IMPRS Block Course 2012

"'Experimental and Theoretical Methods in Surface Science'"

Surface Reactions on Transition Metal Cluster Models

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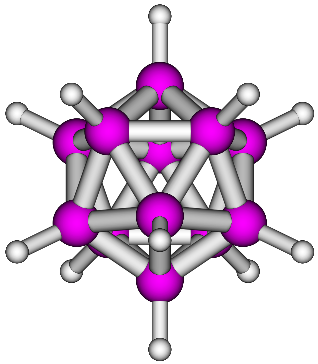
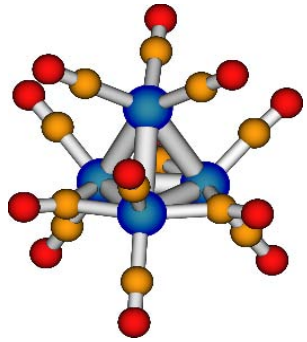
How can free clusters help the understanding of heterogeneous catalysts?

Cluster molecules

- Thermodynamically and kinetically stable
- Chemical synthesis in large quantities
- Characterizations with “classical” spectroscopic techniques (IR, NMR, XRD etc)



$B_{12}H_{12}^{2-}$



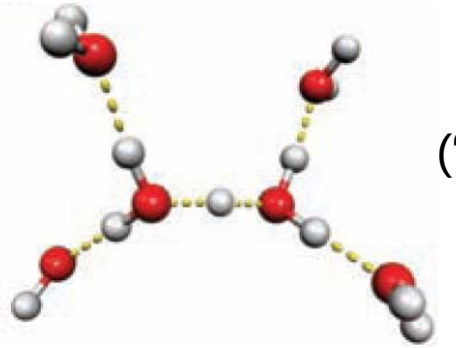
$Co_4(CO)_{12}$

Isolated clusters

- Most clusters are not stable towards aggregation

  → formation of the bulk condensed phase
- Experimental investigations are usually performed in the gas-phase (or in low temperature matrices)

  → Molecular (ion) beam techniques



$H_5O_9^+$ (“Zundel” cation)

Pt_5^+

Literature

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

U. Heiz, U. Landman (eds.), **Nanocatalysis**, 2007 (Springer). Chapter 1: Chemical and catalytic properties of size-selected free and supported clusters

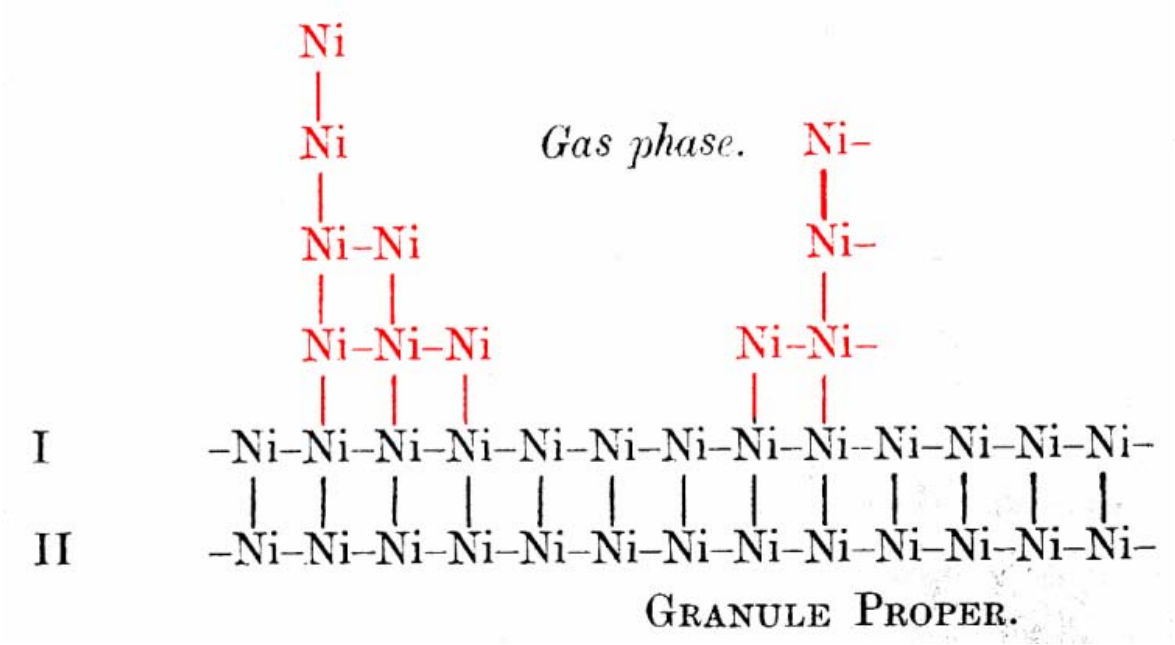
M. B. Knickelbein, **Reactions of Transition Metal Clusters with Small Molecules,** Ann. Rev. Phys. Chem. 50 (1999) 79.

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.)

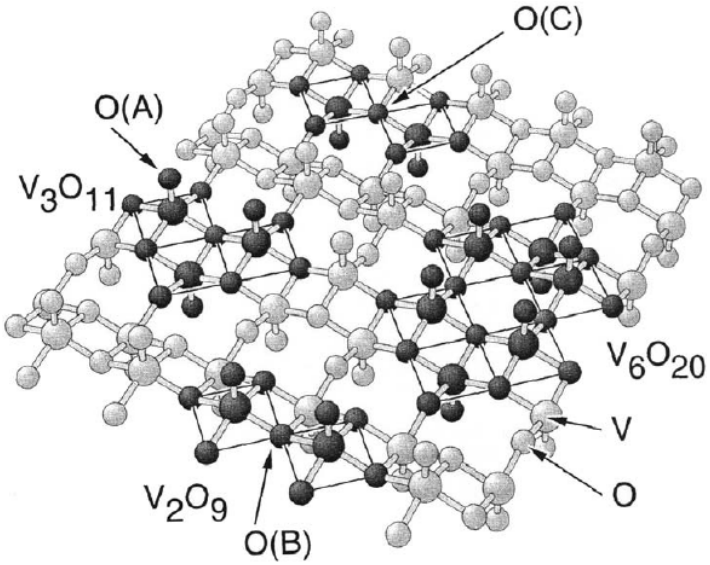


CO hydrogenation on Ni

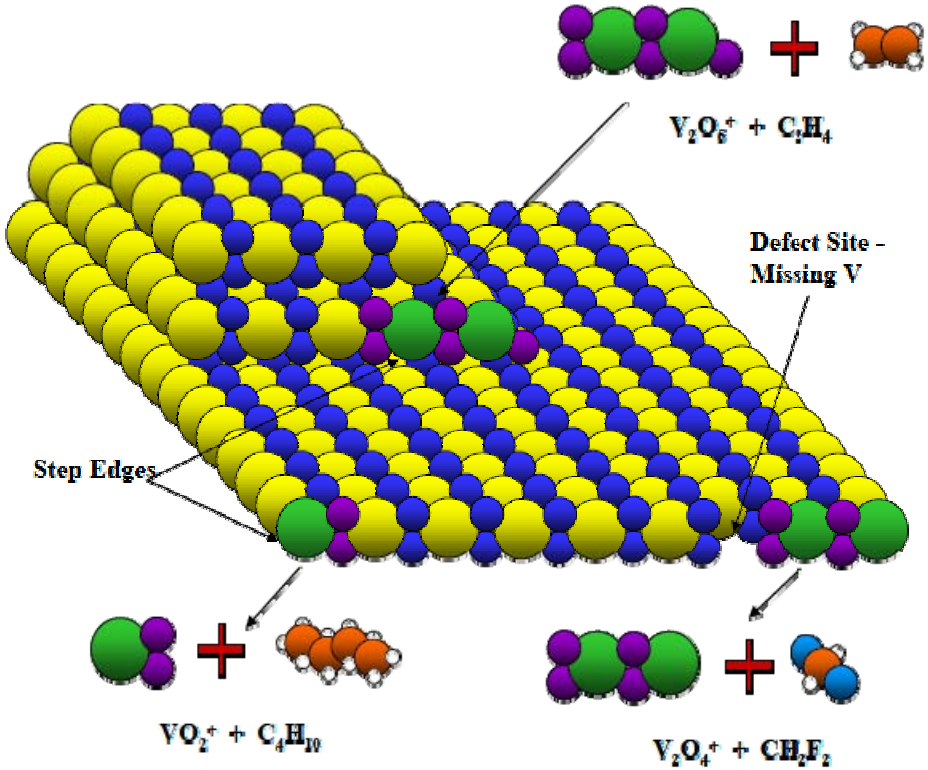
Observation: Catalyst can be deactivated by very small amounts of a poison

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

Clusters as subunits of surfaces?



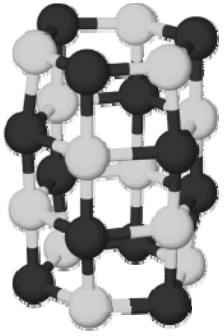
M. Witko, M.; Hermann, K.; Tokarz, R., *J. Electron. Spec. Rel. Phenom.,* **69** (1994) 89.



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

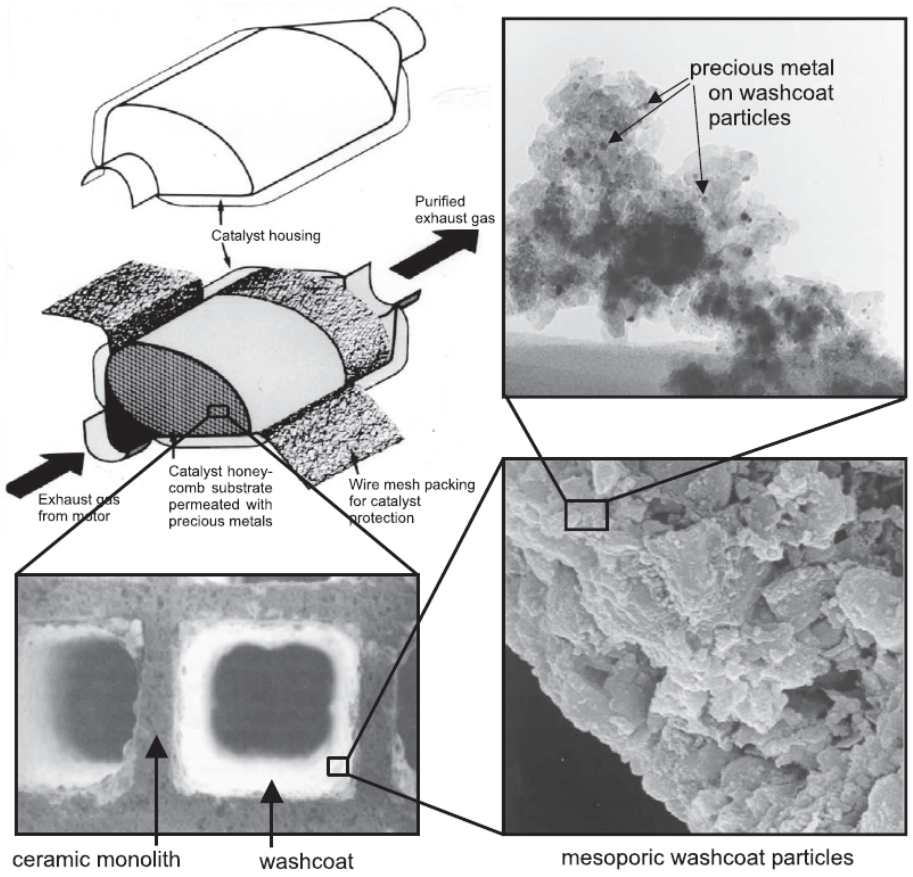
Neglects binding within the surface

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

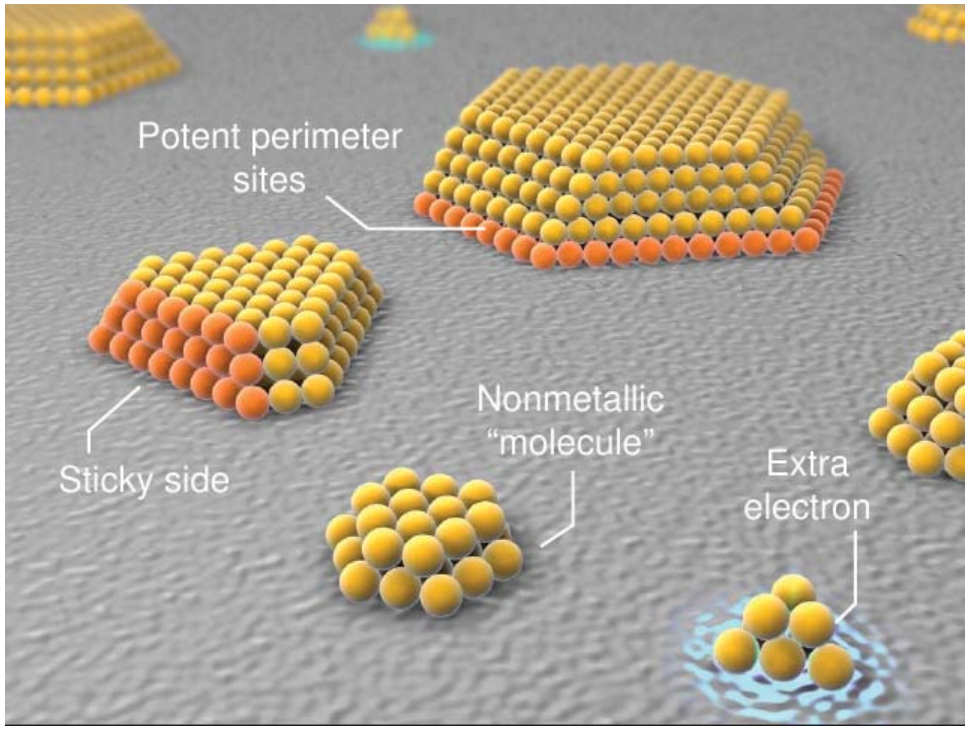


$(MgO)_{12}$

Supported metal particles



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



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

Interaction of the metal particles with the substrate may significantly affect reactivity

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

Limited size = limited complexity

- Properties can be in detailed characterized experimentally
- Different levels of theory can be employed

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

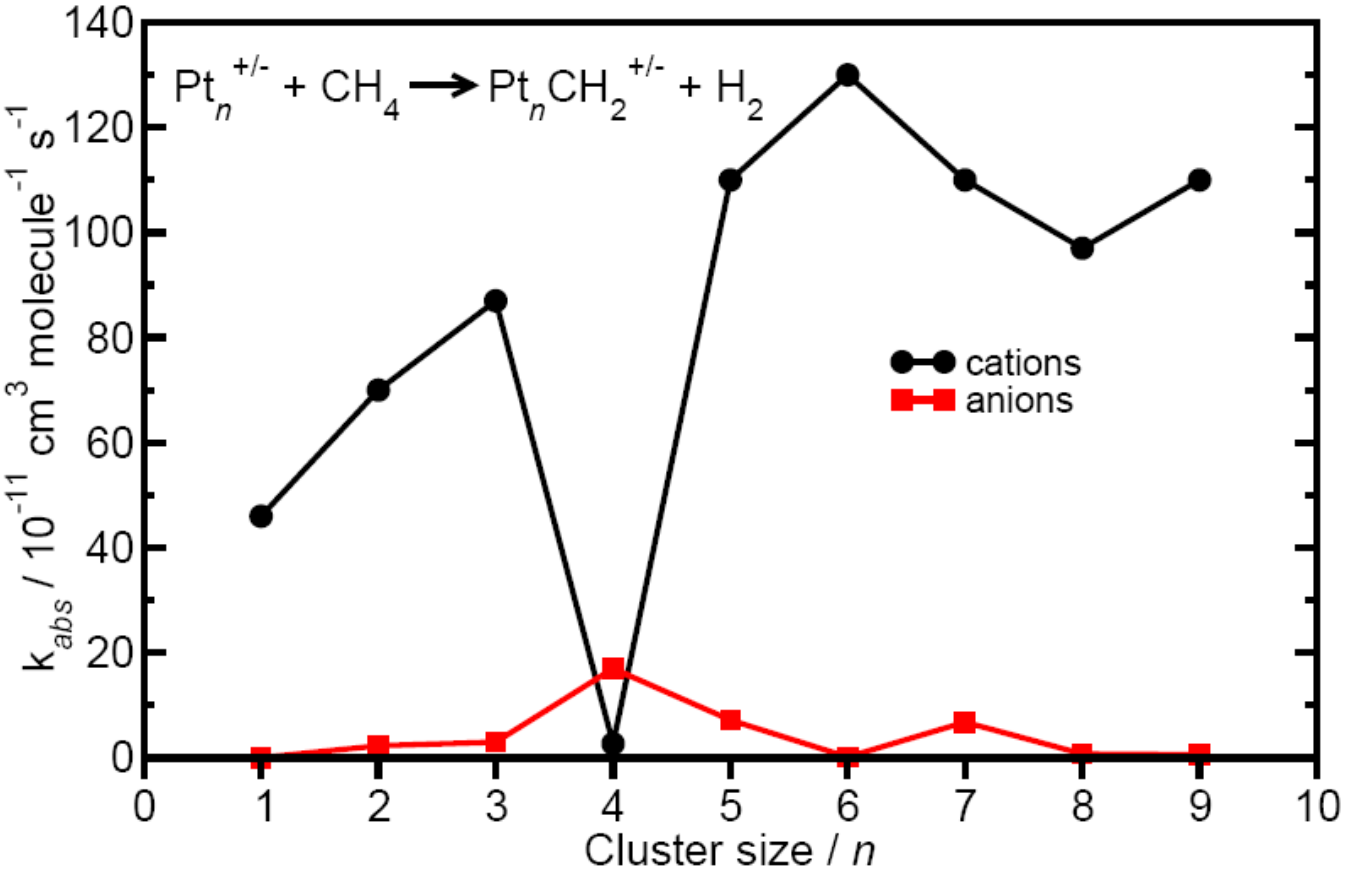
	Cluster				*nano/micro crystals*				
	„micro"		*„small"*	*„large"*					
Number of atoms	1	10	10^2	10^3	10^4	10^5	10^6	10^7	10^8
Surface atoms		10	10^2		10^3	10^4	10^5		
radius [nm]			1			10			10^2

- 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.

Size matters (or: every atom counts)



$$Pt_n^{\pm} + CH_4 \rightarrow Pt_nCH_2^{\pm} + H_2$$

U. Achatz et al. *Chem. Phys. Lett.* **320** (2000) 53.
K. Koszinowski, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **107** (2003) 4999.
G. Kummerlöwe et al., *Int. J. Mass Spectr.* **254** (2006) 183.

Chemistry of gas-phase clusters

- **Structure of reactants and products**
  (electronic + geometric)
- **Thermodynamics**
  (binding energies, equilibrium constants)
- **Reaction kinetics**
  (mechanisms, catalysis)

Today:

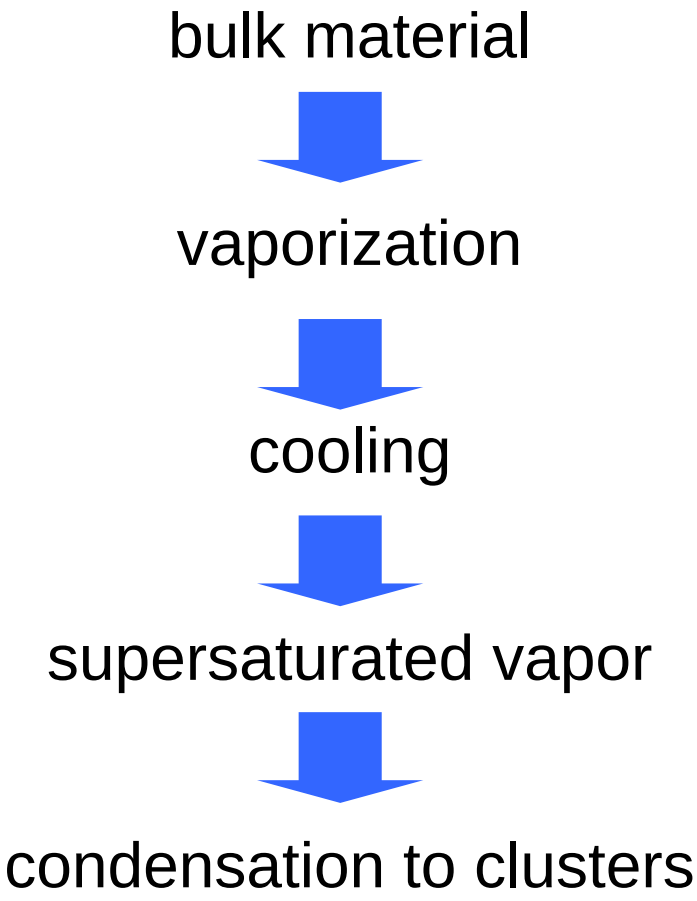
1. CO oxidation on Pt
2. CH_4 activation on Pt

1. Making and characterizing free metal clusters

Experimental techniques for Cluster studies

Cluster production

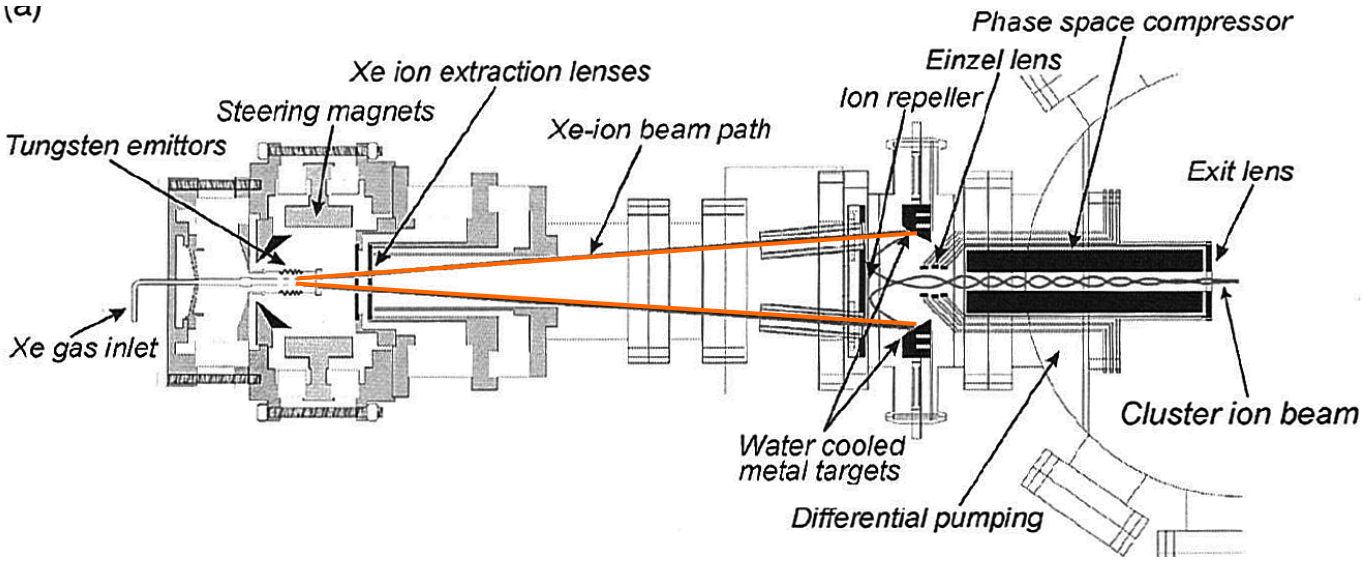
Aggregation of the constituents



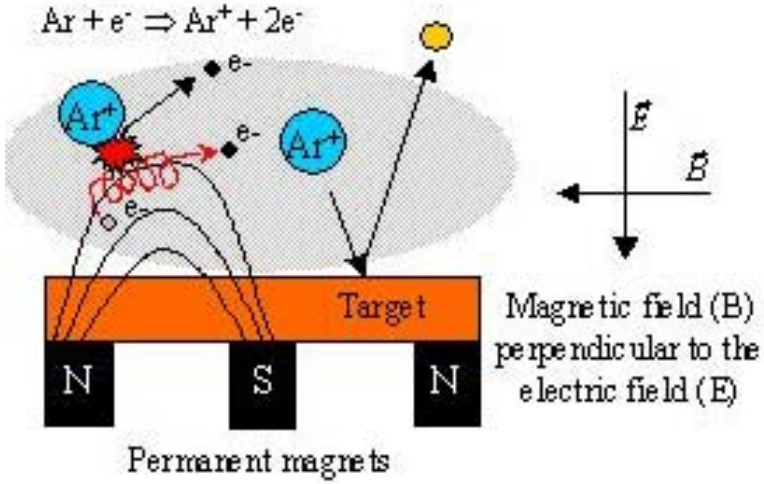
Cluster Production

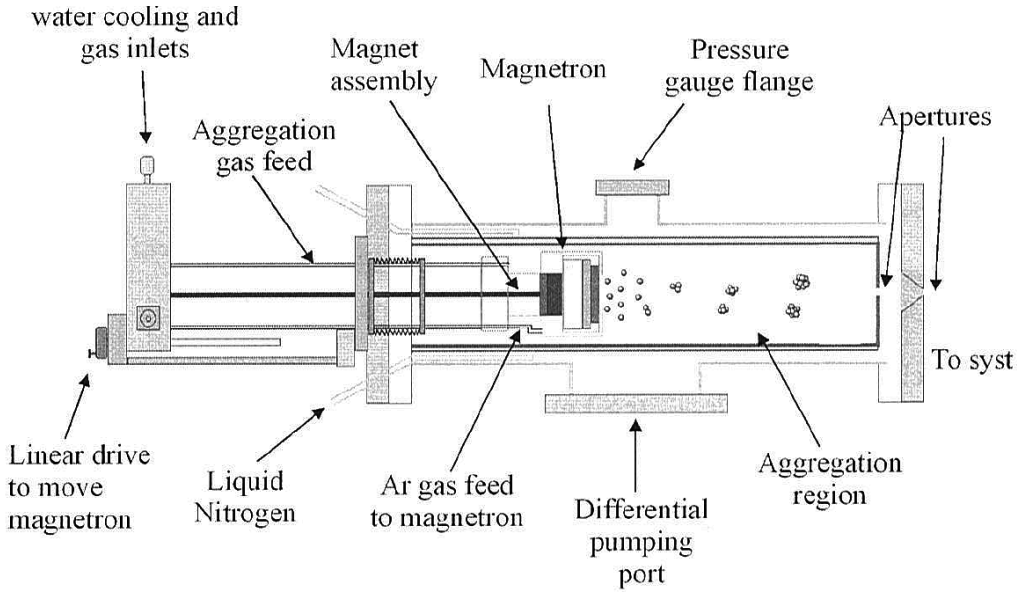
Ion sputtering

CORDIS (cold ion reflection discharge ion source)



Magnetron sputter source





Cluster Production

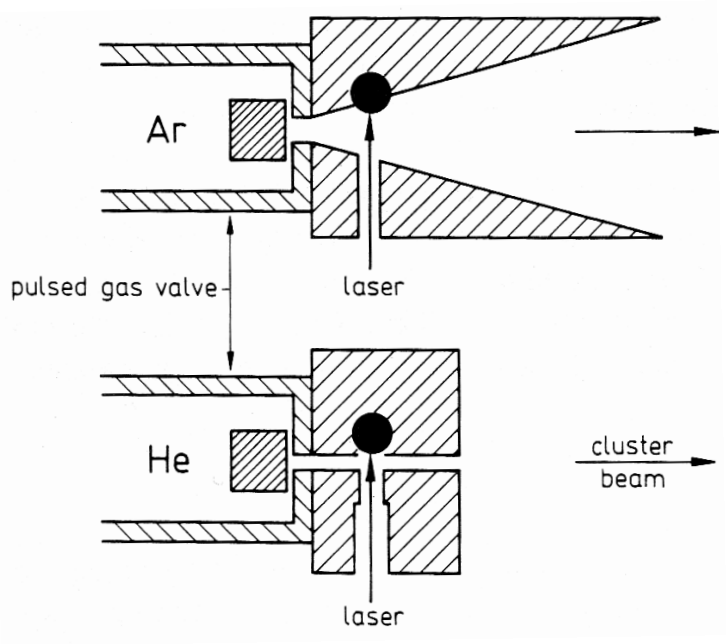
Laser ablation

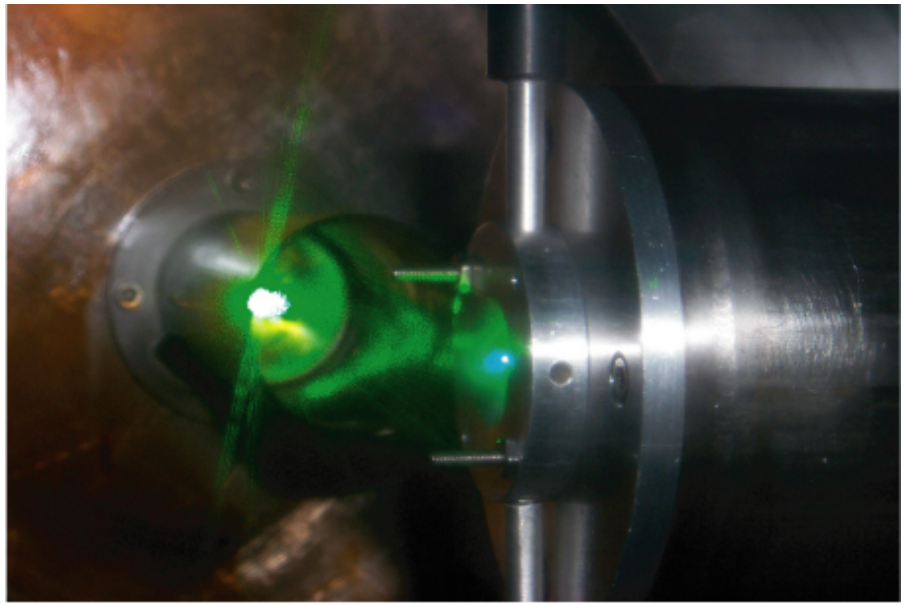
heating of a small surface part of a solid target by a focused, intense short-pulse laser (typically Nd-YAG, 532 nm)

formation of a plasma that contains ions and electrons

cooling with rare gas induces aggregation

→ formation of neutral and charged (anionic and cationic) clusters



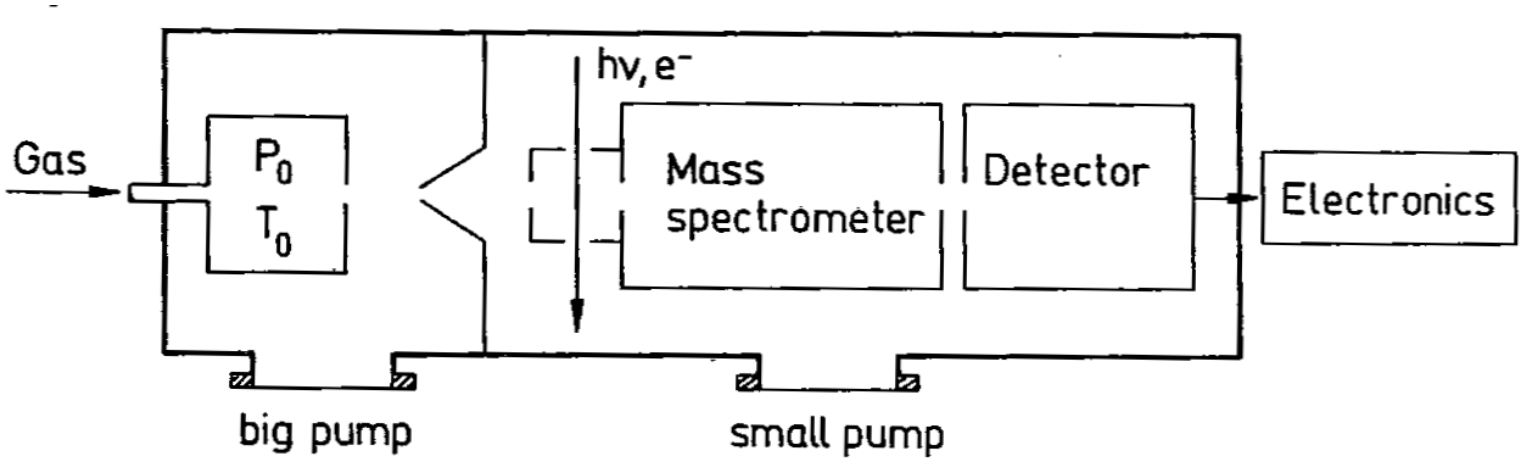


Converts practically any solid into clusters, very frequently used!

Can be easily combined with reaction or thermalization channels, etc.

A molecular beam cluster experiment

Experiments under collision-free conditions



$$\ell = \frac{k_B T}{\sqrt{2}\pi d^2 p}$$

Mean free path length (identical particles)

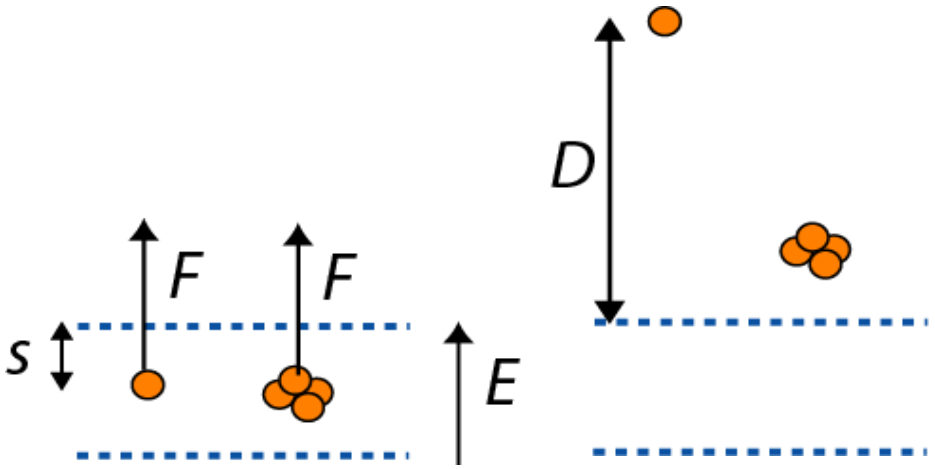
Vacuum range	Pressure in mbar	Molecules / cm^3	mean free path
Ambient pressure	1013	$2.7*10^{19}$	68 nm
Medium vacuum	$1\text{-}10^{-3}$	$10^{16}\text{-}10^{13}$	0.1-100 mm
High vacuum	$10^{-3}\text{-}10^{-7}$	$10^{13}\text{-}10^{9}$	10 cm - 1 km
Ultra high vacuum	$10^{-7}\text{-}10^{-12}$	$10^{9}\text{-}10^{4}$	1 km-10^5 km

Mass spectrometric characterization

Time-of-flight mass spectrometry

acceleration of charged particles (ions) in an electric field

particles having the same charge but different mass are accelerated to the same kinetic energy



$$zeEs = \frac{mv^2}{2}$$

$$v = \sqrt{\frac{2zeEs}{m}}$$

$$t = \sqrt{\frac{m}{2zeEs}}D \qquad (D >> s)$$

Measurement of the arrival time on the detector gives mass information

typical experimental conditions: s=1 cm, D=10-300 cm, E=100-10000 kV/cm

A single mass spectrum can be measured within 5-100 µs.

Mass resolution up to 10 000 amu can be achieved

Mass spectrometric characterization

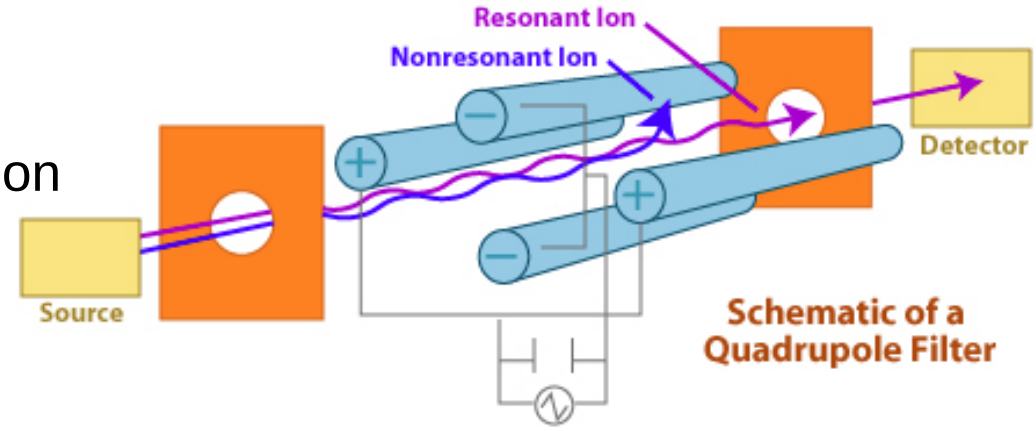
Other types of mass spectrometers

I Magnetic sector field

II Quadrupole

moderate to high (10^4) resolution

experiments on beams of mass selected ions (MS/MS)



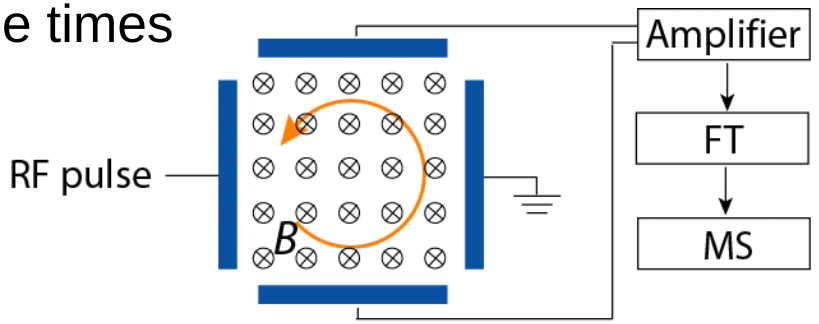
III Ion traps, FT-ICR (ion cyclotron resonance)

very high resolution (10^6), long storage times

simultaneous detection of all ions

expensive

$$\omega = \frac{zeB}{m}$$



I-II are often used as mass filters, measurement of a full mass spectrum requires scanning (of voltages) and is relatively time consuming.

Experiments are often performed on pulsed molecular beams, usage of a ToF-MS allows rapid and full mass analysis of a single ion pulse.

2. Investigating the chemistry of clusters

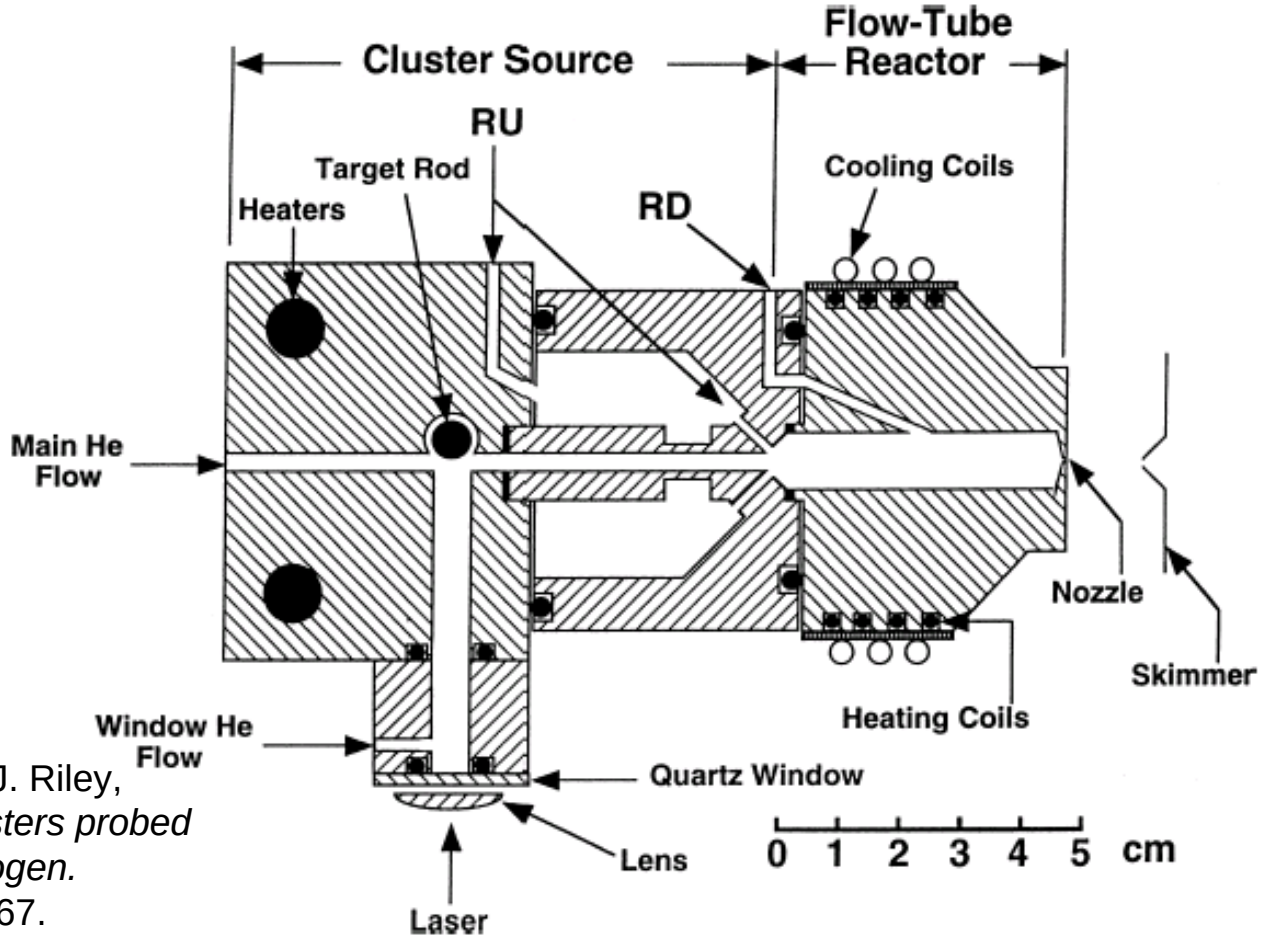
Experimental studies of cluster reactivity

Flow tube instruments

Reaction channel is often an extension of the cluster source

For reactions of neutrals and ions

Reactions under “high-pressure” (few 10 mbar) conditions at defined temperatures



E.K. Parks, K.P. Kerns, and S.J. Riley,
The structure of nickel-iron clusters probed by adsorption of molecular nitrogen.
Chem. Phys. 262 (2000) 151-167.

Cluster size specific reactivity (Fe_n+D_2), qualitatively

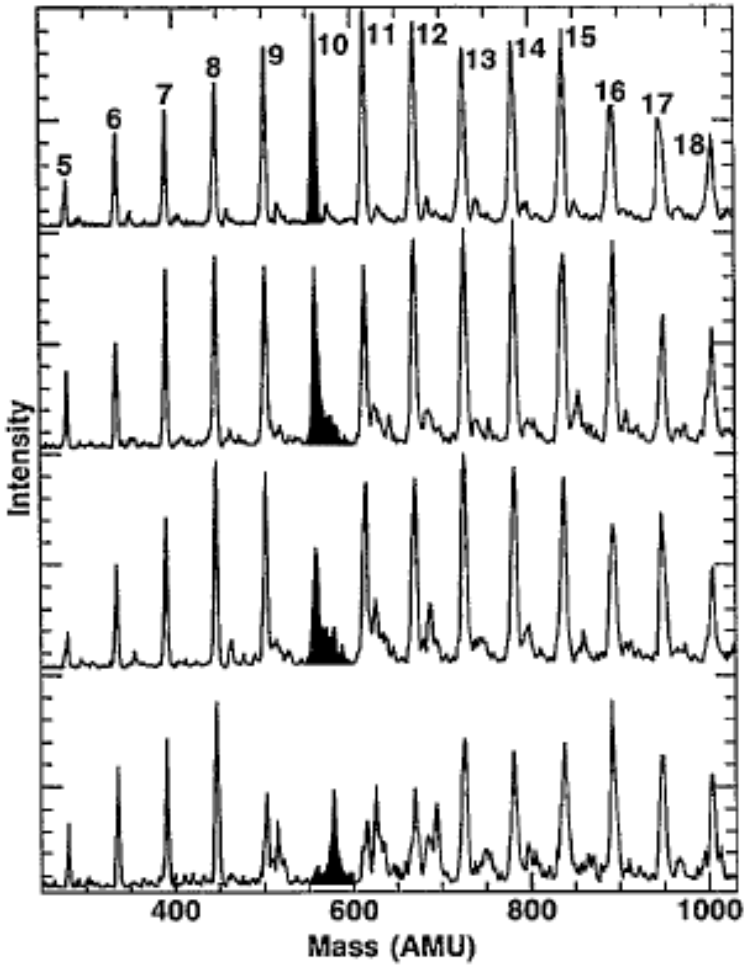


FIG. 1. Chemisorption of D_2 on certain small Fe clusters is seen from these photoionization time-of-flight mass spectra in the preferential depletion of bare clusters Fe_x, accompanied by appearance of products of masses corresponding to $Fe_x(D_2)_y$. The three lower frames correspond to different time lengths (nominally 100, 250, and 600 μsec) of the secondary gas pulse, which is a 25% mixture of D_2 in He.

R. L. Whetten, D. M. Cox, D. J. Trevor, and A. Kaldor,
Phys. Rev. Lett. 54 (1985) 1494.

H_2 addition follows pseudo–first order kinetics

formation $Ni_n + H_2 \rightarrow Ni_nH_2^*$

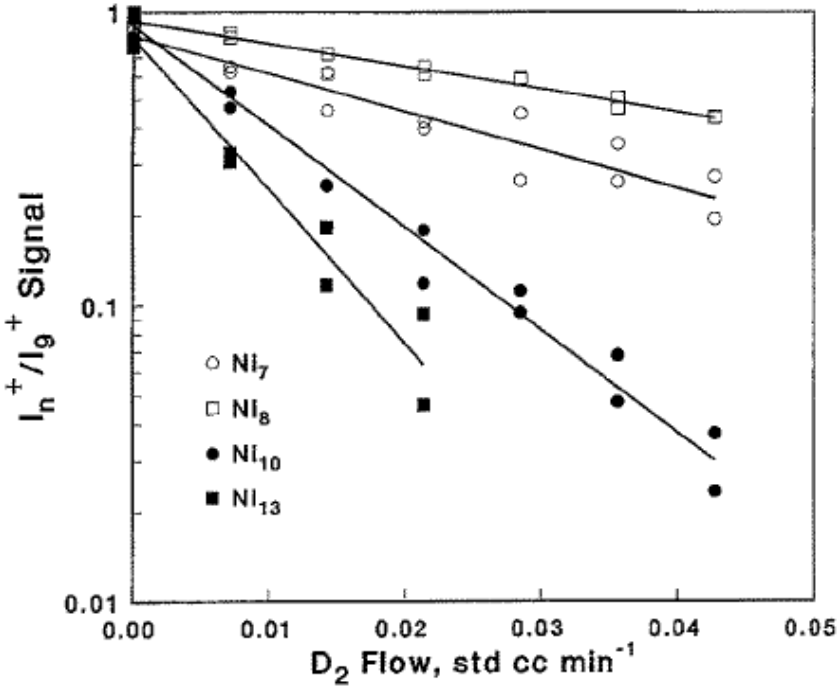
decay $Ni_n + H_2 \leftarrow Ni_nH_2^*$

stabilization $Ni_nH_2^* \rightarrow Ni_nH_2$

$$-d[Ni_n]/dt = k[H_2]\,[Ni_n] - k_r[Ni_nH_2^*],$$

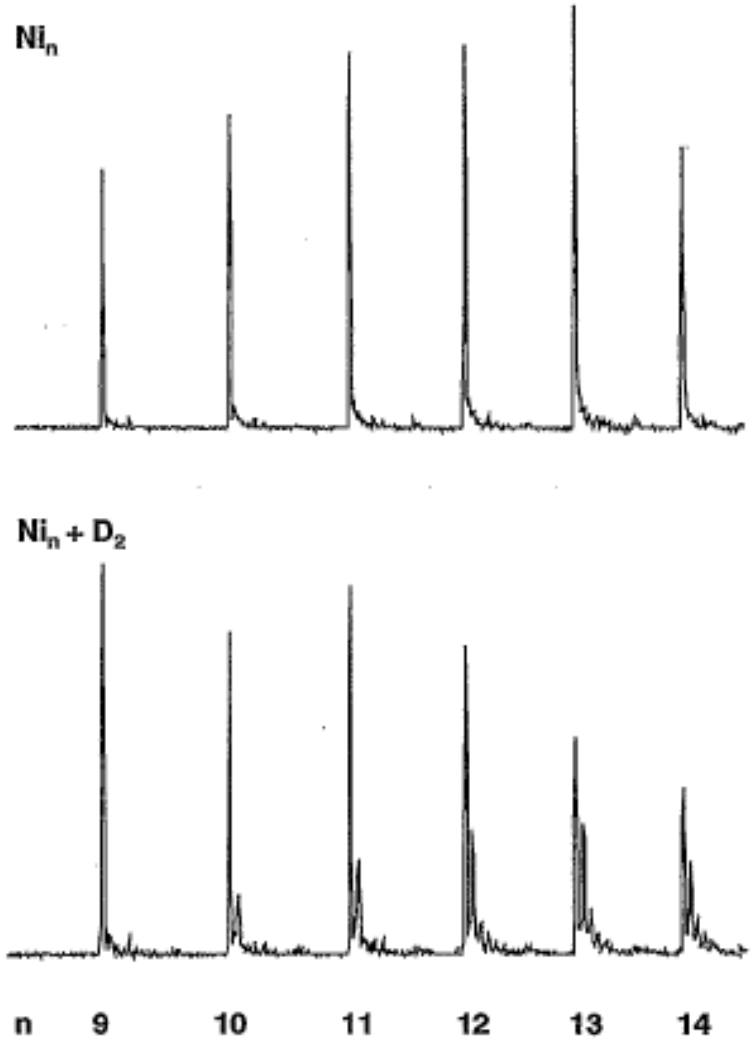
$$-d[Ni_n]/dt = k[H_2]\,[Ni_n] \qquad [H_2] = \text{const}$$

$$\ln\left(\frac{[Ni_n]}{[Ni_n]_0}\right) = k[H_2]t$$



W. F. Hoffman III, E. K. Parks, G. C. Nieman, L. G. Pobo, and S. J. Riley
Z. Phys. D 7 (1987) 83.

Cluster size specific reactivity (Ni_n+H_2), quantitively



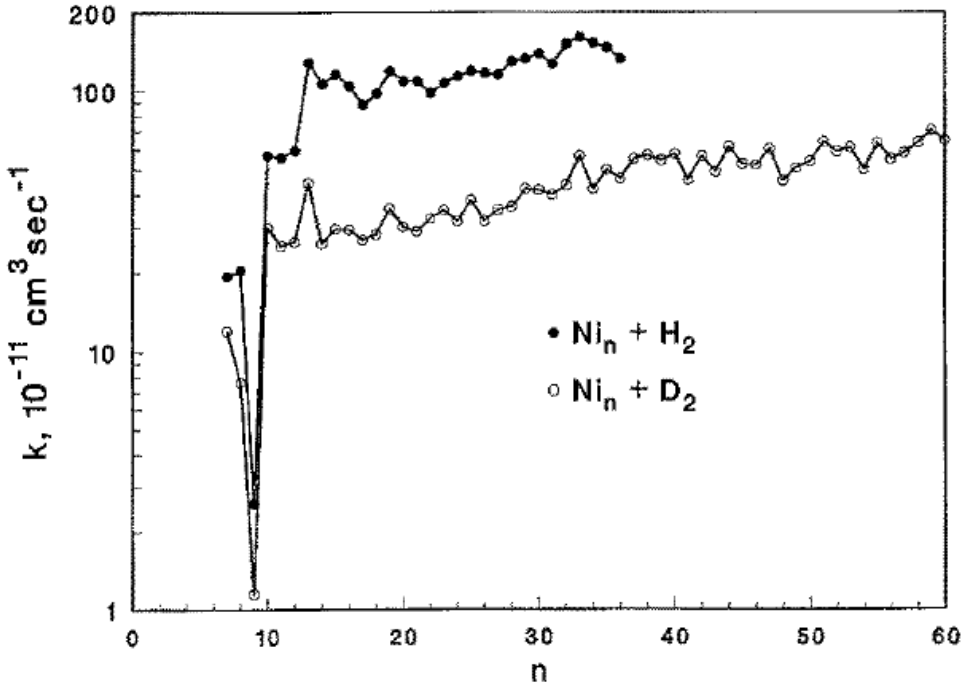


Fig. 3. Absolute rate constants for reactions of nickel clusters with H_2 (filled symbols) and D_2 (open symbols)

L. Zhu, J. Ho, E. K. Parks, and S. J. Riley, J. Chem. Phys. 98 (1993) 2798.

W. F. Hoffman III, E. K. Parks, G. C. Nieman, L. G. Pobo, and S. J. Riley Z. Phys. D 7 (1987) 83.

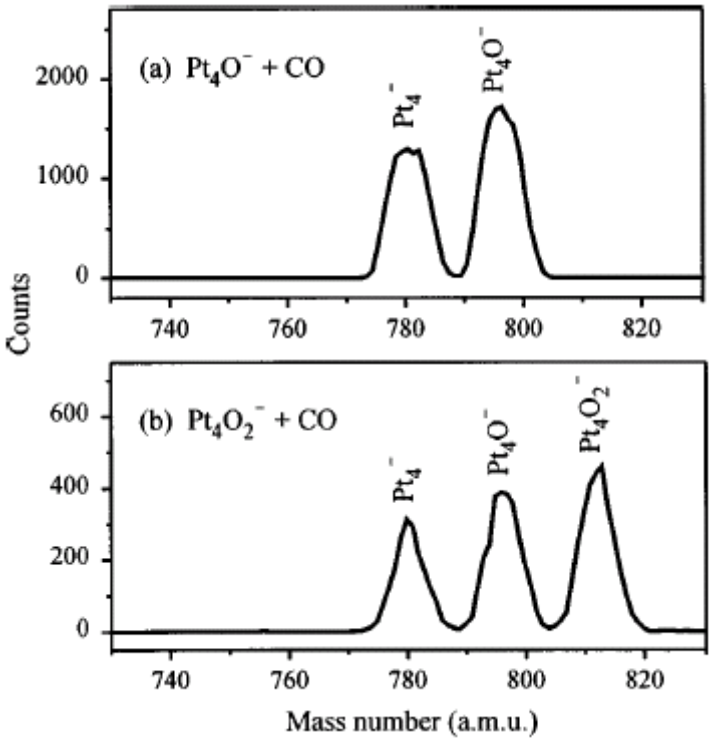
Experimental studies of cluster reactivity

Ion trap experiments

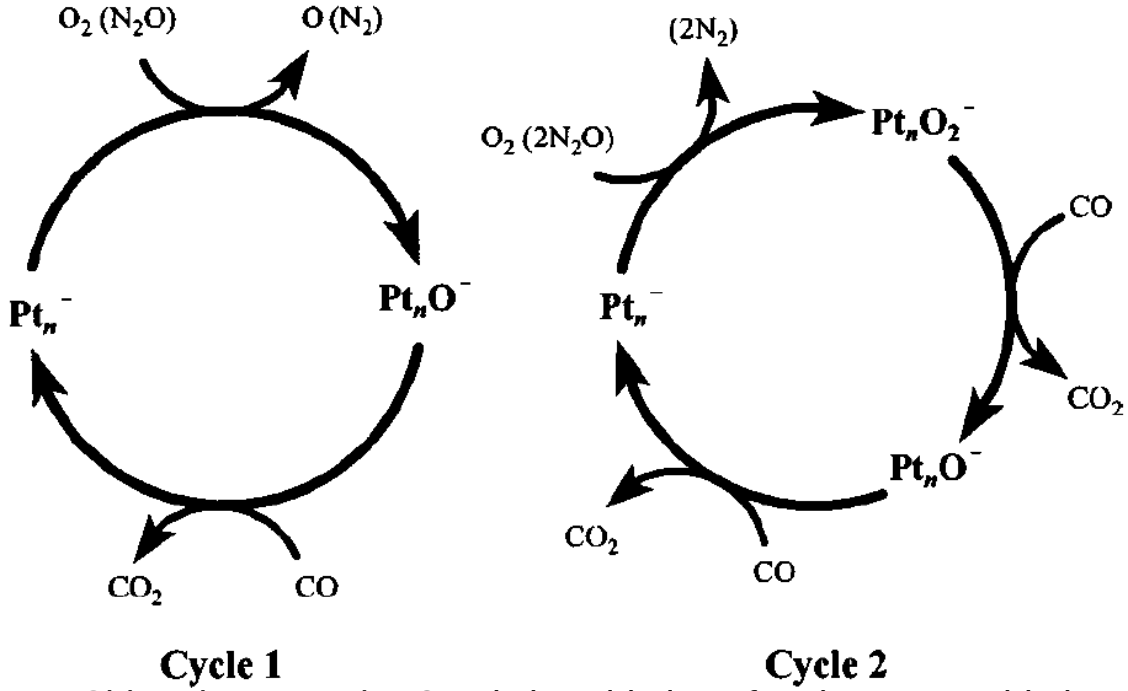
Study of mass selected ionic species

Reactions under single-collision conditions

Reaction sequences



Catalytic cycles for the oxidation of CO on platinum cluster anions

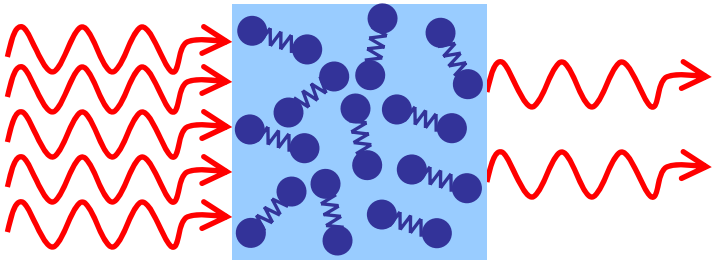


Y. Shi and K.M. Ervin, *Catalytic oxidation of carbon monoxide by platinum cluster anions.* J. Chem. Phys. 108 (1998) 1757.

Can we probe the identity of the intermediates?

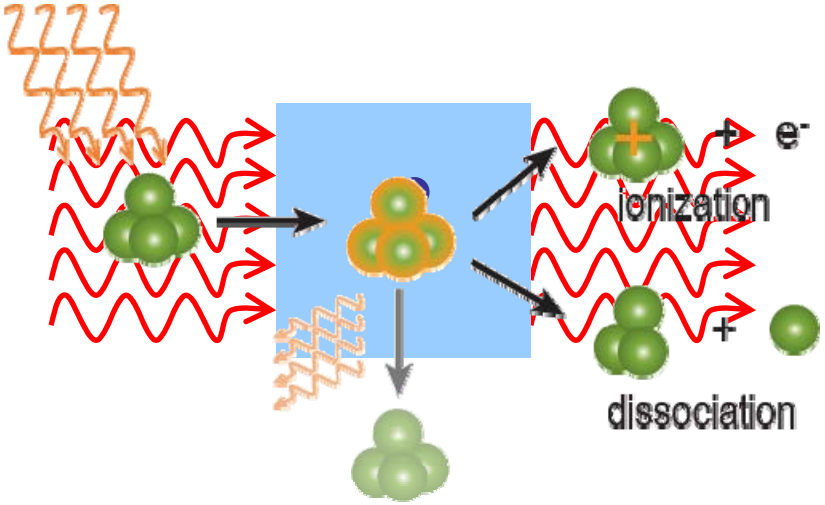
Vibrational spectroscopy as structure probe for gas-phase cluster complexes

IR spectroscopy of clusters in molecular beams



Direct measurement of absorption

- Not sensitive enough (low particle density)
- Not species specific (cluster distribution)

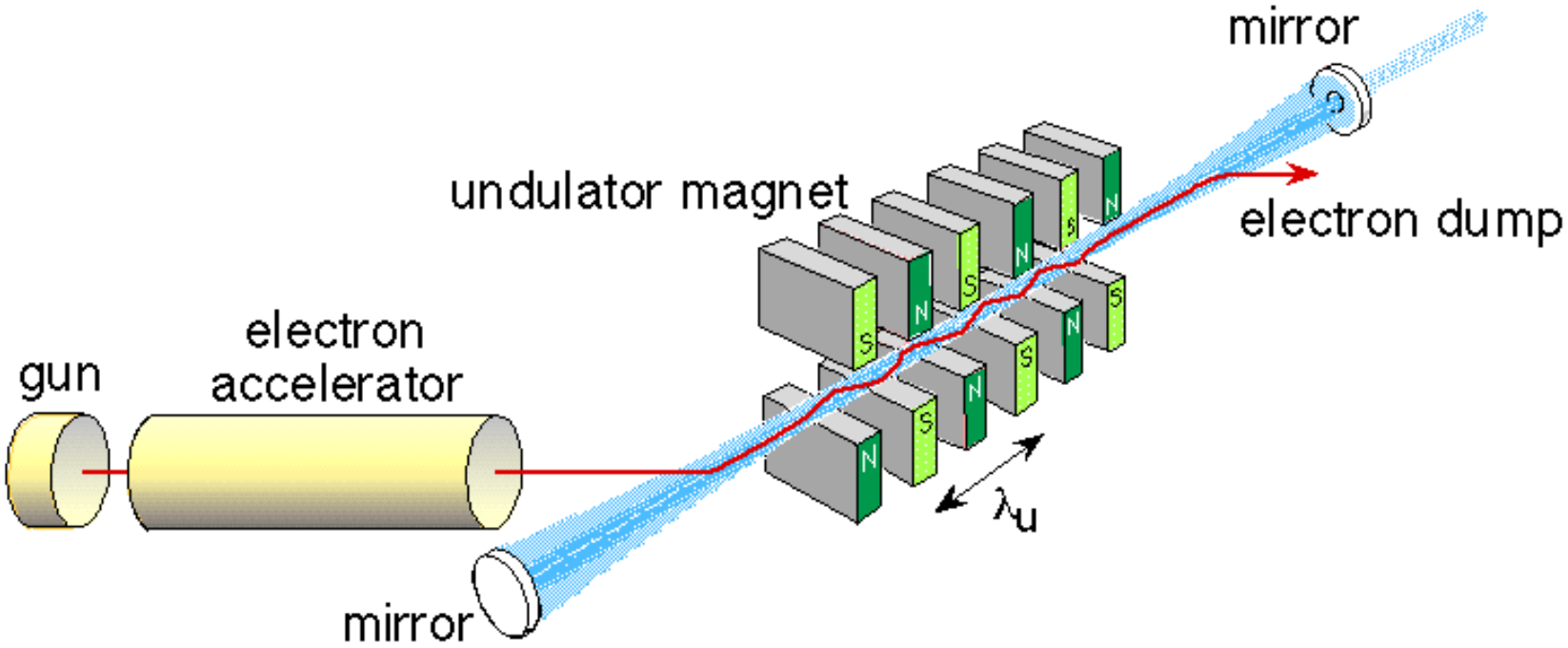


More sensitive and selective:
Mass spectrometric detection of absorption via "Action Spectroscopy"

- Changes of the charge state (ionization)
- Changes of particle mass (dissociation)

➧ **An intense and tunable IR source is needed for the excitation**

Principle of Free Electron Lasers



Wavelength depends on:

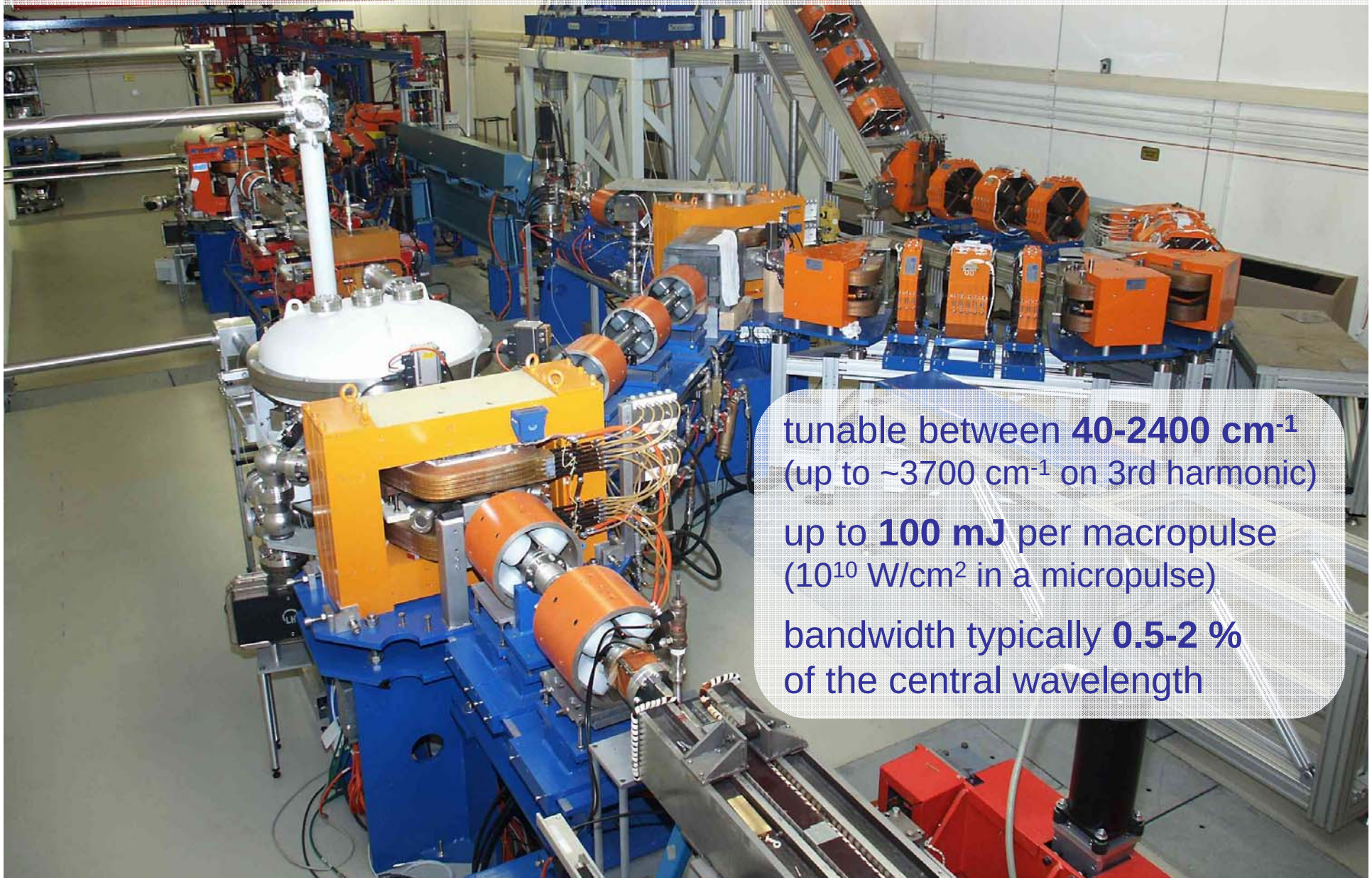
- kinetic energy of the electrons
- Undulator period λ_u
- magnetic field

$$\lambda = \frac{\lambda_U}{2\gamma^2}(1+K^2)$$

$$\gamma = 1 + \frac{E}{m_e c^2}$$

The Free Electron Laser for Infrared eXperiments (FELIX)

FOM Institute for Plasma Physics “Rijnhuizen”, Nieuwegein, The Netherlands

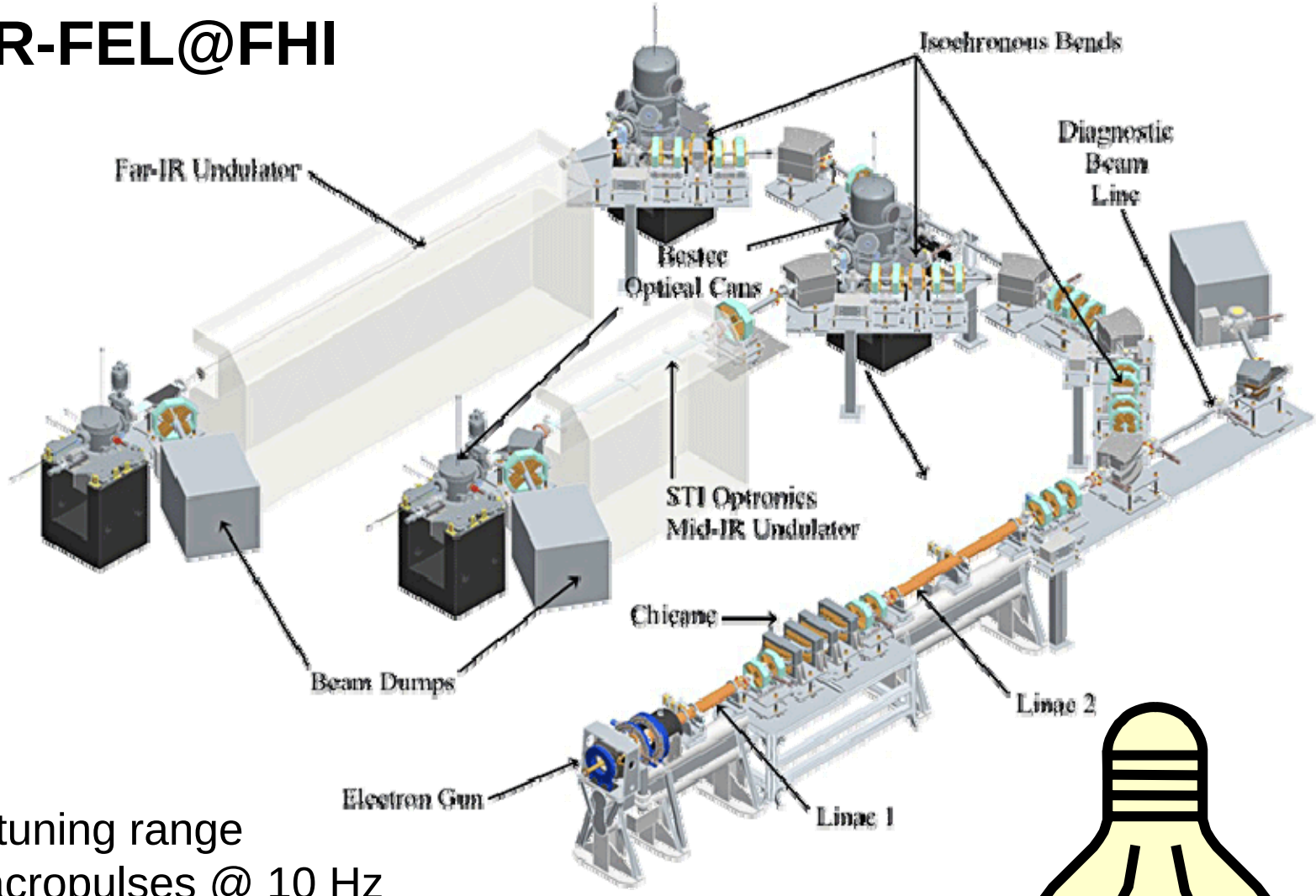


tunable between **40-2400 cm^{-1}**
(up to ~3700 cm^{-1} on 3rd harmonic)

up to **100 mJ** per macropulse
(10^{10} W/cm^2 in a micropulse)

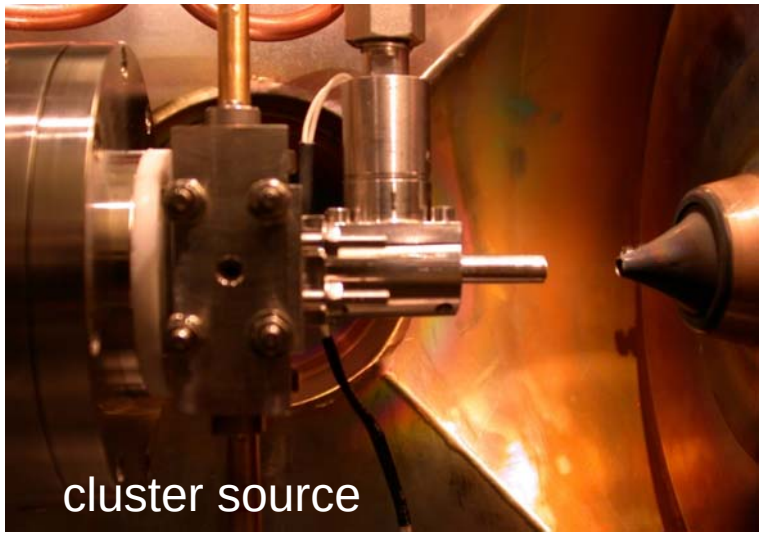
bandwidth typically **0.5-2 %**
of the central wavelength

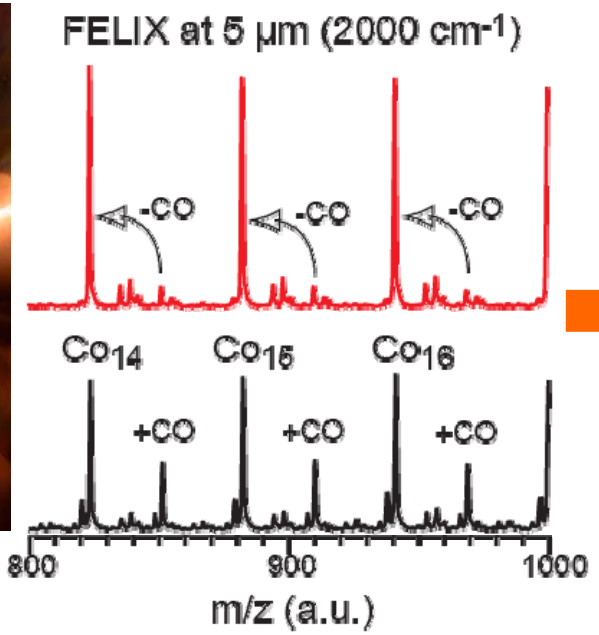
The IR-FEL@FHI

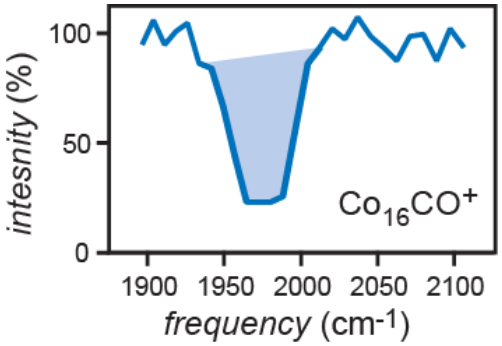


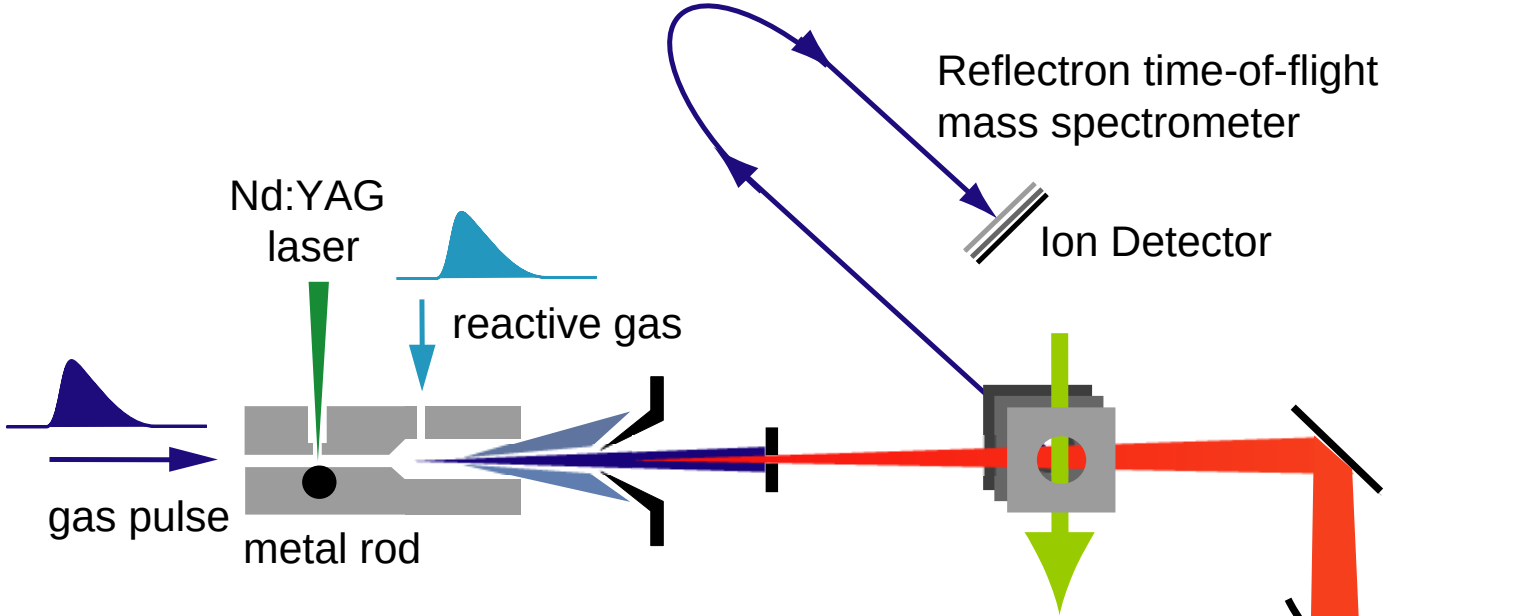
4 – 500 μm tuning range
5 – 10 μs macropulses @ 10 Hz
≈ 100 mJ/macropulse
0.3 – 5 ps micropulses
FT-limited bandwidth
0.3 – 5% of the central frequency

First light
14.02.2012



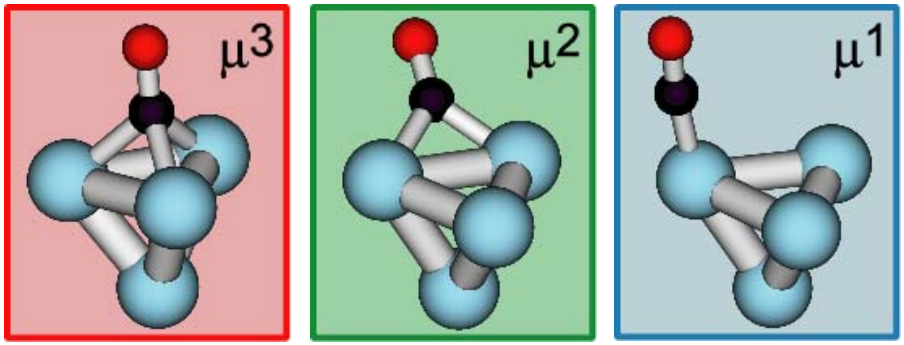




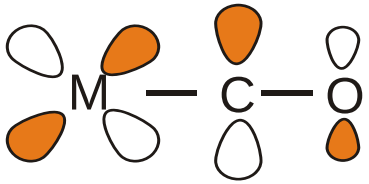


IR Multiple Photon Dissociation (IR-MPD)
Spectroscopy of neutral and charged clusters

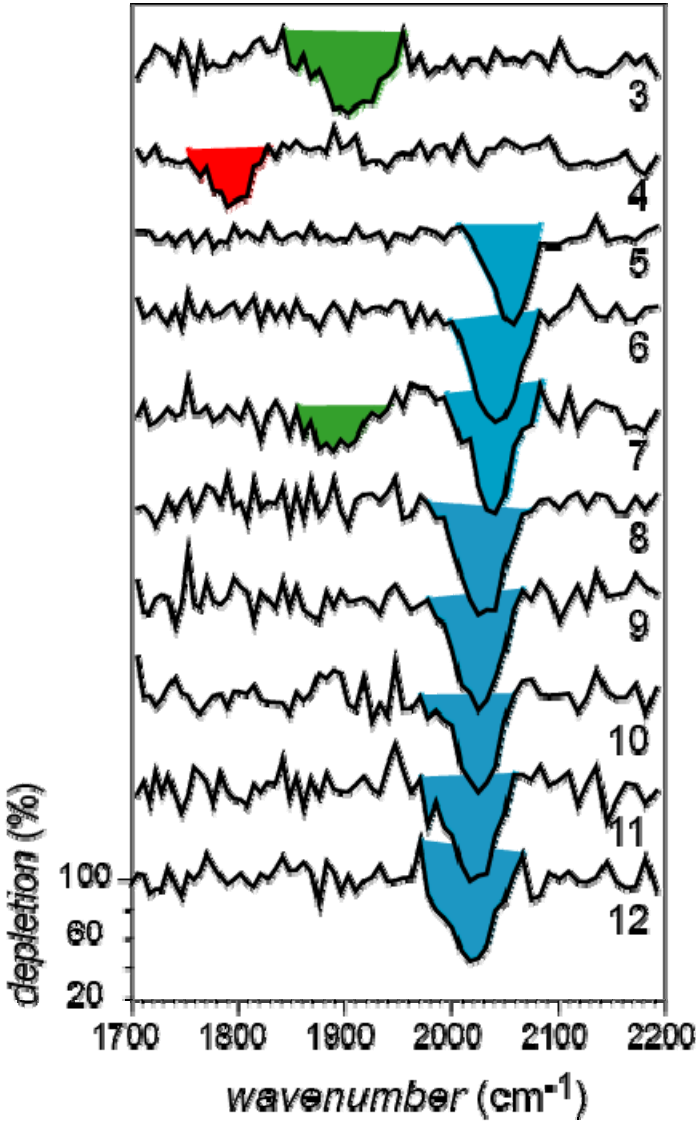
CO at Rh_n^+: Size dependence of the binding site



M(σ)← CO(5σ)
σ donation



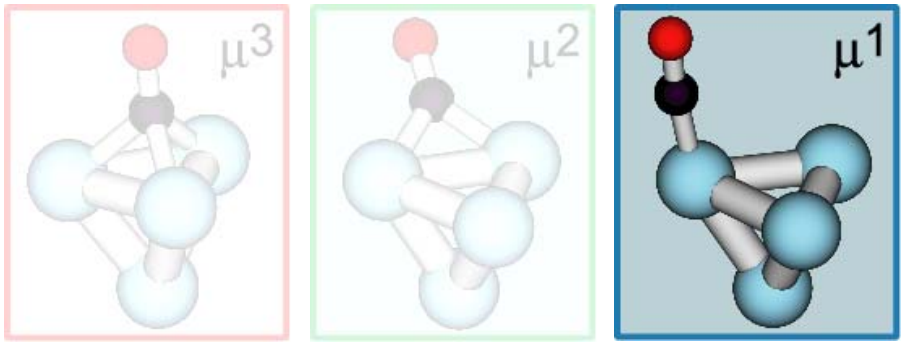
M(δ) → CO(2π)
π back donation



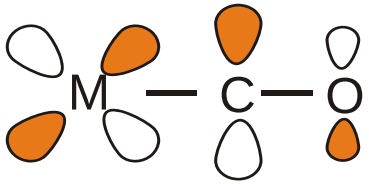
JACS **125** (2003) 15716.
J. Phys. Chem. B **108** (2004) 14591.

Simplifying the CO/Pt(111) puzzle: the cluster case

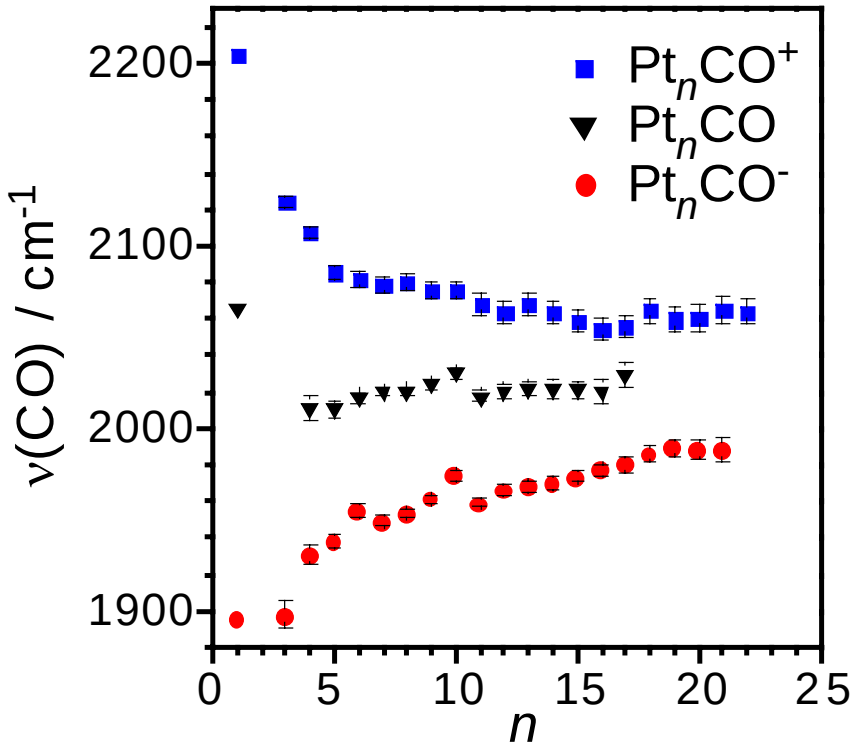
P.J. Feibelman et al. *J. Phys. Chem. B* **105** (2001) 4018



M(σ)← CO(5σ)
σ donation



M(δ) → CO(2π)
π back donation

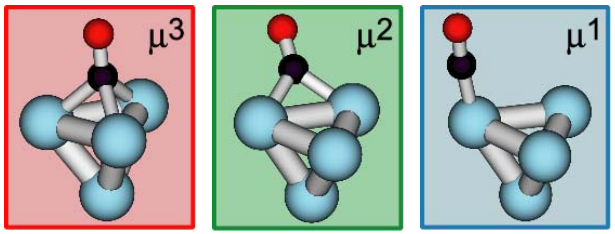


$$\nu(\mathrm{CO}) = \nu_{\infty} + \Delta\nu_{\mathrm{ES}} + \gamma'\frac{z}{n_{\mathrm{S}}}$$

Dependence of ν(CO) for the ionic complexes is mainly due to charge delocalization

PCCP **10** (2008) 6144.

Trends in the binding geometry of CO on transition metal clusters



atop (μ_1) only

21 Sc	22 Ti	23 V C	24 Cr	25 Mn	26 Fe N	27 Co A N C	28 Ni N C	29 Cu	30 Zn
39 Y	40 Zr	41 Nb N	42 Mo	43 Tc	44 Ru A C	45 Rh A N C	46 Pd A C	47 Ag N C	48 Cd
57 La	72 Hf	73 Ta N	74 W N	75 Re C	76 Os	77 Ir N	78 Pt A N C	79 Au A N C	80 Hg

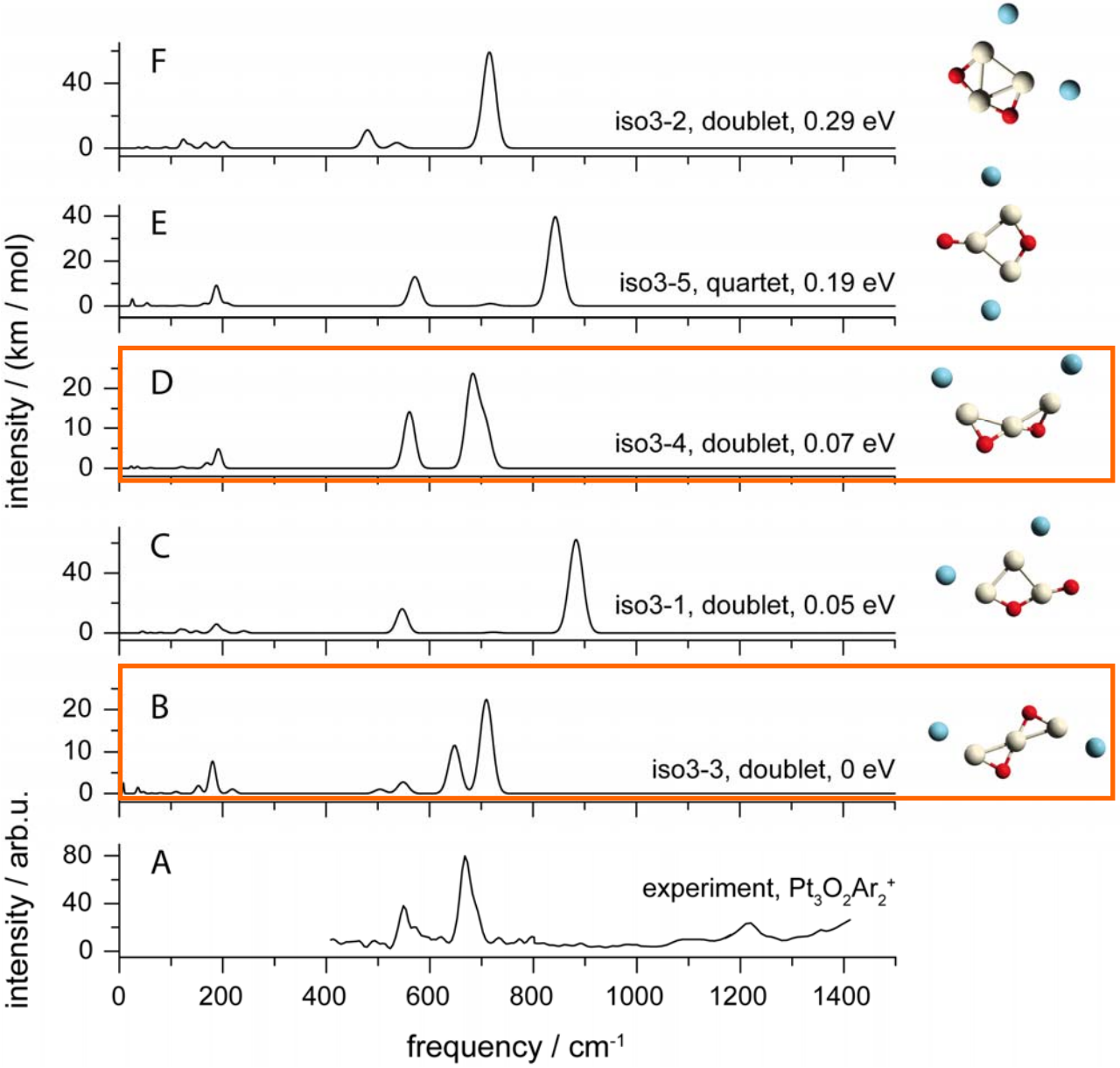
atop (μ_1) and/or bridging (μ_2, μ_3)

Stabilization of atop bound CO for late 5d metals (Ir, Pt) due to relativistic effects

G. Pacchioni, S.-C. Chung, S. Krüger, and N. Rösch, *Surf. Sci.* **392** (1997) 173.

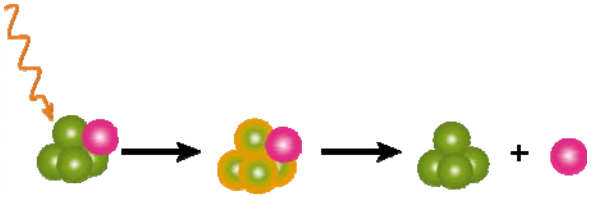
Surf. Sci. **603** (2009) 1427.

Platinum oxide clusters



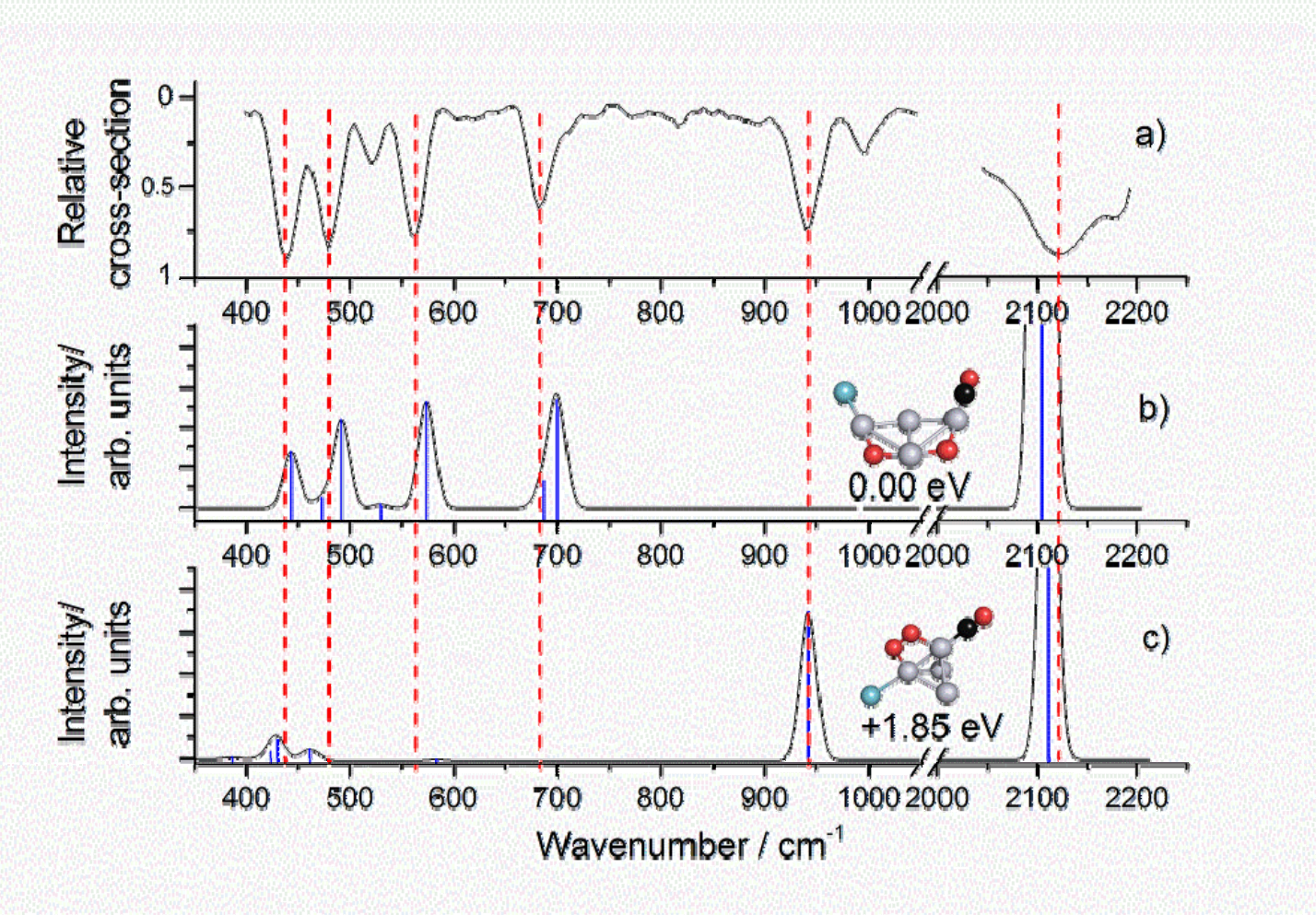
$Pt_3O_2.Ar_2^+$

Ar atoms as ‘inert’ messenger of IR absorption



Structural assignments by comparison with predicted IR spectra using density functional theory

Now, including CO: $Pt_4O_2(CO)Ar^+$

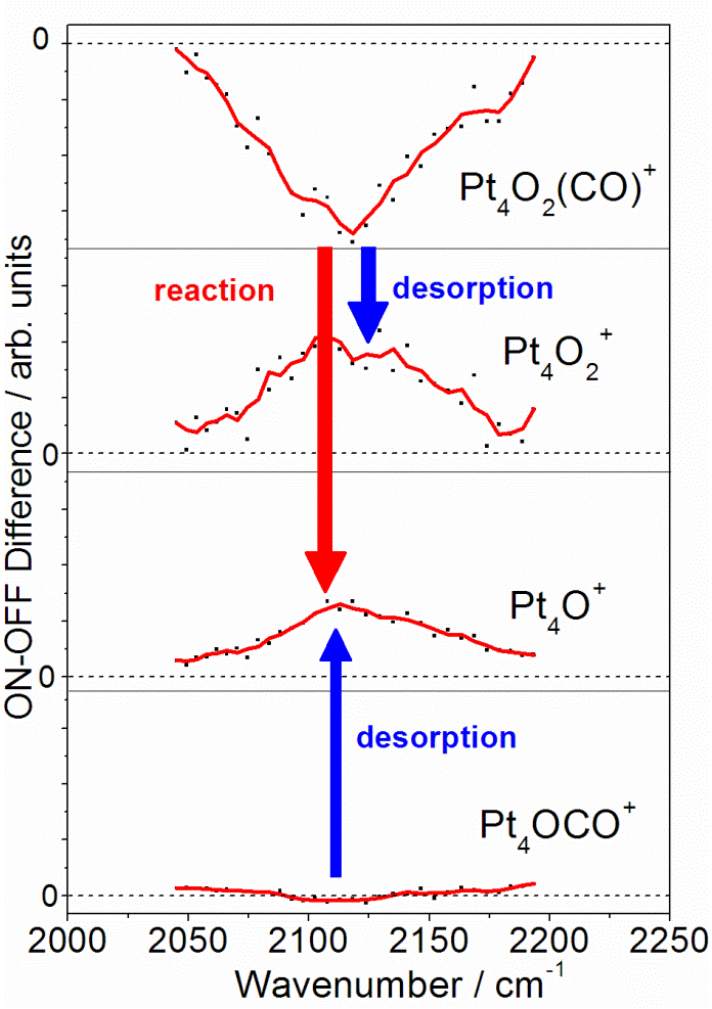


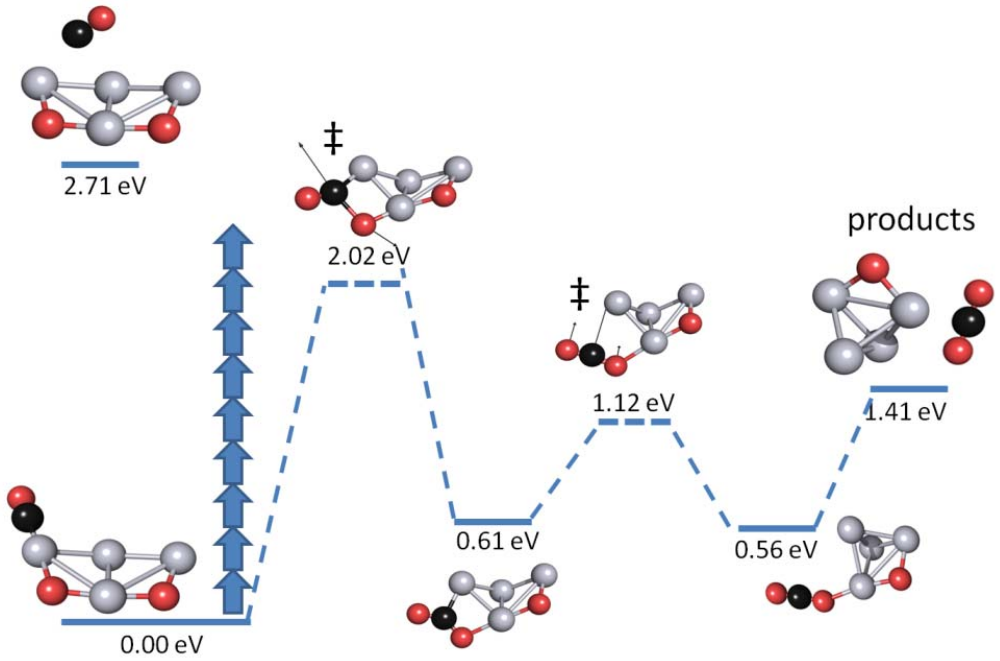
Linearly bound CO molecule

2 isomers: a) with bridging O

b) with an O_2^{2-} (peroxo) unit

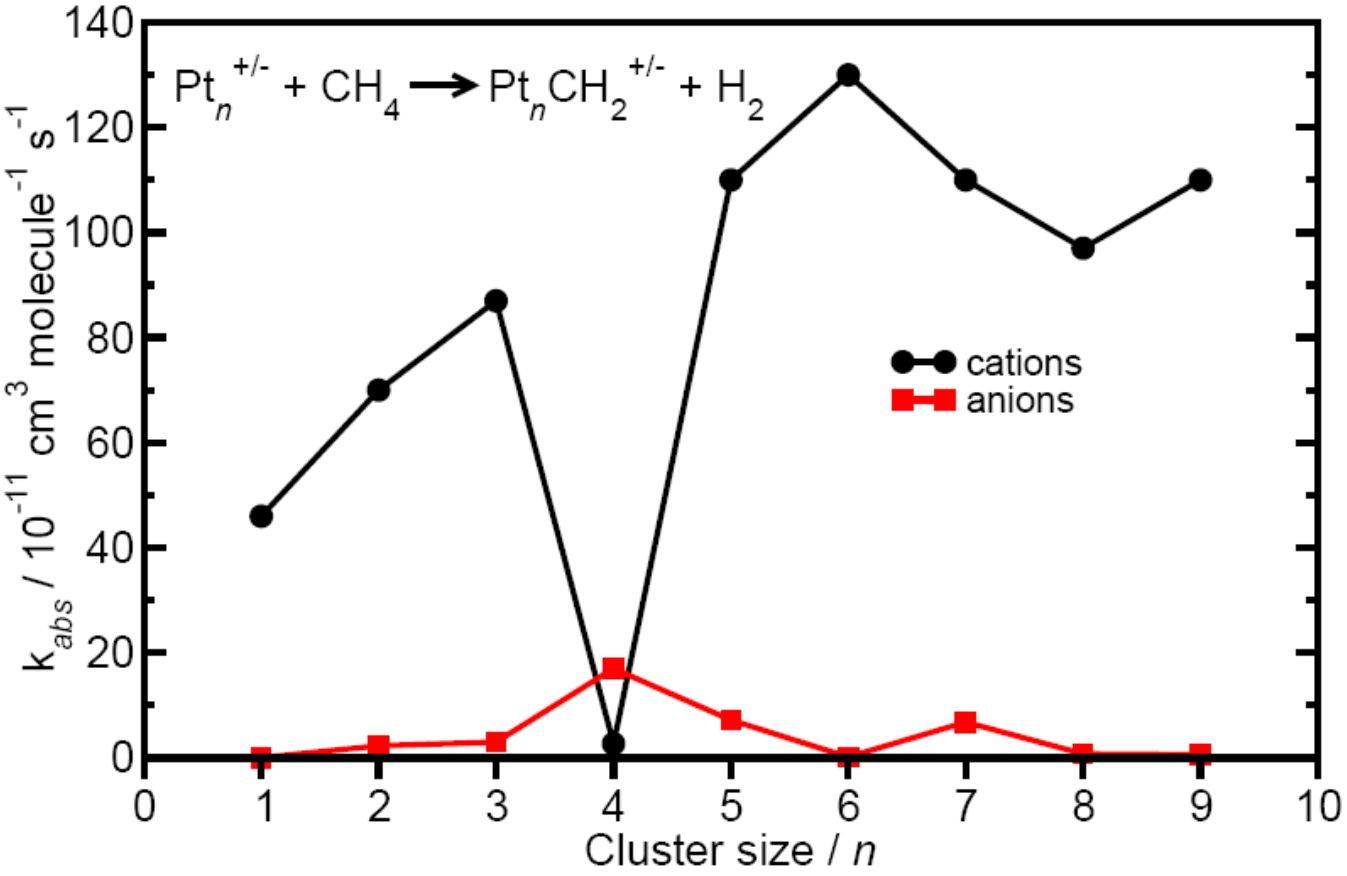
IR heating of the CO complex induces the reaction





possible pathway for formation of CO_2

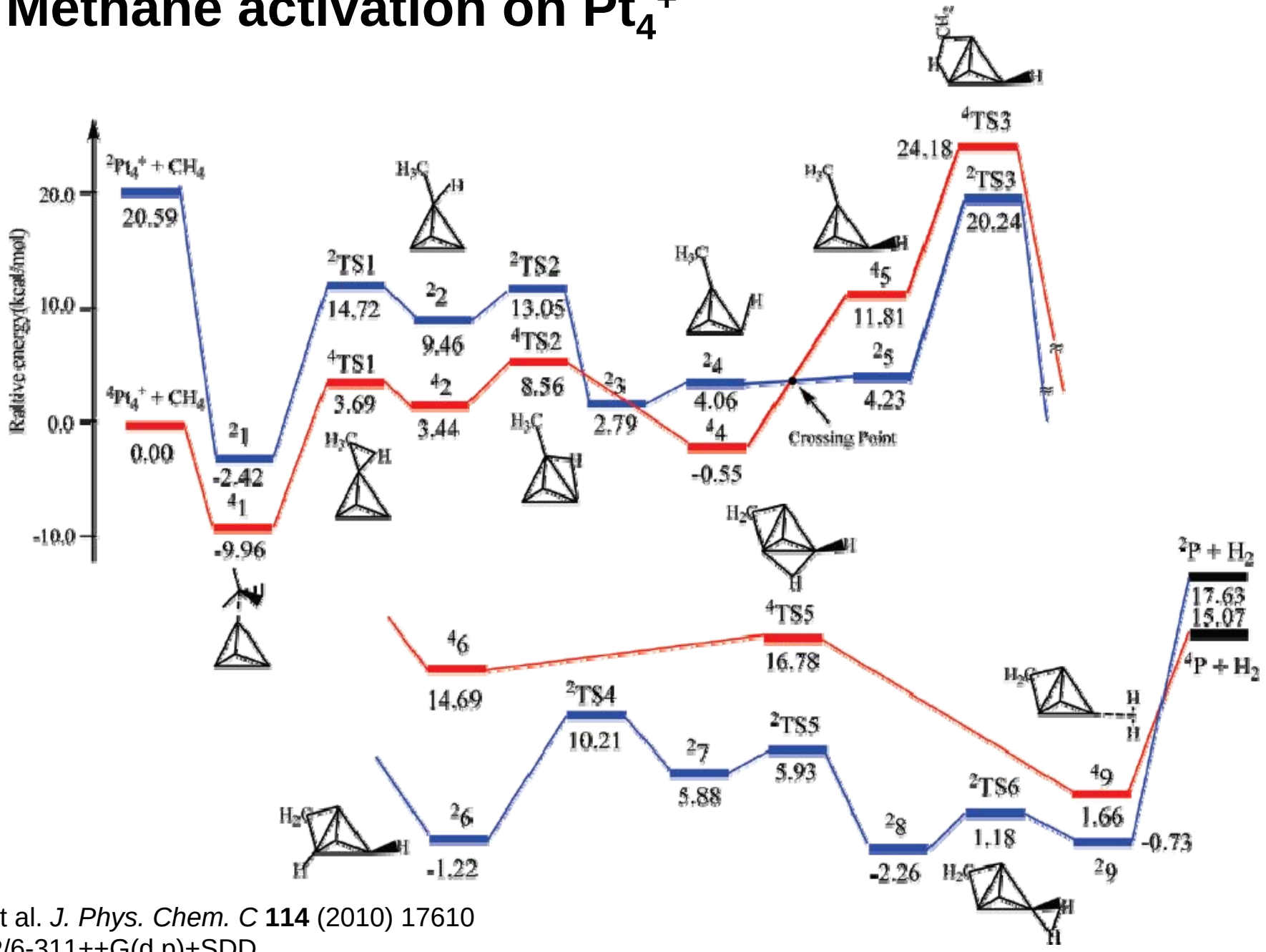
Methane activation on platinum clusters



$$Pt_n^{\pm} + CH_4 \rightarrow Pt_nCH_2^{\pm} + H_2$$

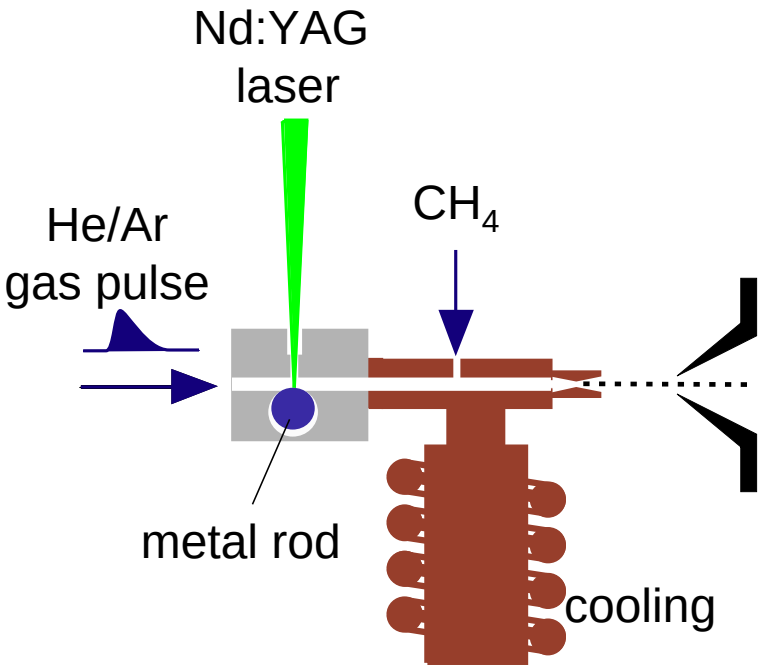
U. Achatz et al. *Chem. Phys. Lett.* **320** (2000) 53.
K. Koszinowski, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **107** (2003) 4999.
G. Kummerlöwe et al., *Int. J. Mass Spectr.* **254** (2006) 183.

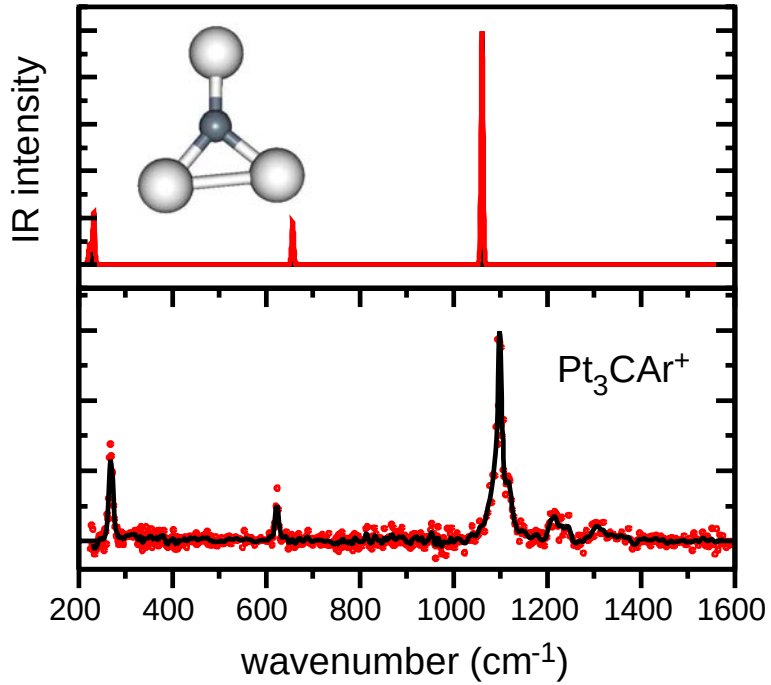
Methane activation on Pt_4^+



L. Lv et al. *J. Phys. Chem. C* **114** (2010) 17610
B3LYP/6-311++G(d,p)+SDD

Experiment I: introducing CH_4 in the reactor

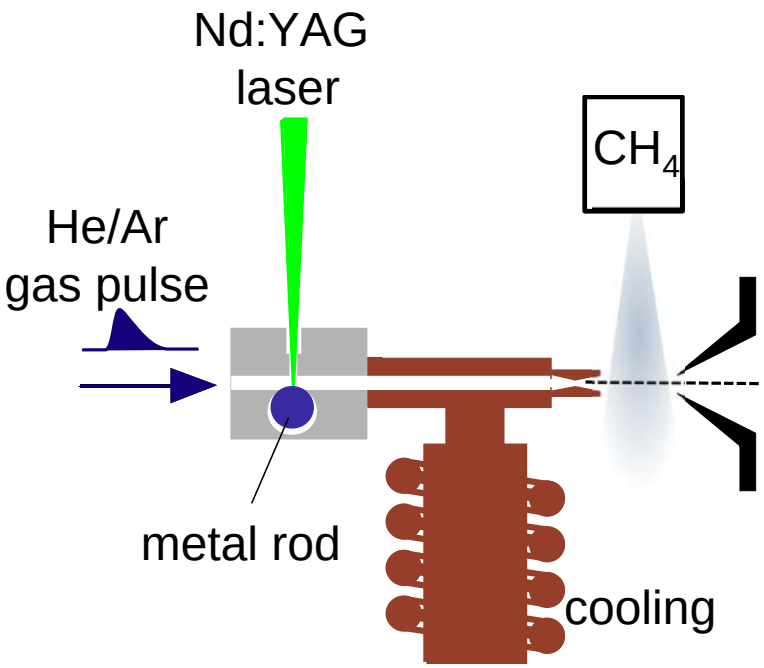




Complete dehydrogenation:

$Pt_n^+ + CH_4 \rightarrow Pt_nC^+ + 2H_2$

Experiment II: CH_4 in a crossed beam



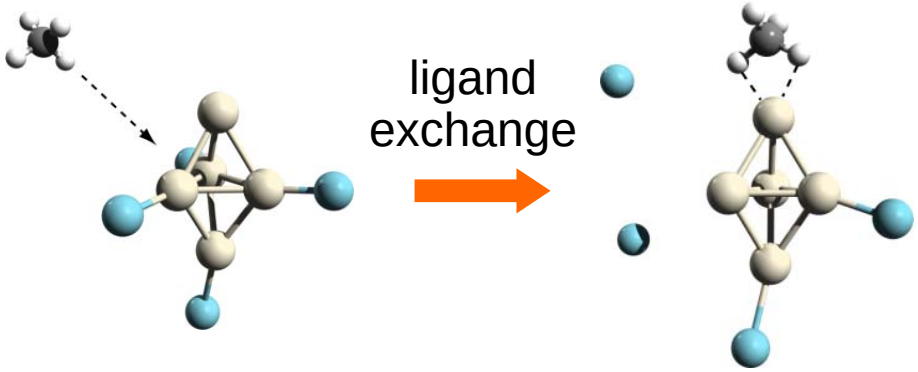
Single collision conditions,
similar to FT-ICR-MS

Pure Pt clusters:

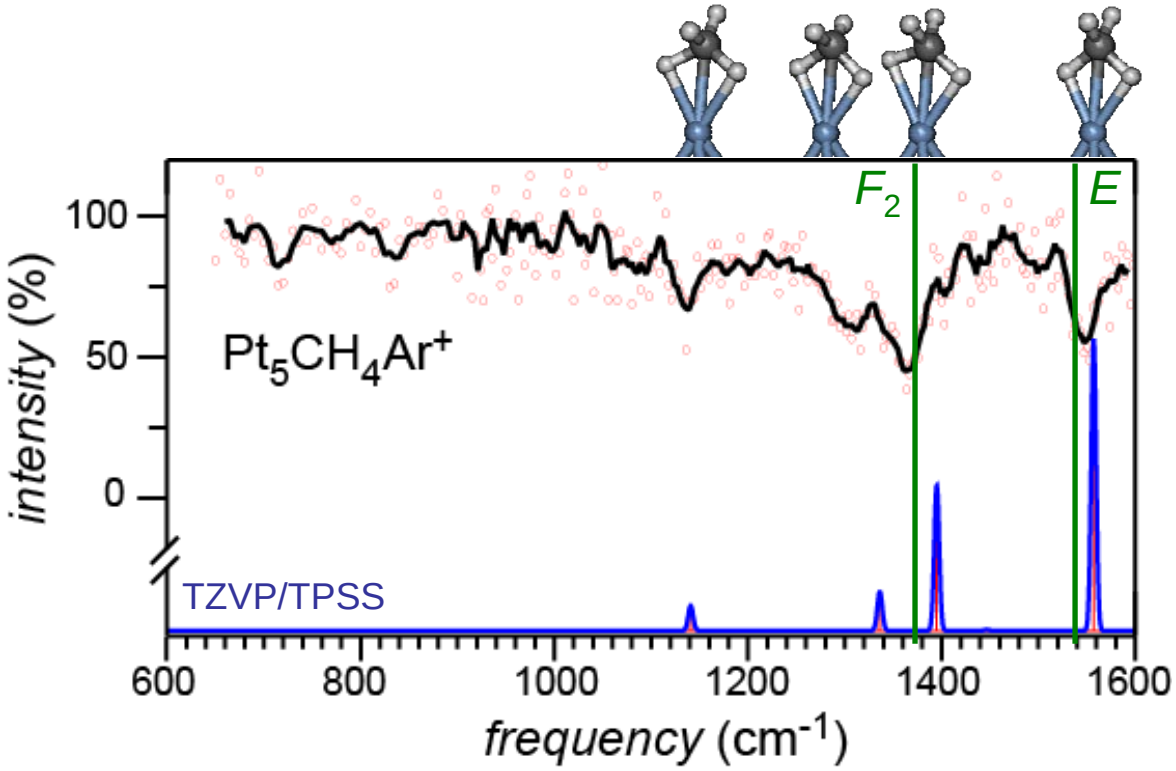
$Pt_n^+ + CH_4 \rightarrow Pt_n[C,2H]^+ + H_2$

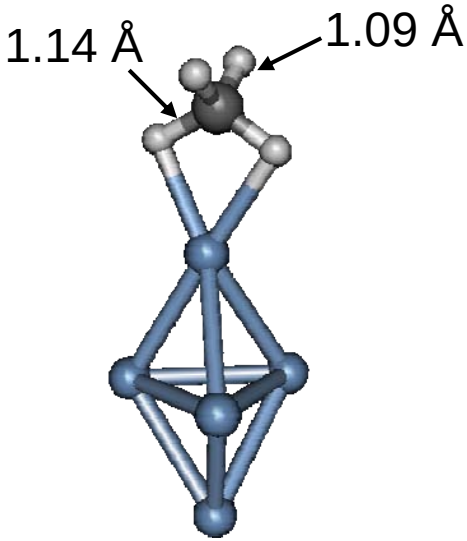
Ar complexes:

$Pt_nAr_m^+ + CH_4 \rightarrow Pt_nAr_{m-p}[C,4H]^+ + pAr$



Complexes of Pt_n^+ with methane





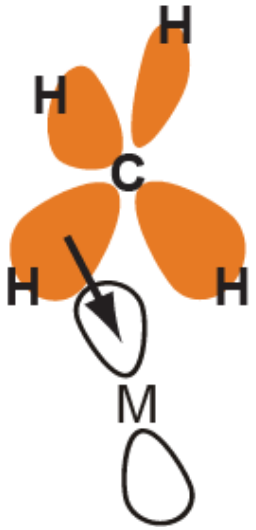
^4A

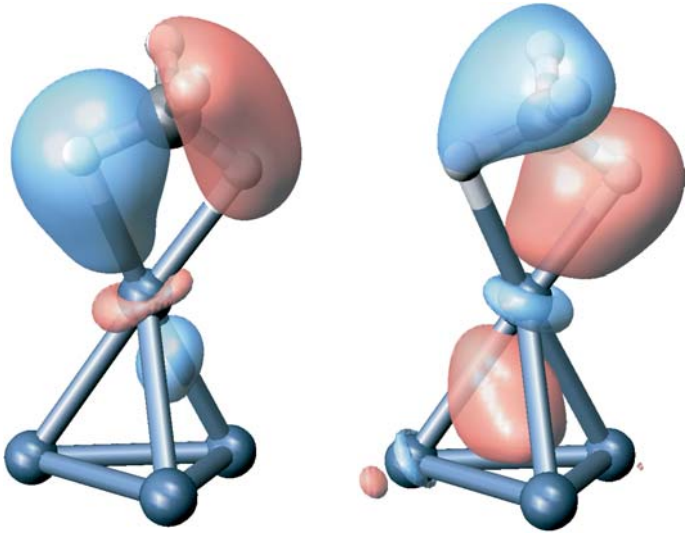
BDE: ~0.8 eV

Strongly bound molecular complex with activated C-H bonds for $Pt_{3,4,5}^+$

Angew. Chem. Int. Ed. **51** (2012) 817.

C–H → Pt binding

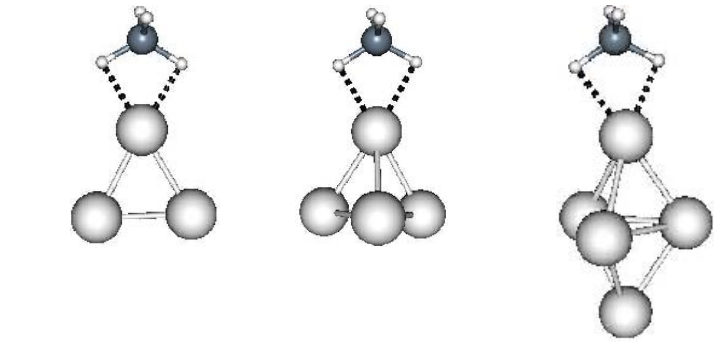


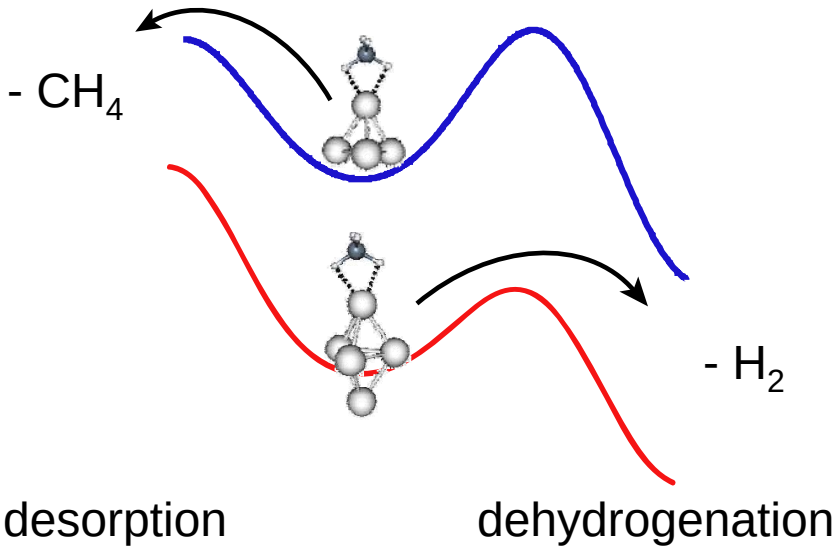


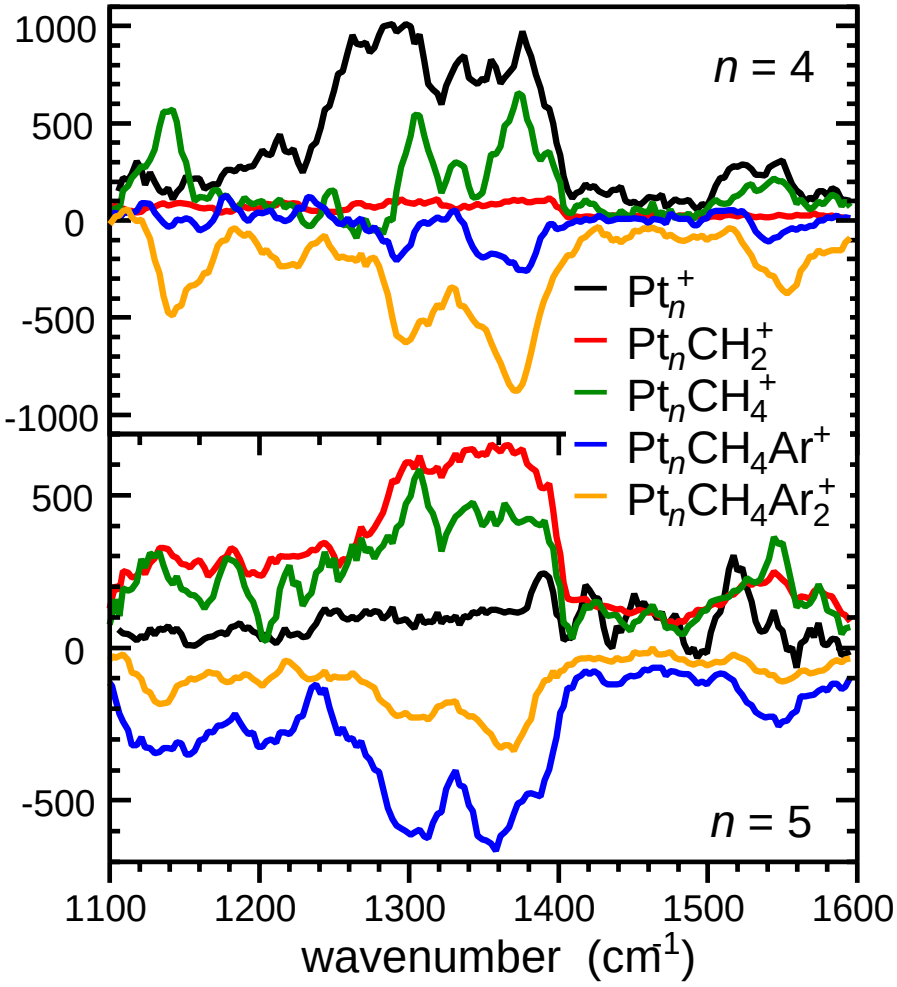
“Agostic” bond: 3-center 2-electron binding

∠C-H-Pt is nearly 90°
Strength is typically 40-60 kJ/mol

Nothing special for Pt_4^+ ?

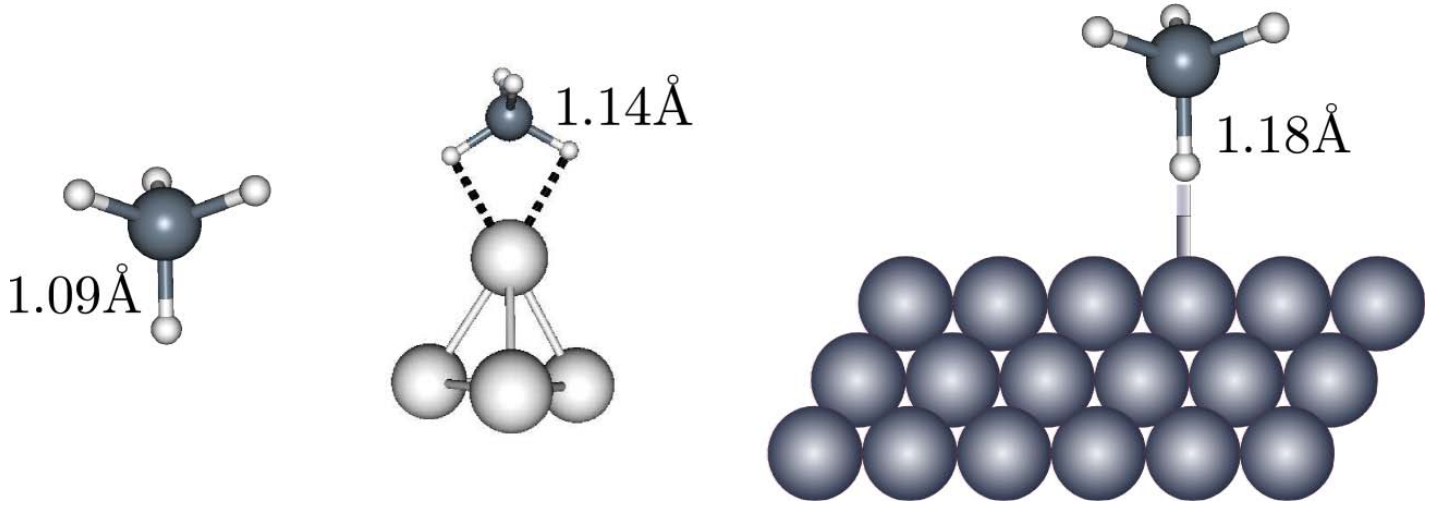






Angew. Chem. Int. Ed. **51** (2012) 817.

Comparison to Pt surfaces



- Different binding motif on extended surface
- C–H bond more activated on surface than cluster

Öström et al., *Phys. Rev. Lett.,* **96** (2006) 146104

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.

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