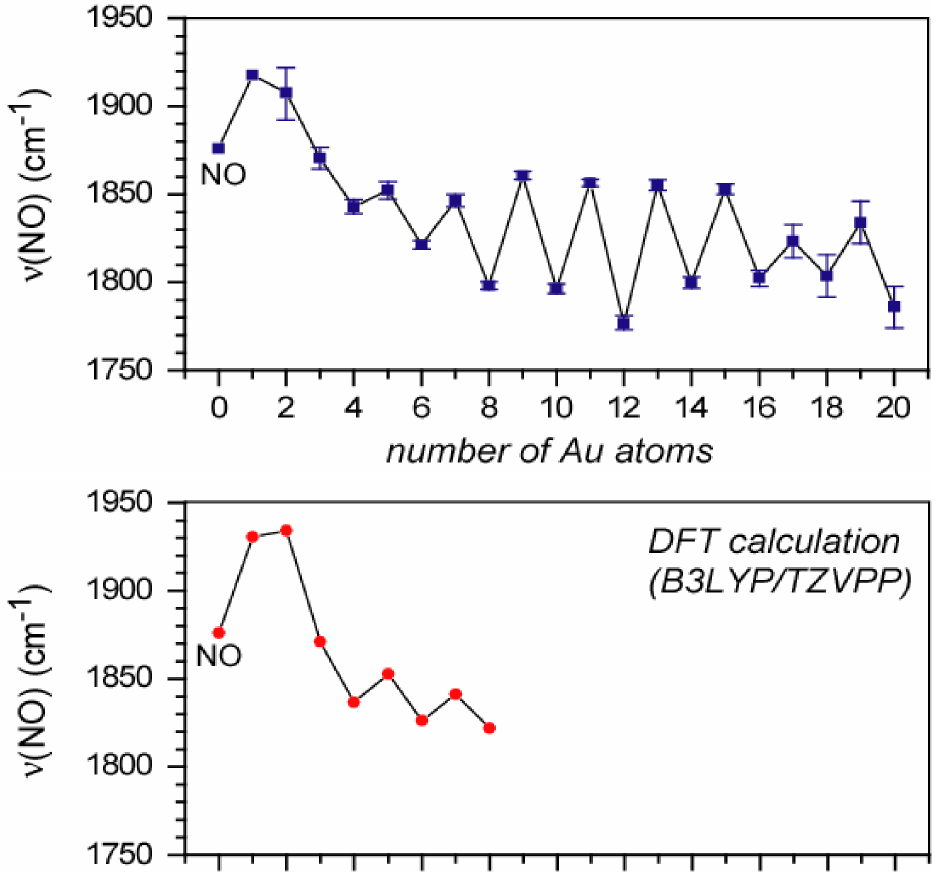
σ_s^*

σ_s

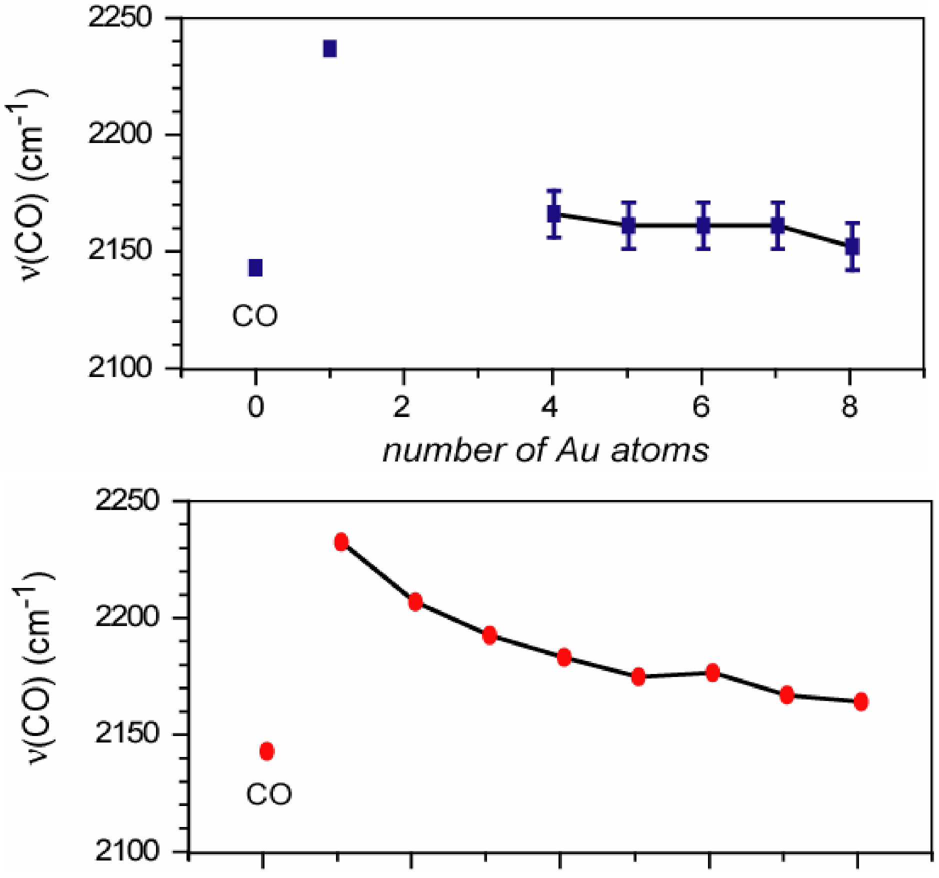
Comparison between NO and CO complexes of Au_n^+

Vibrational spectroscopy probes electron transfer

Au_nNO^+

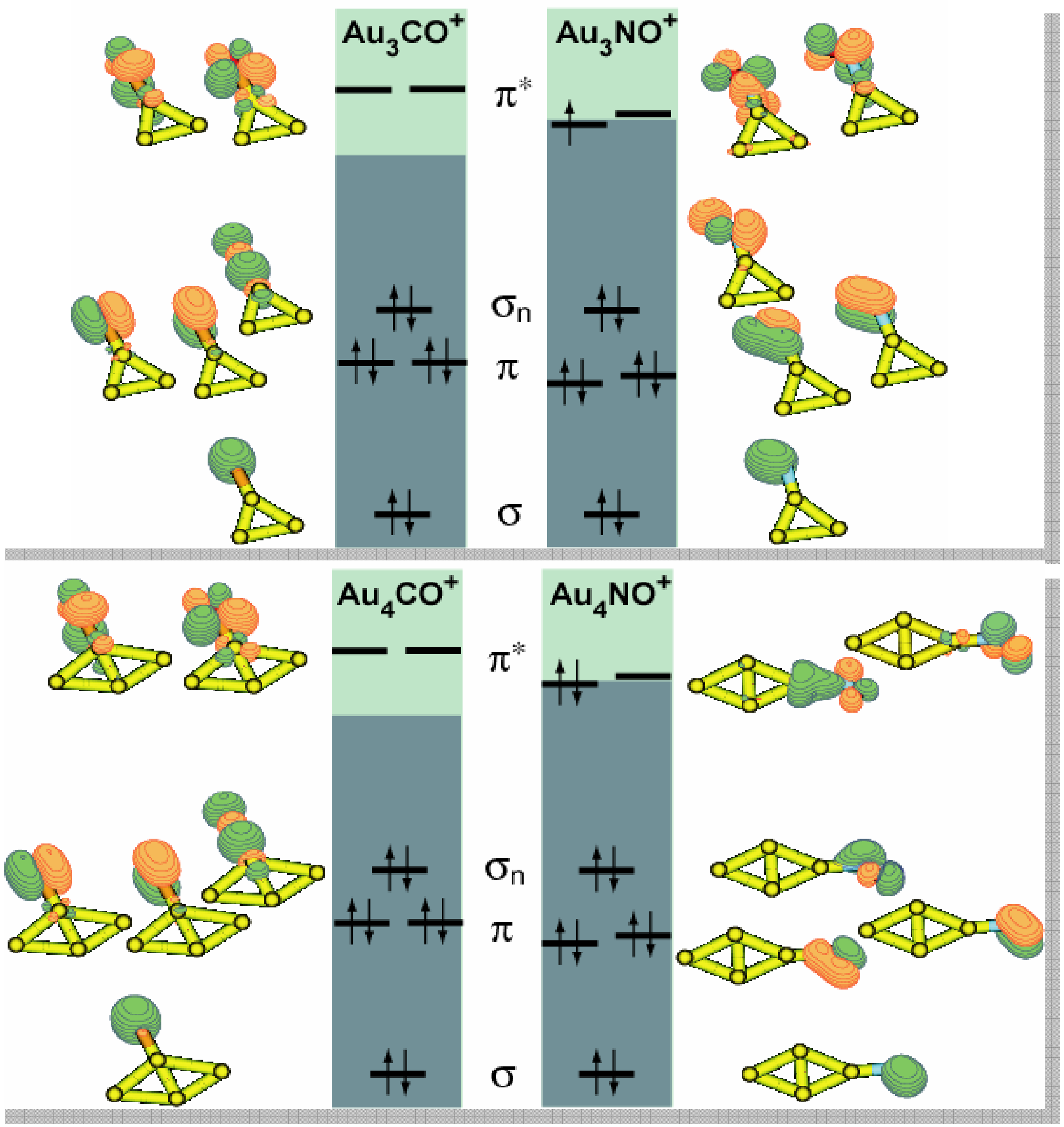


Au_nCO^+



PCCP, **7**, 3906 (2005).

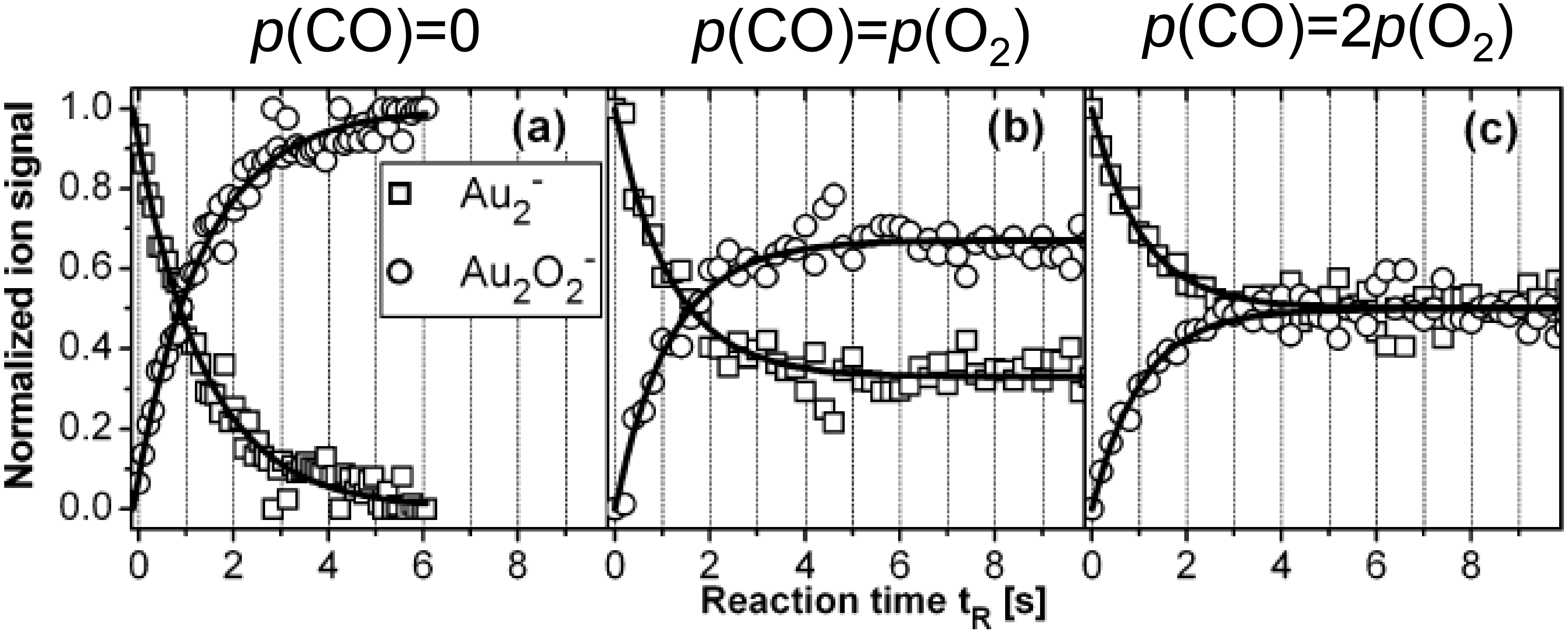
Bonding in the CO and NO complexes of Au_n^+



→ Cluster size dependent activation of NO on Au_n^+

PCCP, **7**, 3906 (2005).

Reaction kinetics of Au_2^- with O_2 in the presence of CO

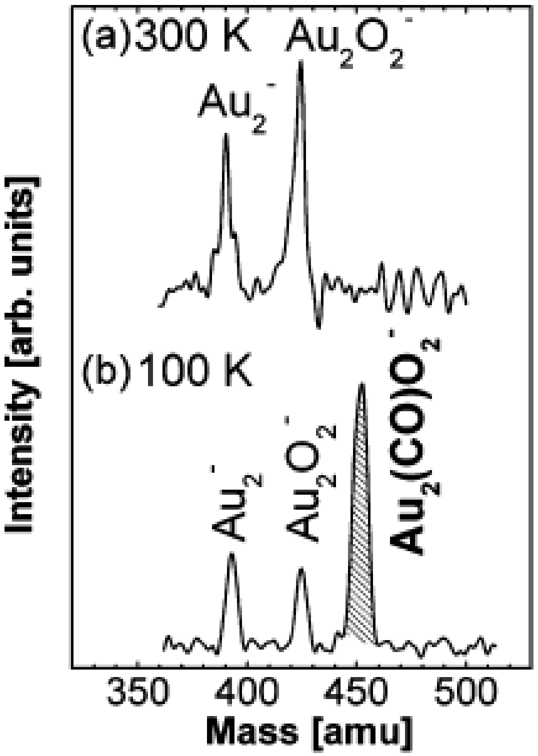


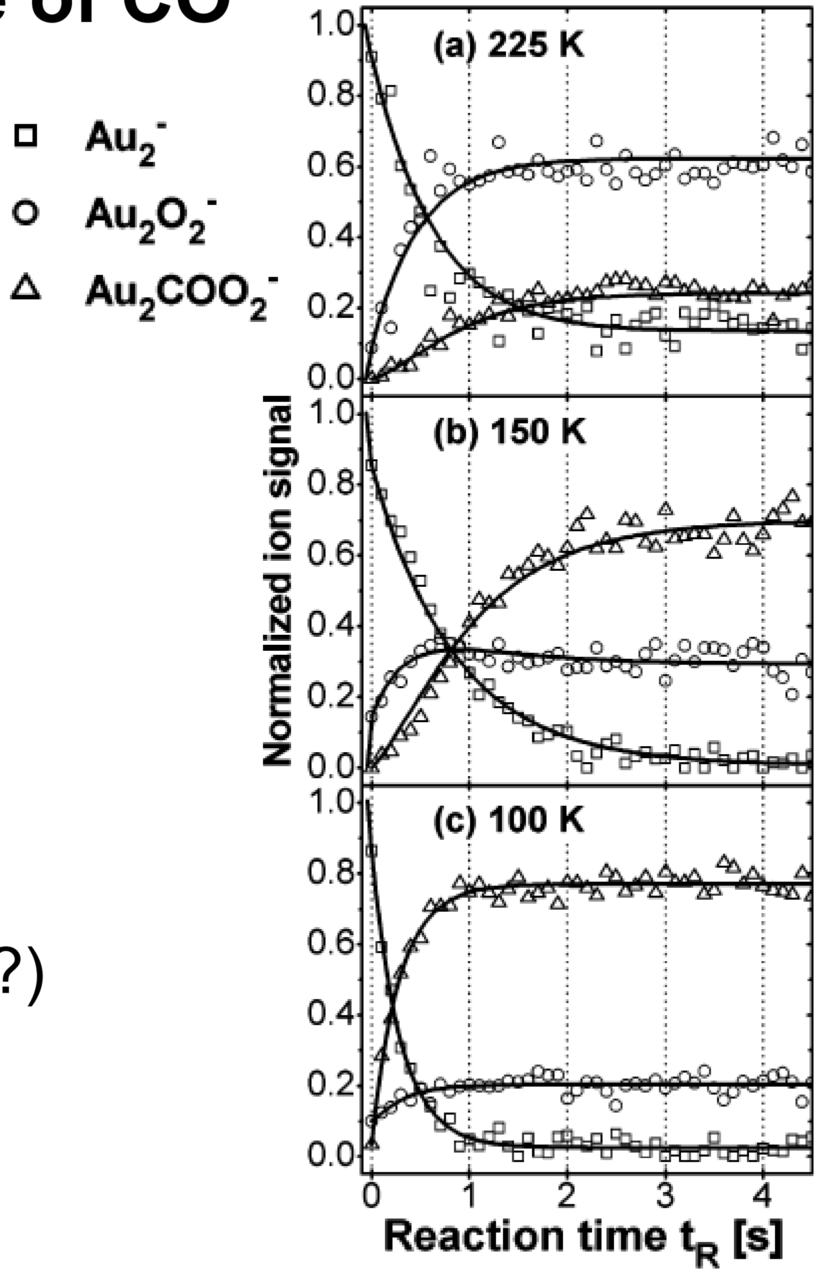
$$Au_2^- + O_2 \rightleftharpoons Au_2O_2^-$$

Although at 300 K only complexes containing O_2 are observed, the reaction mechanism must involve CO.

L. D. Socaciu et al. *J. Am. Chem. Soc.* **125** (2003) 10437

Reaction kinetics of Au_2^- with O_2 in the presence of CO



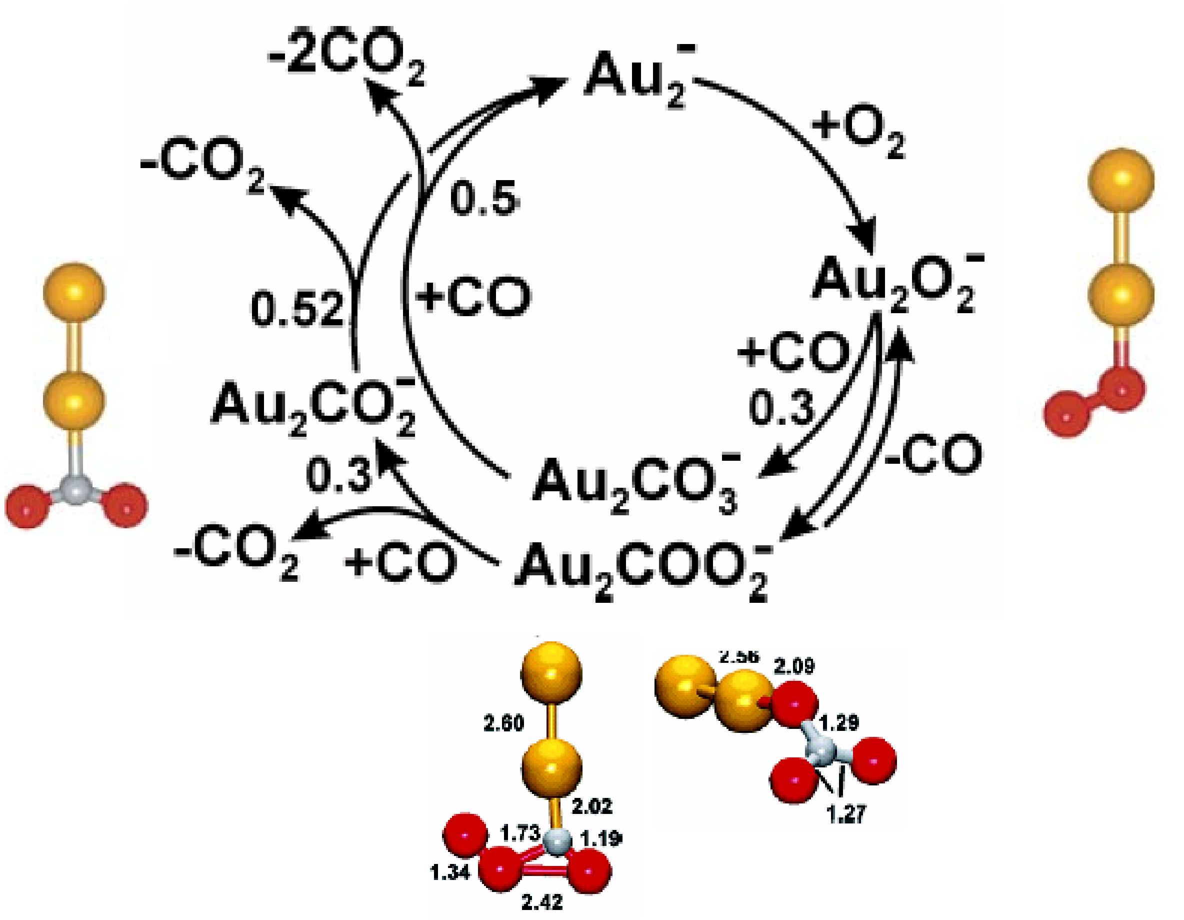


$Au_2(CO)O_2^-$ co-adsorbates (?) are observed in the mass spectra at low temperatures

L. D. Socaciu et al. *J. Am. Chem. Soc.* **125** (2003) 10437

Oxidation of CO by O_2 on gold clusters

Mechanism of CO oxidation on Au_2^- from kinetic measurements and DFT calculations

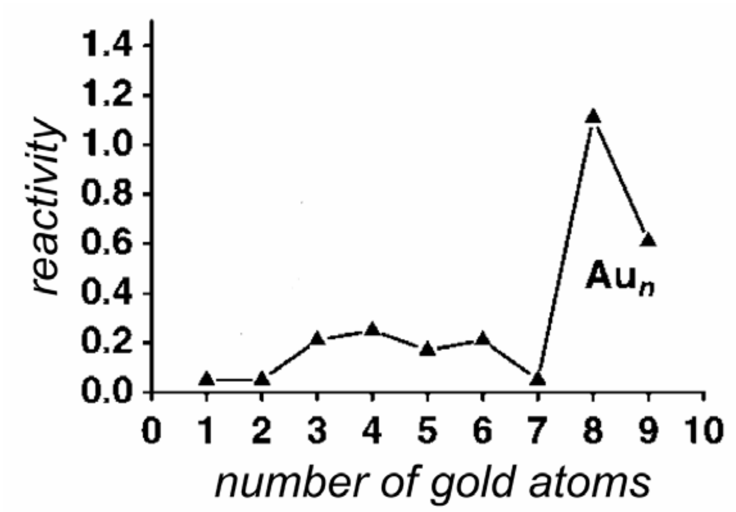


L. D. Socaciu et al. *J. Am. Chem. Soc.* **125** (2003) 10437

CO oxidation mechanism on gas phase gold clusters

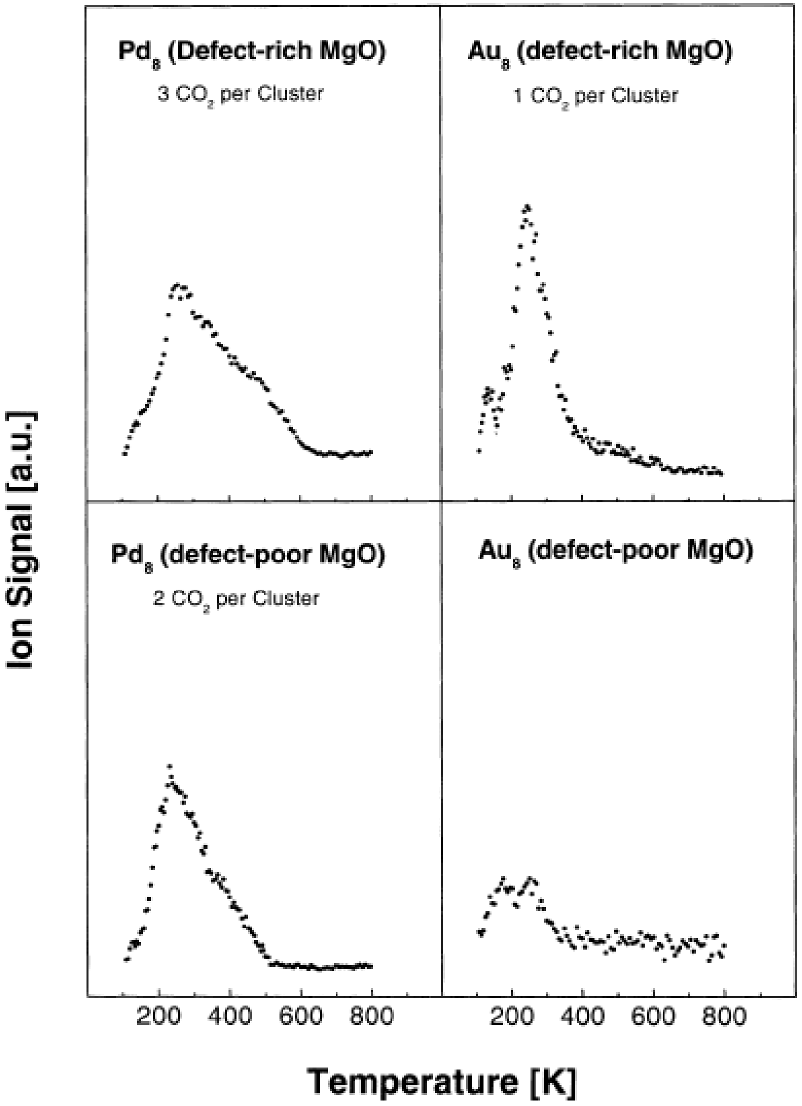
- Activation of molecular oxygen on gold clusters occurs via electron transfer and formation of O_2^- species
- This demands that electron transfer is energetically feasible
- CO oxidation via **Eley–Rideal Mechanism**

CO combustion on small deposited Au clusters



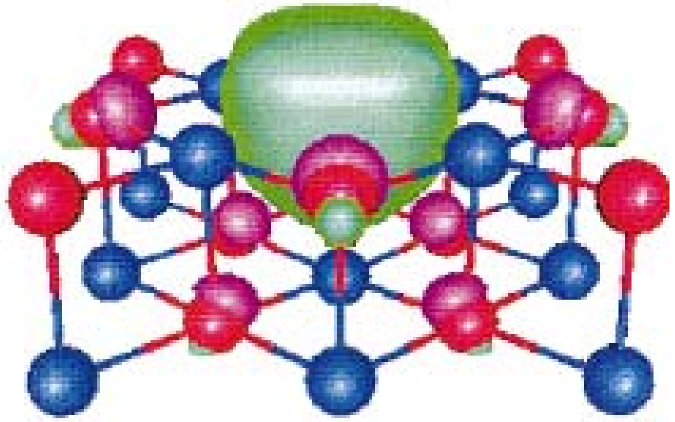
Experiments of U. Heiz et al.:

- Mass selected Au$_n$ clusters are deposited on a MgO substrate
- Effectivity of catalytic CO_2 formation from CO and O_2 is measured
- Au_8 is highly active!
- Reactivity is related to defect centers

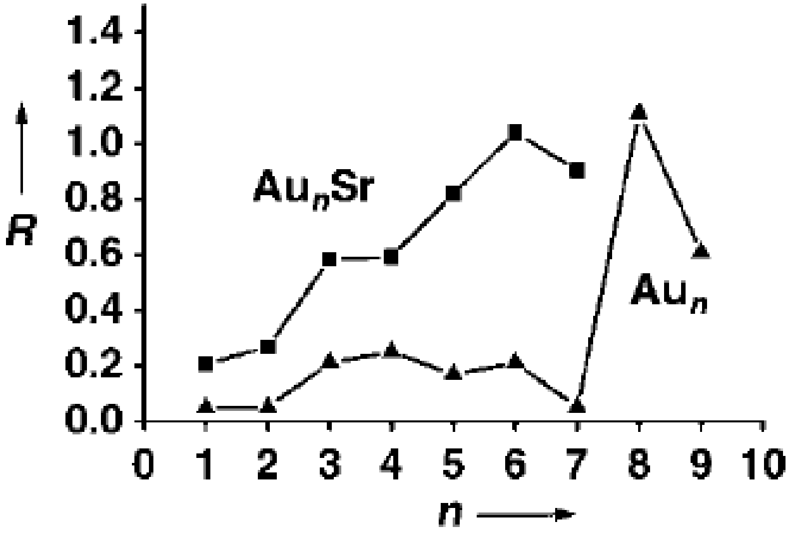


U. Heiz et al. *Chem. Phys.*, **262**, 189 (2000).

What determines reactivity of deposited gold clusters?



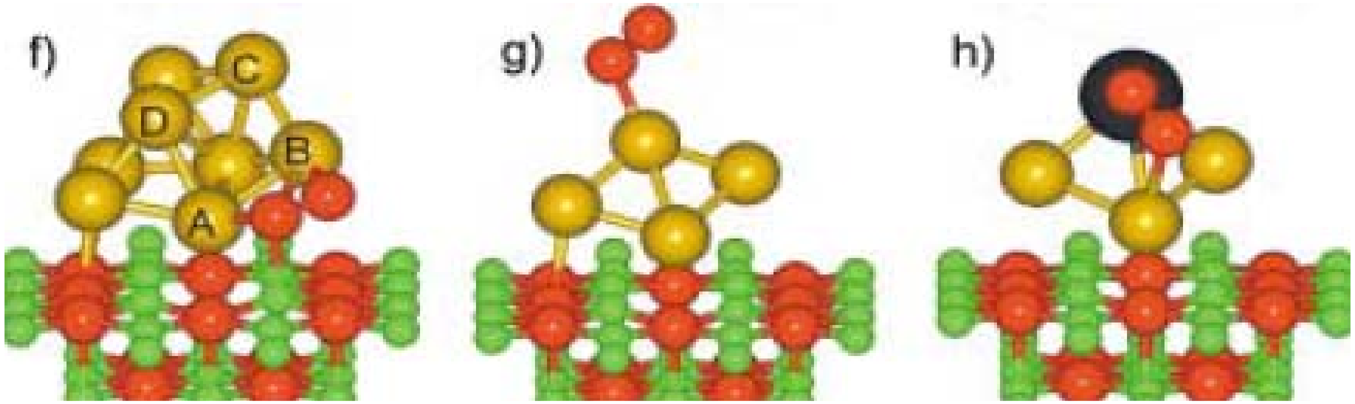
Au_n binds to a $2e^-$ color center on MgO (oxygen vacancy)



Electropositive dopants of Au_n enhance reactivity

A. Sanchez et al., *J. Phys. Chem. A*, **103**, 9573 (1999).
H. Häkkinen et al. *Angew. Chem. Int. Ed.*, **42**, 1297 (2003).

The binding of O_2 to deposited gold clusters



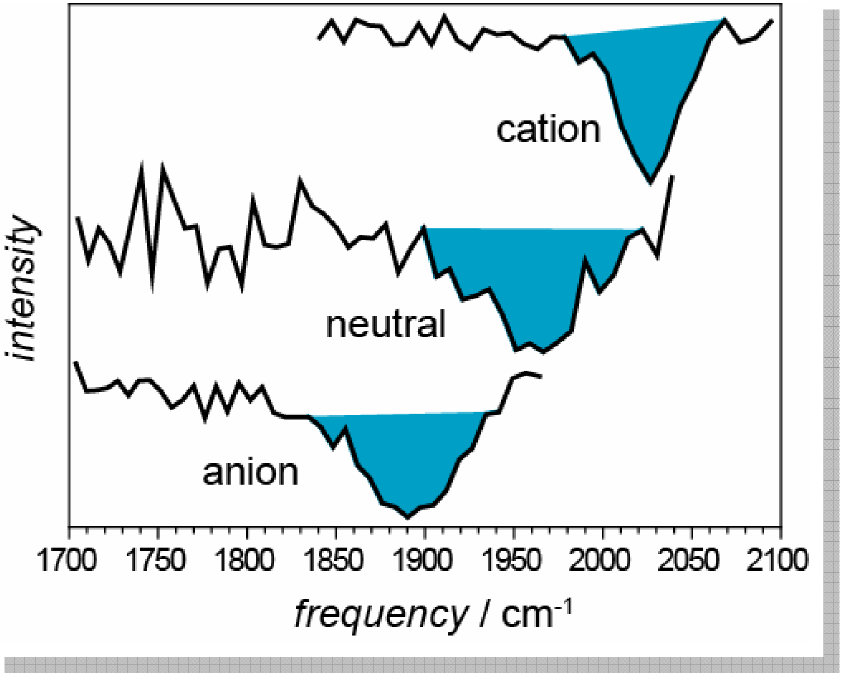
	Au_8	**Au_4**	**Au_4Sr**
E_{ads} / eV	1.43	1.28	1.37
d(O-O) / Å	0.47	0.18	1.94

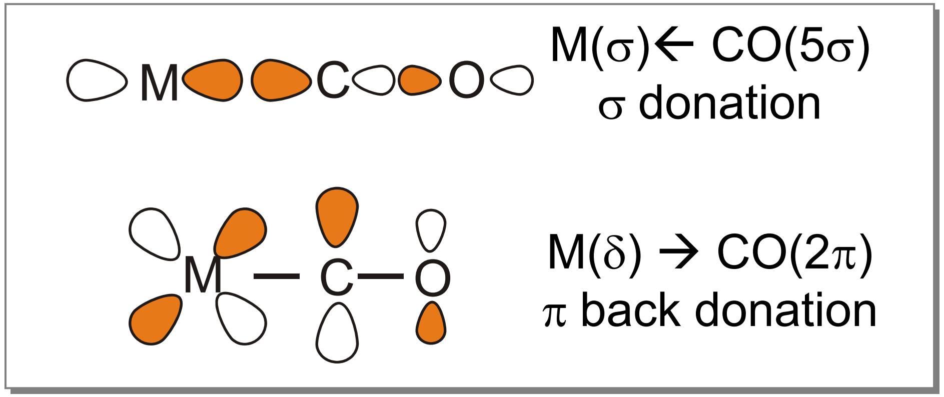
O_2 activation proceeds via electron transfer
from (partially) negatively charged Au clusters.

Can we probe the charge (electron density) on the cluster?

H. Häkkinen et al. *Angew. Chem. Int. Ed.*, **42**, 1297 (2003).

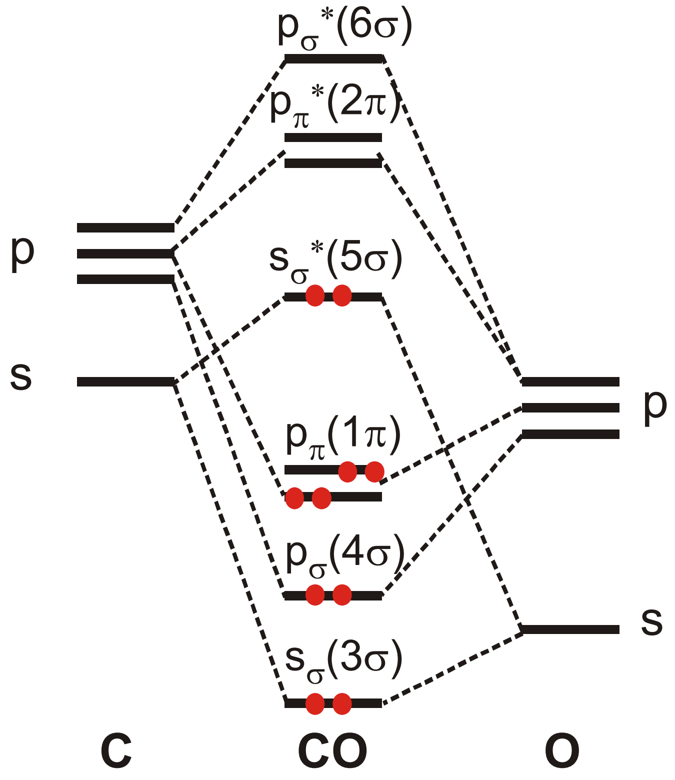
Effect of charge on ν(CO): example of $Rh_8CO^{+/0/-}$



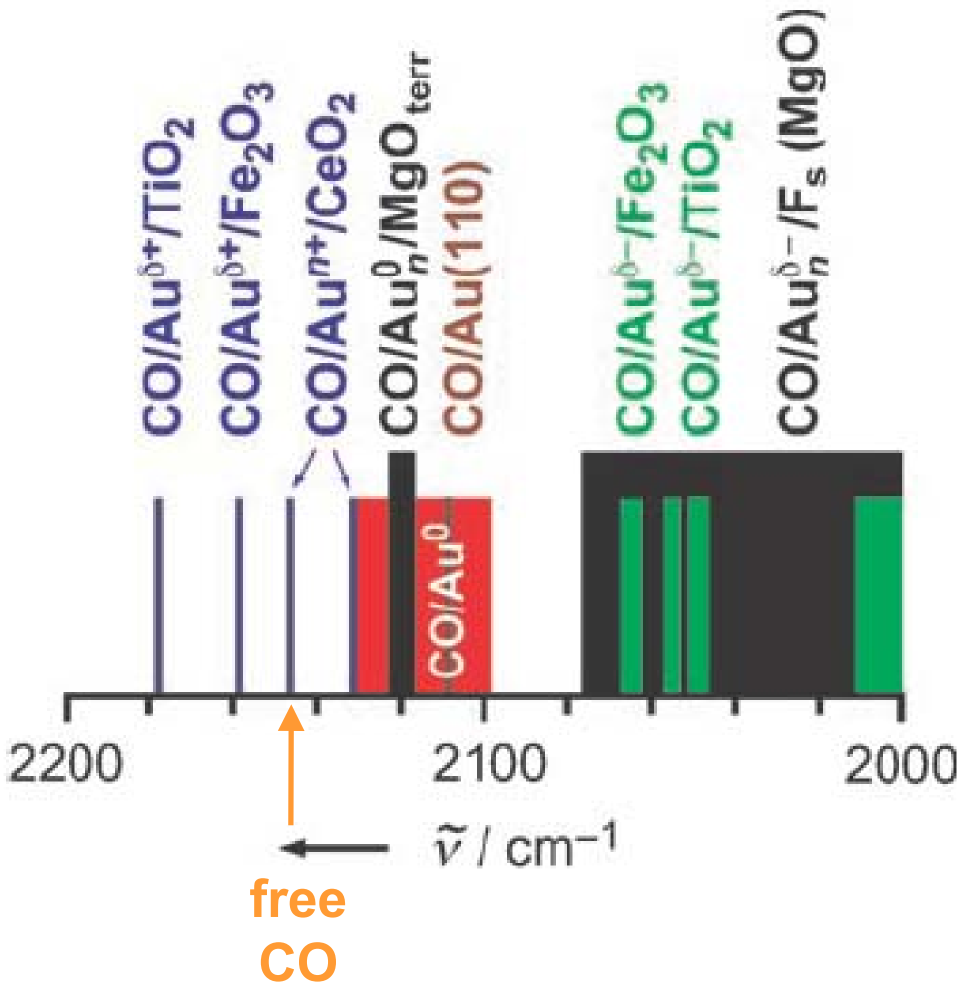


M(σ)← CO(5σ)
σ donation

M(δ) → CO(2π)
π back donation



Observed values of ν(CO) for various systems



Assignments base on the dependence of ν(CO) on:

Particle growth method

Dispersion / mean particle size

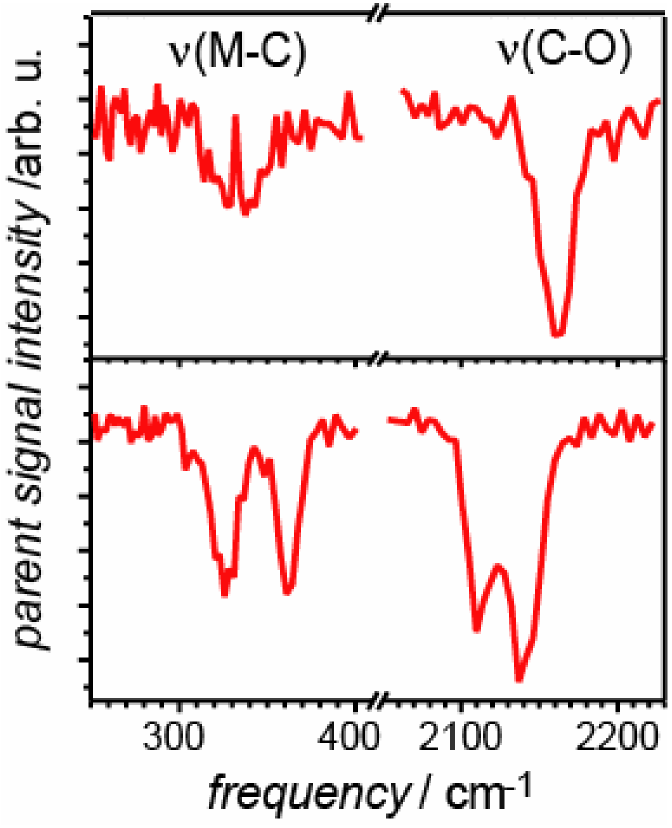
Substrate

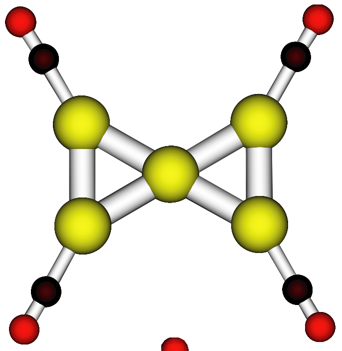
Presence of substrate defects

and on comparison with theory

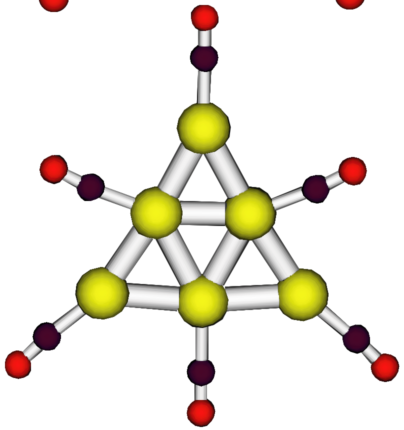
M. Sterrer et al., *Angew. Chem. Int. Ed.* 45, 2630 (2006).

IR spectra of CO complexes of gold cluster in the gas-phase





$Au_5(CO)_4^+$

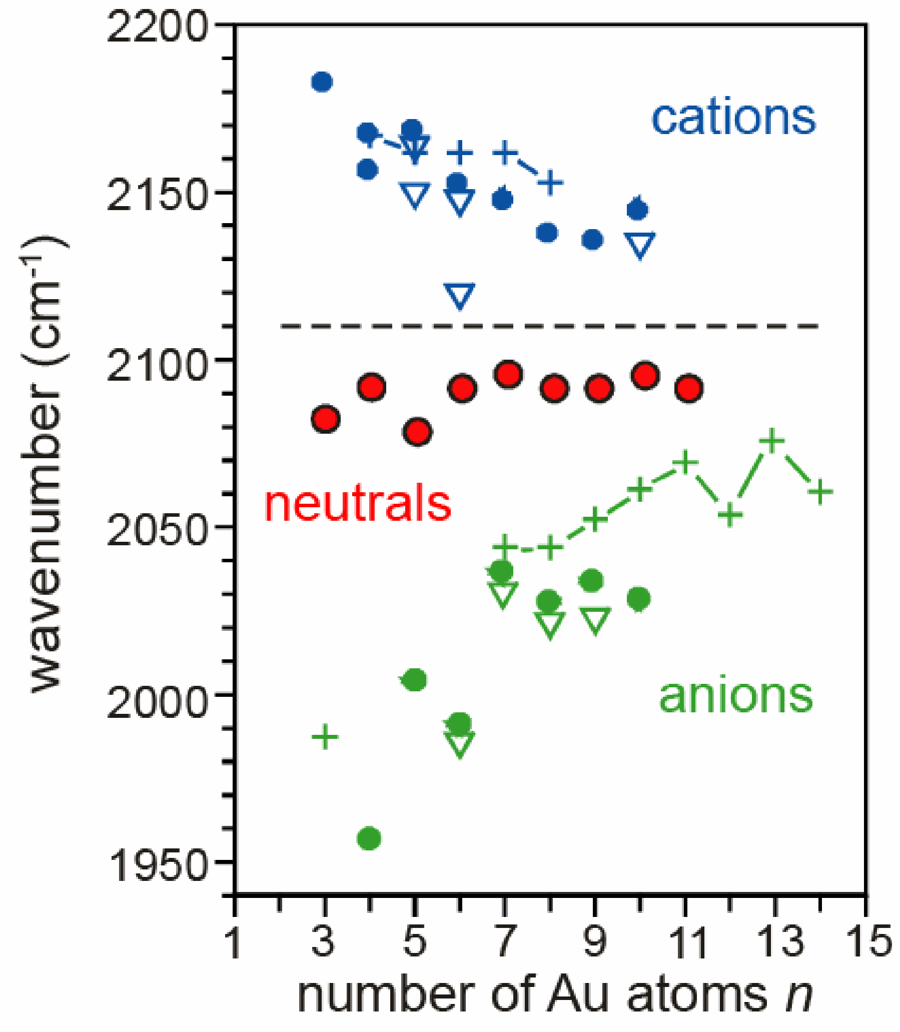


$Au_6(CO)_6^+$

Direct way to determine the dependence of ν(CO) on

cluster size
charge state
coverage
adsorption site

Size and charge dependence of ν(CO) for gold clusters



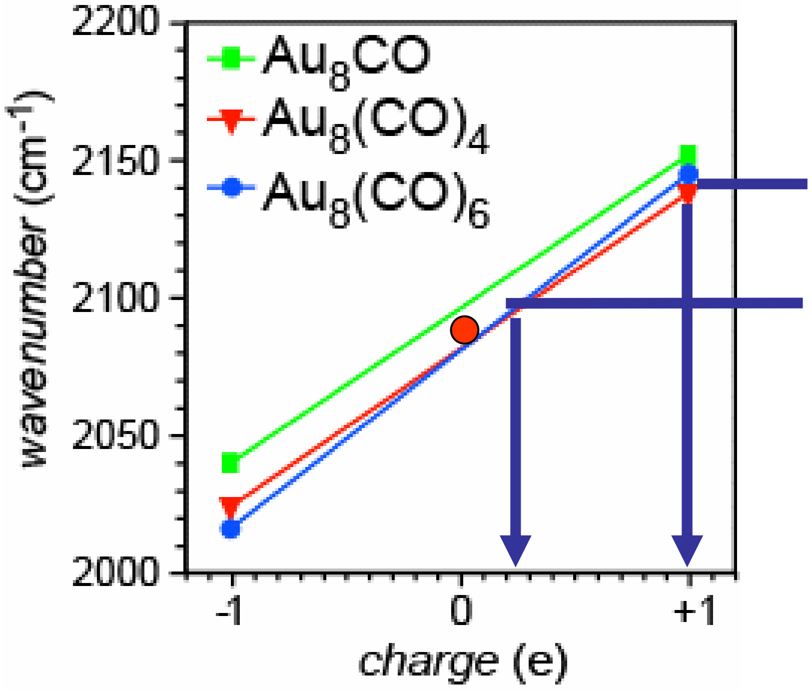
CO binds atop (μ_1)

only to low coordinated Au atoms ($n_{coord} < 5$)

ν(CO) is highly sensitive to charge

Data from gas-phase clusters can be used as reference to probe partial charges of deposited clusters

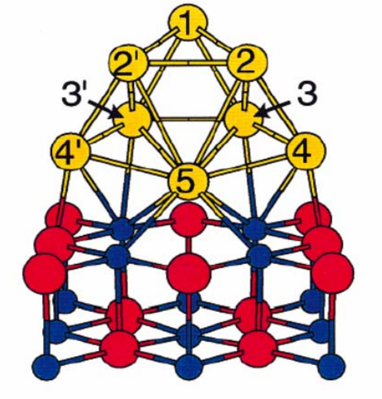
Probing the charge: CO on gold clusters



Au_8@MgO (defect-free)

Au_8@MgO (defect-rich)

B. Yoon et al. *Science* **307** (2005) 403



DFT calculations: Charge on Au_8 bound to an F-centre on MgO ~ -0.5 e

CO is bound to positively polarized clusters

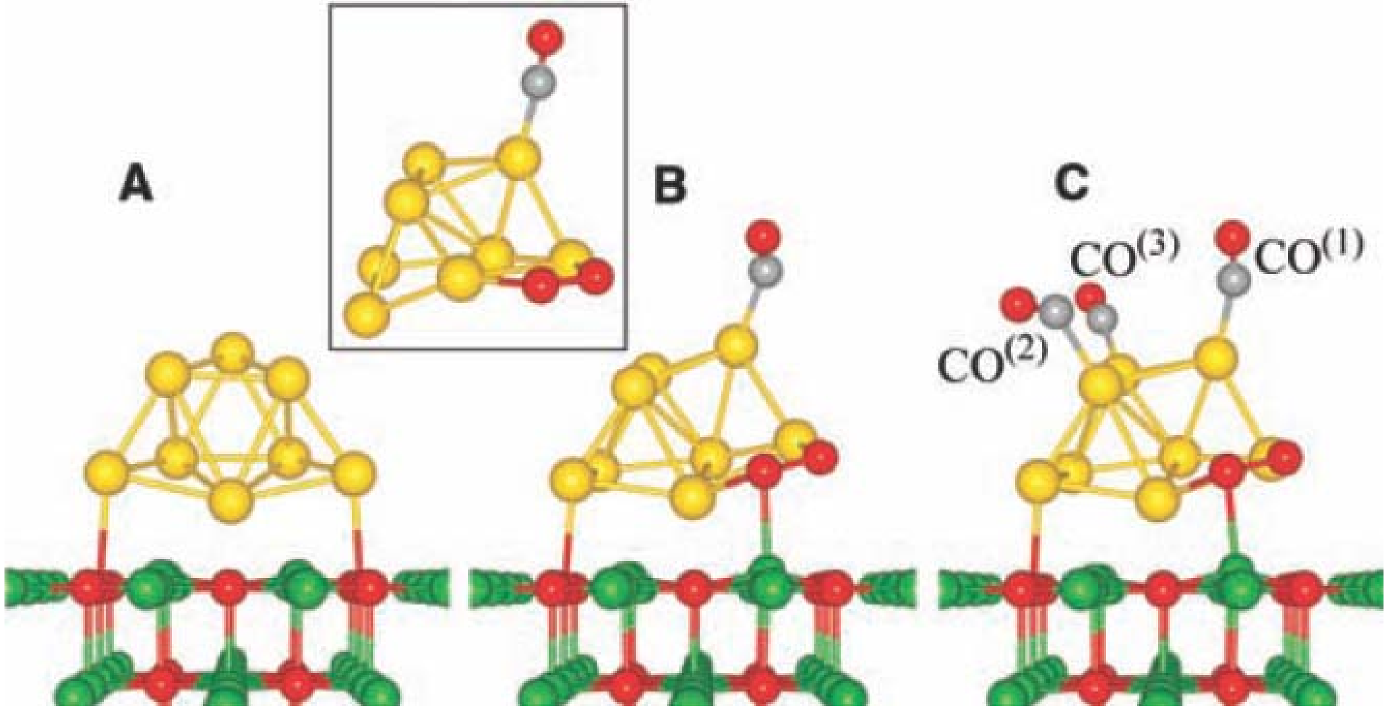
Not the bare clusters are probed but co-adsorbates with molecular oxygen

Binding of O_2 reduces initial charge on the cluster by ~ 1 e (assuming binding as O_2^-)

Initial charge on Au_8 is ~ -0.7 e

JACS **127** (2005) 8416
J. Phys. Chem. B **109** (2005) 23935

CO oxidation mechanism



1. *Langmuir-Hinshelwood* type

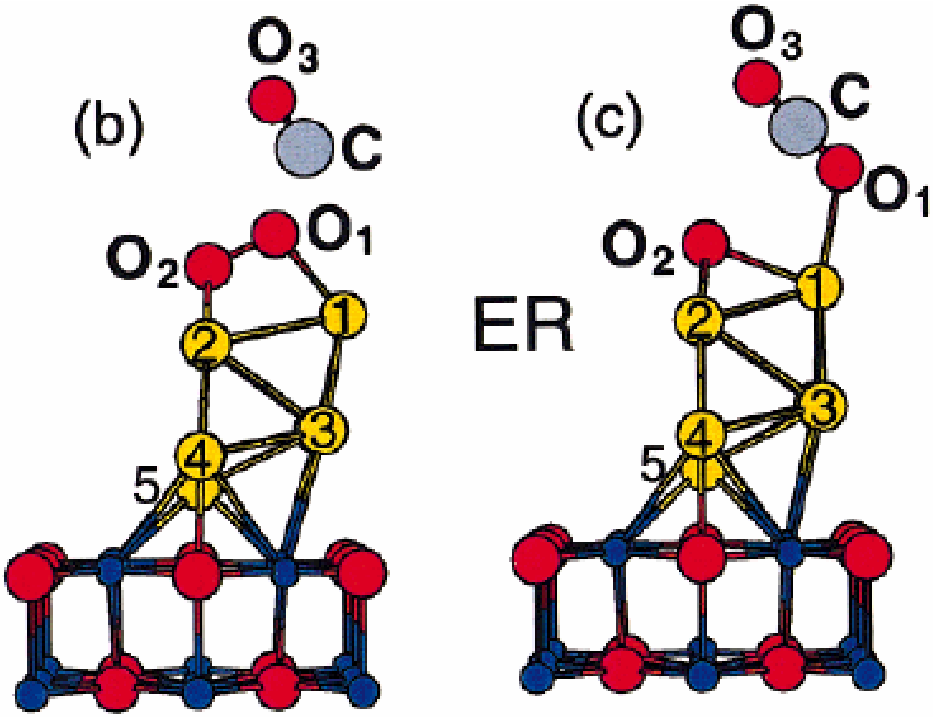
Initial binding of CO to an exposed gold atom

Migration to the super-oxo group

Reaction proceeds with low barrier (0.1 eV)

B. Yoon et al., U, *Science*, **307**, 403 (2005).

Alternative direct mechanism



2. *Eley-Rideal* type

O_2 is bound atop

Direct reaction of O_2^- with CO

Reaction proceeds without barrier

A. Sanchez et al., *J. Phys. Chem. A*, **103**, 9573 (1999).

LH or ER?

- Depends on how O_2 is bound
- Theory suggests that O_2 at the interfacial site can be stronger bound after distortion of the Au_8 cluster
- Spectroscopic studies on Au_8@MgO are in line with CO adsorbed on top of the cluster and co-adsorbed oxygen →LH
- Identification and localization of O-O species needed

- Gas-phase clusters: direct reaction of CO and adsorbed O_2 (ER)

Summary

Physical and chemical properties of small metal clusters (<100 atoms) are often strongly *size-dependent*.

Clusters are suitable *model systems* to develop and test concepts that can be transferred to deposited particles.

Compositions of cluster complexes in the gas phase can be unambiguously determined; reacting species are therefore clearly defined.

Size and composition specific characterization (kinetics, thermochemistry, spectroscopy etc.) is possible.

Clusters are suitable reference systems to identify effects related to charging.