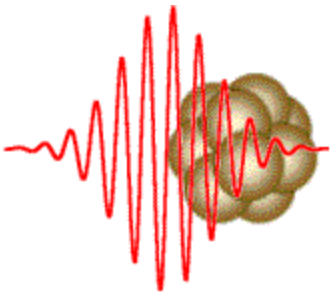


**Photoelectron spectroscopy on Clusters as new material**

The exciting potential of nanotechnology founds on the size-dependent properties of matter. Cluster, which are new materials with a well defined number of atoms, serve as ideal candidates to study size-dependent properties by changing the size of a nanoparticle by just one atomic unit. This makes them unique for tracing the development of chemical and physical properties from the atom to the solid in a continuous manner. Due to the large surface-to-bulk ratio small clusters are particularly attractive for applications in heterogeneous catalysis or as magnetoelectric devices of enhanced magnetic moment. Thus hunting for new nanomaterials and a conceptual understanding of quantum-size effects, clusters are of interest for both fundamental as well as material science. The most famous cluster $C_{60}$ has been discovered in experiments on free carbon clusters of various sizes and its properties are completely different from the ones of smaller and larger clusters, e.g., $C_{59}$ and $C_{61}$, which do not belong to the class of fullerenes. In contrast to normal carbon cluster the fullerenes are enormous stable ("magic") and after the discovery of $C_{60}$ it has been proposed immediately as building block for a new kind of bulk carbon material with new properties, e.g. $C_{60}$-based transistors and superconductors. Today this new material called "fullerit" is commercially available.

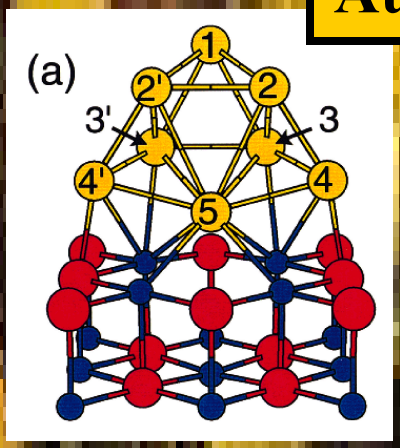
Nevertheless, there are large and systematically blank areas in cluster physics with respect to the geometry and electronic structure. In order to study the intrinsic properties of clusters a mass-selected exploration of isolated gas phase clusters is obligatory. However, mass selection extremely reduces the target densities which are by 5-7 orders of magnitude smaller than in comparable experiments on stable molecules. Only an extraordinary machine, such as a free electron laser, has sufficient brillance, wavelength range and temporal resolution to get insight into the inner electronic structure of mass-selected clusters. For the first time this will provide unique structural, chemical, magnetic and dynamical information of monodisersed clusters in a similar way as it has been achieved for surfaces and adsorbates with synchrotron and ultrafast laser radiation in the past.

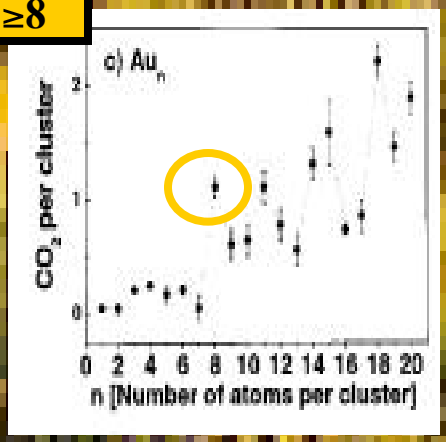
# Photoelectron spectroscopy on clusters as new materials

M. Neeb, N. Pontius, W. Eberhardt, BESSY GmbH, Berlin
former coworkers: G. Lüttgens, P.S. Bechthold, FZ-Jülich

## *Gold clusters as new catalysts:*

**$Au_{\geq 8}$**

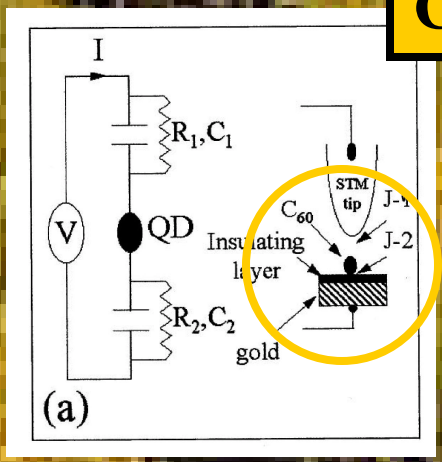


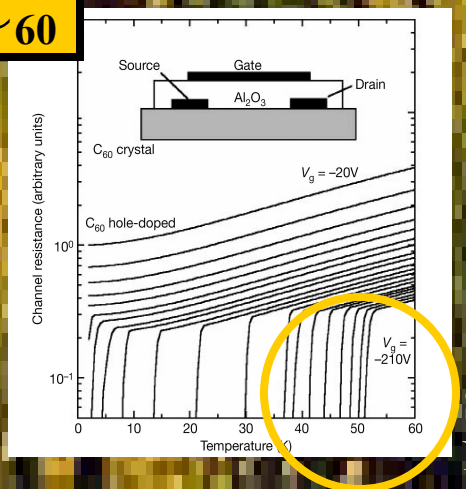




A. Sanchez et al., JCP A 103,(1999).

## *Fullerenes as new SET and SC:*

**$C_{60}$**



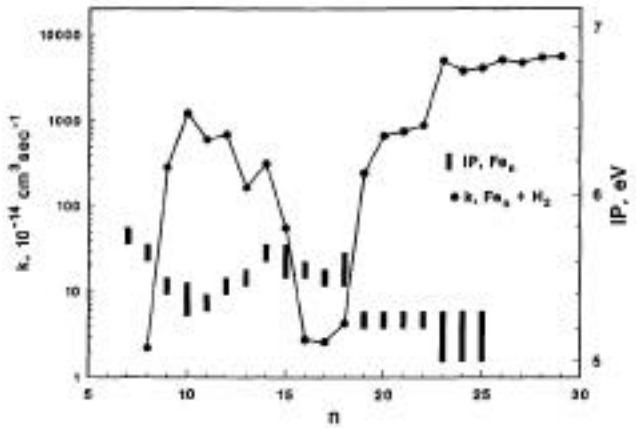




D. Porath et al., PRB 56, (1997).

Schön et al., Nature 408 (2000).

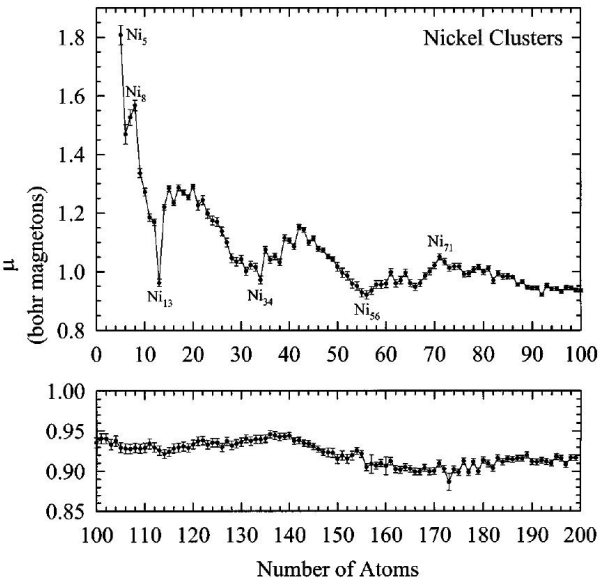
# *Each atom counts!*

## **Reactivity** ($Fe + H_2$)



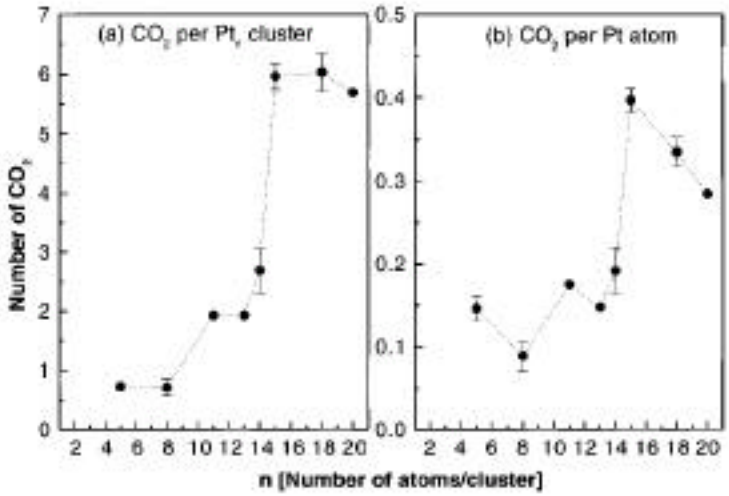

Parks *et al*.,
JCP **88** (1988)

## **Magnetism** ($Ni_n$)



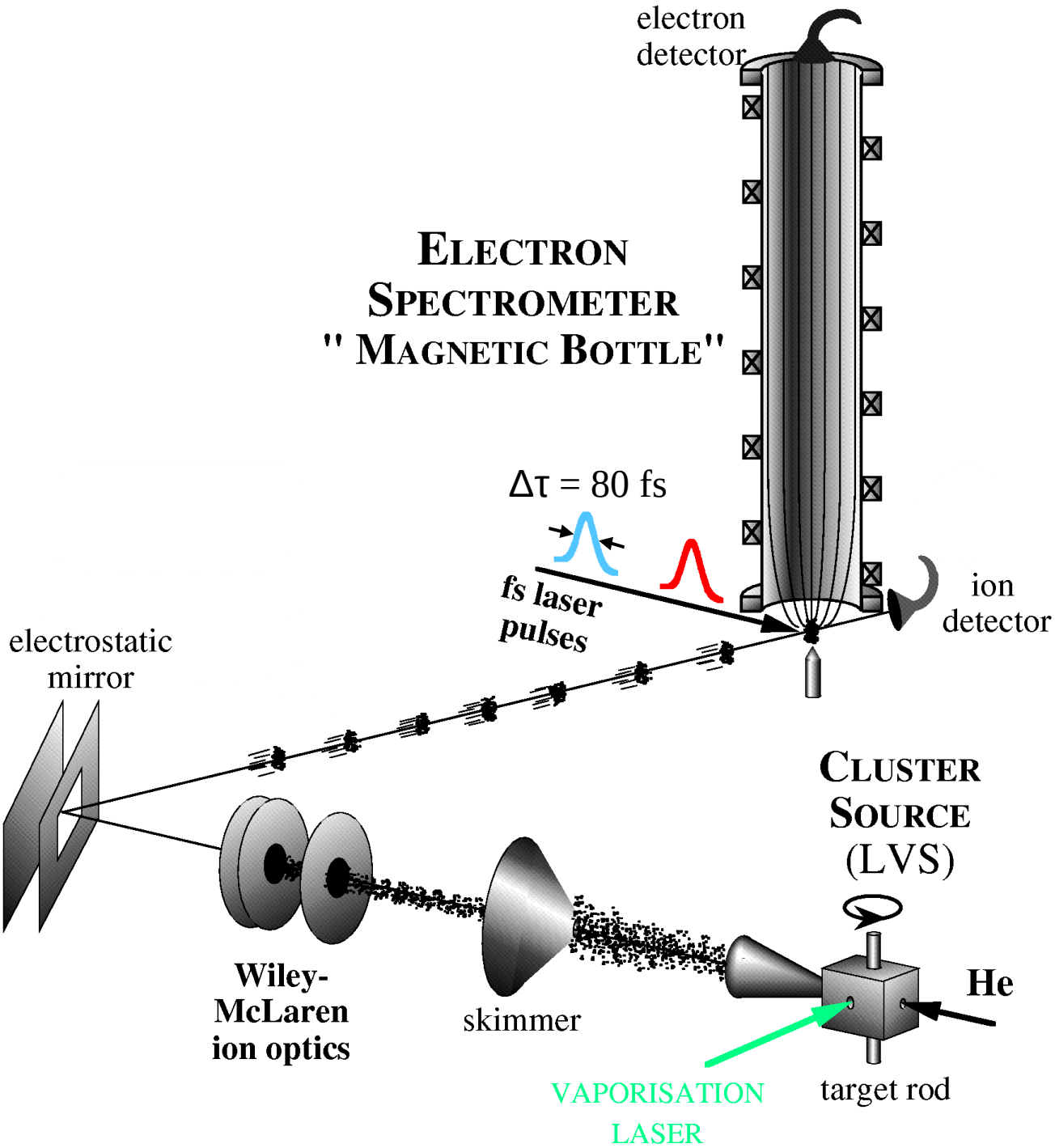

Apsel *et al*.,
PRL **76** (1996)

## **Catalysis** ($Pt_n$)




Heiz *et al*.,
JACS **121** (1999)

# experimental setup

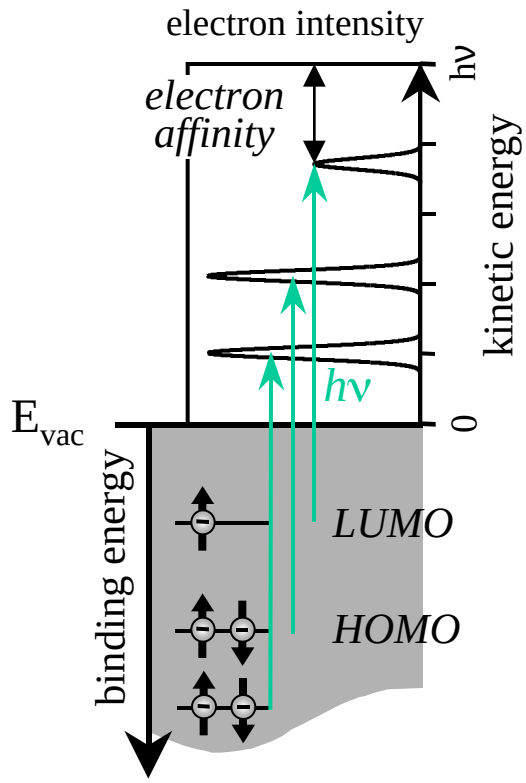



N. Pontius et al., APB 71, 351 (2000).

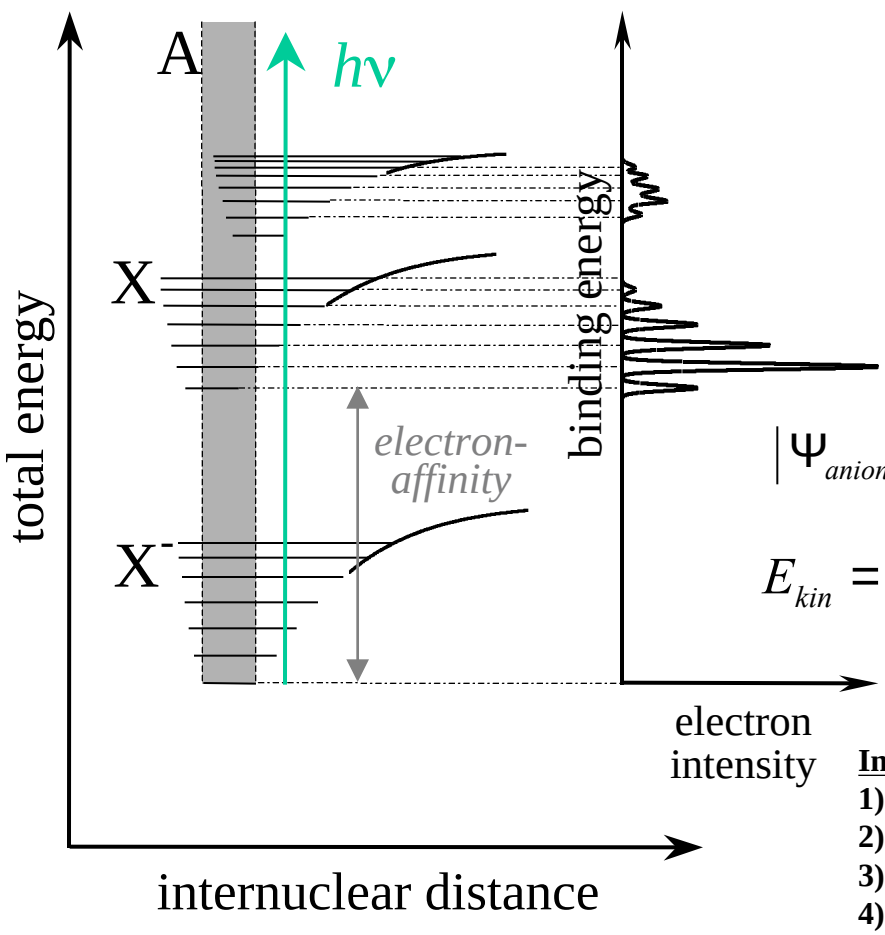
# anion photoelectron spectroscopy

- ***single particle picture:***

$$\left|\varepsilon_{orbital}\right| = E_{bind} = h\upsilon - E_{kin}$$




- ***transition between electronic states:***




$$\left|\Psi_{anion}\right\rangle \blacklozenge \left|\Psi_{neutral}\right\rangle \left|\Psi_{electron}\right\rangle$$

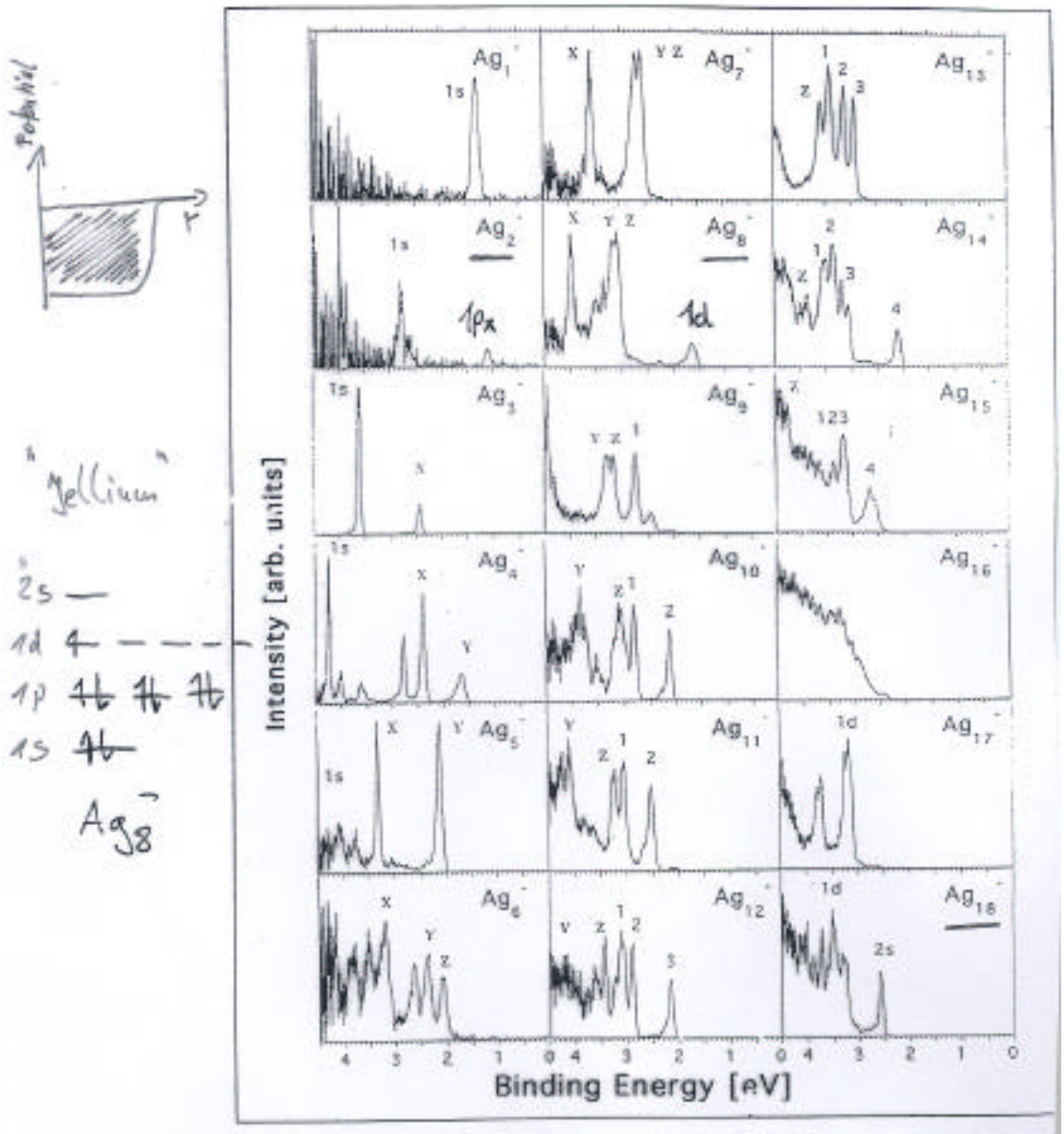
$$E_{kin} = h\upsilon - (E_{\Psi_{anion}} - E_{\Psi_{neutral}})$$

**<u>Information from Anion-PES</u>**

**1) valence electron structure („DOS“)**
**2) HOMO-LUMO gap („band gap“)**
**3) electron affinity („work function“)**
**4) vibrational frequency („phonons“)**
**5) dynamics (nuclear, electron)**

# Photoelectron Spectra of $Ag_n^-$

(C.Y. Cha, PhD Forschungszentrum Jülich GmbH)




"Jellium"

2s —

1d ↑ — — —

1p ↑↓ ↑↓ ↑↓

1s ↑↓

$Ag_8^-$

H. Handschuh et al. JCP 102, 6406 (1995)

# Open d-shell metal: $Ti_n^-$

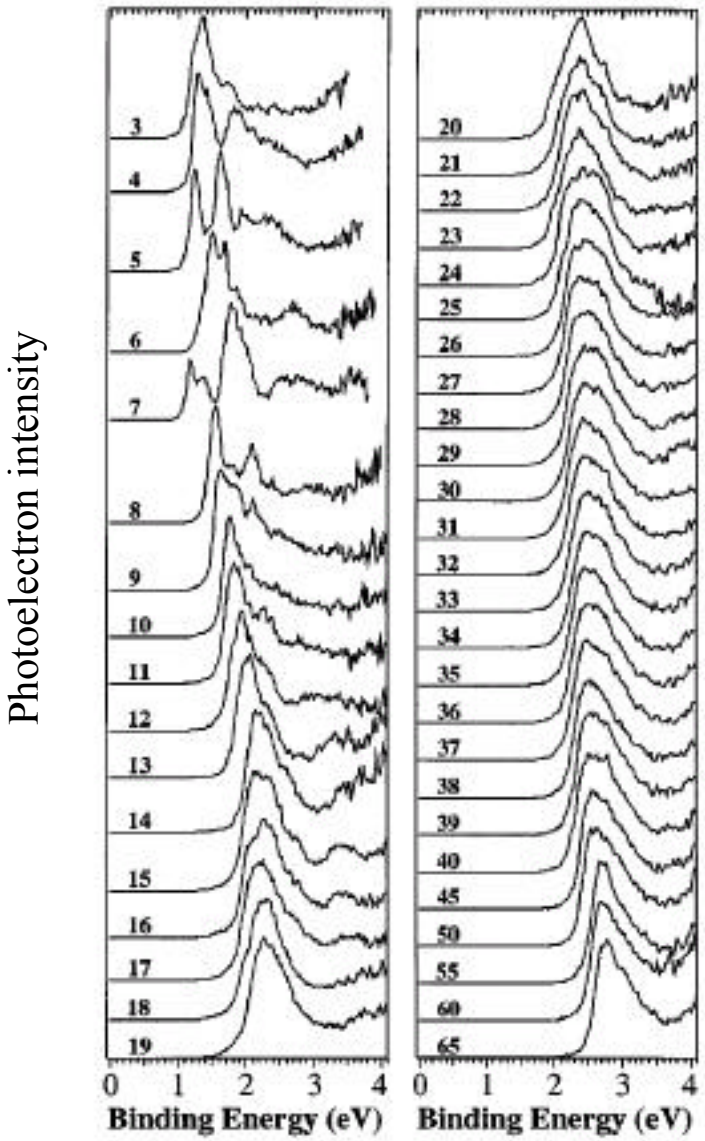
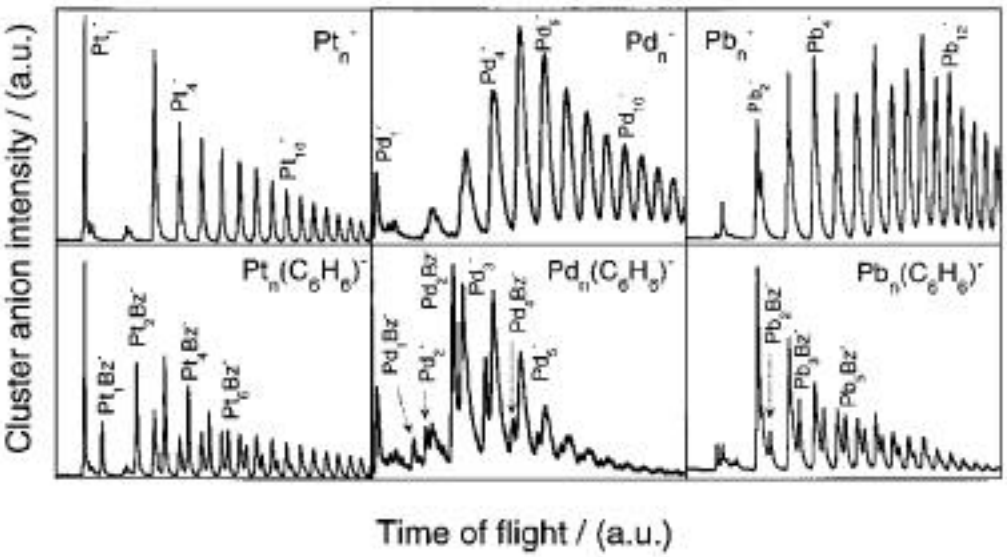



FIG. 1. Photoelectron spectra of size-selected $Ti_n^-$ ($n$ = 3−65) clusters at 4.66 eV detachment energy. Note the change from $n$ = 7 to 8 and the spectral similarity thereafter.

L.S. Wang *et al*., PRL **76**, 215 (1996)

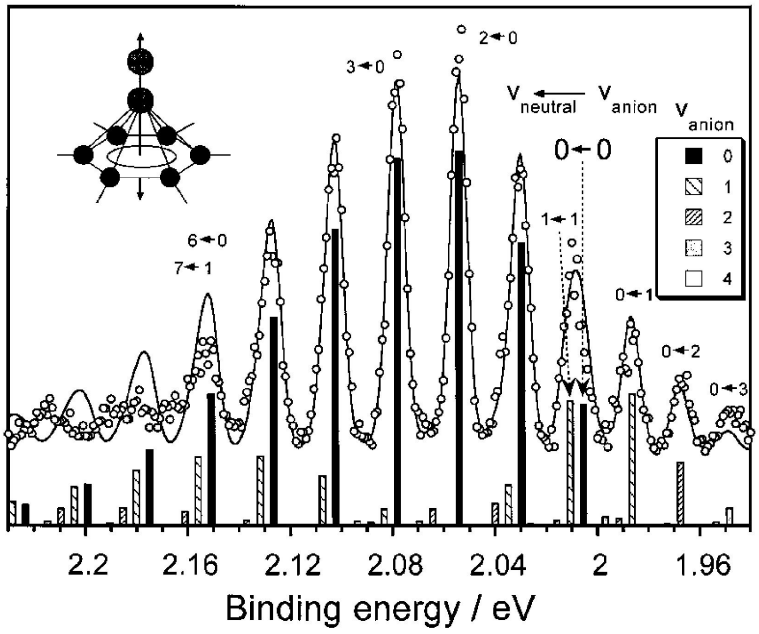
# Mass spectra of benzene-adsorbed metal clusters

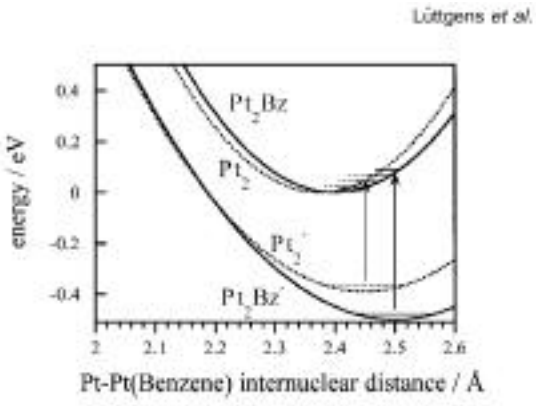



G. Lüttgens *et al*., JCP114, 8414 (2001)

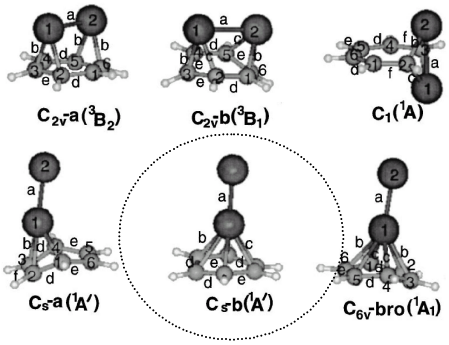
# Vibrationally-resolved PES: $Pt_2(C_6H_6)^-$

8416 J. Chem. Phys., Vol. 114, No. 19, 15 May 2001




10302 J. Chem. Phys., Vol. 114, No. 23, 15 June 2001




Majumdar *et al*. JCP 114, (2001)

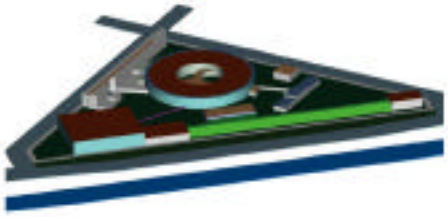
MP2 and DF
Group of Balasubramanian

# Missing information

- core orbitals (ESCA analysis)
- unoccupied level density (NEXAFS, EXAFS)
- adsorbate o rbitals
- d-orbitals of transition metals
- f-orbitals of lanthanoids

**Pulse energy: 1 mJ**
**Repetition rate: 1 kHz-10 kHz**
**Photon energy: 10 eV-1 keV**
**Width: 200 fs (20 fs)**

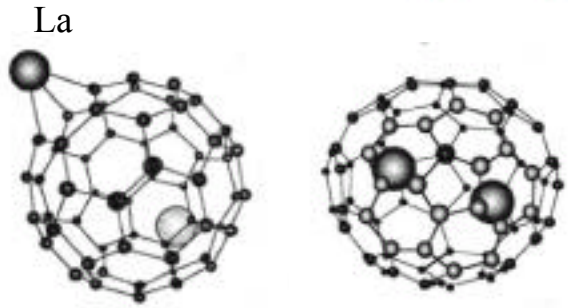
**The BESSY SASE-FEL in Berlin-Adlershof**



## *Using ESCA (Xray FEL) to distinguish between:*

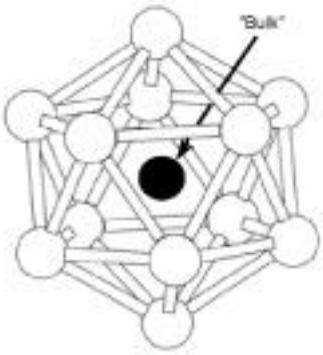
**1) isomers**

**$Pt_3$**



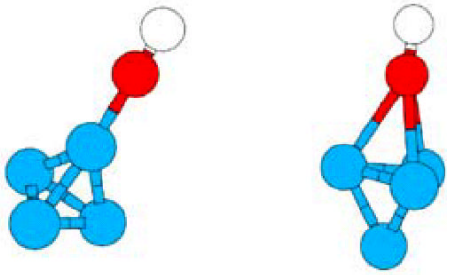

**doped fullerenes**

**2) surface-bulk atoms**



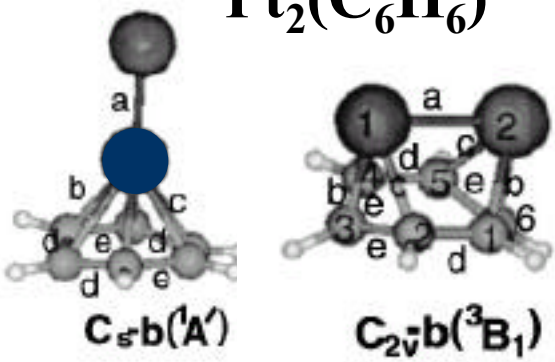

**$Al_{13}$**

**3) adsorption geometry**



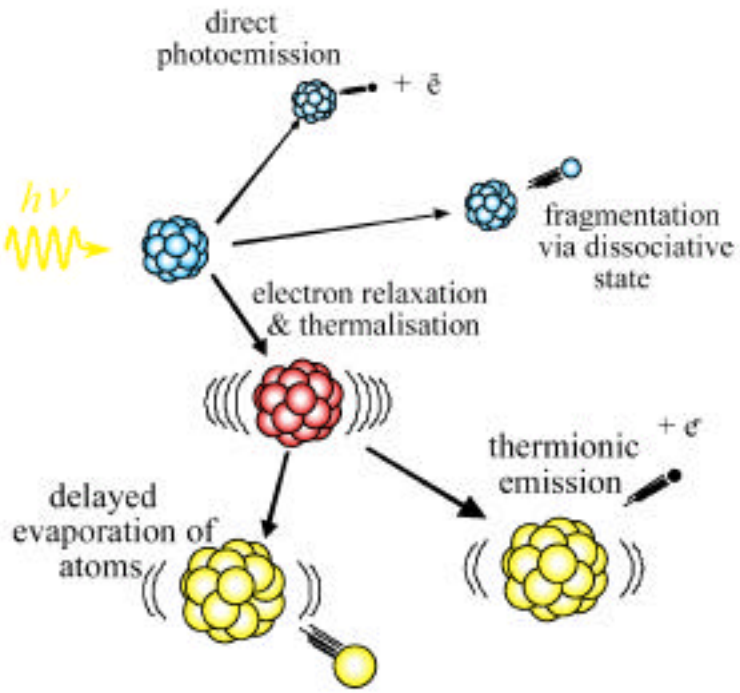
**$Ni_4(CO)$**

**$Pt_2(C_6H_6)$**

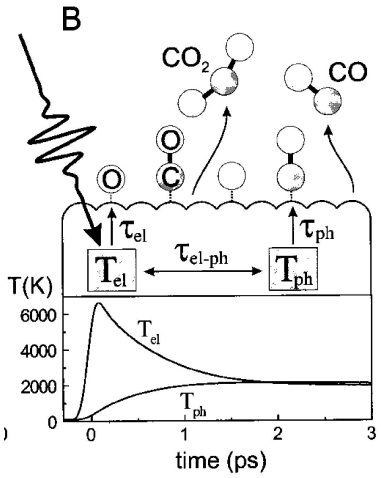



Majumdar *et al*., JCP 114, 10300 (2001)

# Fs-dynamics in clusters probed by pump-probe PES

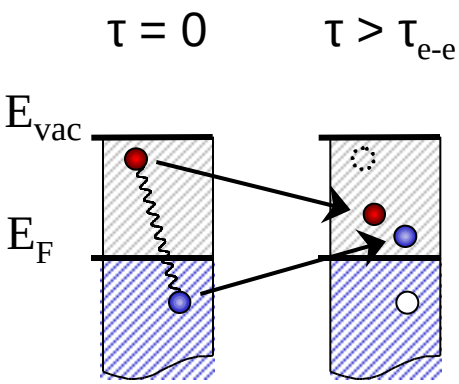



N. Pontius *et al*., JESRP 106 (2000).



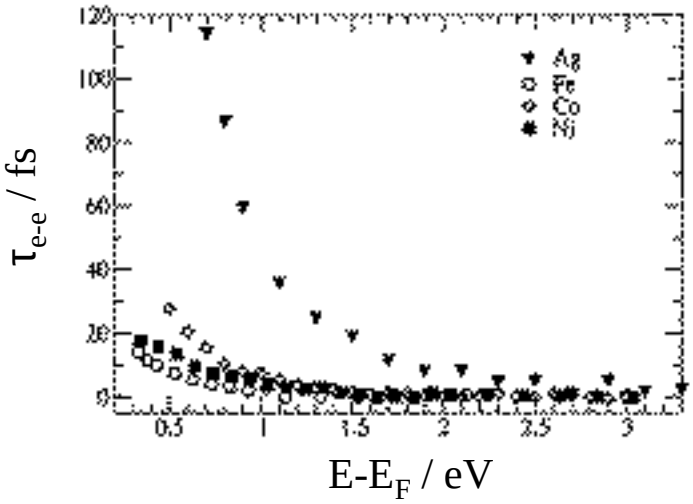

M. Bonn *et al*., Science 285 (1999).

# $e^-$-$e^-$- scattering in bulk metals

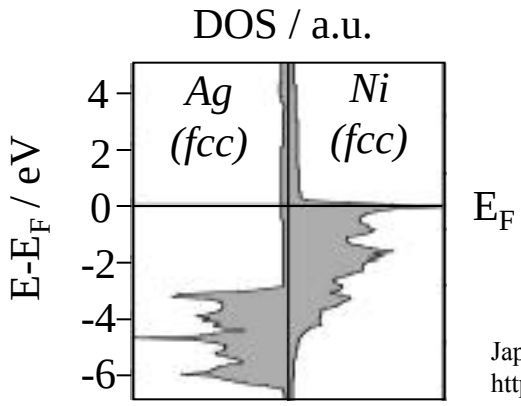



- ***$e^-$- $e^-$ - interaction***
  (Coulomb screening)
- ***DOS around $E_F$***

} $\tau_{e\text{-}e}$

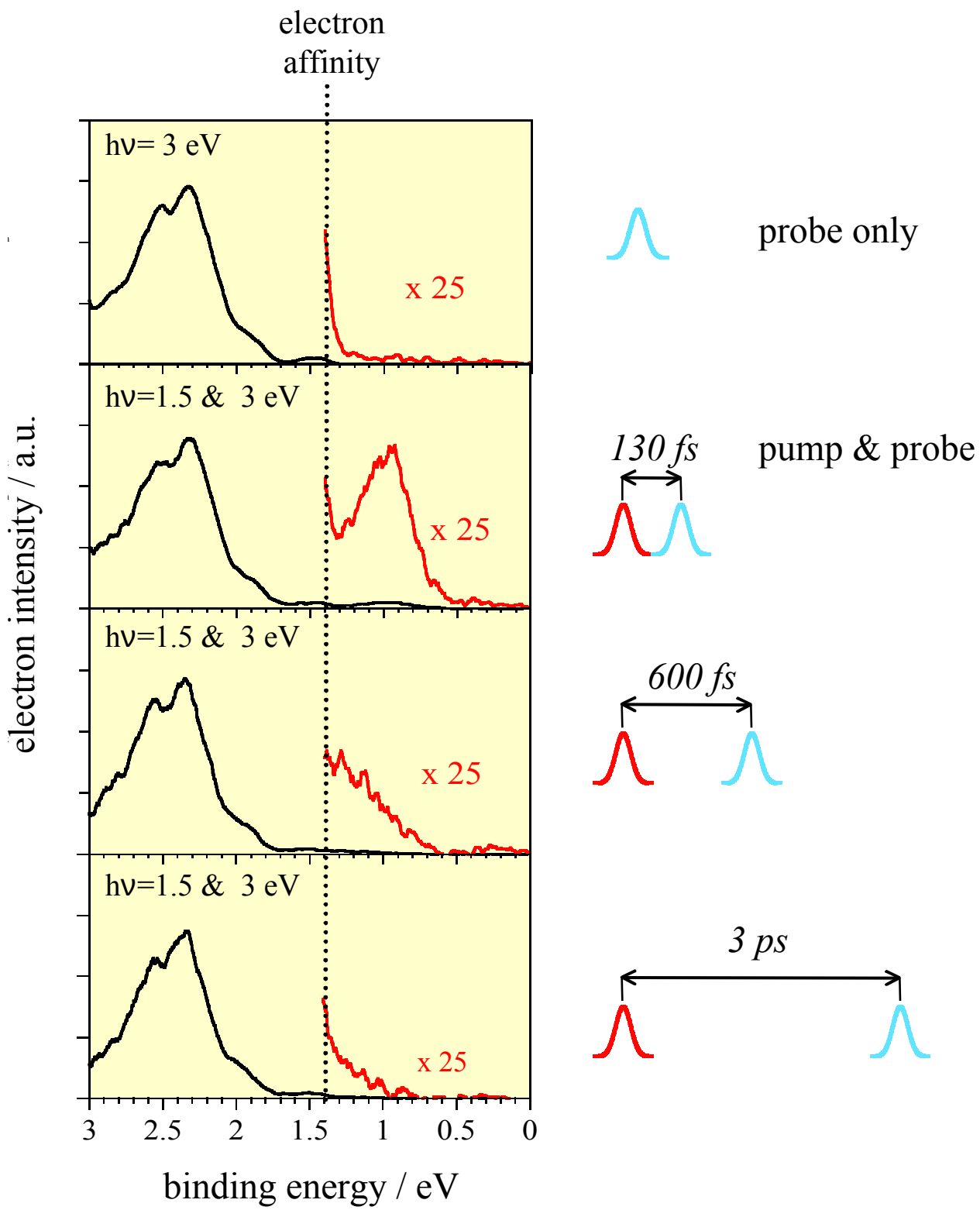



R. Knorren et *al.*,
Phys. Rev. **B 61**, 9427 (2000)



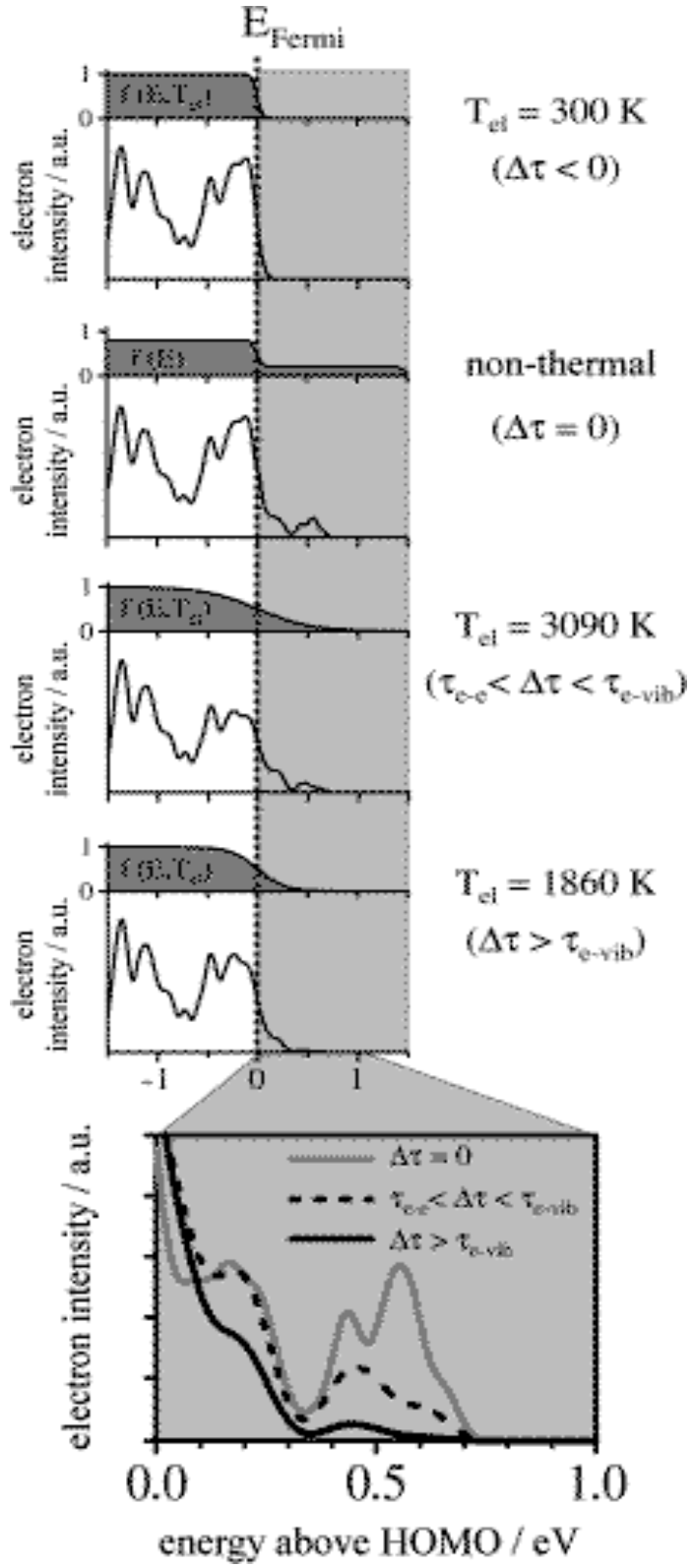

Japan Science and Technology Corporation
http://who.tokyo.jst.go.jp/CALDB/index.html

# optical excitation and electronic relaxation in $Ni_3^-$



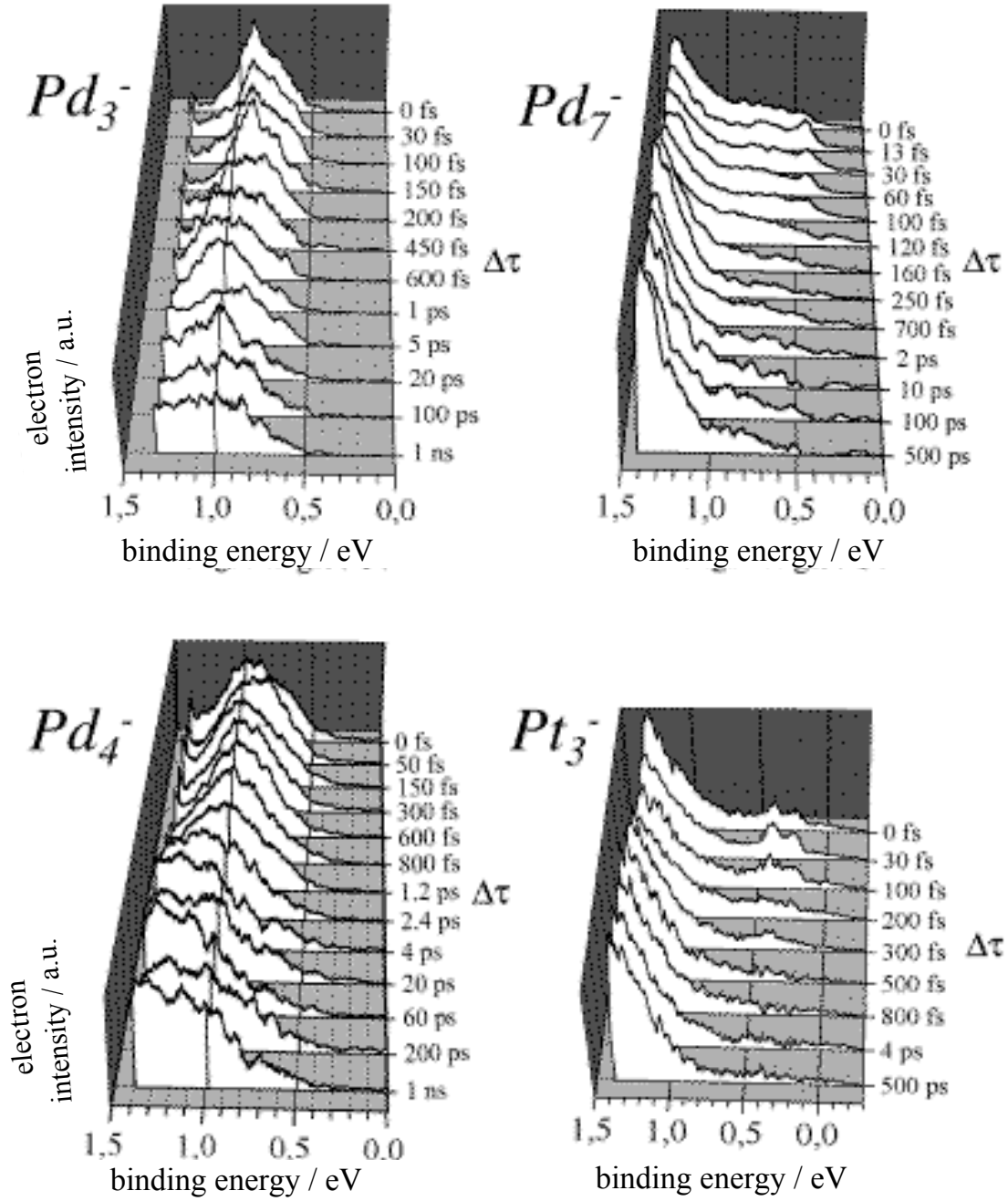

N. Pontius, PhD thesis, Universität Köln, 2001

# energy dissipation simulation in a 4-atom transition metal cluster




N. Pontius et al.
JCP 115, 10479 (2001).

# electronic relaxation in $Pt_3^-$, $Pd_{3,4,7}^-$



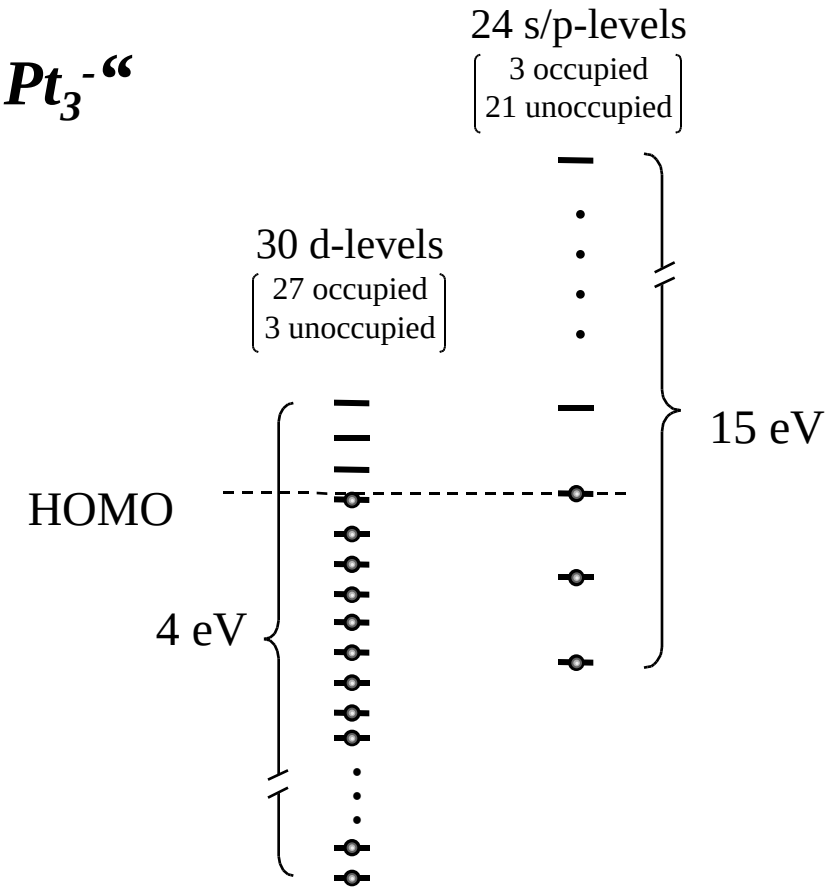

| | $Pt_3^-$ | $Pd_3^-$ | $Pd_4^-$ | $Pd_7^-$ | $Ni_3^-$ | bulk-Ni | bulk-Ag |
|---|---|---|---|---|---|---|---|
| $\tau_{e\text{-}e}$ / fs | < 70 | 40 $\pm$20 | 70 $\pm$20 | 25 $\pm$14 | 230 $\pm$50 | 4 | 30 |
| $\tau_{e\text{-}vib}$ / ps | - | - | 1 $\pm$0.2 | 0.7 $\pm$0.2 | 0.4 $\pm$0.1 | - | 0.9 |

R. Knorren et *al.*, PRB **61**, 9427 (2000)
Del Fatti et *al.*, PRL 81, 922 (1998)

# number of excited states in a 3-atom transition metal cluster

***„Ni$_3^-$, Pd$_3^-$, Pt$_3^-$“***

*($d^9 s^1$)*




for 0 eV < E* < 1,5 eV: **~ 250** excited states

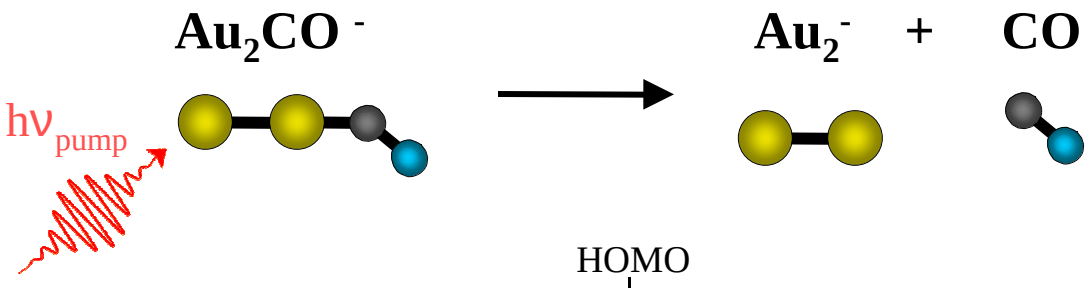
**by comparison:** ***„Cu$_3^-$, Ag$_3^-$, Au$_3^-$“*** *($d^{10} s^1$)* :

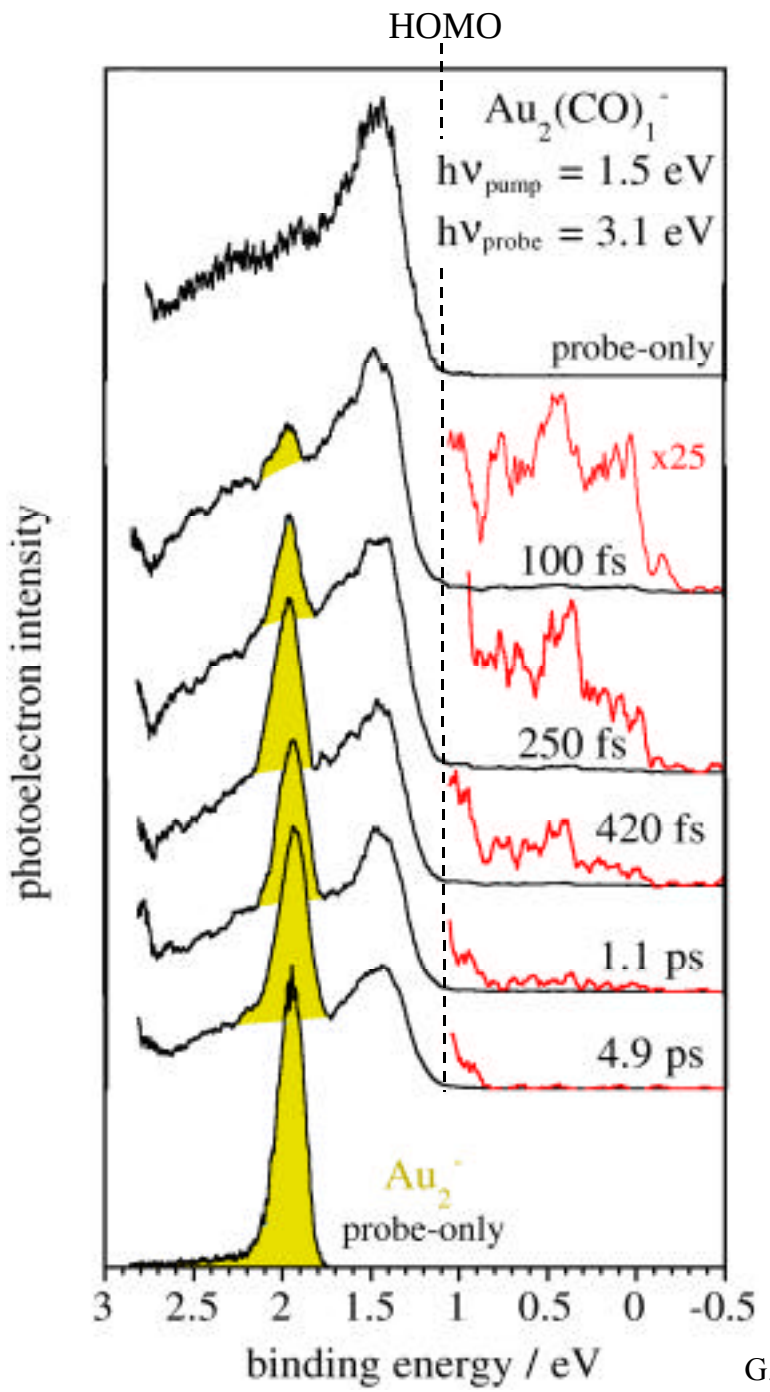
for 0 eV < E* < 1,5 eV: **~ 3** excited states

**outlook:** ***„ Ag$_{15}^-$ “***: **~ 270** excited states

N. Pontius, PhD thesis, Universität Köln 2001

# photon-induced desorption :

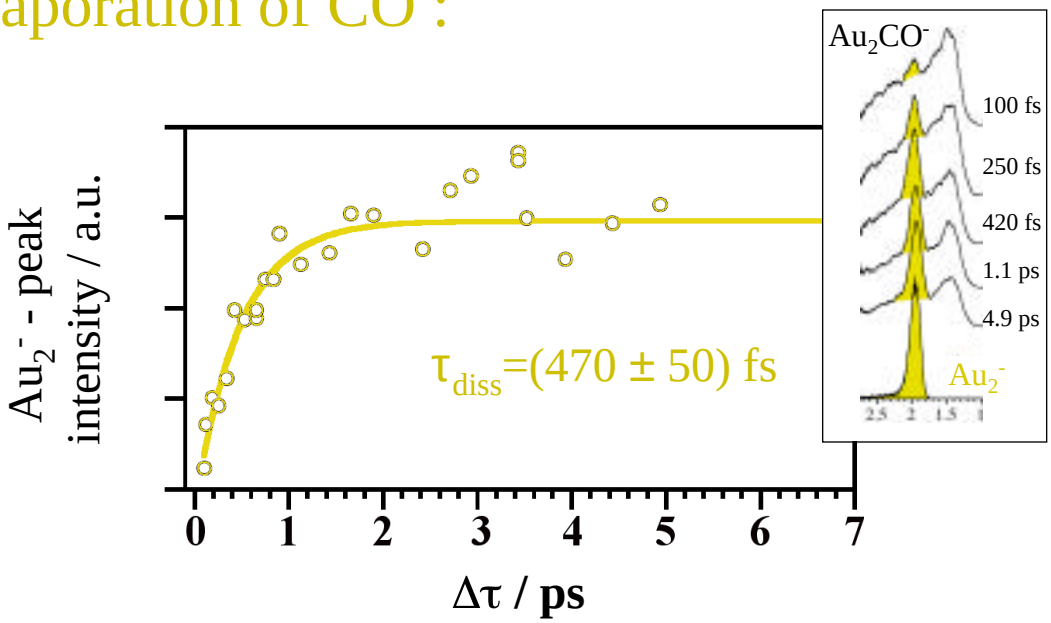


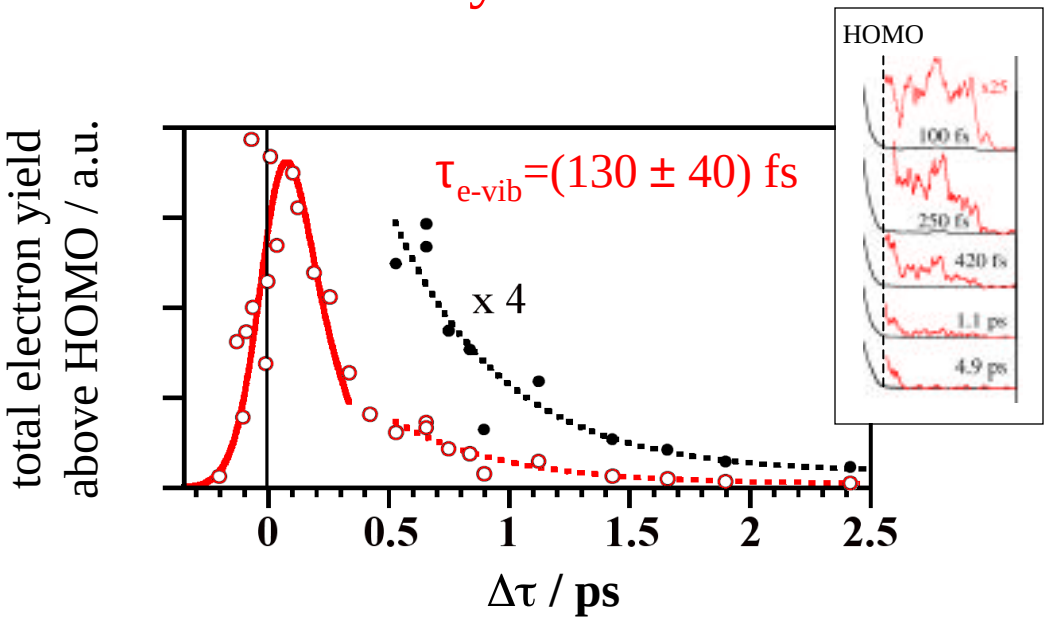

G. Lüttgens et al.
PRL **88**, 076102-1 (2002)

# photon-induced thermal desorption in $Au_2CO^-$:

evaporation of CO :




electron relaxation dynamics:




G. Lüttgens et al., PRL **88**, 076102 (2002)

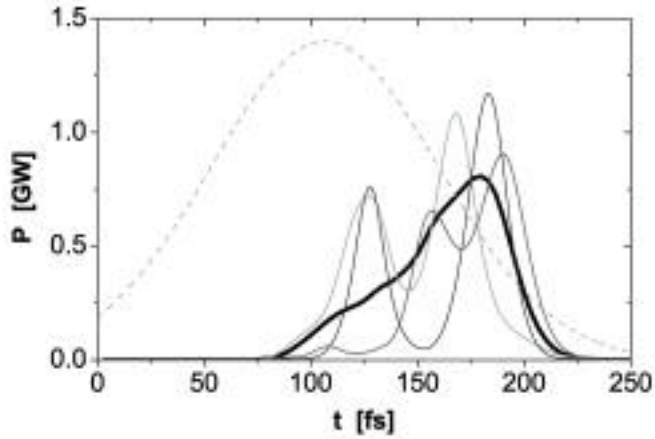
Electron and electron-vibrational relaxation times of clusters as measured by time-resolved photoelectron spectroscopy

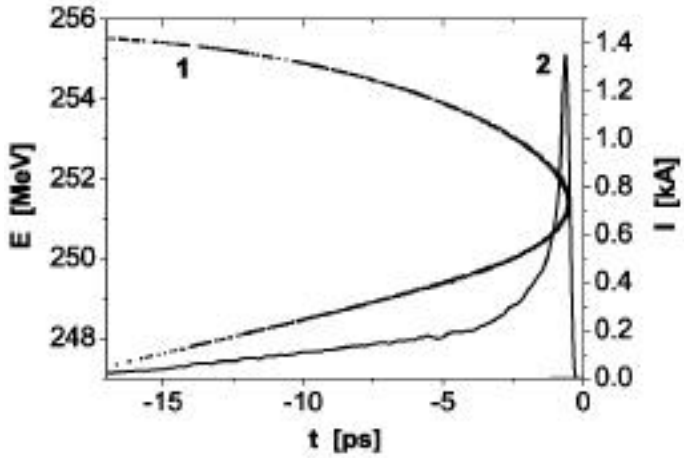
***Time constants by pump-probe 2PPE***

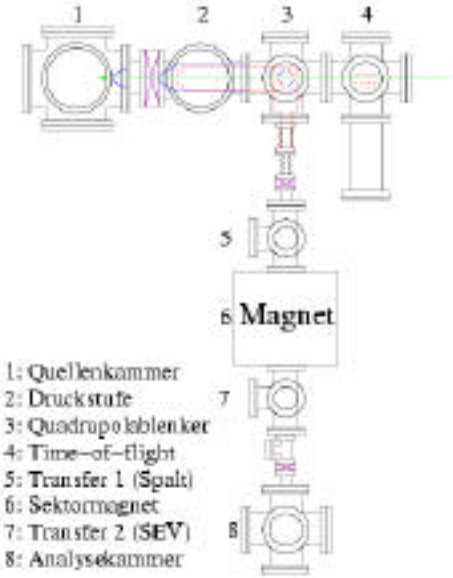
| | $Au_2(CO)^-$ | $Pt_2(CO)_5^-$ | $Pt_2N_2^-$ |
|---|---|---|---|
| $\tau_{e\text{-}e}$ | 65±35 fs | < 20 fs | |
| $\tau_{e\text{-}vib}$ | 130±40 fs | 36±12 fs | |
| $\tau_{diss}$ | 470±50 fs | 3 ± 2 ps | 30-100 ps |
| $E_{diss}$ | 0.9±0.1 eV | < 1.5 eV | <1.5 eV |

G. Lüttgens *et al*., PRL 88, 076102 (2001)

# TTF@DESY (HH):
# SASE FEL (presently:100 nm; Phase II: down to 6 nm)




BMBF project „VUVFEL“:
Uni Rostock, Uni Hamburg, Bessy, Desy/Hasylab,
Uni Konstanz, Uni Osnabrück

**Intense X-ray FEL for exploring mass-selected clusters**:
1) conventional XPS (core orbitals, isomers, adsorbate levels, ESCA, Auger, resonant PES, NEXAFS
2) time-resolved 2PPE (chemistry: bond formation, products, intermediates; site-specific spectroscopy)

**Feasibility**

| | |
|---|---|
| Inner-shell PI cross section σ (adsorbate) | 1-10 Mb |
| σ (metal) | 0.5-5Mb |
| photon intensity (desired) | $>10^{14}$/pulse |
| mass-selected cluster anion intensity | $10^5$-$10^7$/pulse |
| repetition rate | 1000 Hz |
| electron detection efficiency (ToF) | 1- 100(MB) % |
| electron count rate (1Mb) | 100-10000 Hz |