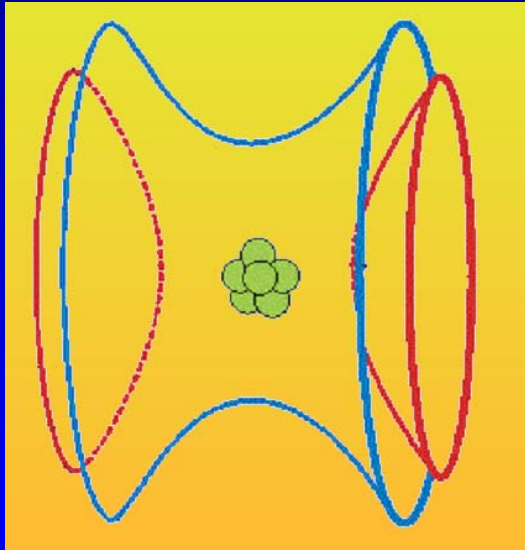


# ClusterTrap: A Penning Trap for Cluster Research

(Ion Trapping for Cluster Research)



**ClusterTrap**

**Lutz Schweikhard**

Institut für Physik  
Ernst-Moritz-Arndt-Universität  
17487 Greifswald  
Germany



## Overview

### **Other traps and applications**

**FT-ICR MS**, precision MS of radionuclides,  
EBIT, (electrostatic ion-beam traps => Wada)

### ClusterTrap

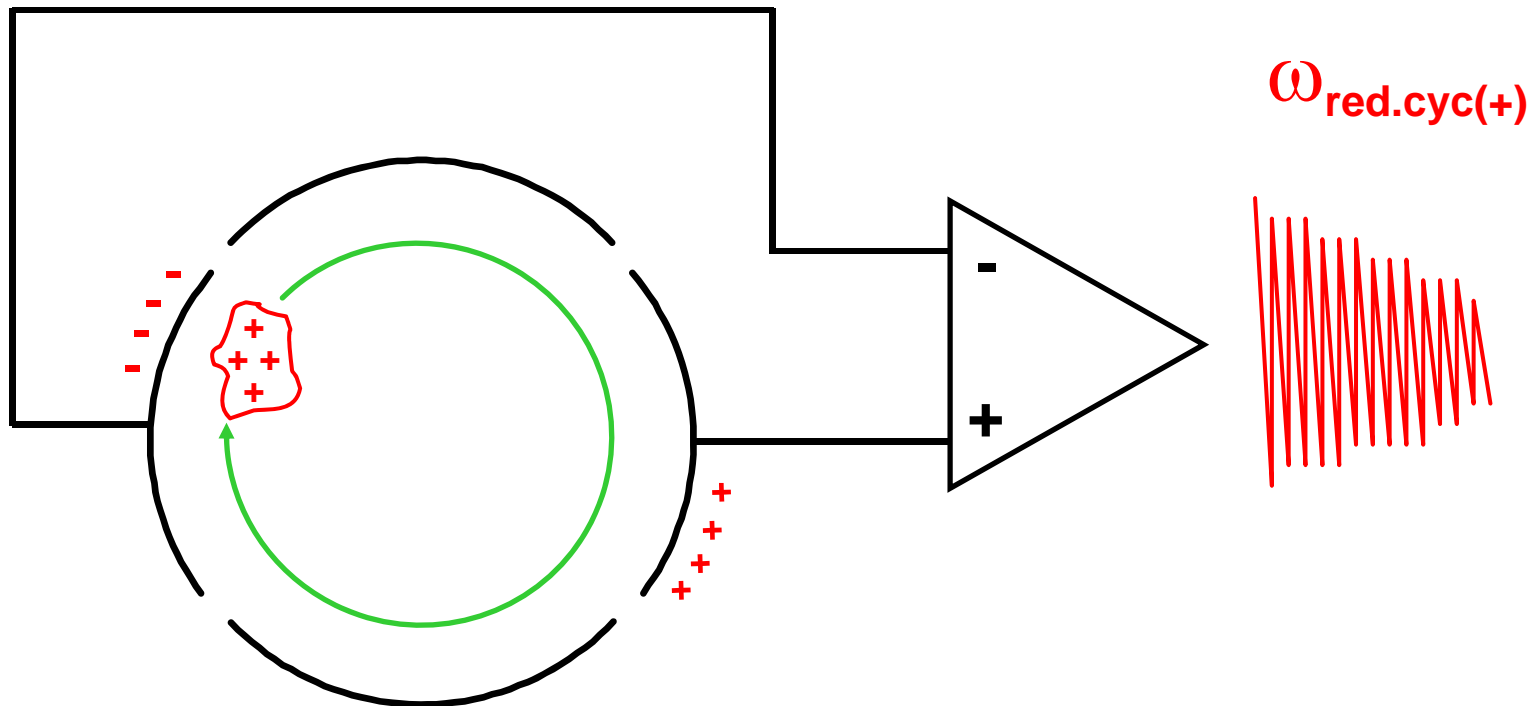
why? how? what?

Other cluster-storage devices

# FT-ICR MS = FTMS

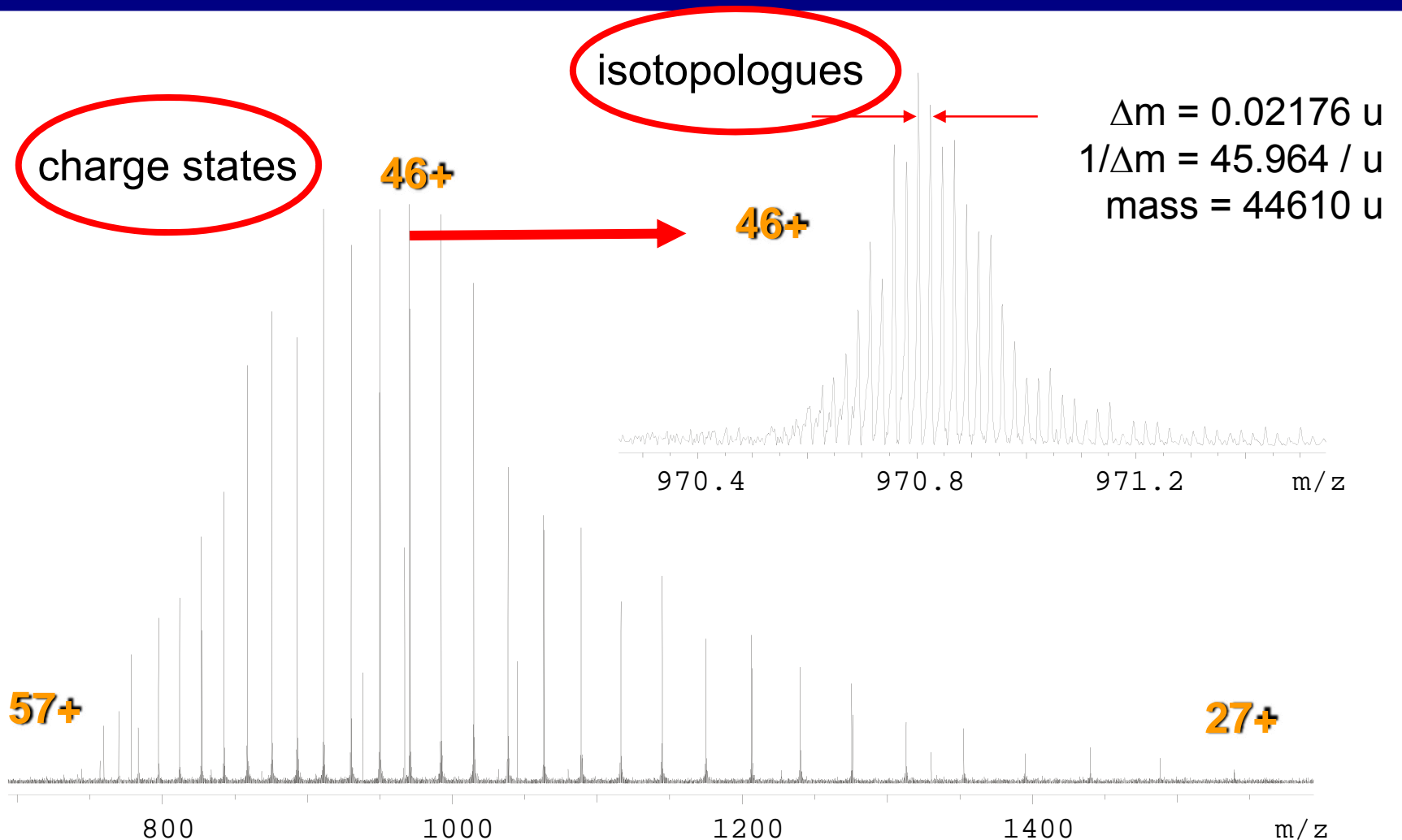
Fourier Transform (Ion Cyclotron Resonance) Mass Spectrometry

## Detection of Ion Motion (after broad-band excitation)



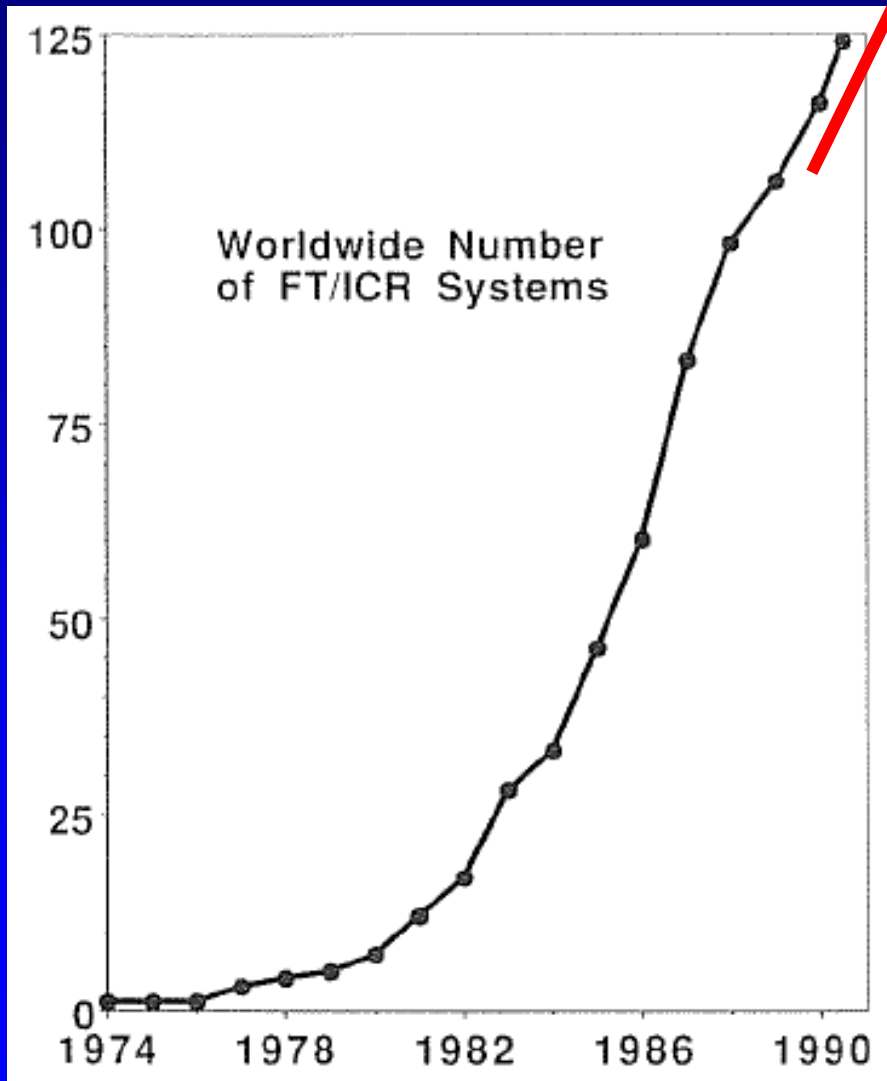
Courtesy of Roland Jertz, Bruker Daltonik/Bremen

# Protein A (44 kDa) Broad-Band Spectrum



Courtesy of Roland Jertz, Bruker Daltonik/Bremen

# FT-ICR MS systems in use (as a function of time)



Typically > 500 k€ a piece

Three independent companies developing and selling FT-ICR systems

A.G. Marshall and LS,  
IJMS 118/119 (1992)

## Overview

### **Other traps and applications**

FT-ICR MS, precision MS of radionuclides,  
EBIT, (electrostatic ion-beam traps => Wada)

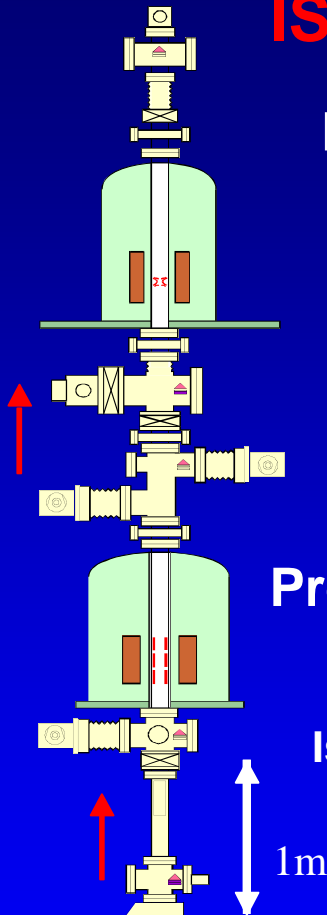
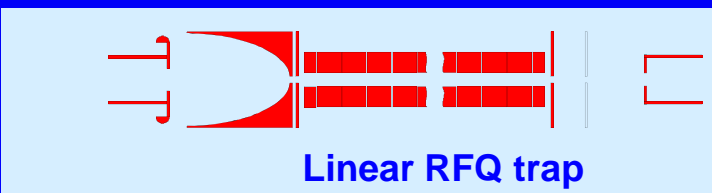
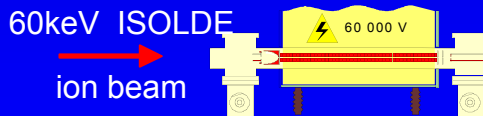
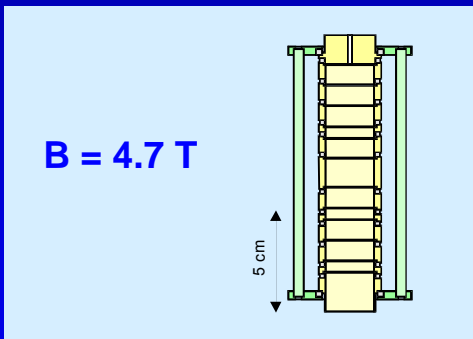
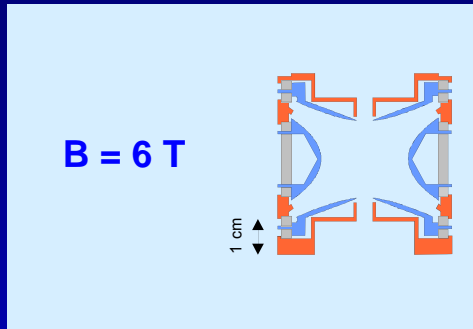
### ClusterTrap

why? how? what?

Other cluster-storage devices

# Precision mass measurements of short-lived nuclides

## ISOLTRAP AT ISOLDE/CERN



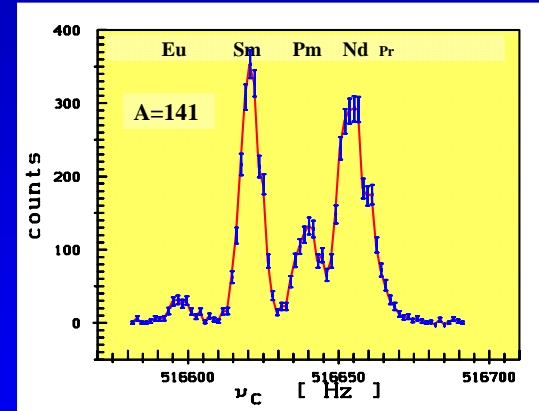
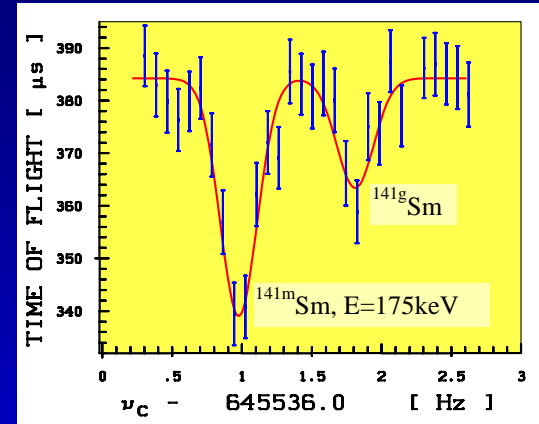
**Precision Trap:**  
Determination  
of cyclotron  
frequency  
Isomer separation

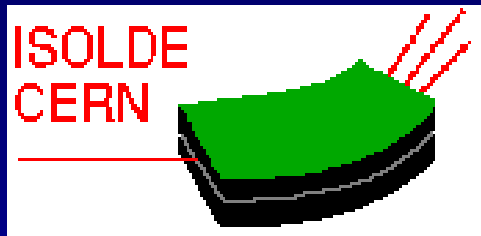
**Preparation Trap:**  
Accumulation  
Cooling  
Isobar separation

Retardation  
Cooling  
Accumulation  
Bunching

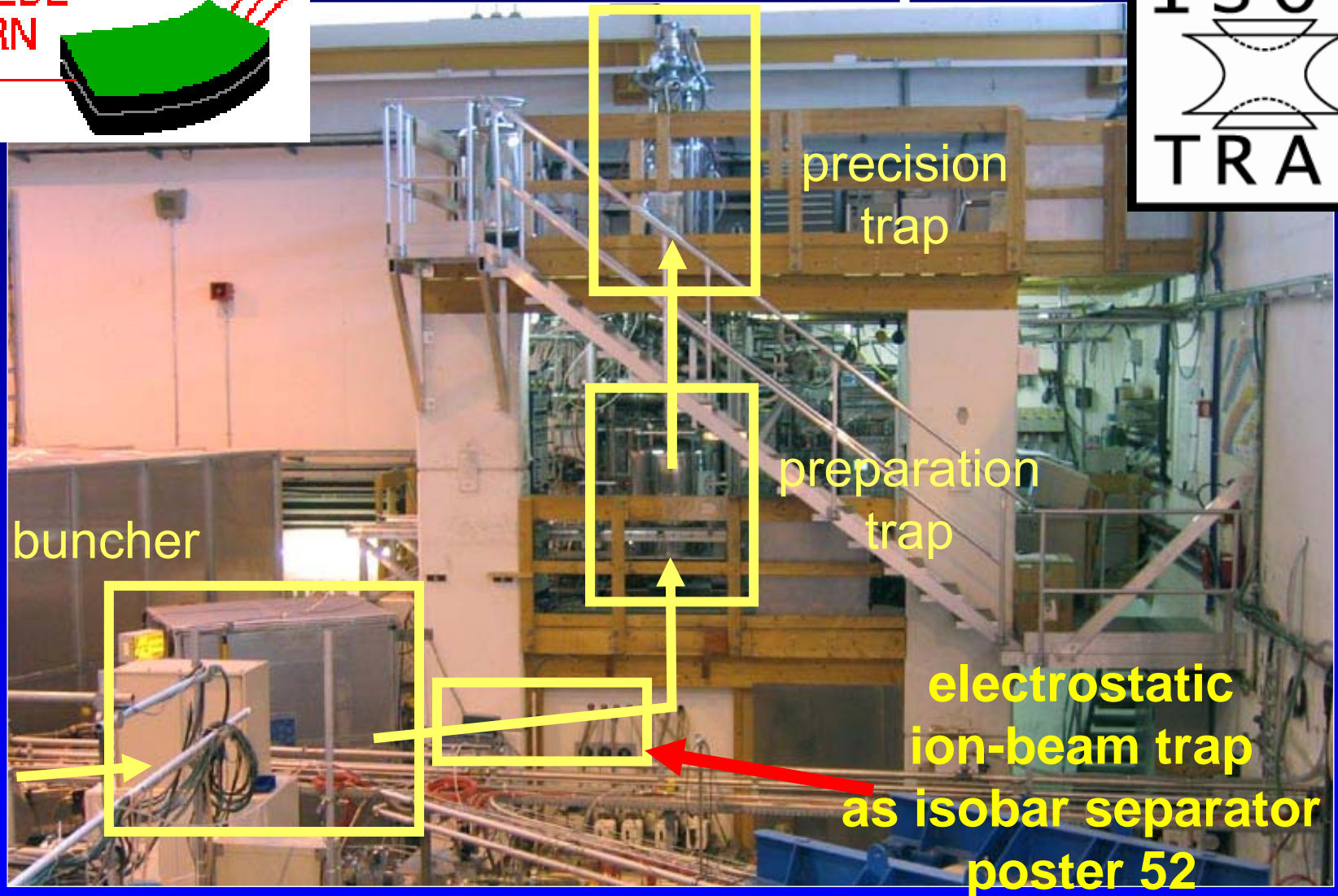
Setup:

- H. Stolzenberg et al., PRL 1990
- G. Bollen et al., NIM A 1996
- H. Raimbault-Hartmann et al., NIM B '97
- F. Herfurth et al., NIM A 2001





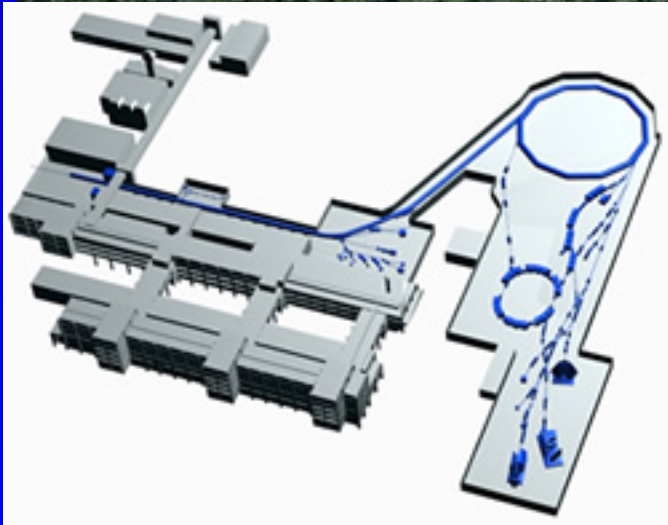
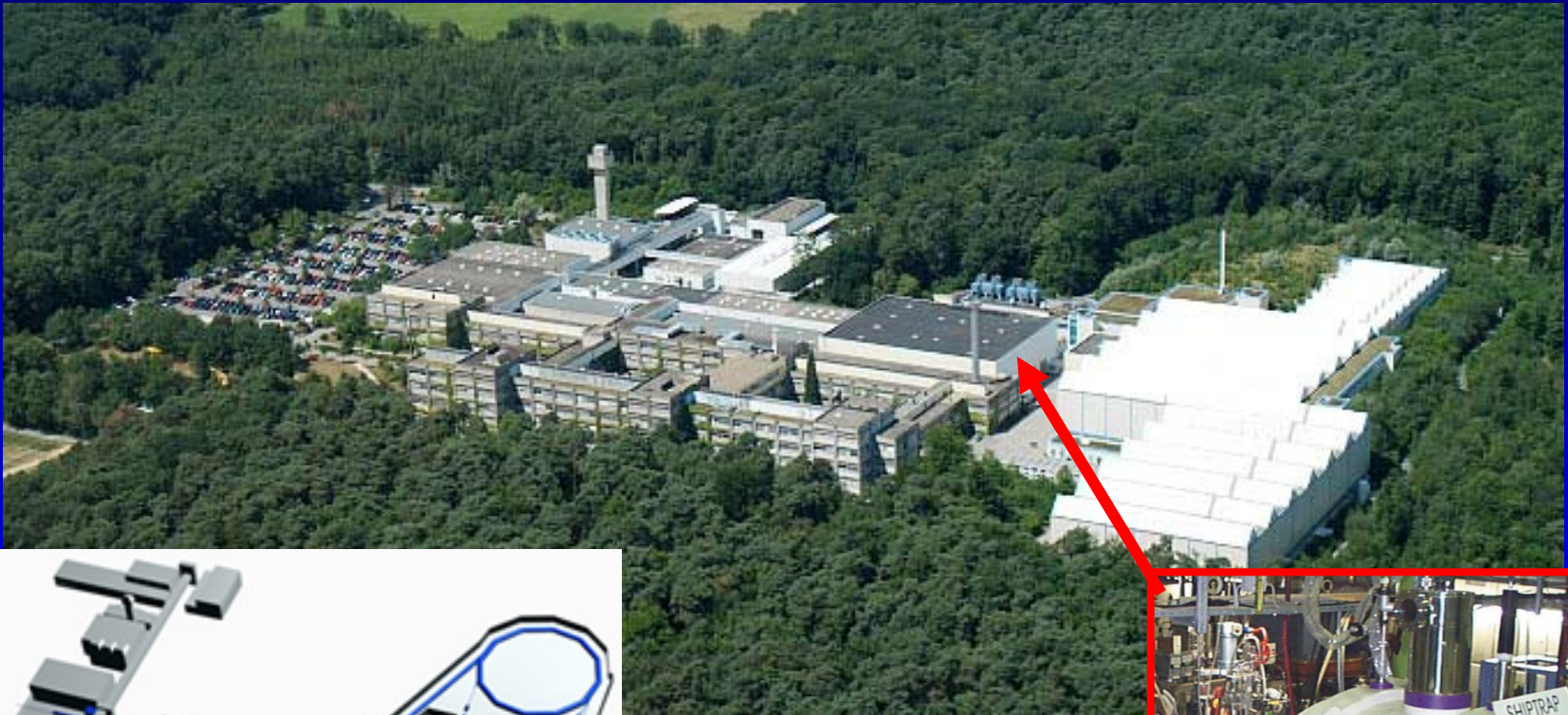
# ISOLTRAP setup



Recent exp. results, e.g.: PRL **98**, 162501(2007); **100**, 072501(2008); **101**, 252502(2008); **101**, 262501(2008); **102**, 112501(2009); **105**, 032502(2010)



# One of the off-springs: **SHIPTRAP** at GSI/Darmstadt



# First direct mass measurements above uranium

M. Block et al., **Nature** 463 (2010) 785

$^{252-254}\text{No}$  ( $Z=102$ )

with production rates

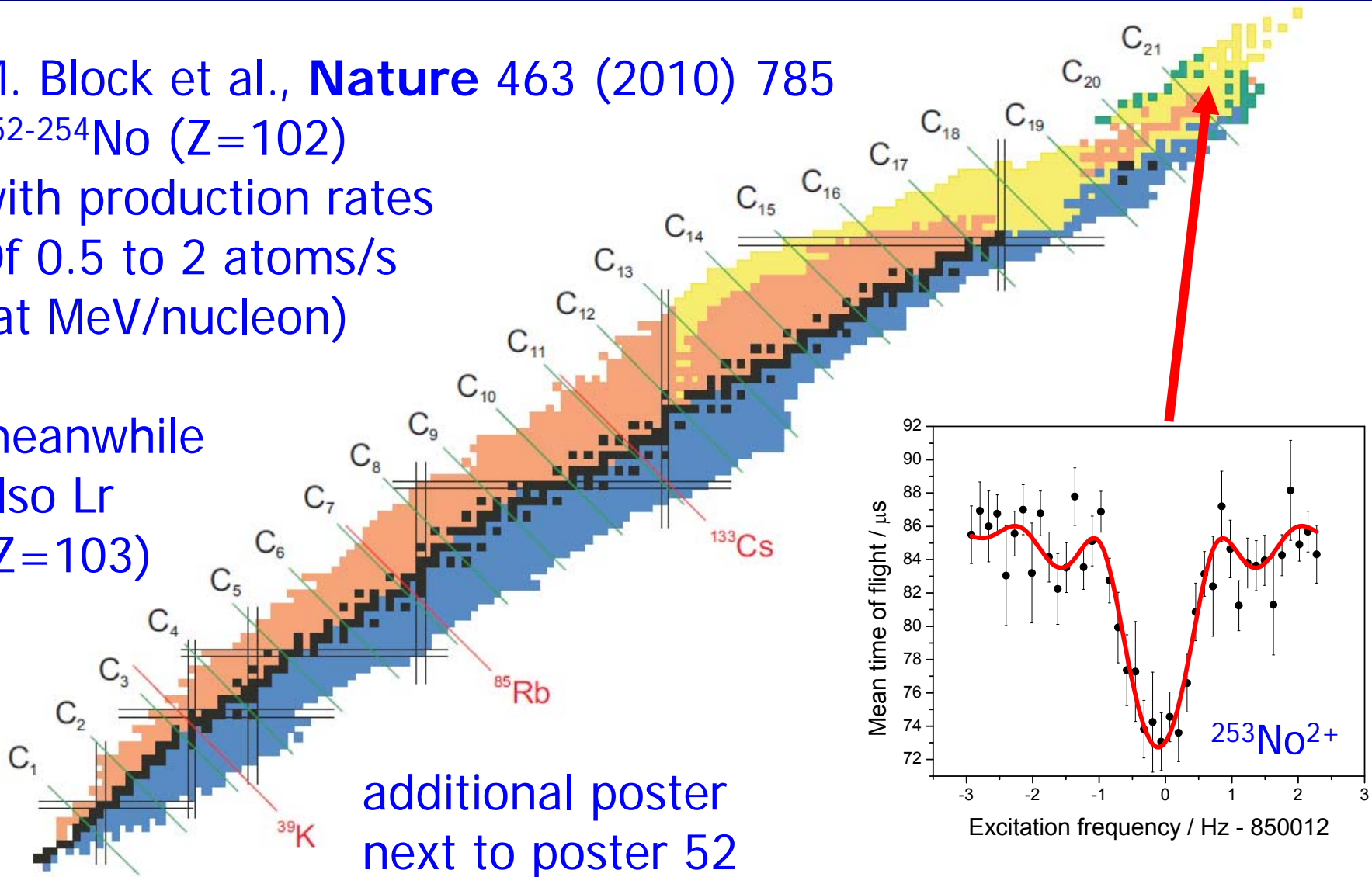
Of 0.5 to 2 atoms/s

(at MeV/nucleon)

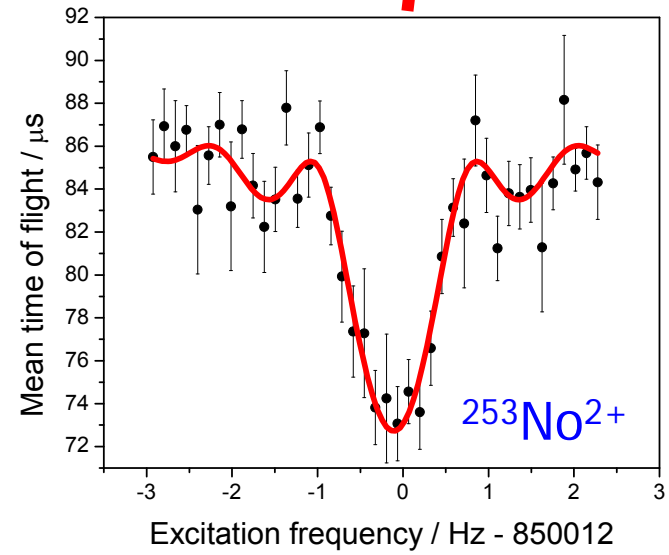
meanwhile

also Lr

( $Z=103$ )



additional poster  
next to poster 52



## Overview

### **Other traps and applications**

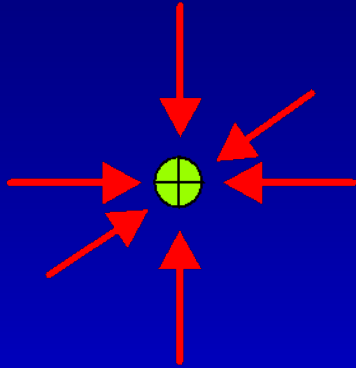
FT-ICR MS, precision MS of radionuclides,  
**EBIT**, (electrostatic ion-beam traps => Wada)

### ClusterTrap

why? how? what?

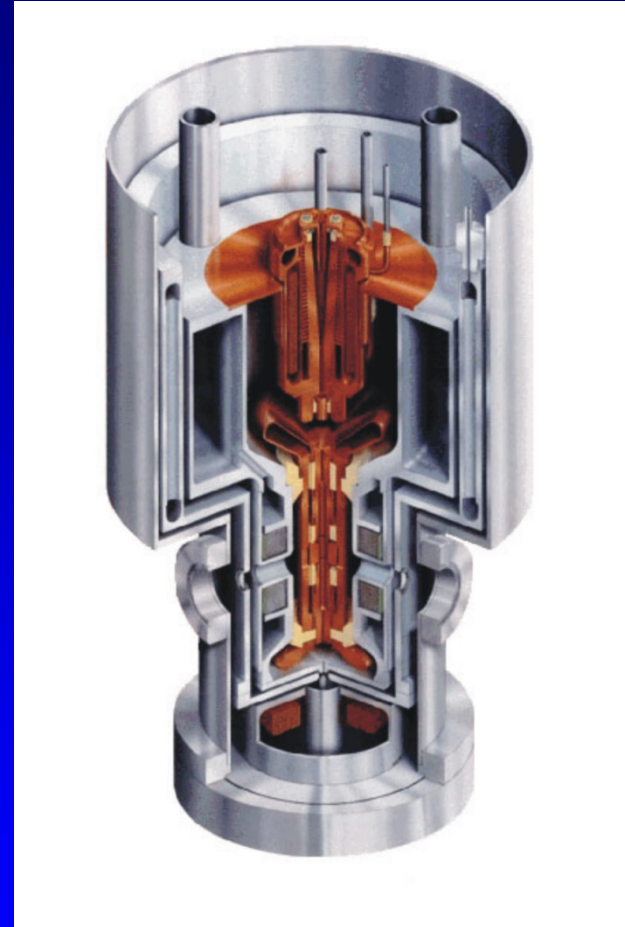
Other cluster-storage devices

# EBIT: Electro-Beam Ion Trap or How to produce and confine highly-charged ions?



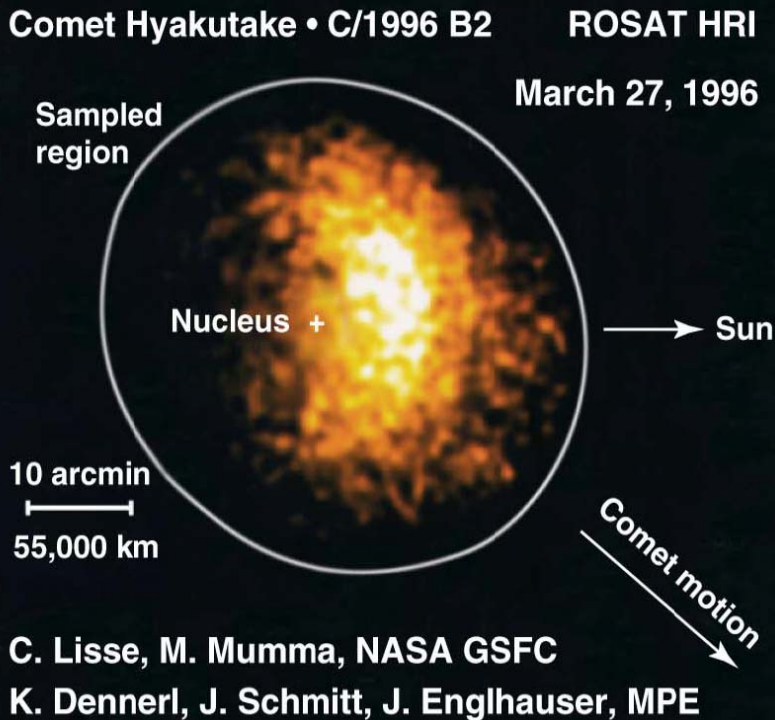
Electrostatic trapping  
is not possible by  
static electric fields only  
unless space charge allowed

Here by compression  
of an electron beam  
by strong B-field



Replace Laplace:  $\Delta\phi = 0$   
by Poisson:  $\Delta\phi = \rho/\epsilon_0$

# FIRST X-RAY IMAGE OF A COMET

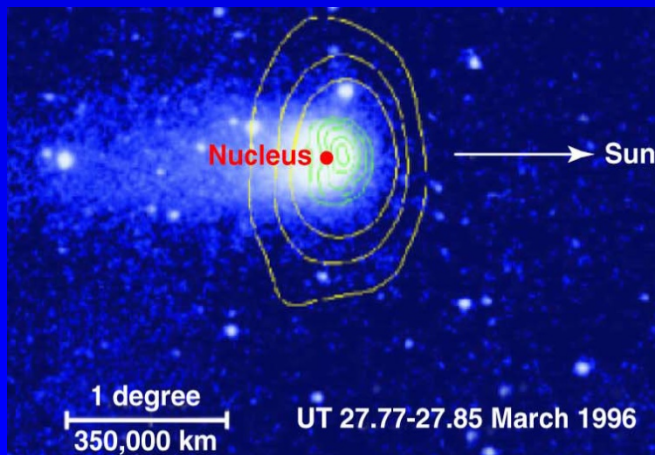


## X-ray emission from comets

due to charge transfer from highly-charged ions of solar wind colliding with neutral atoms of the comets

Such reactions as well as lifetimes of metastable states are studied in the

“magnetic-trapping mode” of EBIT P. Beiersdorfer, LS et al., RSI 67, 3818 (1996)



Lisse et al.,  
Science 274, 205 (1996)

## Overview

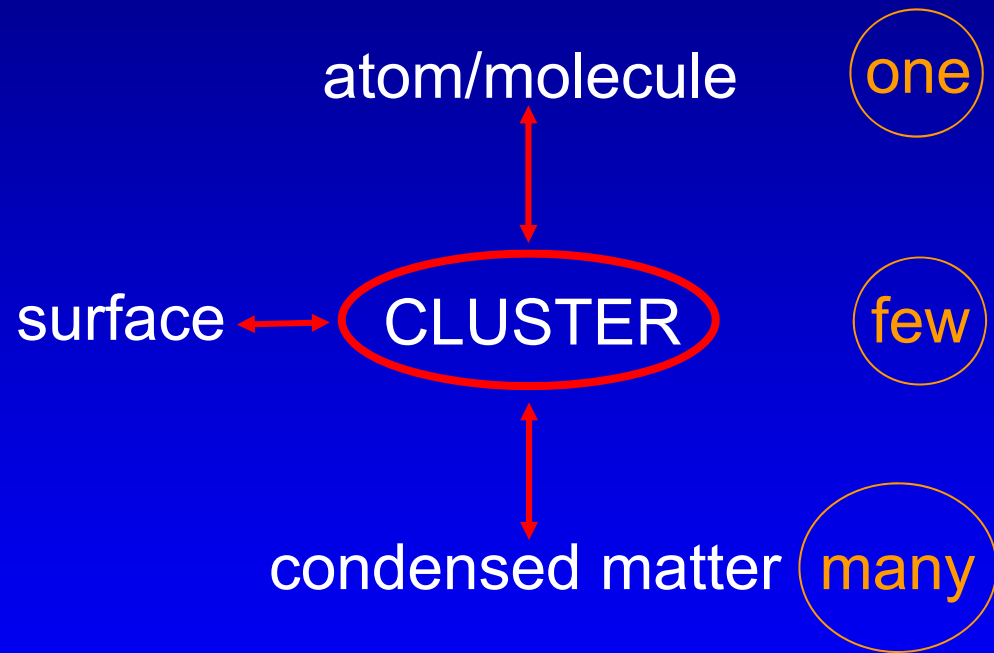
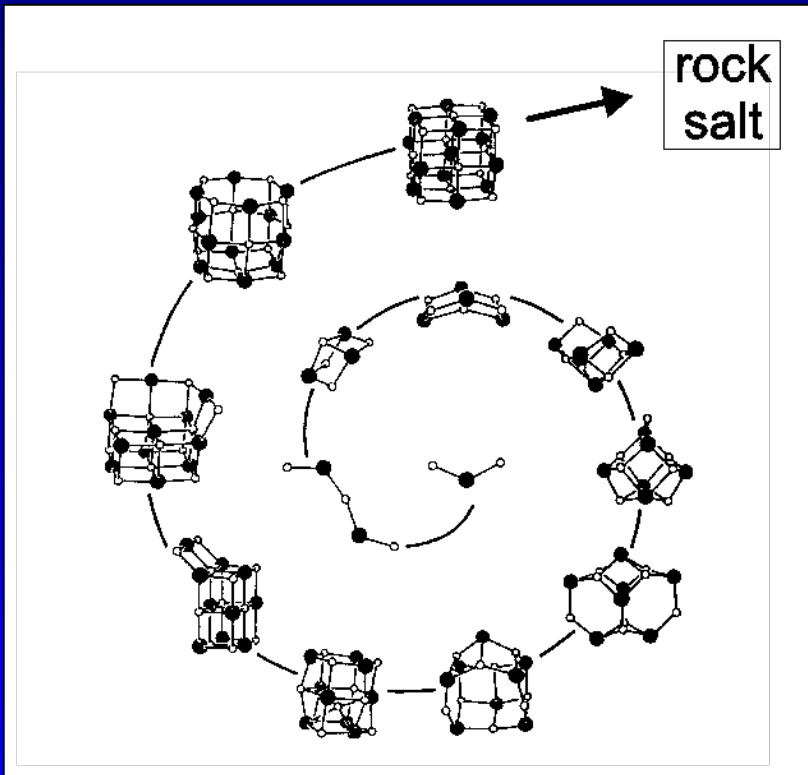
# Other traps and applications

## ClusterTrap

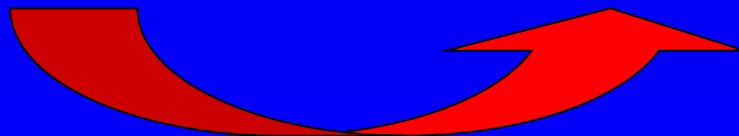
clusters? why? how? what?

Other cluster-storage devices

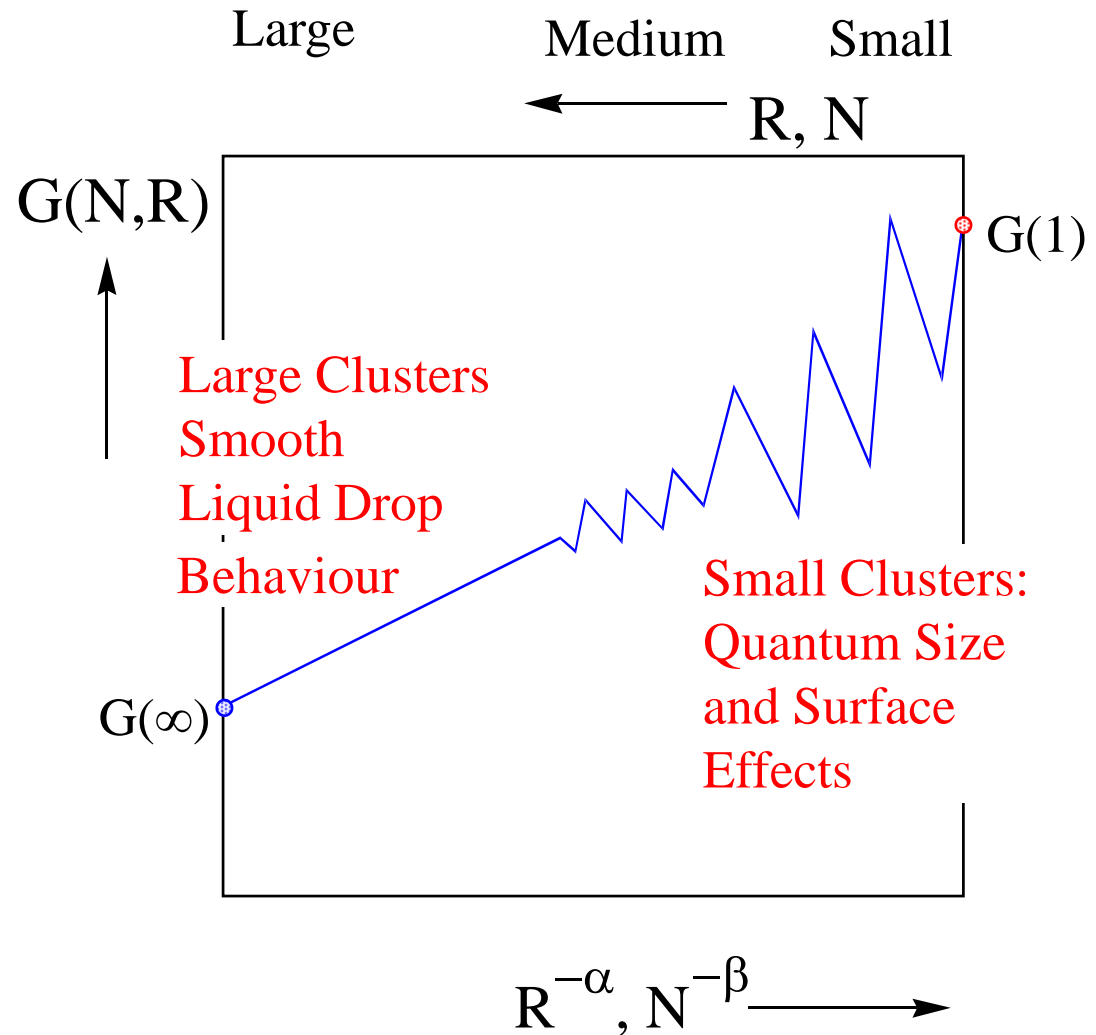
# From Atoms to Bulk Matter: Clusters



T.P. Martin (1984)



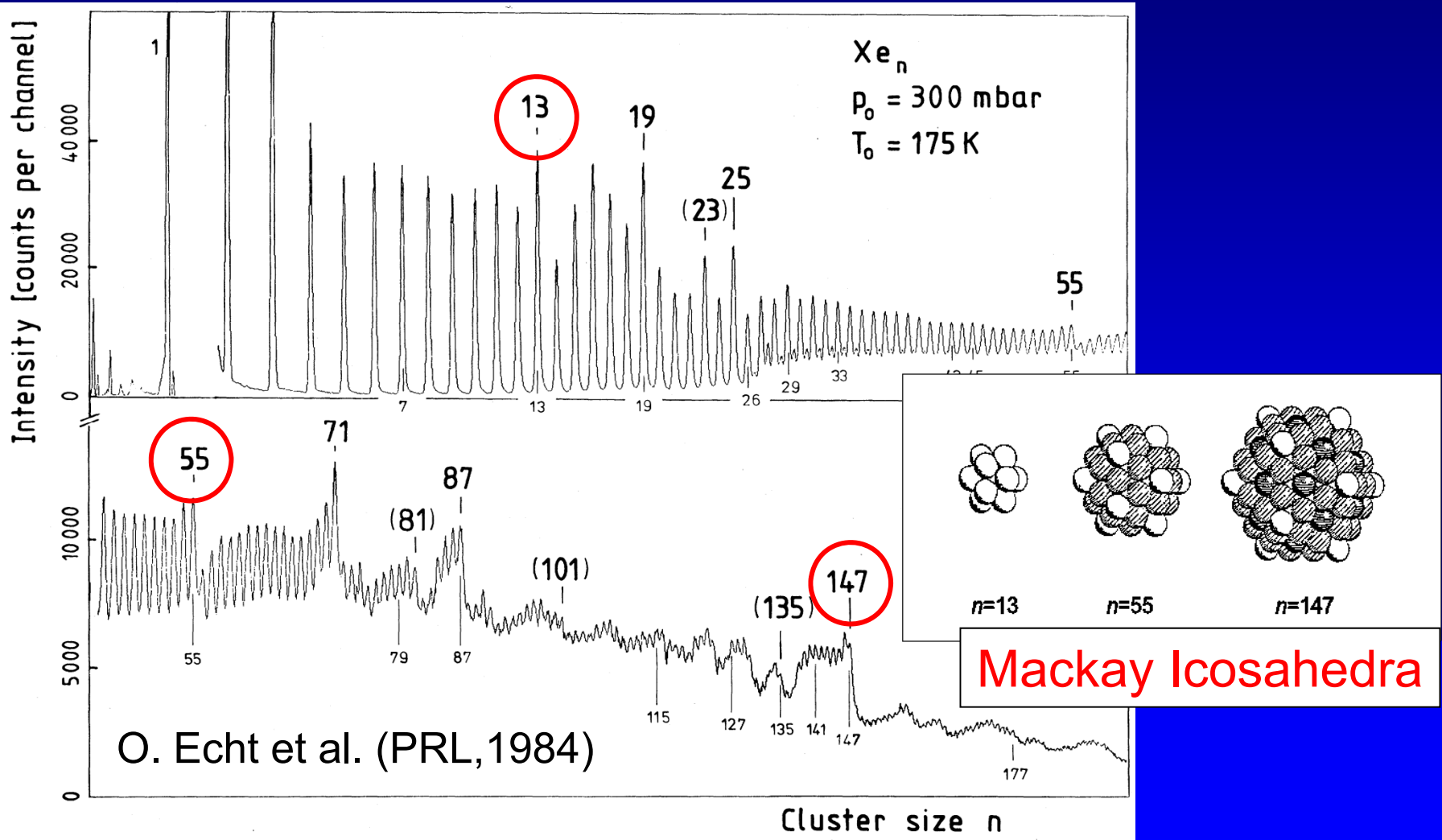
# Scaling Laws

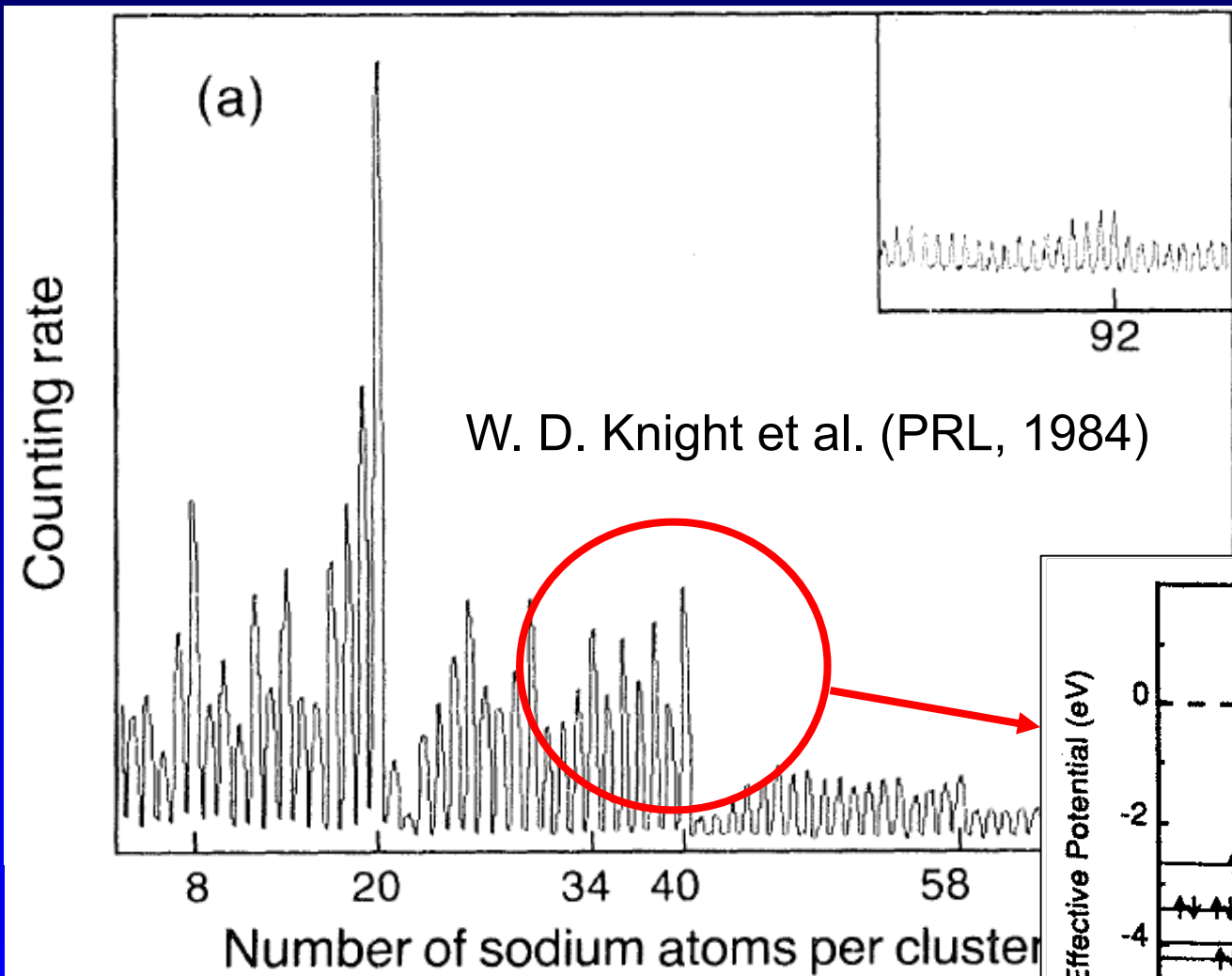


from  
Roy L. Johnston:  
Atomic and  
Molecular Clusters  
(London, New York, 2002)



# Noble gas clusters: geometric shells



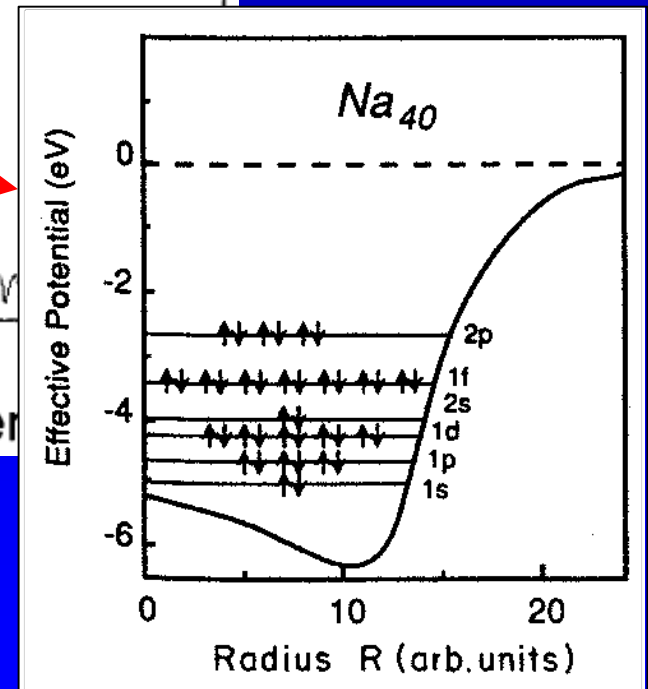


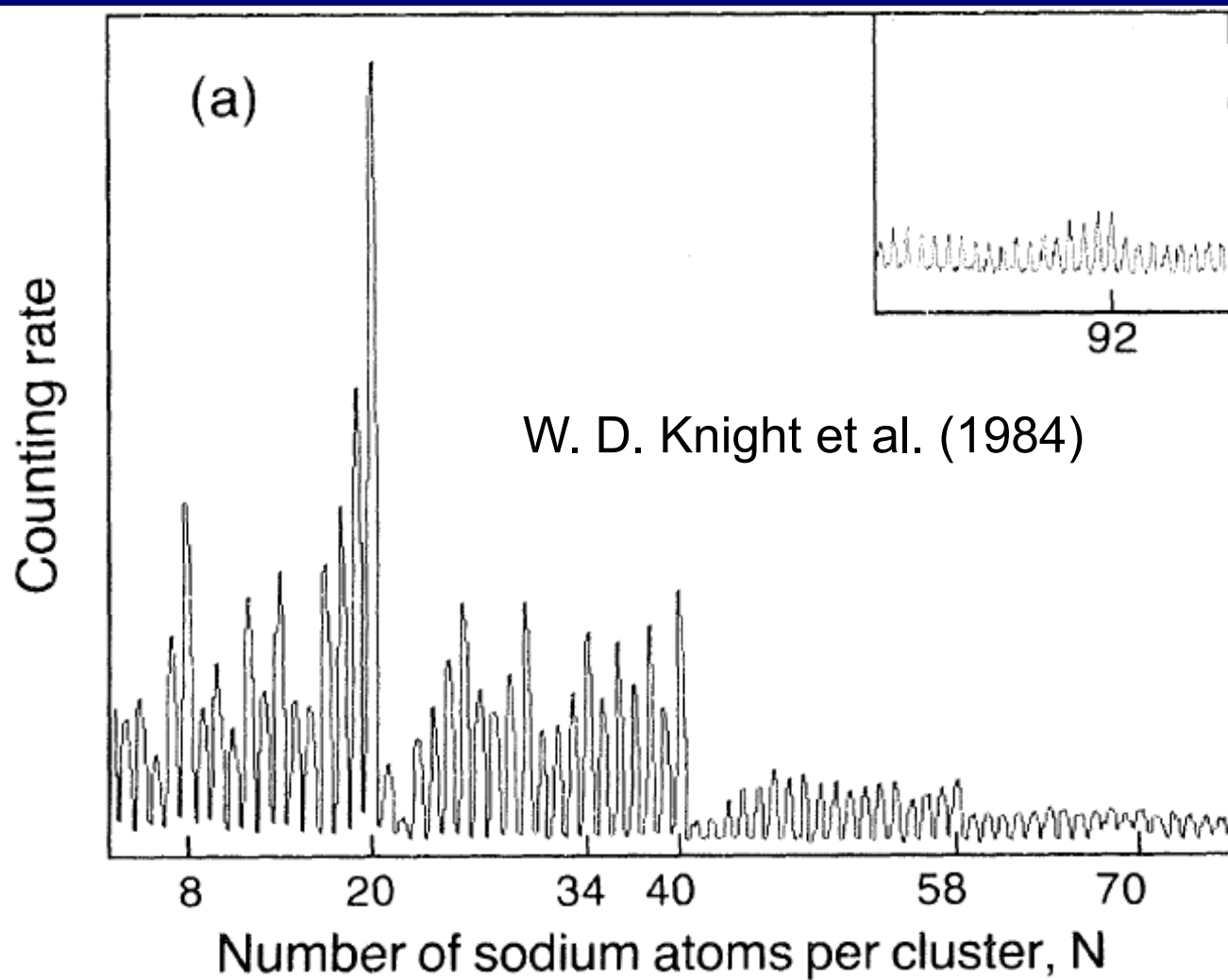
Metal clusters

Jellium model

electronic shells

Experimental distinction betw.  
geom. and electr. effects:  
charge-state dependence





Why  
cluster  
ions?

Size selection by **mass spec.** as **first step** for detailed studies !  
mass spec. also for reaction **product analysis** => **MS-MS**

## Overview

# Other traps and applications

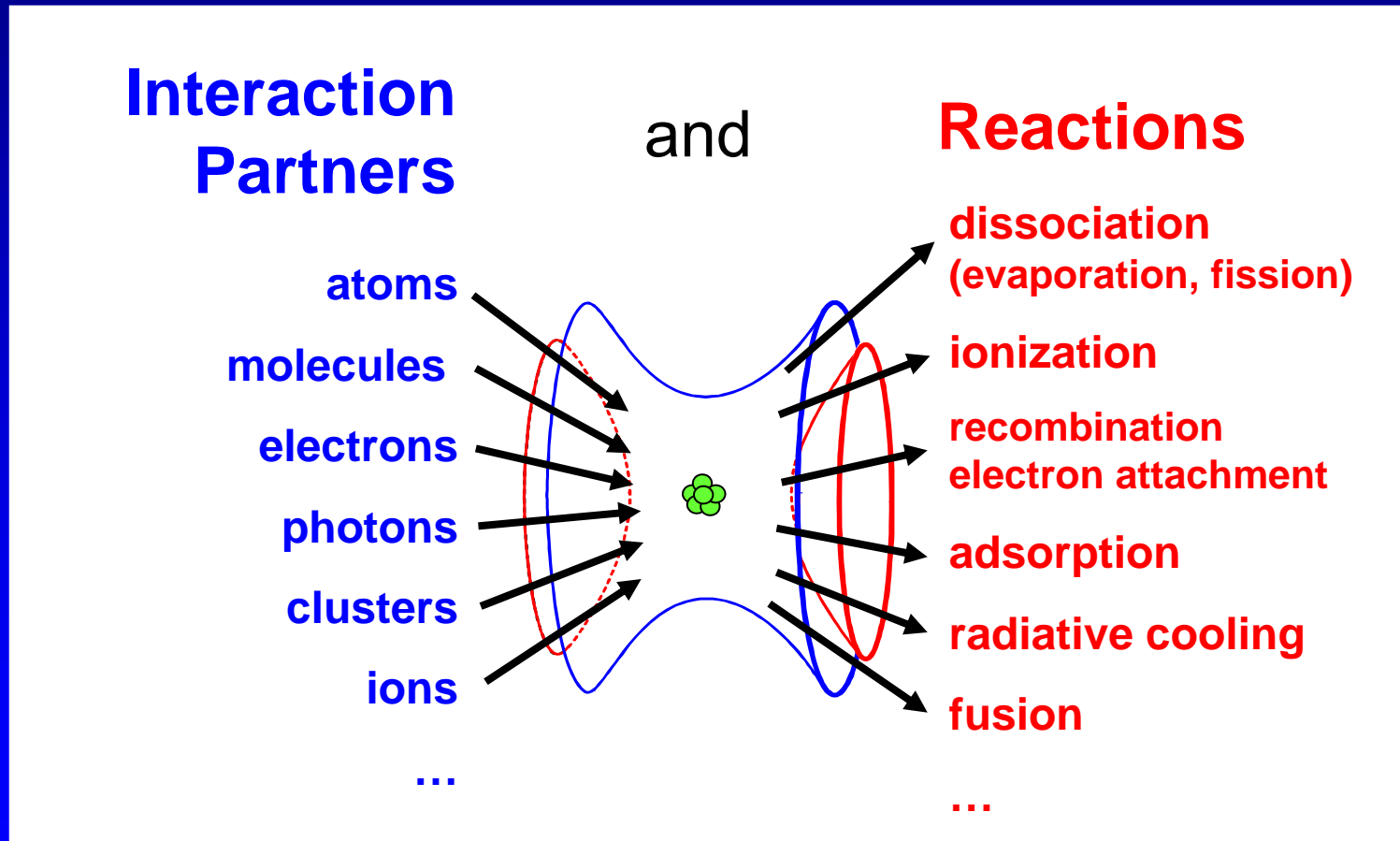
## ClusterTrap

clusters? *why?* how? what?

Other cluster-storage devices

# Why cluster trapping? (as compared to beams)

- extended **interaction** periods
- extended **reaction** periods
- multi-step preparation



## Overview

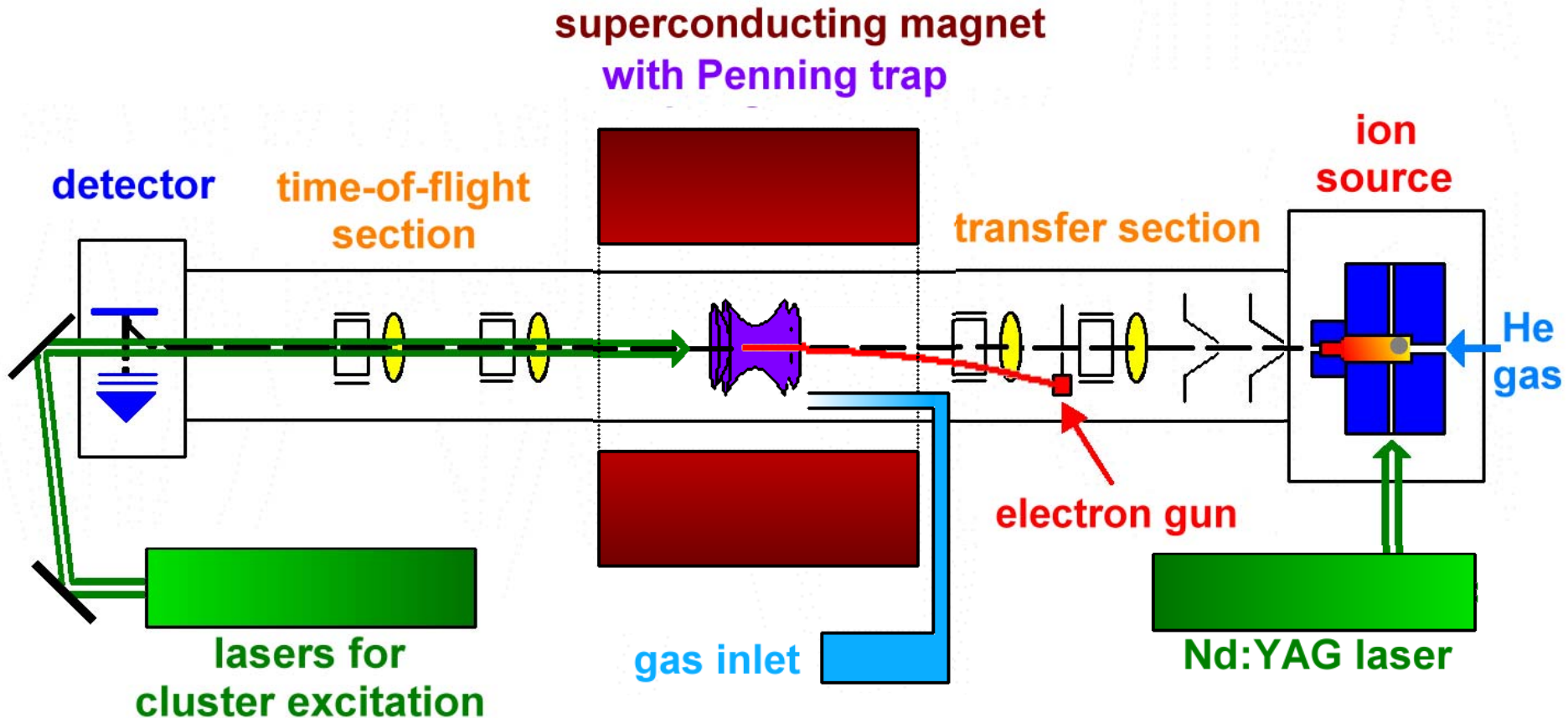
# Other traps and applications

## ClusterTrap

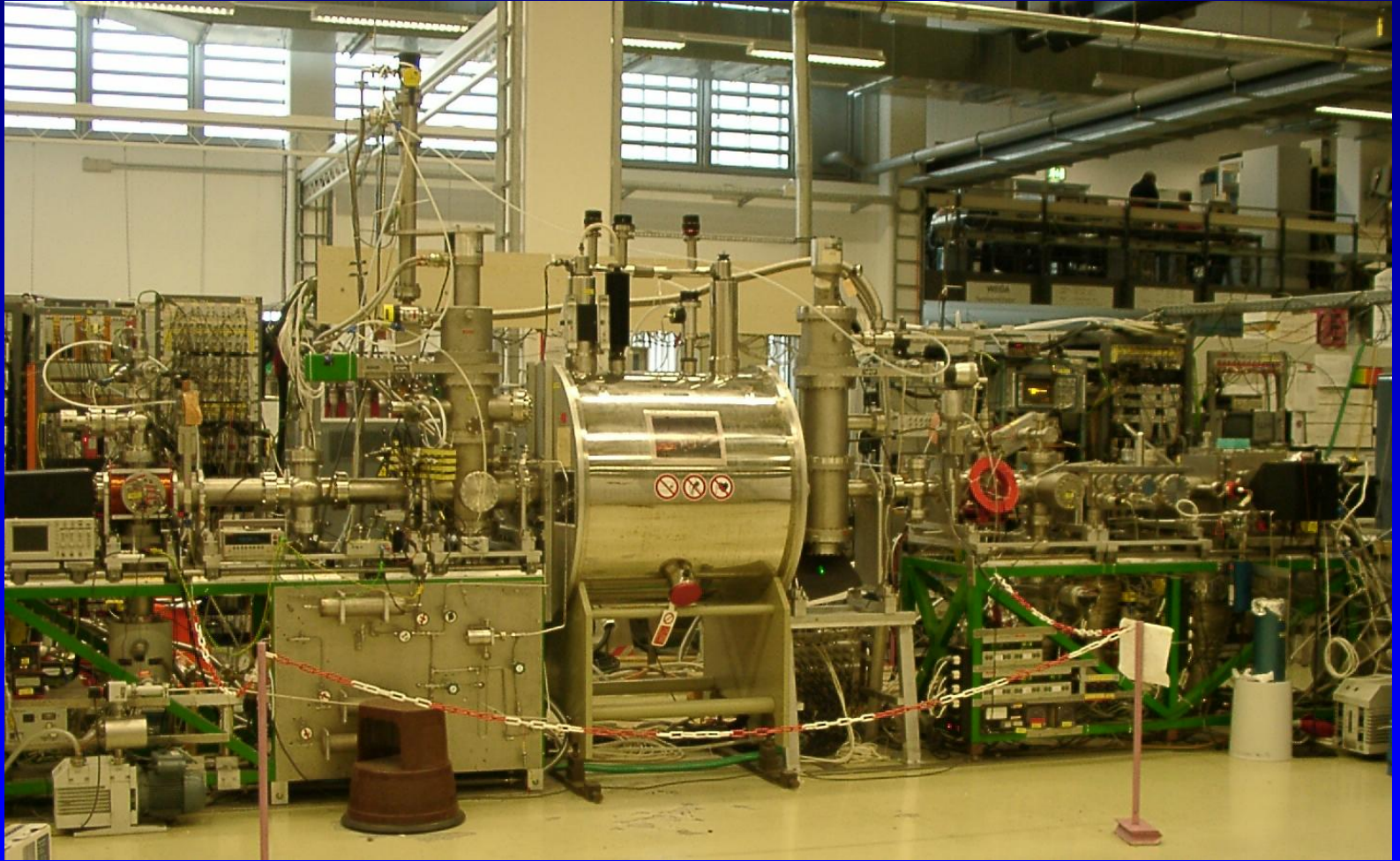
clusters? why? how? what?

Other cluster-storage devices

# Experimental set-up of ClusterTrap @ Greifswald



# Experimental set-up of ClusterTrap @ Greifswald

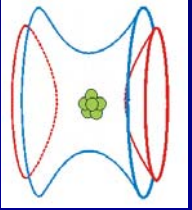


S. Becker et al., RSI (1995)  
LS et al., EPJ D (2003)





# ClusterTrap



at Univ. of Greifswald



founded in 1456  
„full university“  
ca. 12000 students

Obergurgl  
Next ECTI

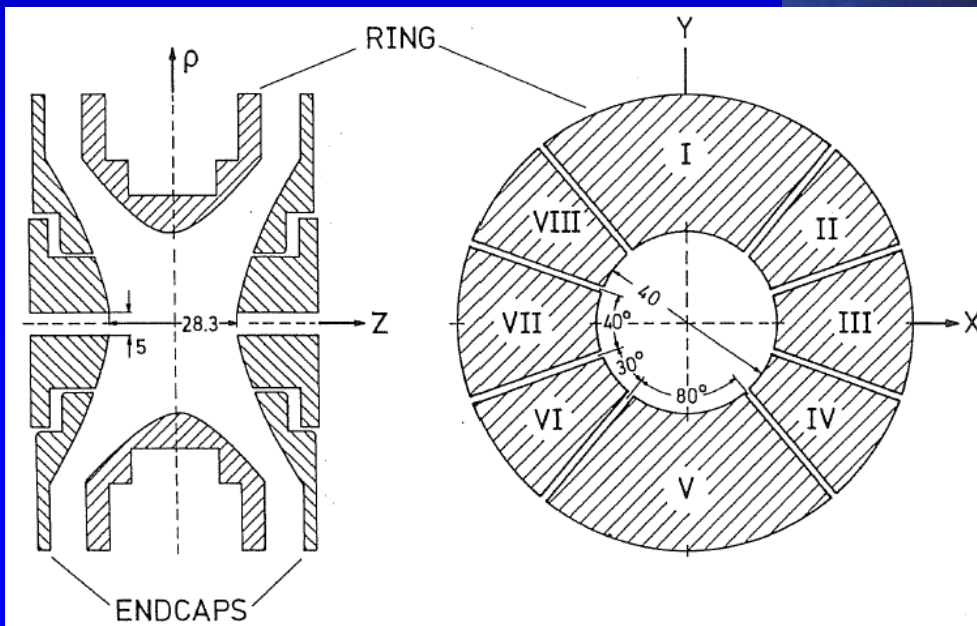
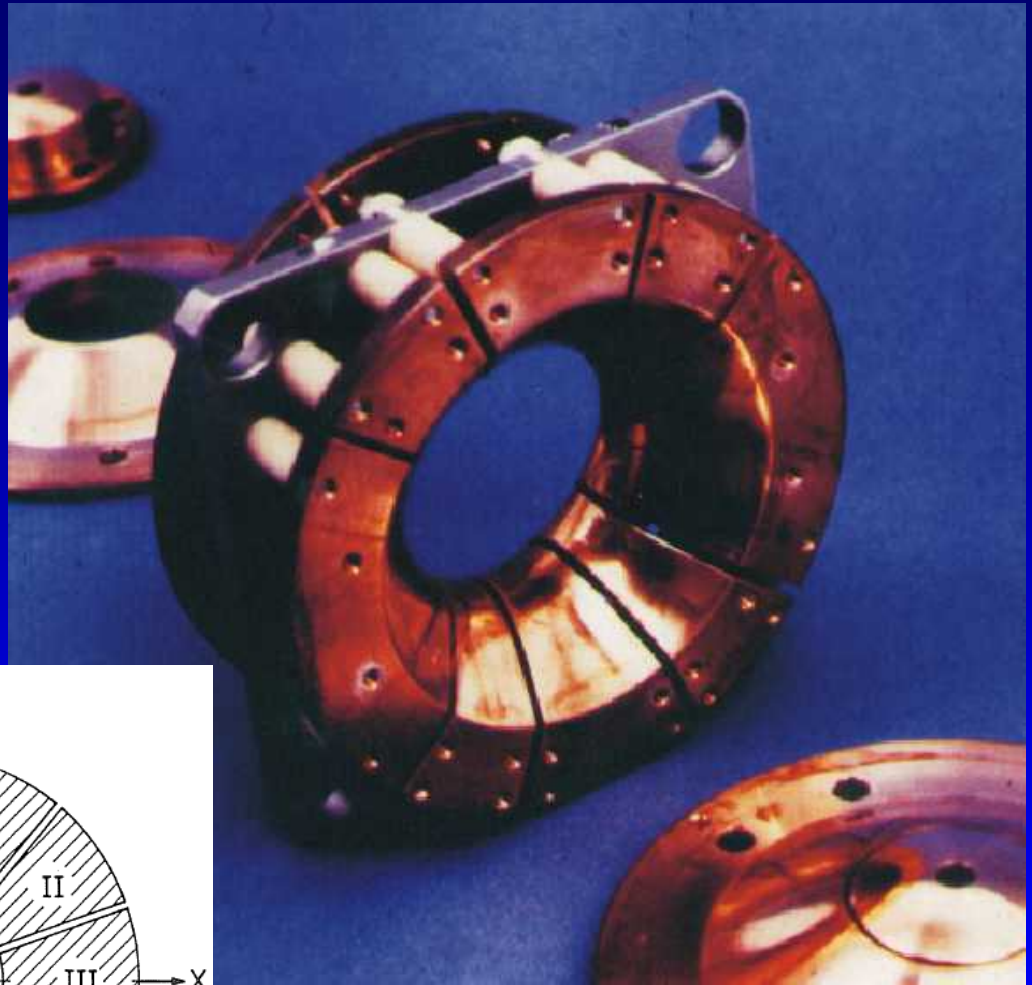
GSI

CERN



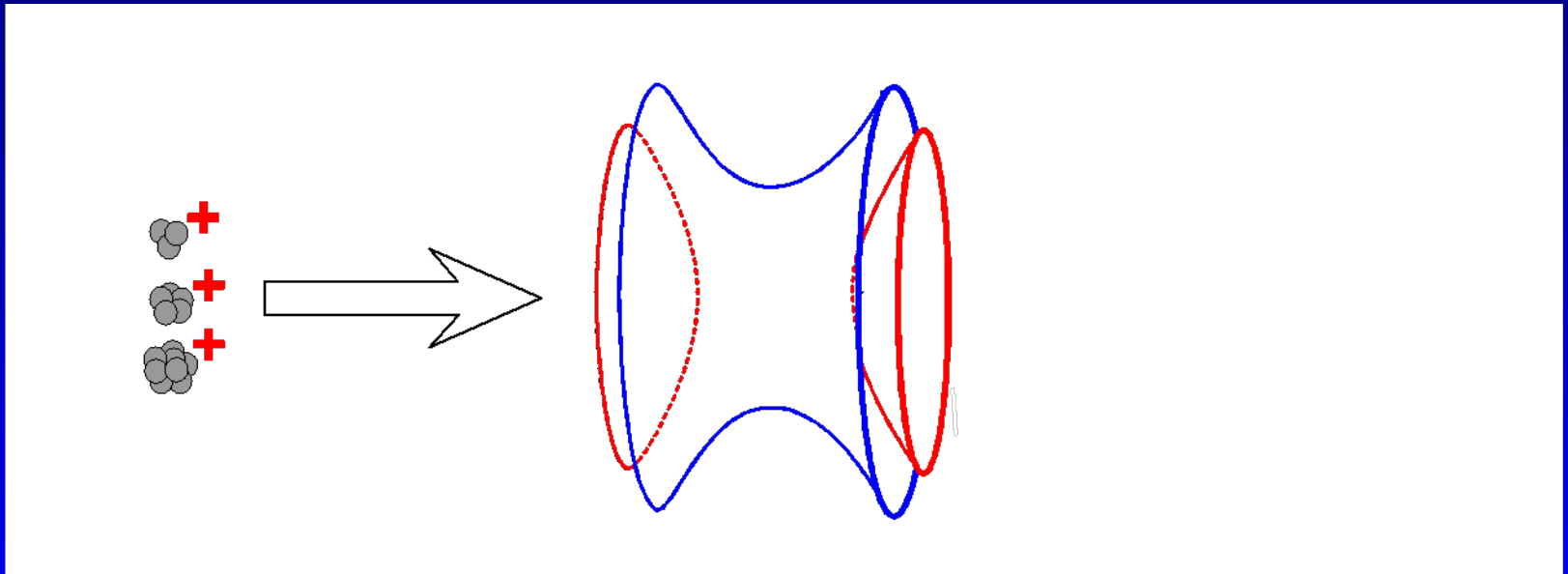
# Trap Electrodes

inner diameter  
of ring electrode  
40 mm



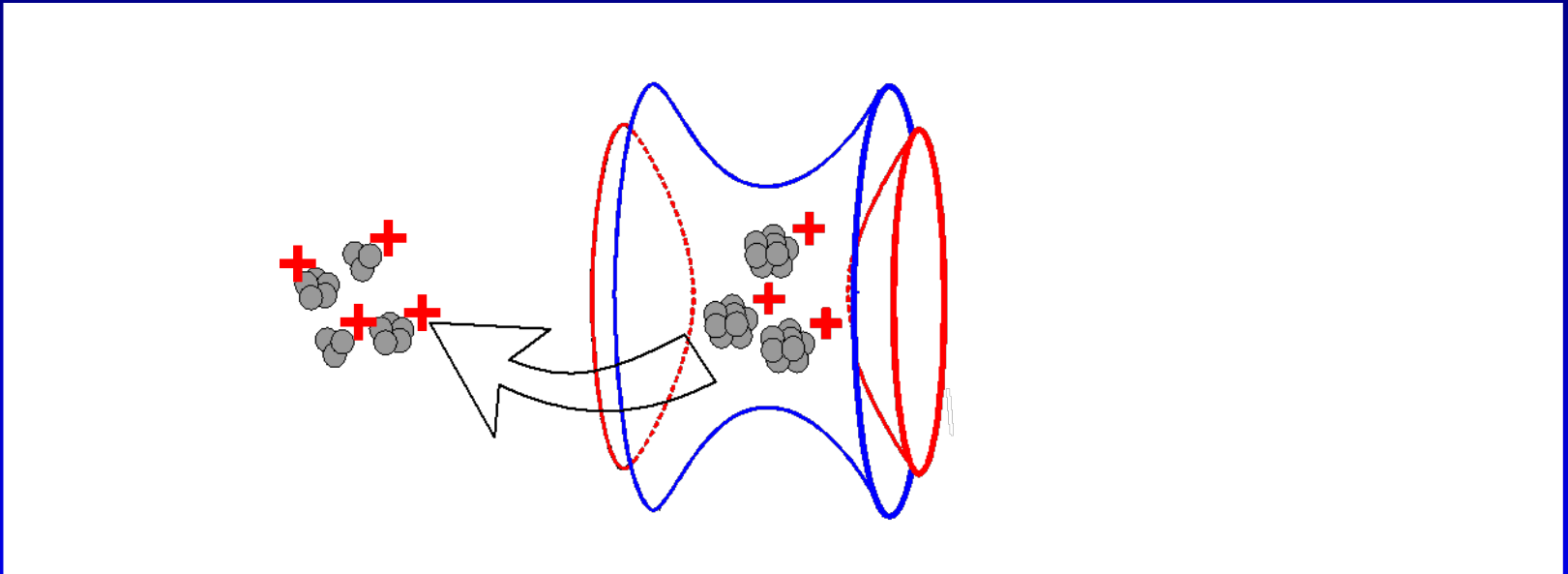
Note:  
Miniaturization is  
not appreciated !

# Typical experimental sequence



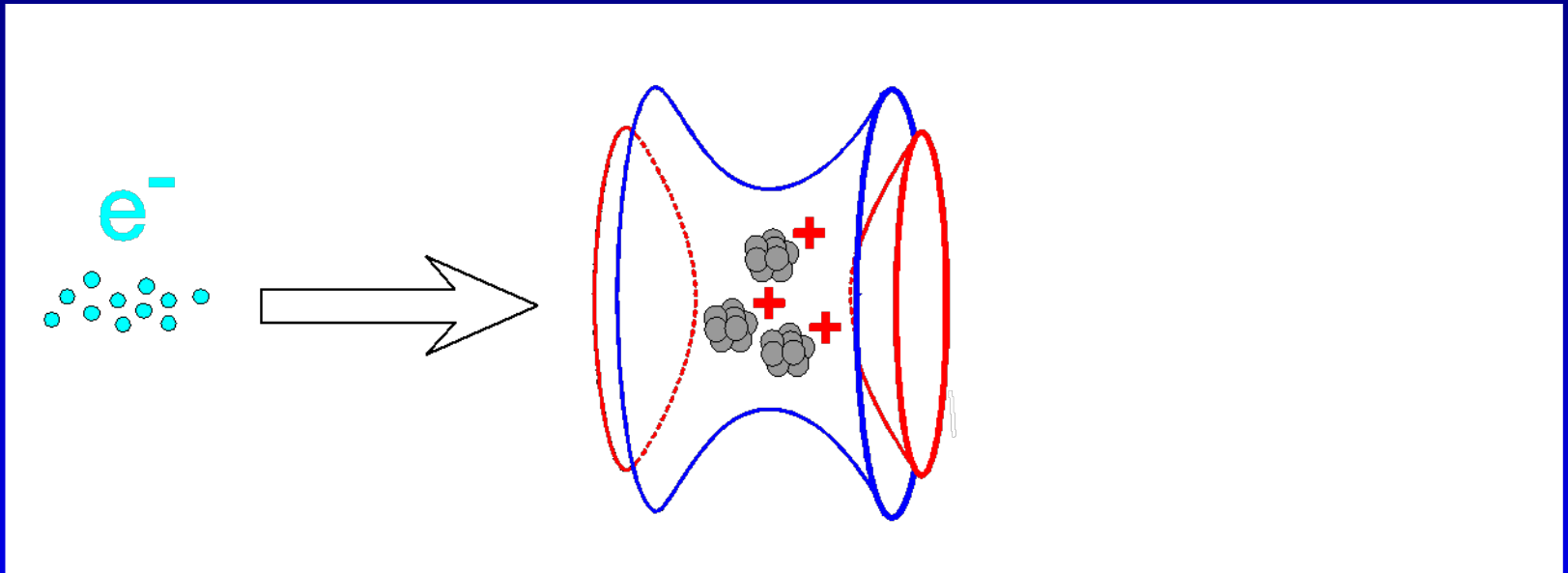
**CAPTURE**

# Typical experimental sequence



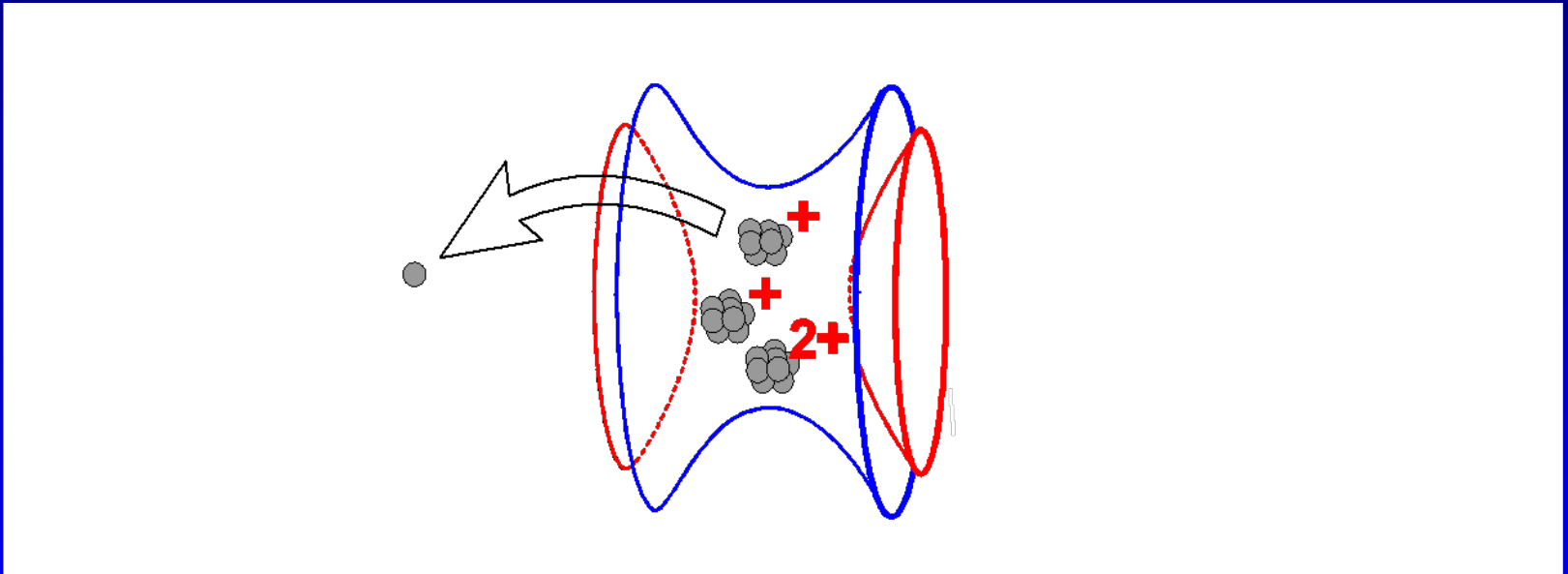
**SELECTION**

# Typical experimental sequence



**INTERACTION**  
(e.g. electron bombardment)

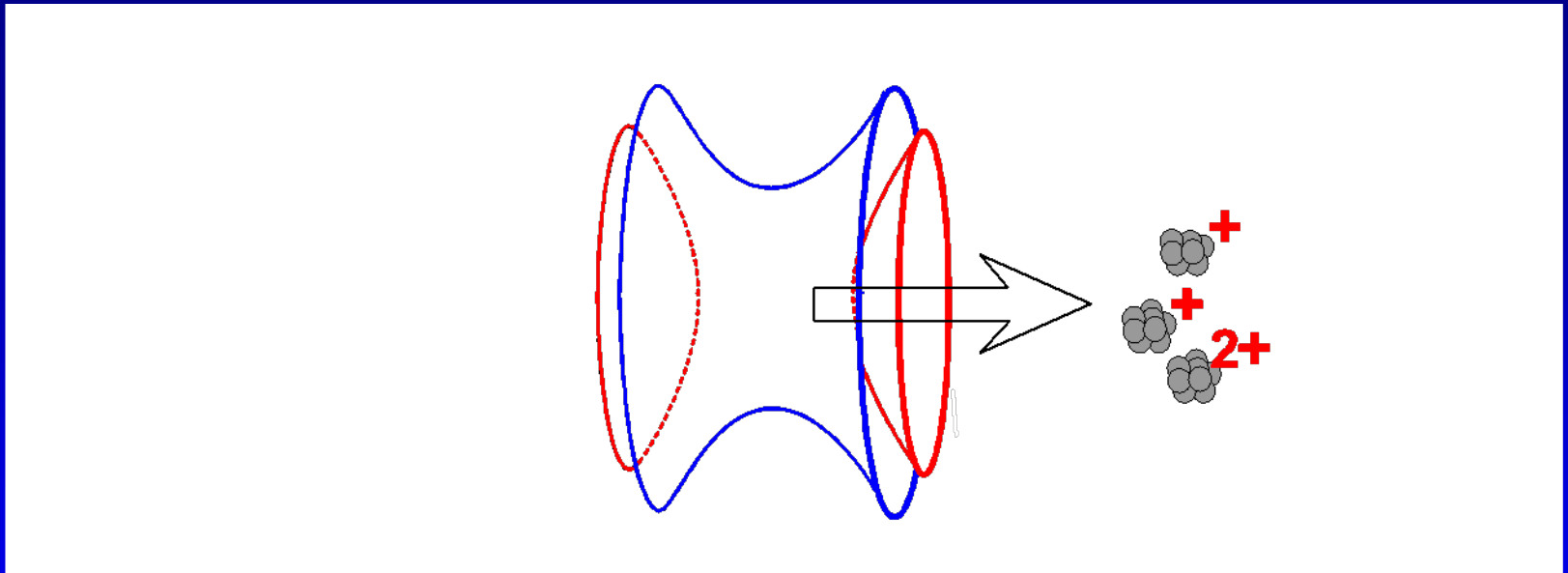
# Typical experimental sequence



**RE-ACTION**

(e.g. ionization and dissociation)

# Typical experimental sequence



**EJECTION**  
for TOF mass analysis

## Overview

### **Other traps and applications**

**FT-ICR MS, precision MS of radionuclides,  
EBITs, electrostatic ion-beam traps**

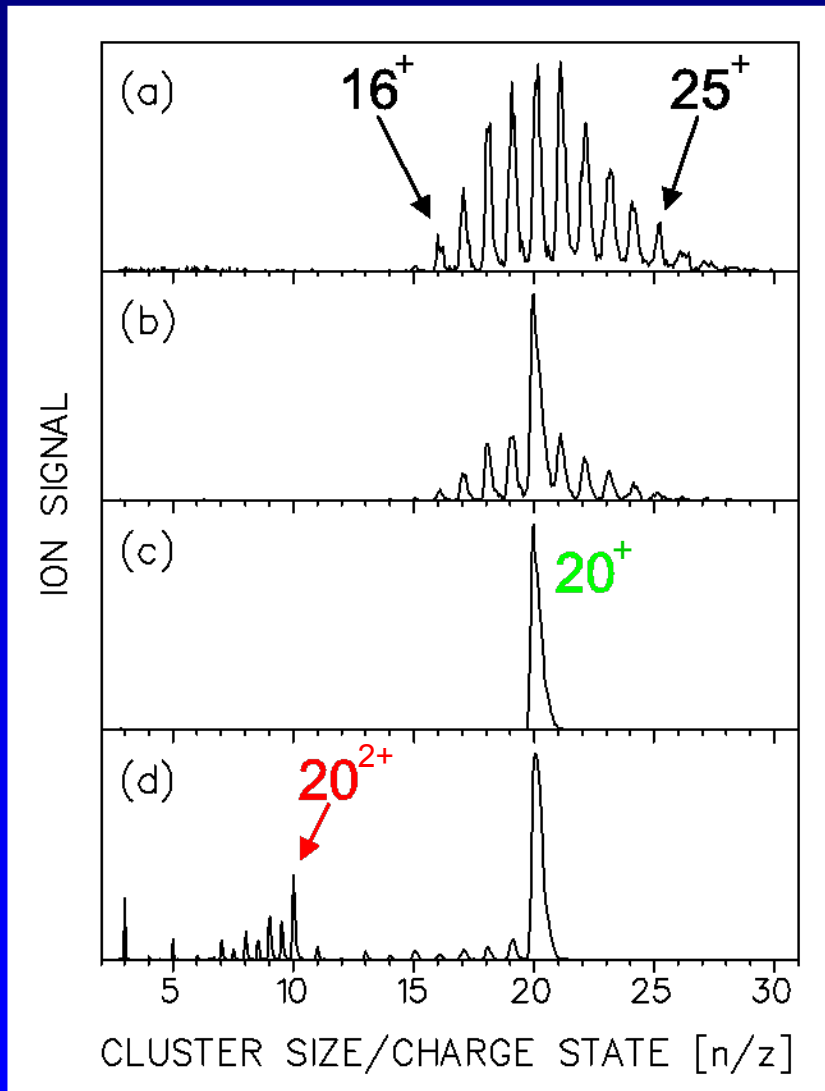
### **ClusterTrap**

clusters? why? how? **what?**

**Other cluster-storage devices**



# electron bombardment of cations time-of-flight spectra (gold clusters)



CAPTURE

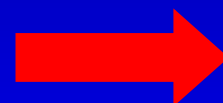
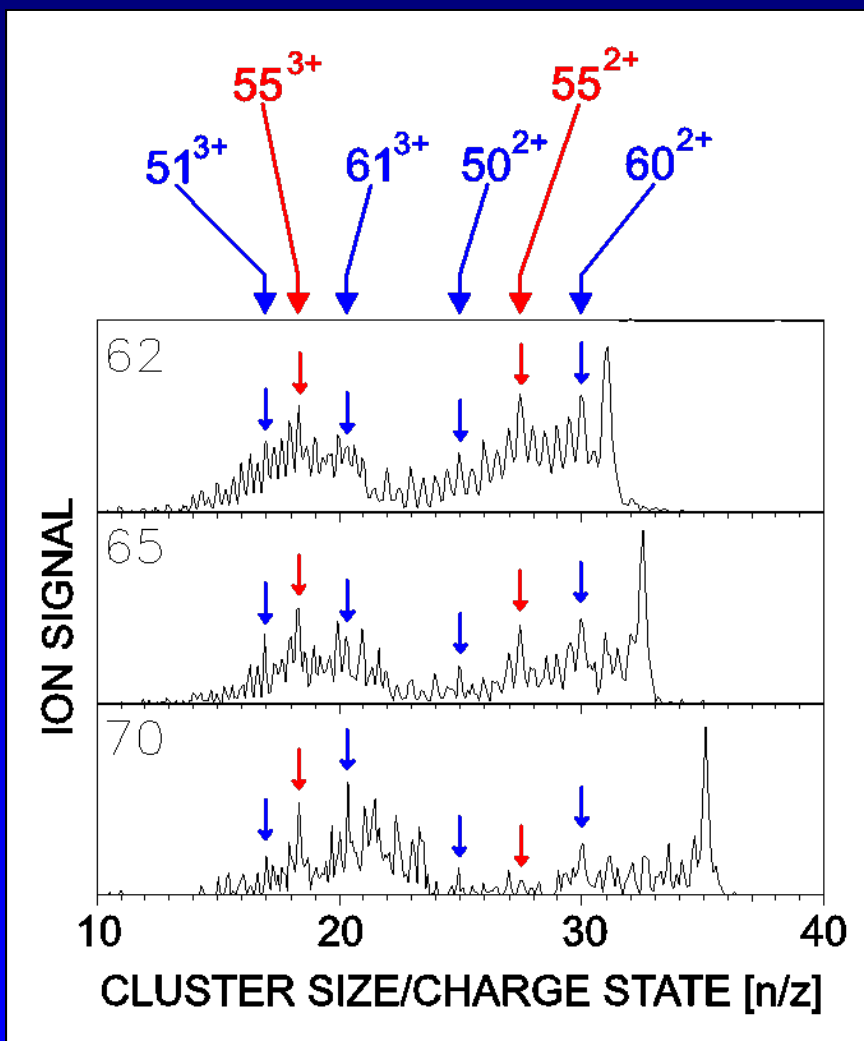
ACCUMULATION

SELECTION

ELECTRON  
BOMBARDMENT

A. Herlert et al.,  
J. Electron Spectrosc. (2000)

# Electron Impact Ionization/Dissociation of Ag-clusters



observation of both

**ELECTRONIC**

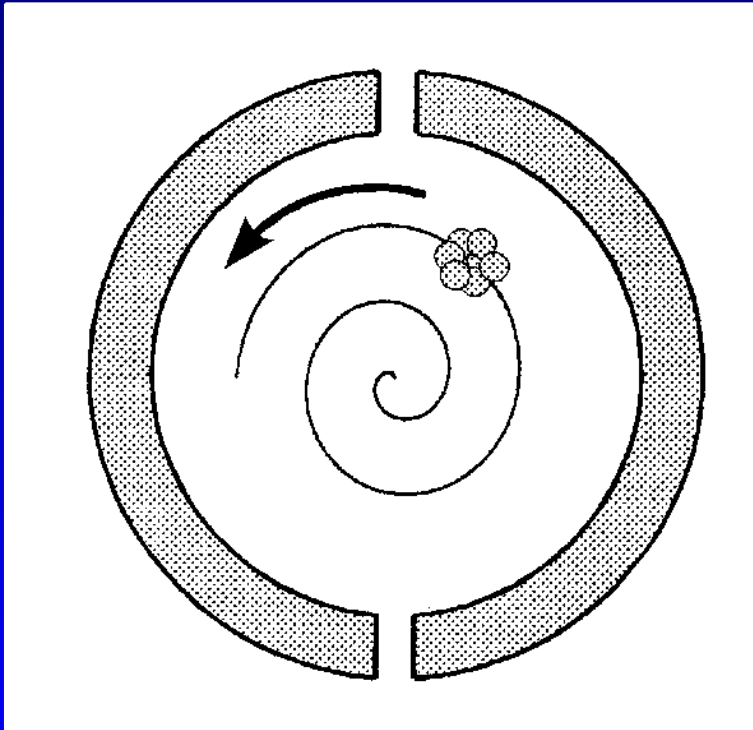
and

**GEOMETRIC**

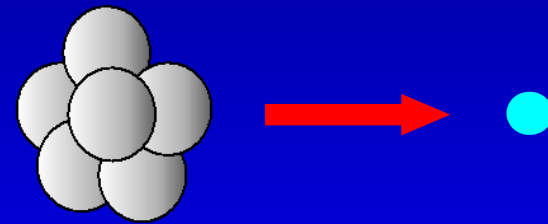
shells

S. Krückeberg et al. (1999)

# Collision Induced Dissociation (CID)

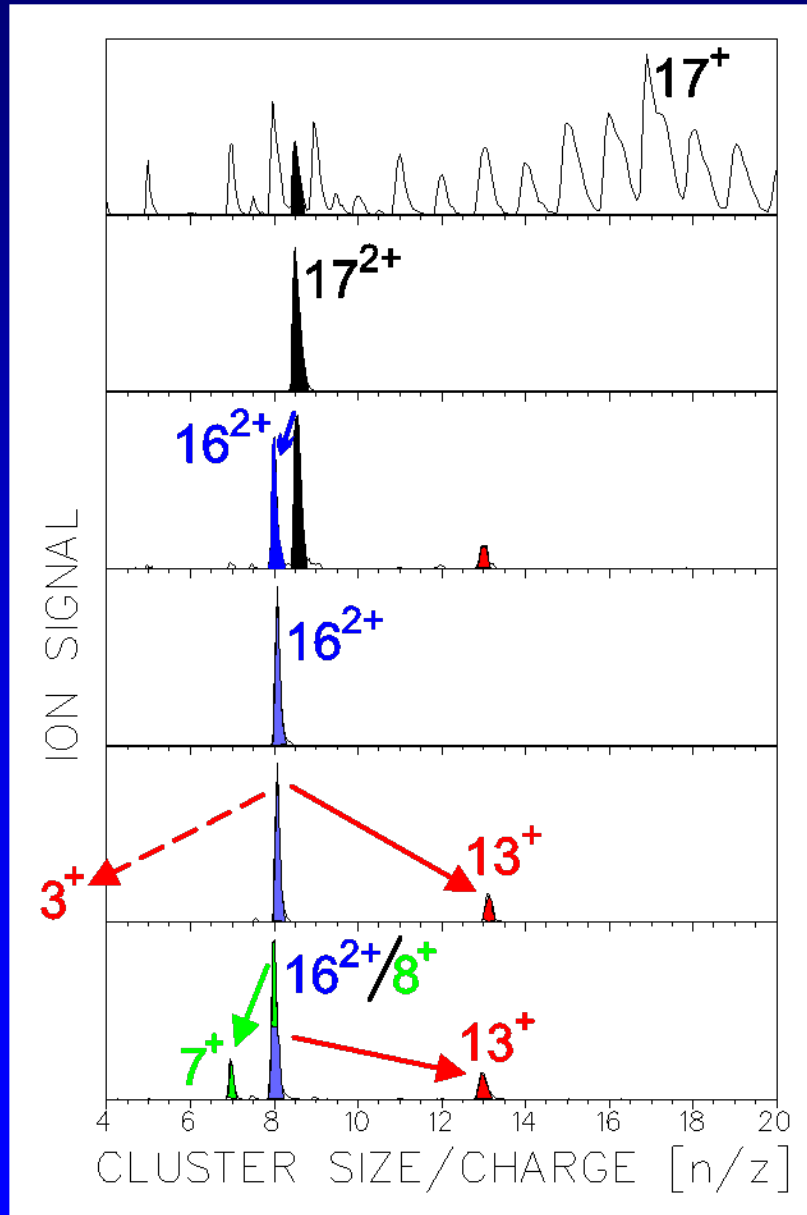


dipole excitation



(Many) collisions  
with noble-gas atoms

# CID of product ions: How do they break apart ? => decay channels



capture/accumulation and  
electron bombardment

1. selection

CID

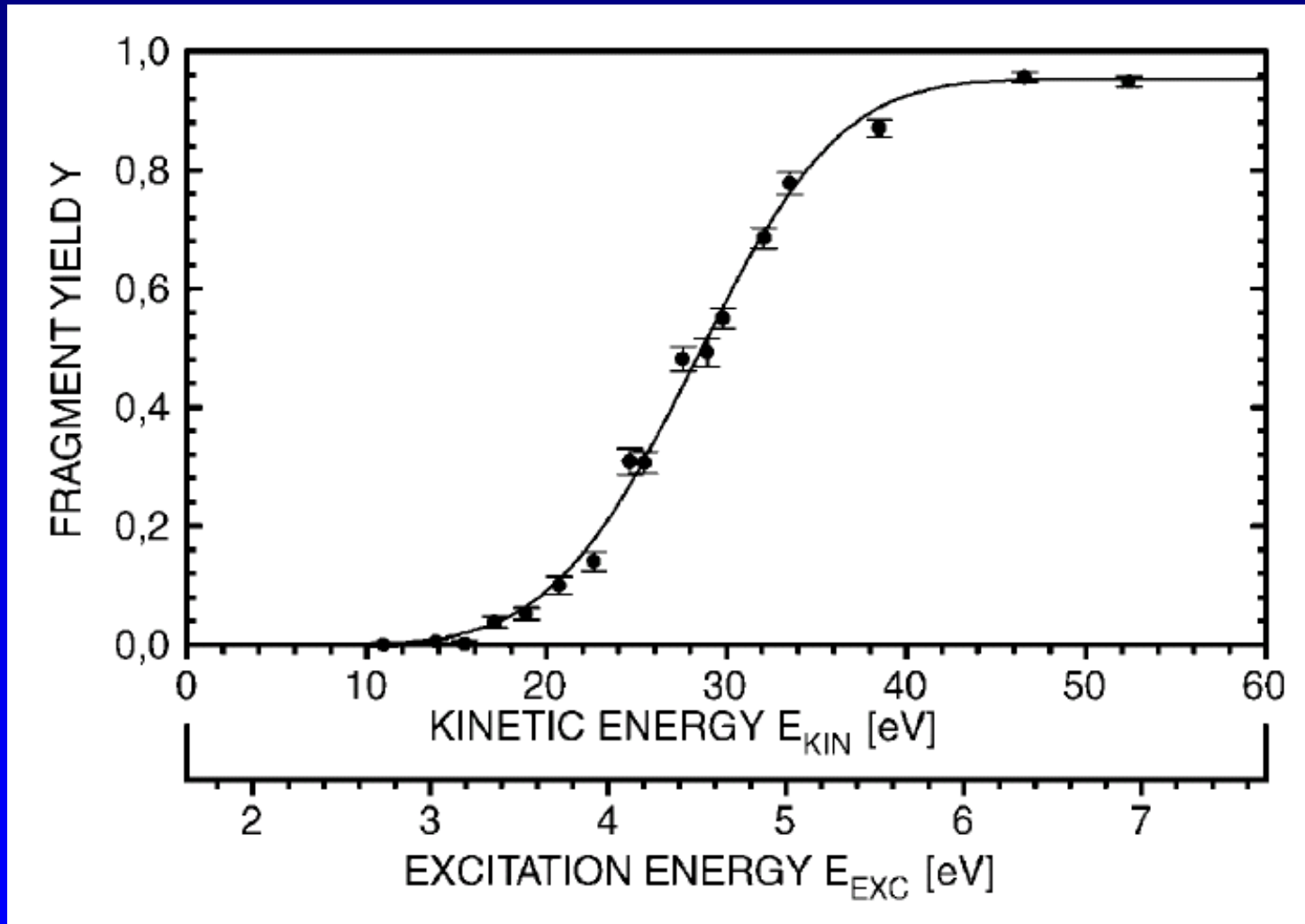
2. selection

CID

CID after first selection

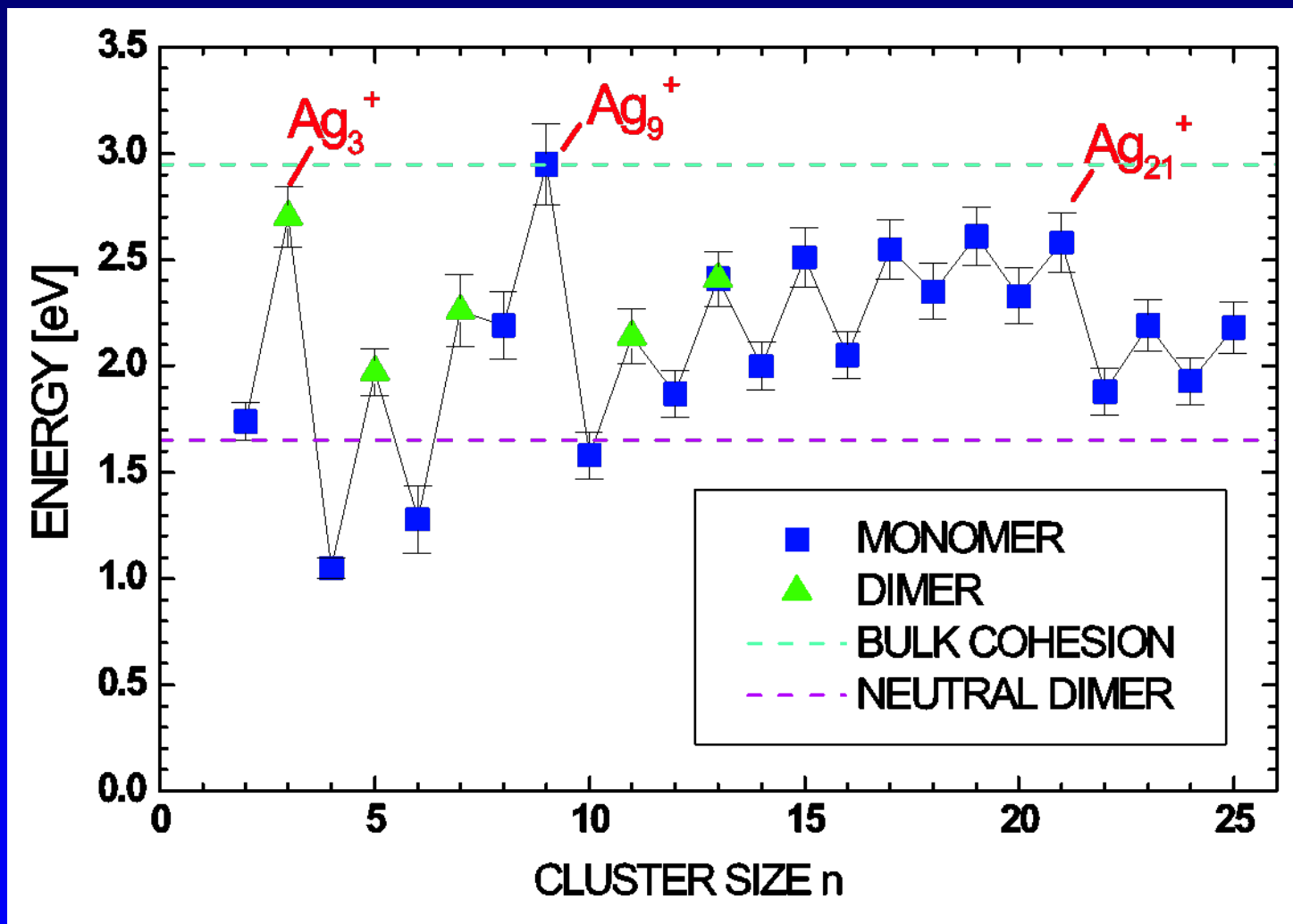
S. Krückeberg et al., ZPD (1997)

CID revisited: **At what energy do they break apart ?**  
**=> dissociation energies**



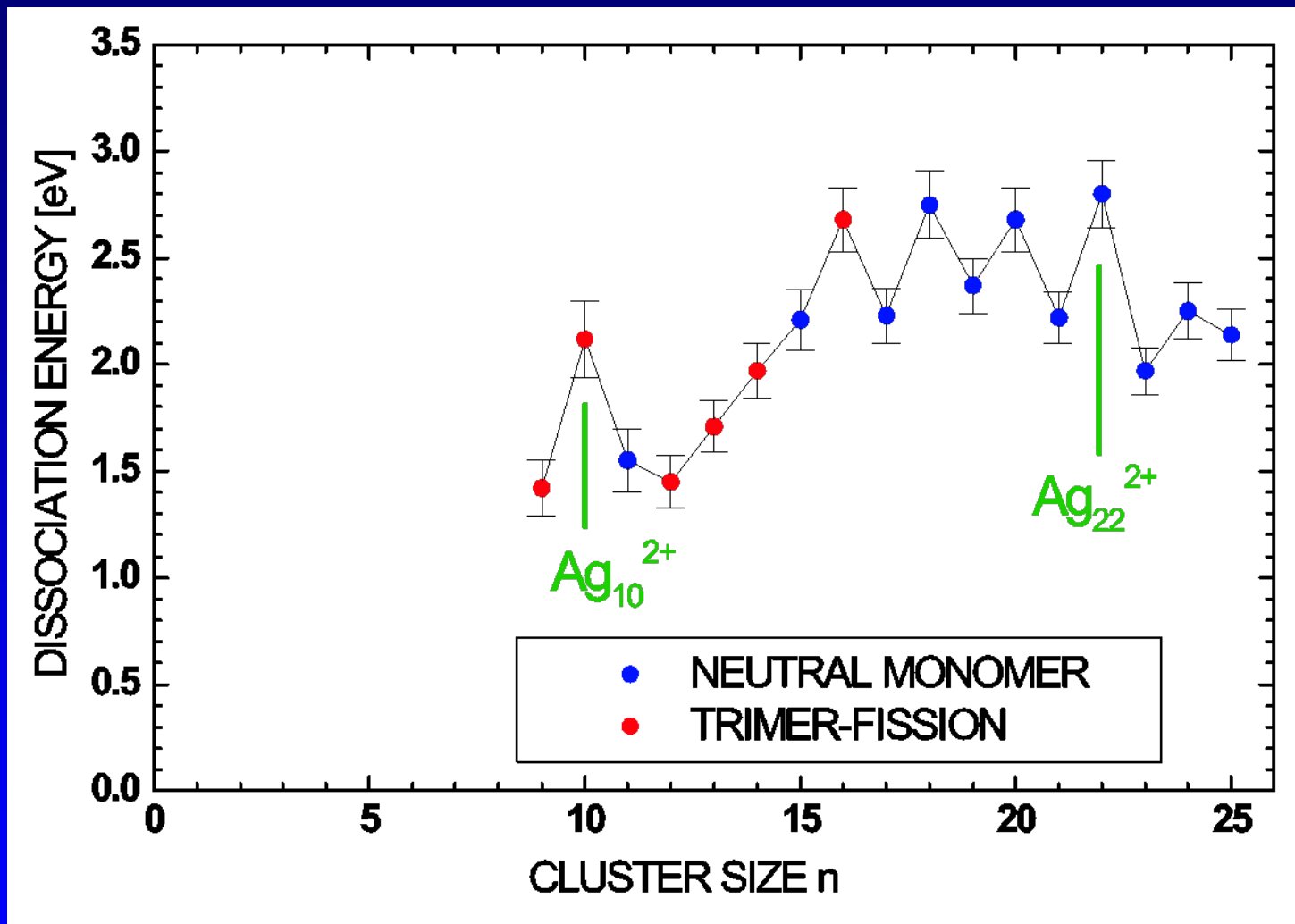
Krückeberg (EPJD, 1999)

# Dissociation energies from CID

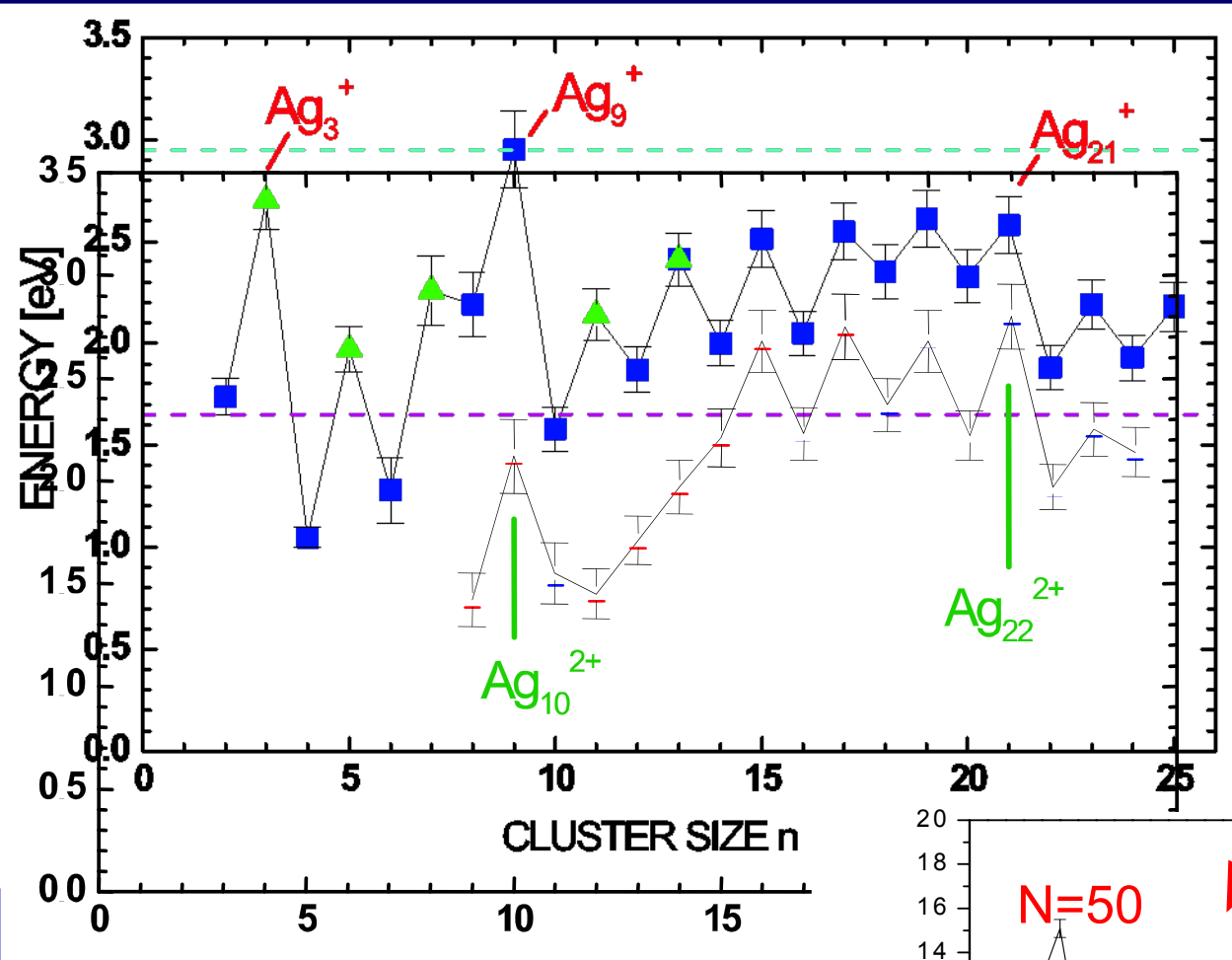


S. Krückeberg et al., JCP (1999)

# Dissociation energies from CID



S. Krückeberg et al., PRA (1999)

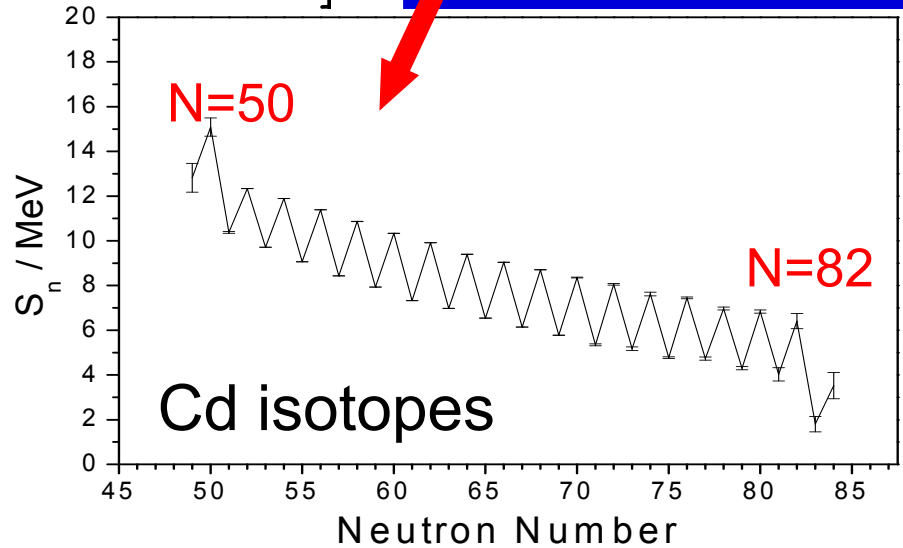


Dissociation energies from CID

cf. neutron-separation energies from mass meas.

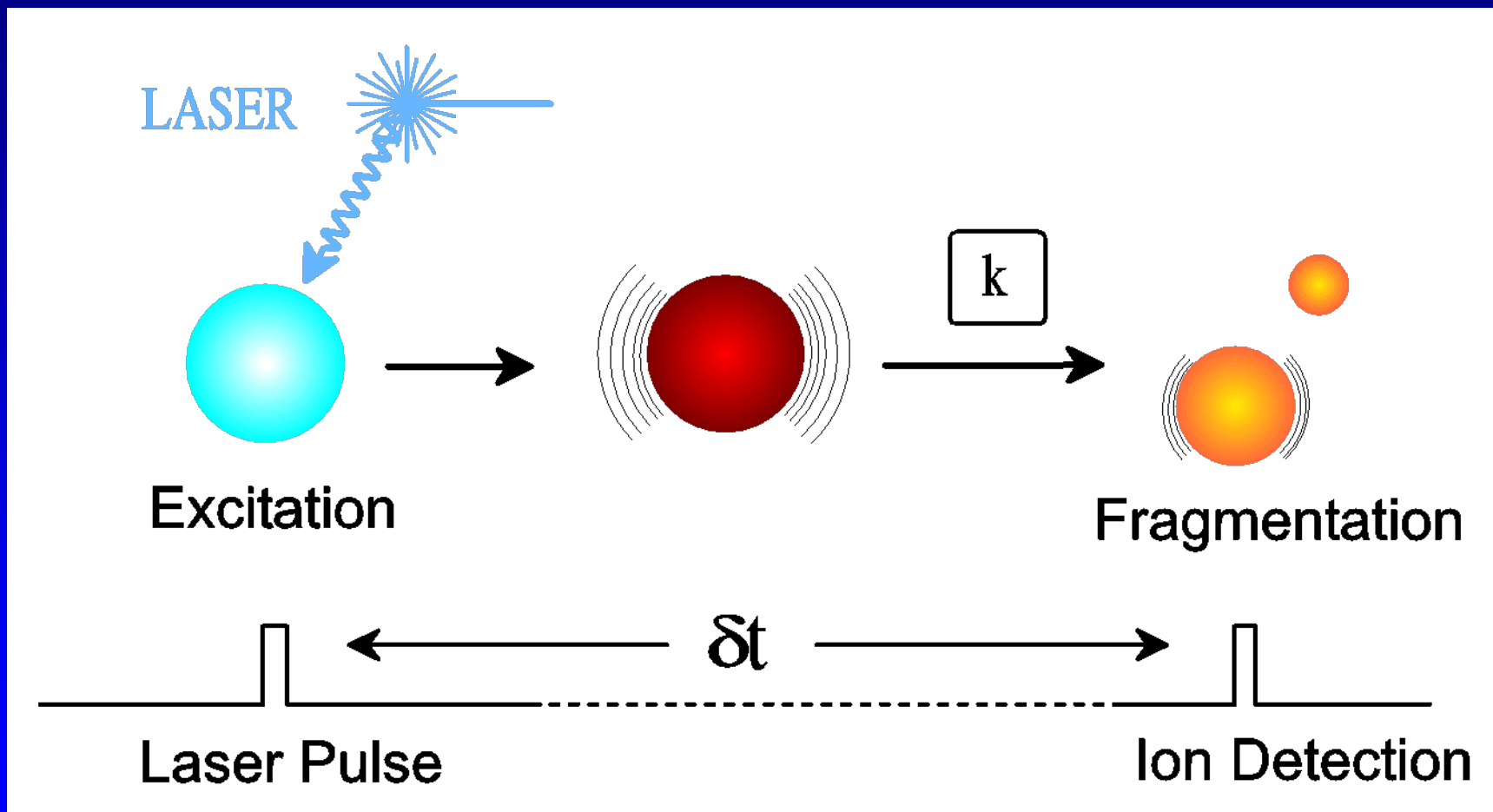
However:

- impact parameter? => energy?
- time of collision?





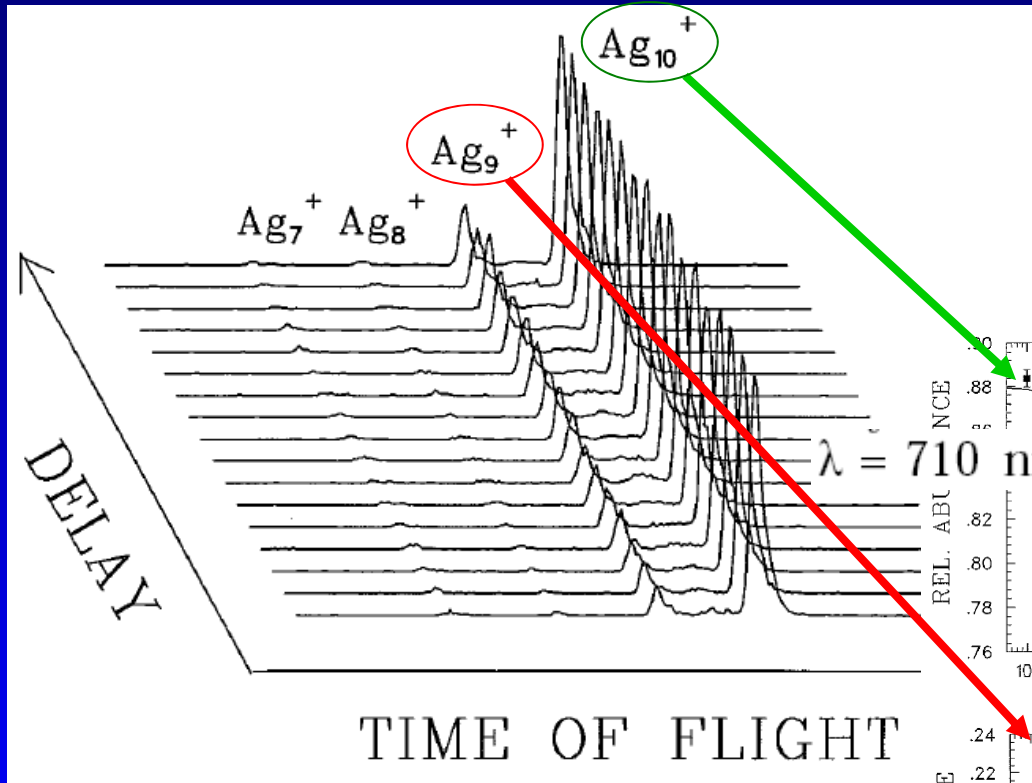
# Dissociation energies from Time – resolved photodissociation



C. Walther et al., CPL (1996), M. Lindinger et al., ZPD (1997)

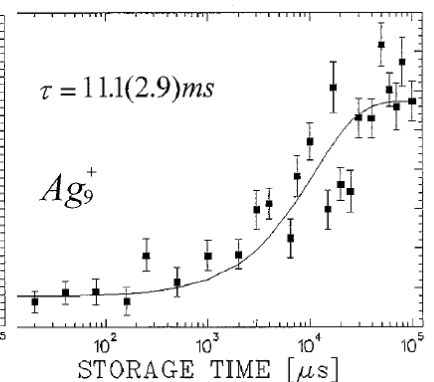
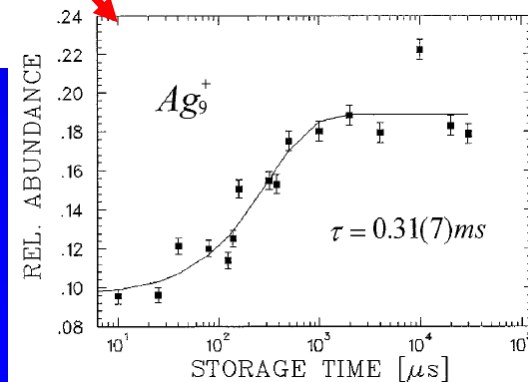
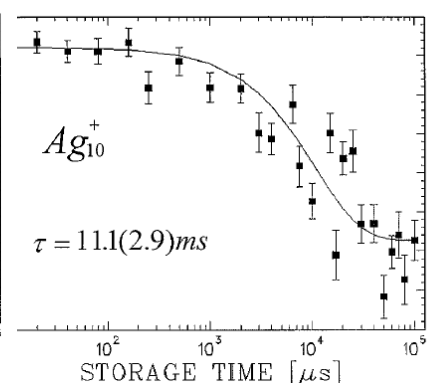
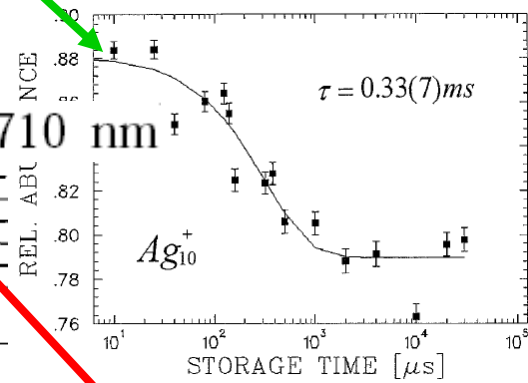
# Time – resolved photodissociation

Defined  
- excitation time and  
- excitation energy



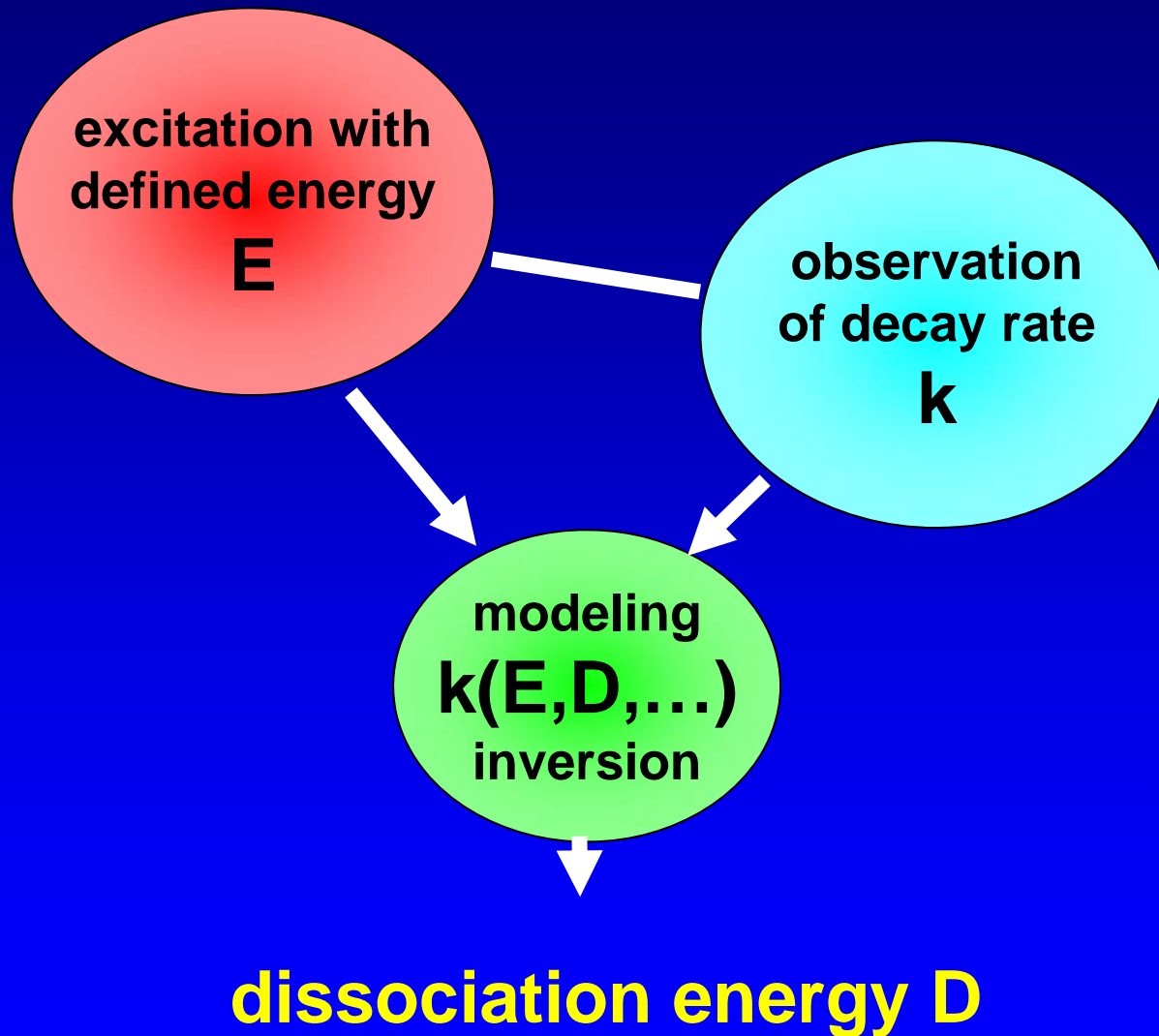
$\lambda = 710 \text{ nm}$

$\lambda = 780 \text{ nm}$

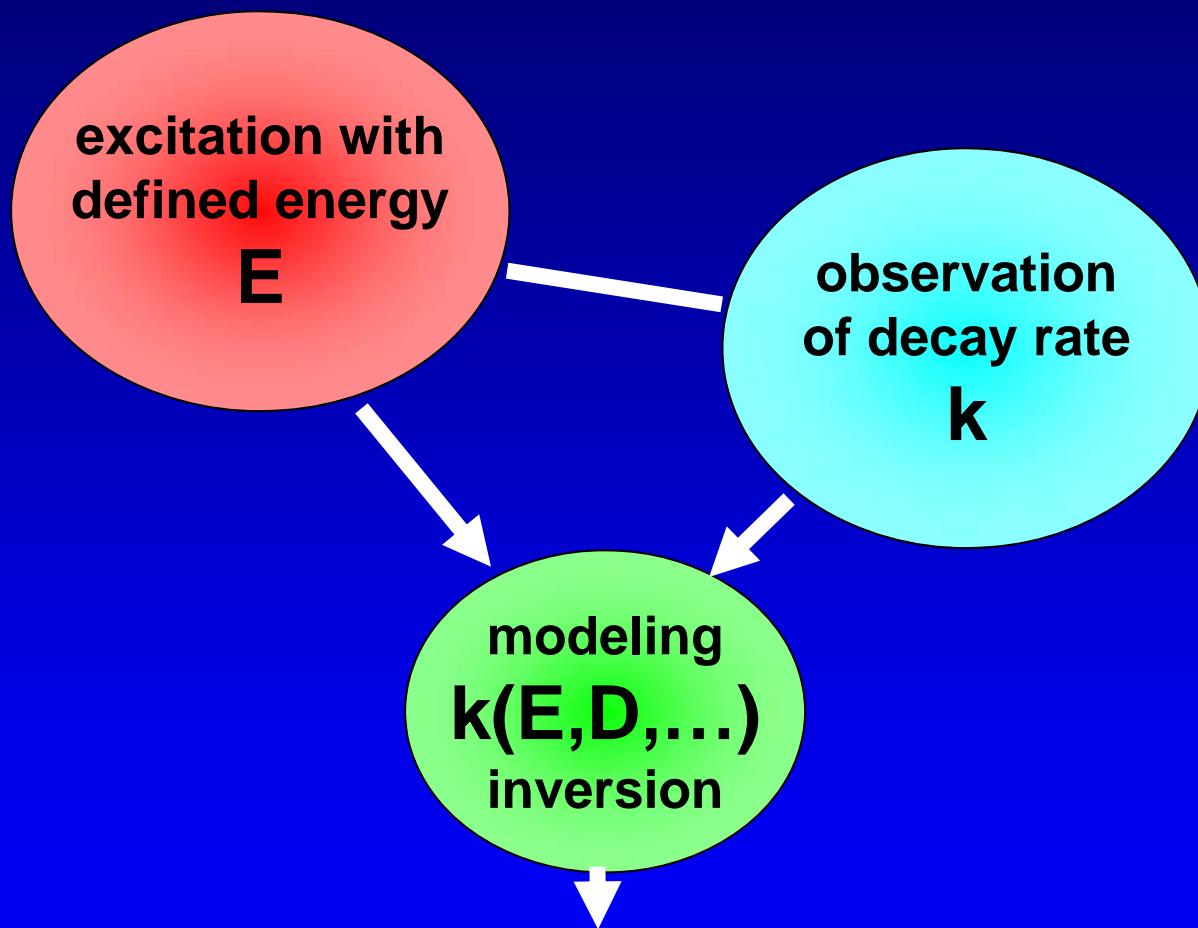


Walther et al., Z. Phys. D., 1996  
Lindinger et al., Z. Phys. D., 1997  
Hild et al., Phys. Rev. A, 1998

# Determination of dissociation energy – in principle



# Determination of dissociation energy – in principle

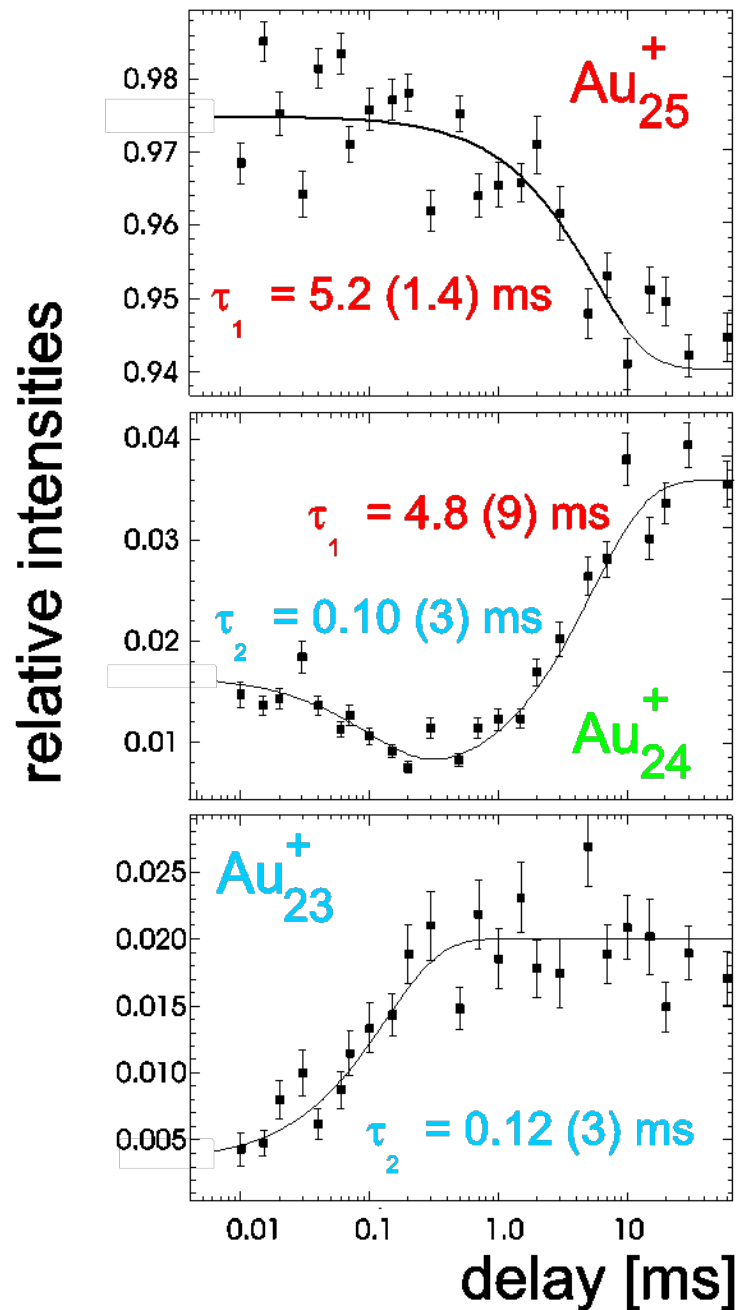


**and in praxis:** - value of  $D$  is model-dependent  
- value of  $D$  is dep. on exc. energy  $E$

Observation of precursor and product(s)

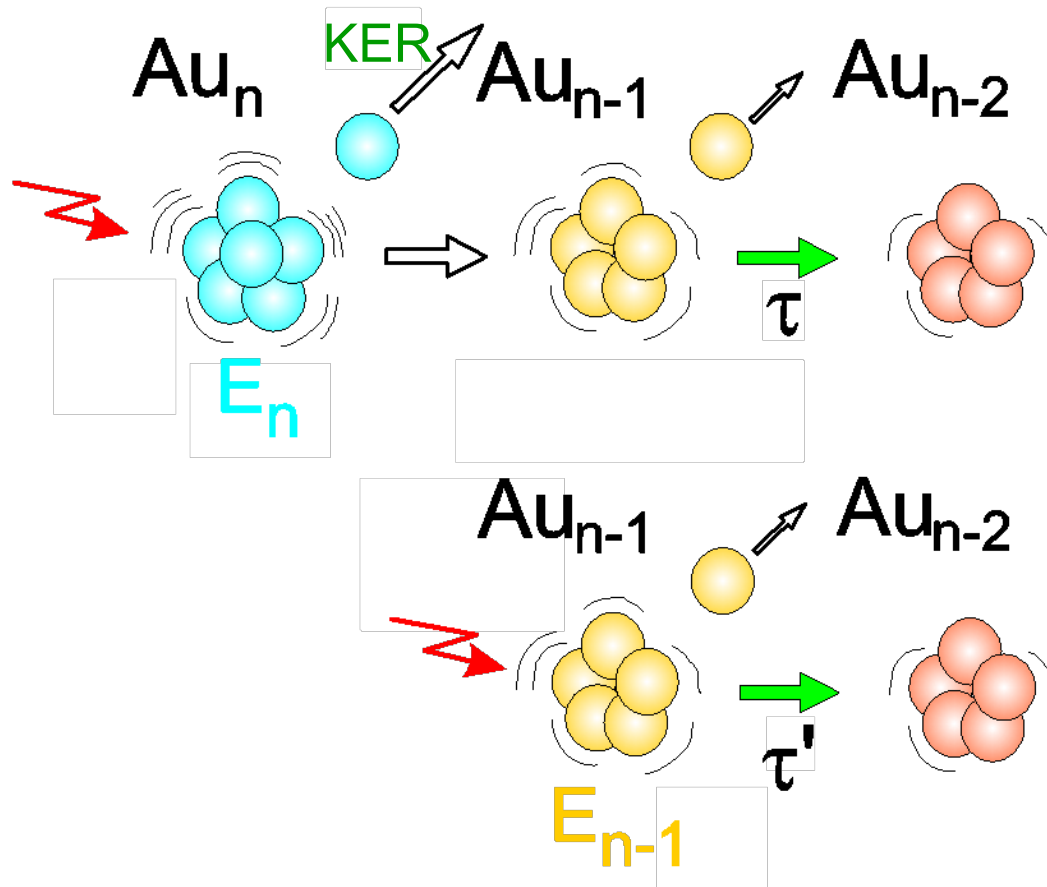
allows

observation of sequential decay



M. Vogel et al., PRL (2001)

# Quasi model-free determination of D



What's the trick?

no need to model the residual excitation energy left after the dissociation

What's the pay-off?

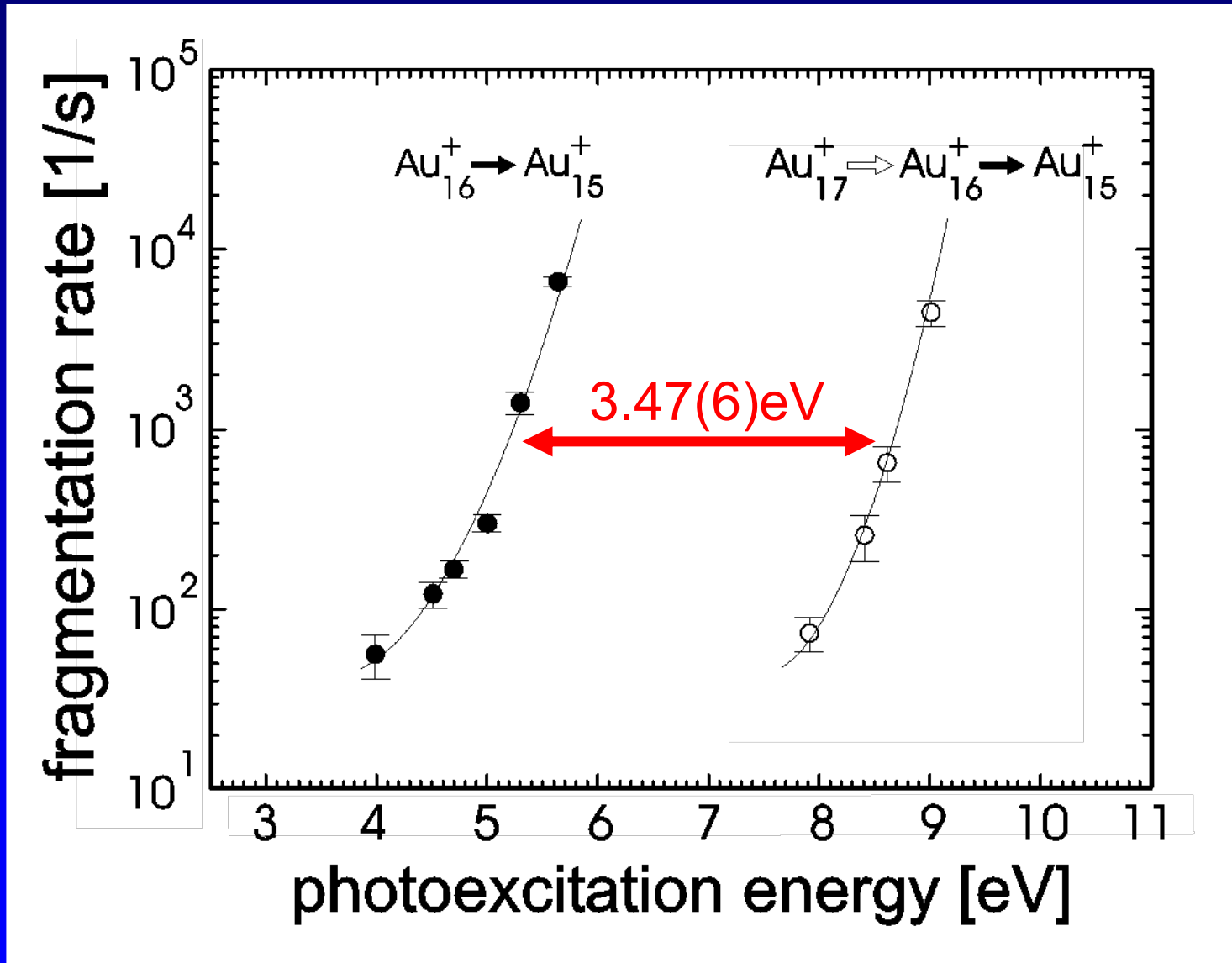
two coordinated measurements needed

$$\text{for } \tau = \tau': \quad E_n - D_n - \text{KER} = E_{n-1}$$

$$\longrightarrow \quad D_n = E_n - E_{n-1} - \text{KER}$$

M. Vogel et al.,  
PRL (2001)

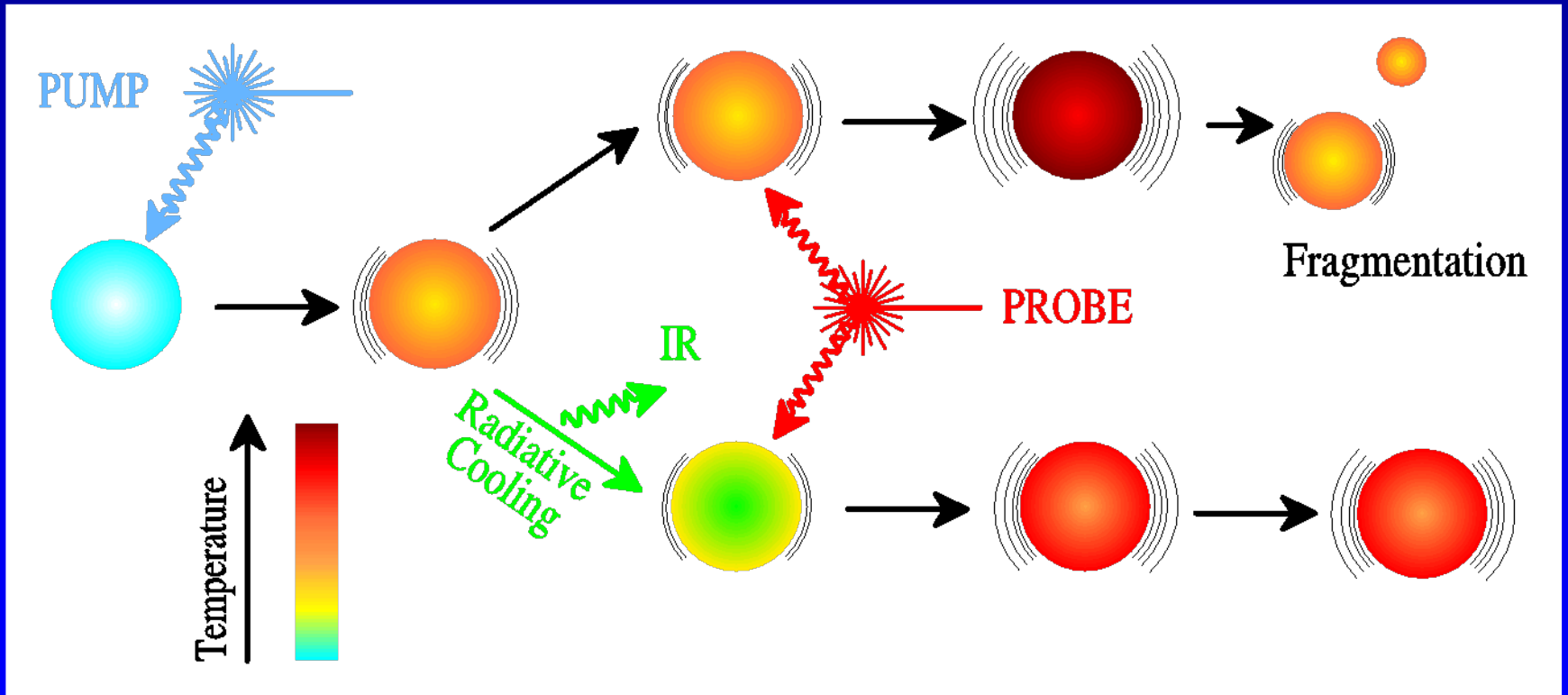
In practise: perform a couple of measurements



# Sequential Excitation

i.e. pump – probe at up to tens of milliseconds

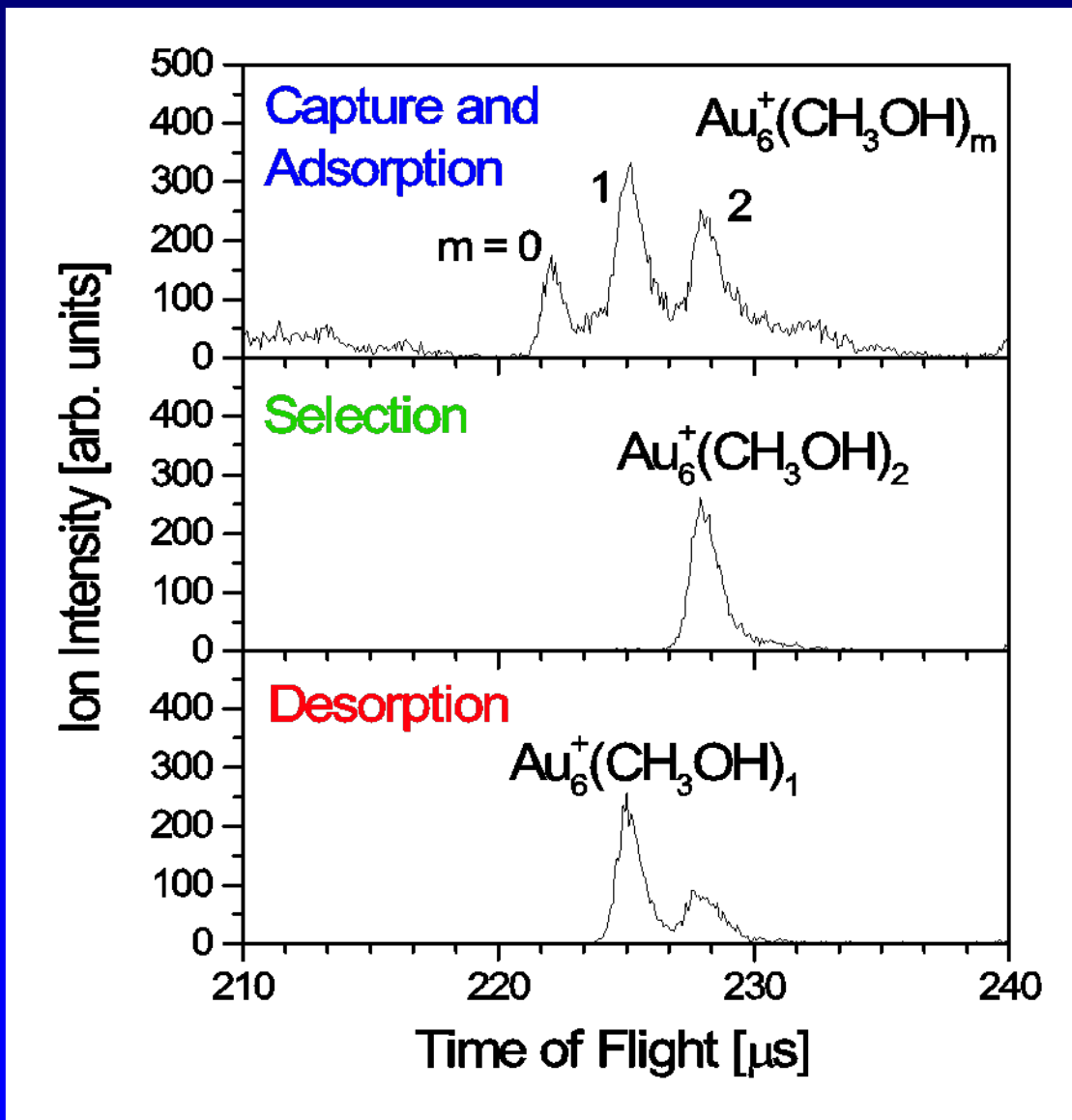
=> Investigation of Radiative Cooling



C. Walther et al., PRL (1999)



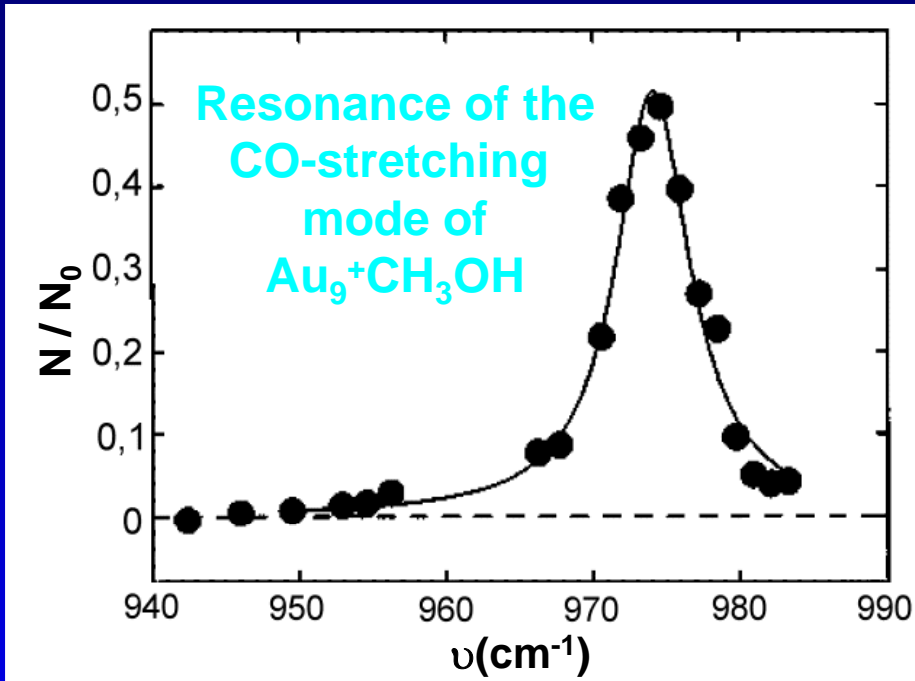
# Attachment and photodetachment of methanol



G. Dietrich et al.,  
CPL (1996), ...  
JCP (2000)

# Infrared Spectroscopy

## Photodetachment of methanol

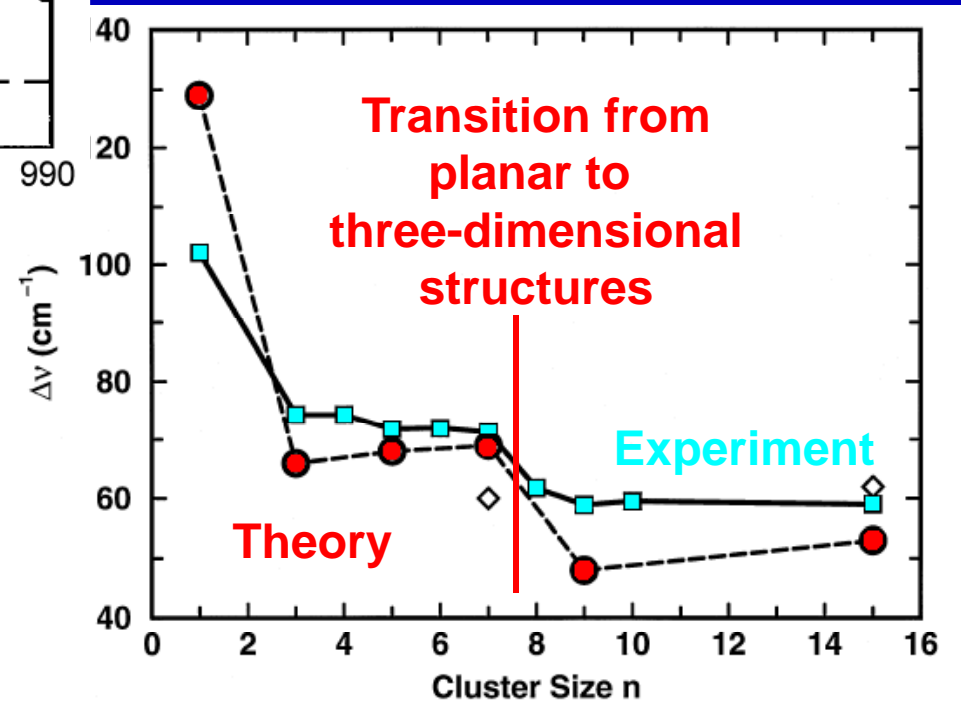


G. Dietrich et al., JCP (2000)

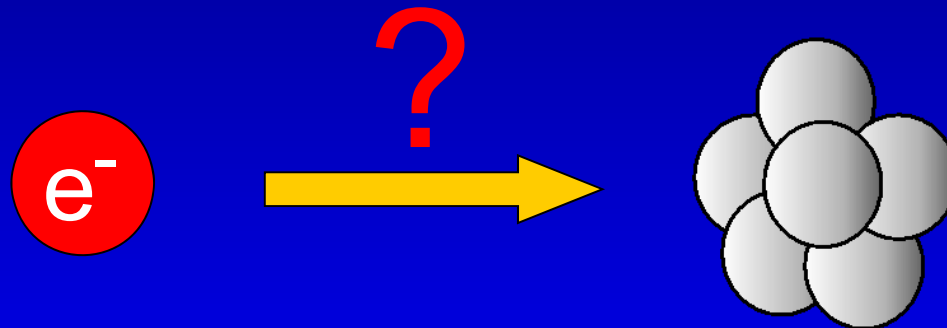
R. Rousseau et al., CPL (1998)

Detachment energies:

M. Vogel et al., JCP (2002)

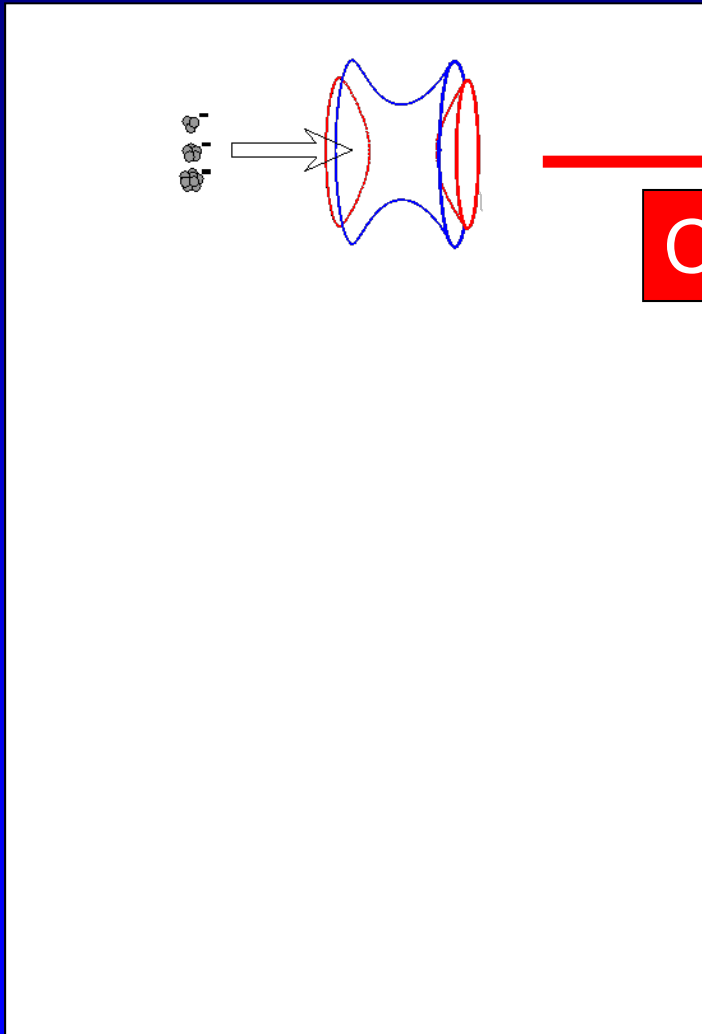


Moving on to further charge states by electron-cluster interaction:

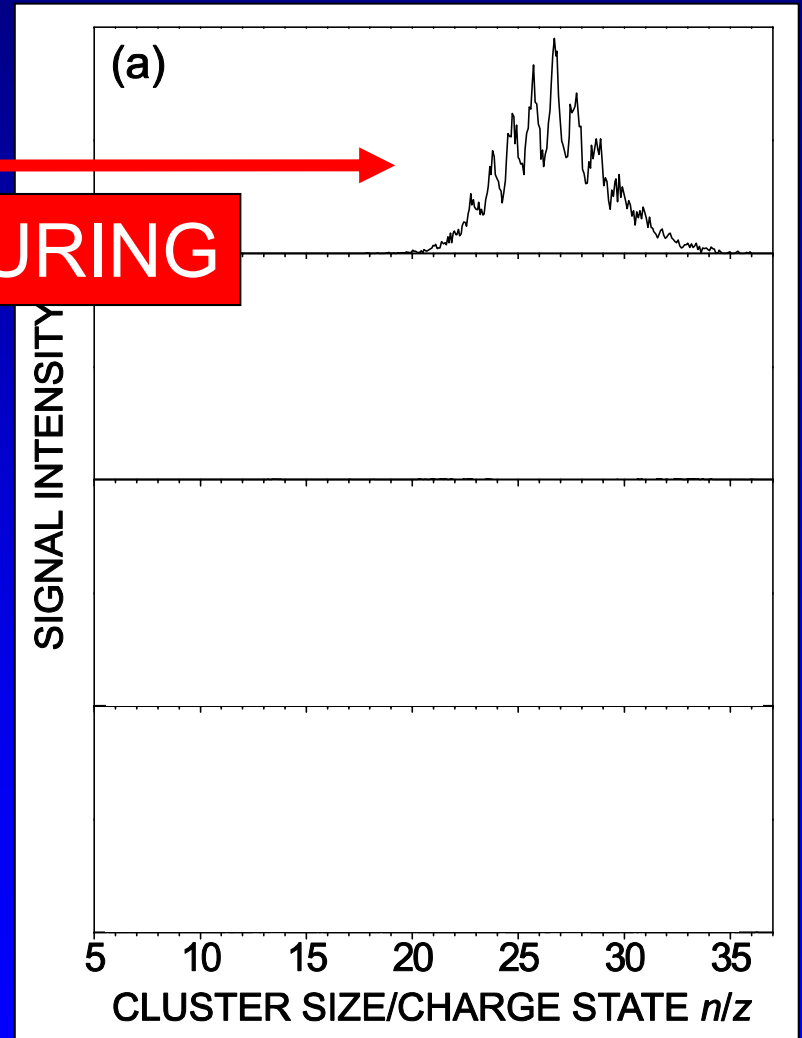


- Electron-impact ionisation for **cationic** clusters (see above)
- Electron attachment for **anionic** clusters

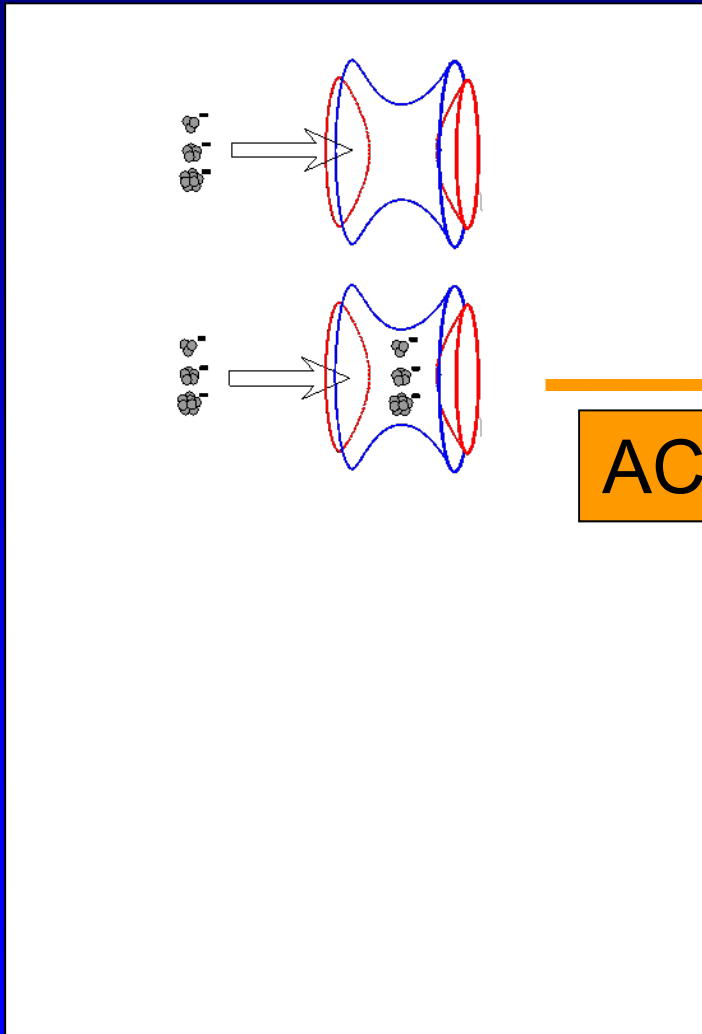
# Dianion production



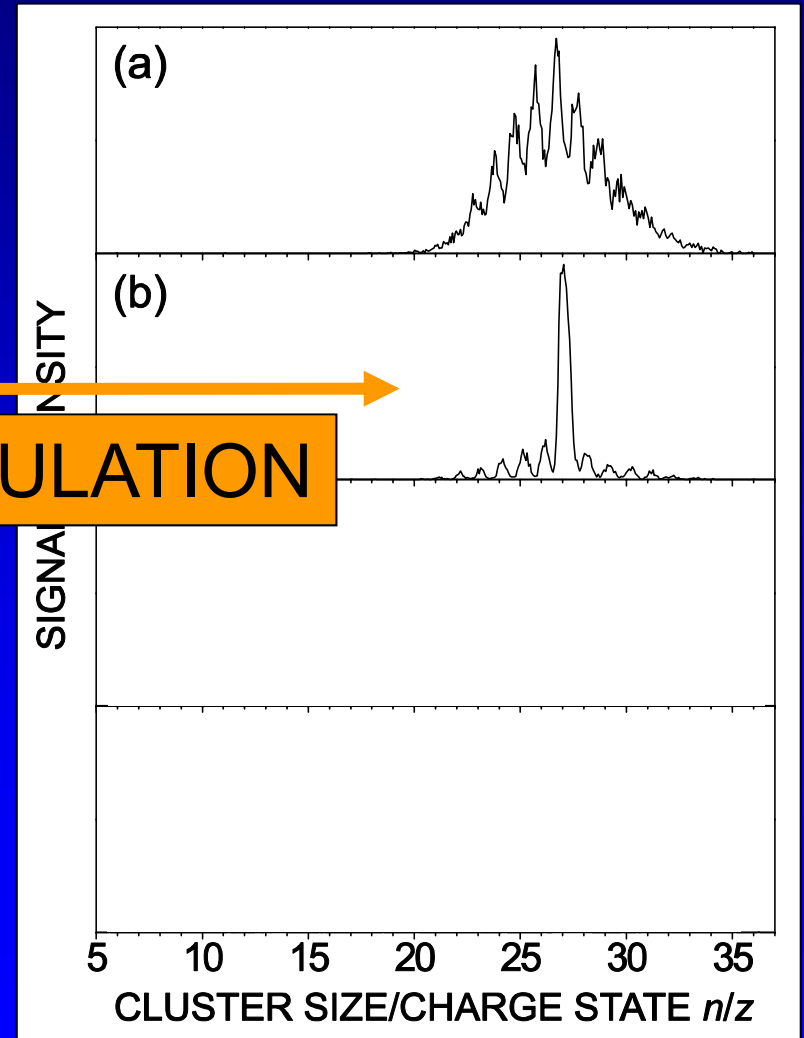
**CAPTURING**



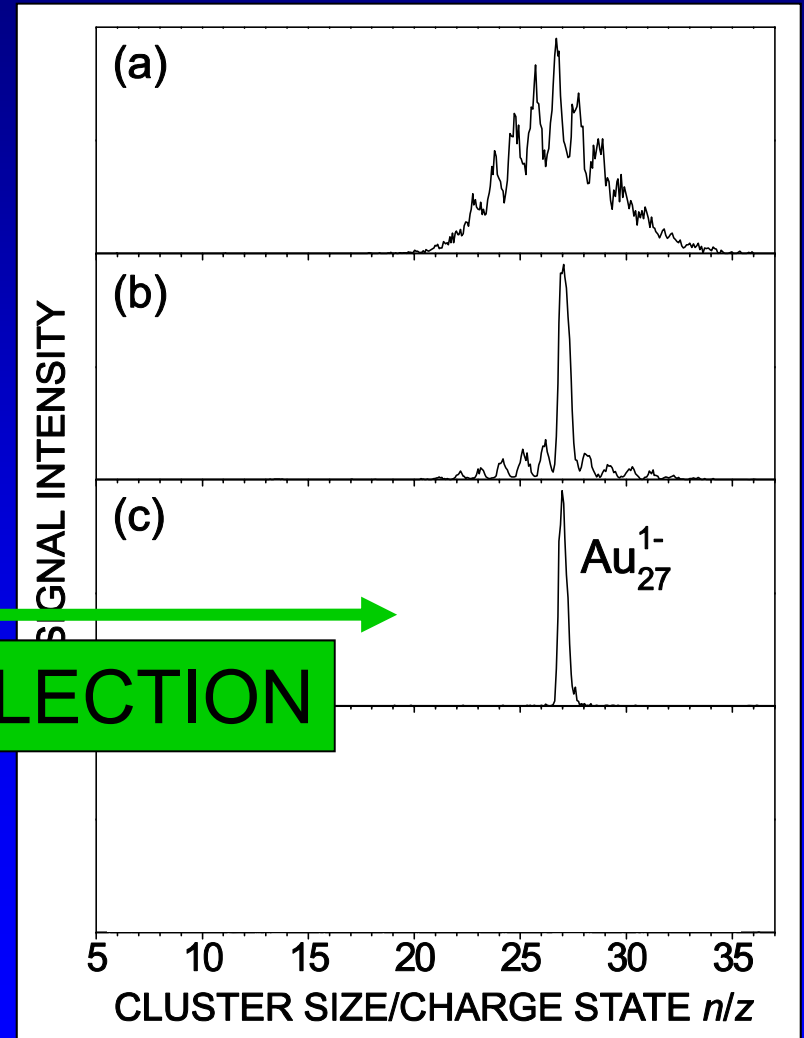
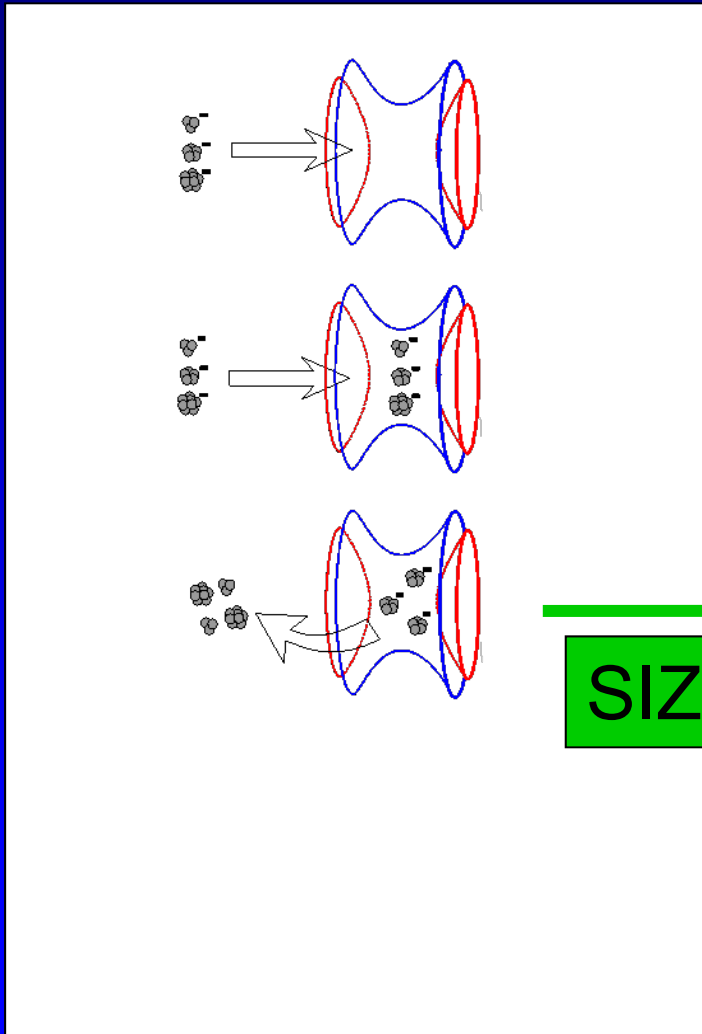
# Dianion production



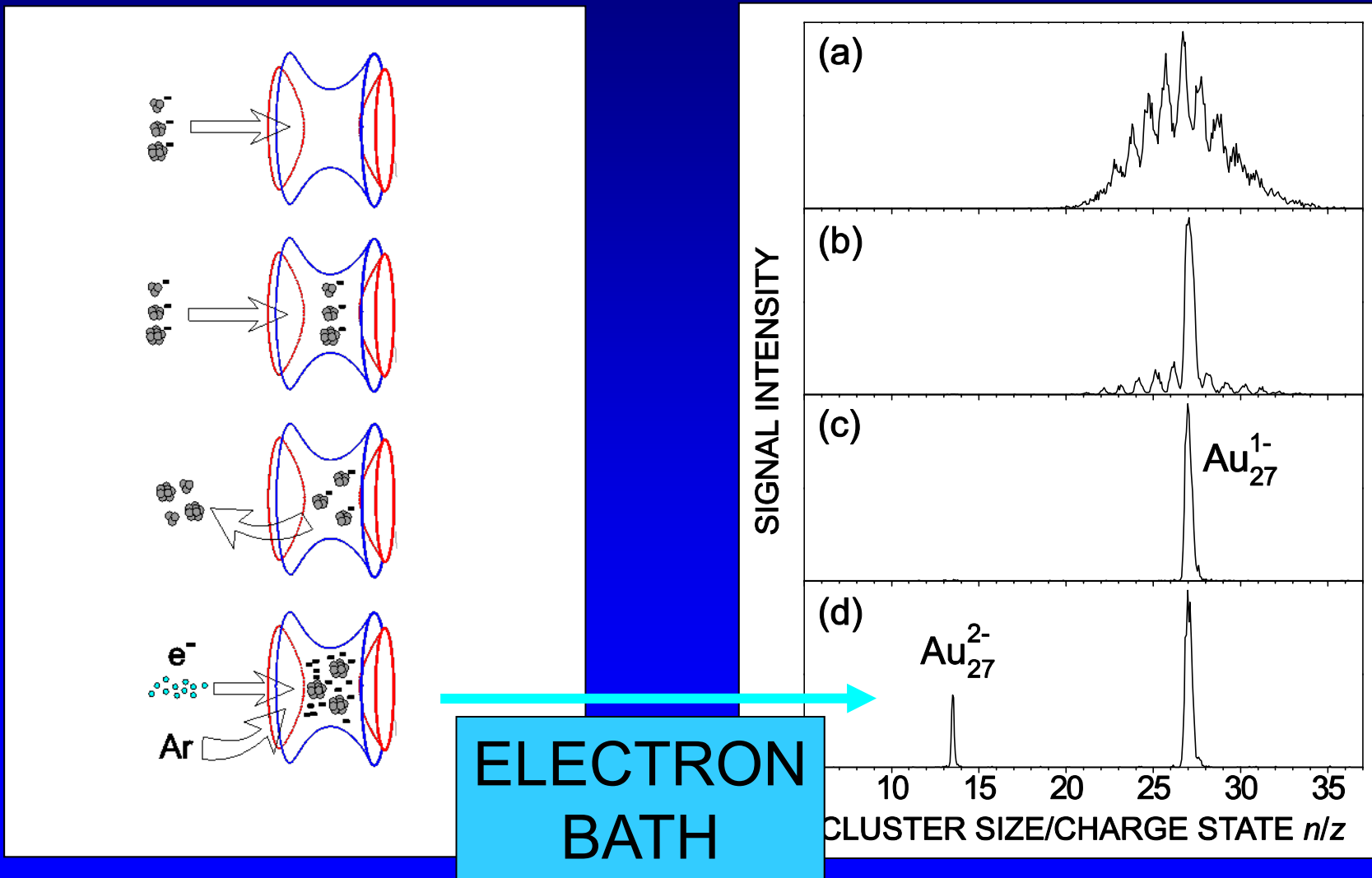
**ACCUMULATION**



# Dianion production

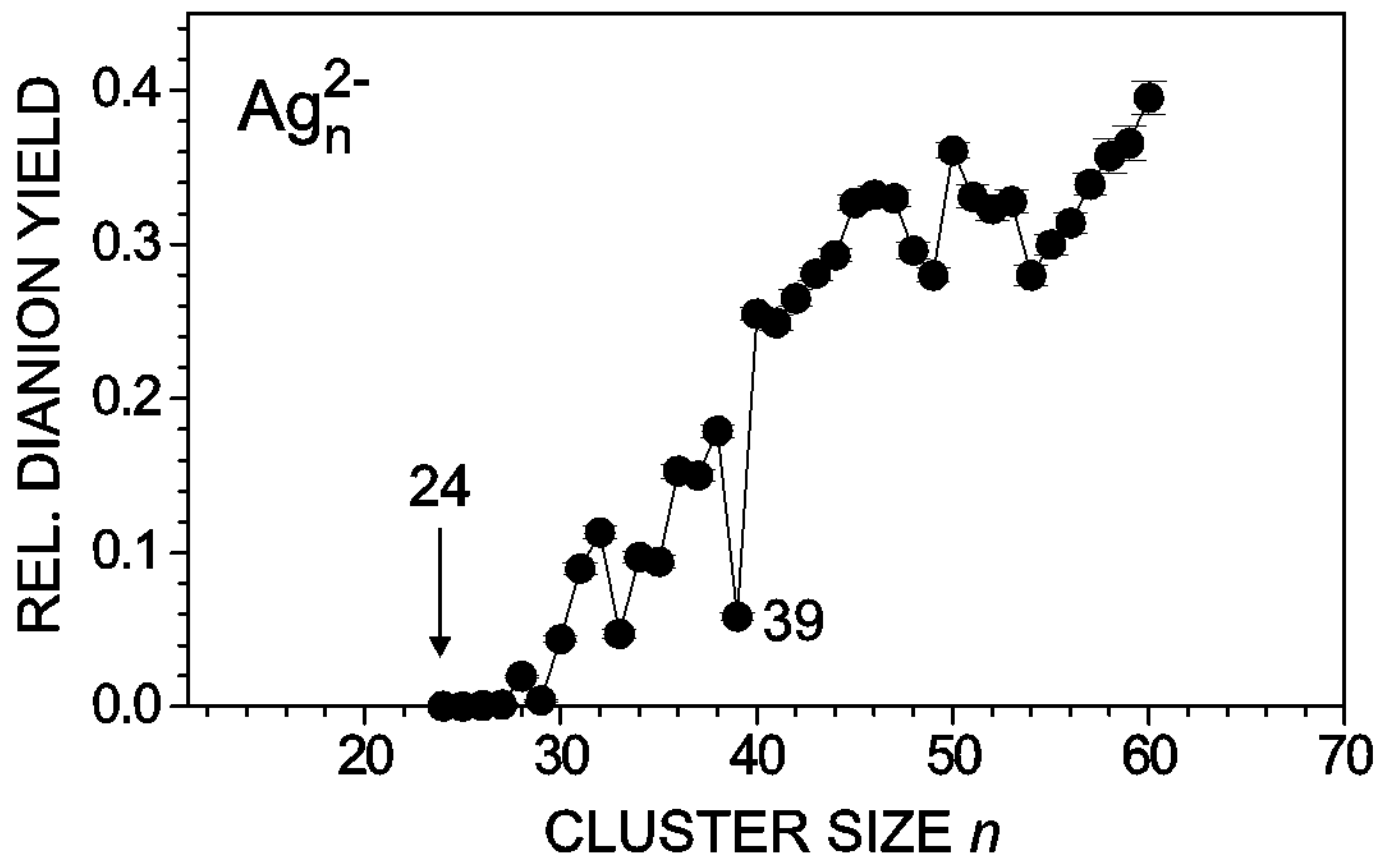


Simultan. storage of clusters,  $m_{\text{cluster}} \approx 5000 \text{ u}$   
and electrons,  $m_e \approx 1/2000 \text{ u}$



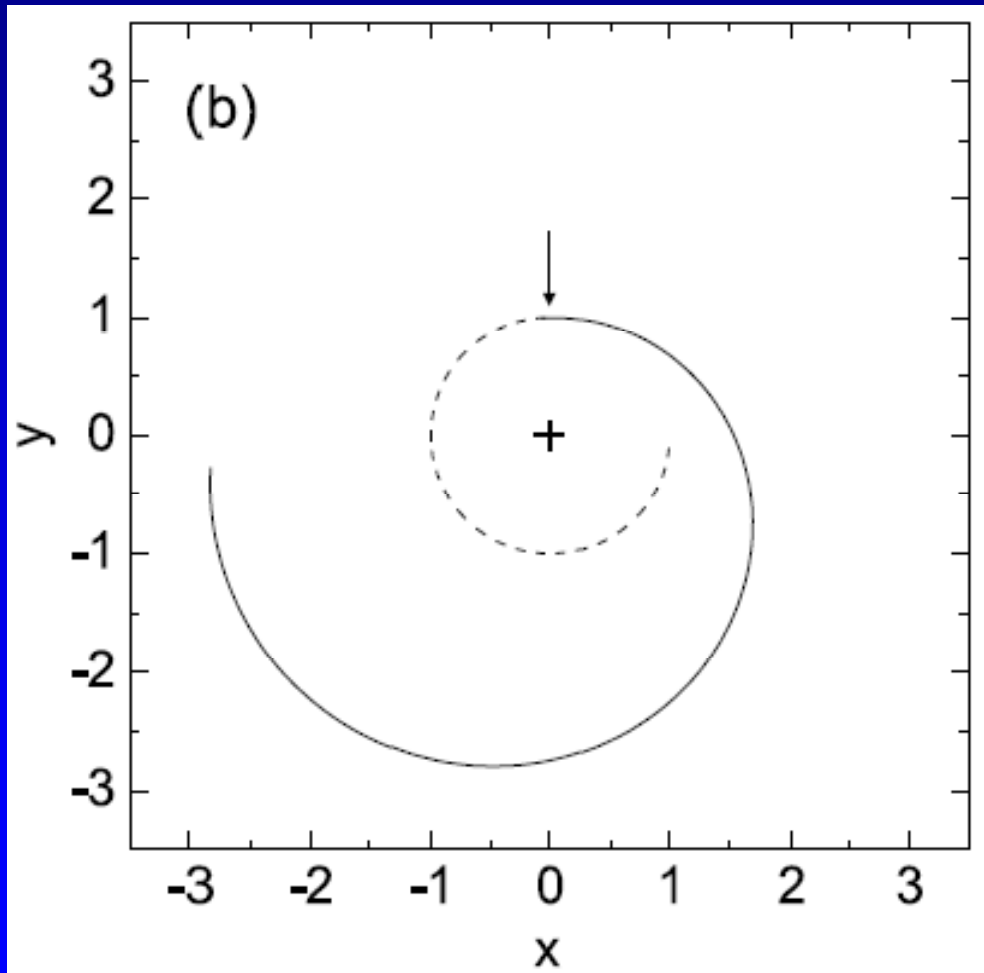
A. Herlert et al. (1999)

# Silver - cluster dianions





CID (collision-ind. dissociation)  
is not always a good idea

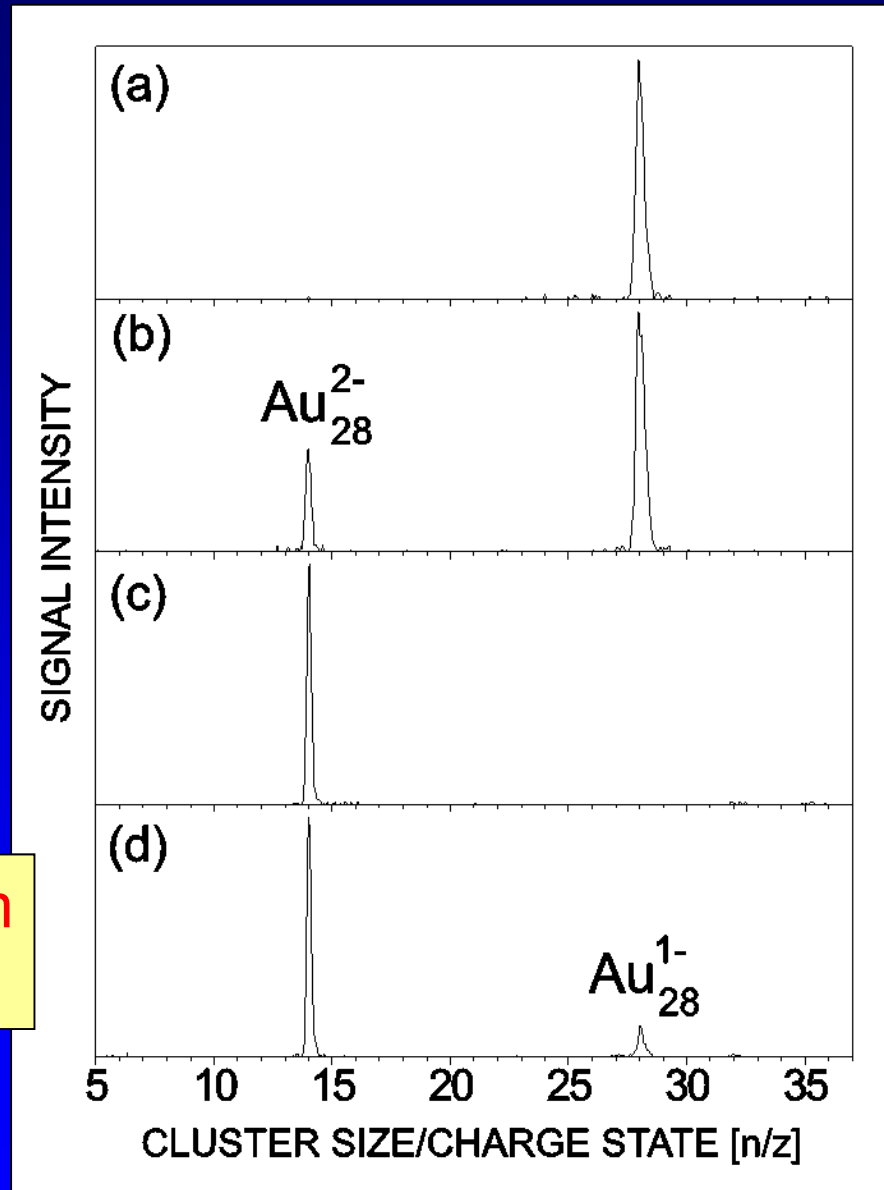


as charge-changing  
reactions  
(here electron emission)  
can lead to ion loss  
due to increased  
motional amplitudes

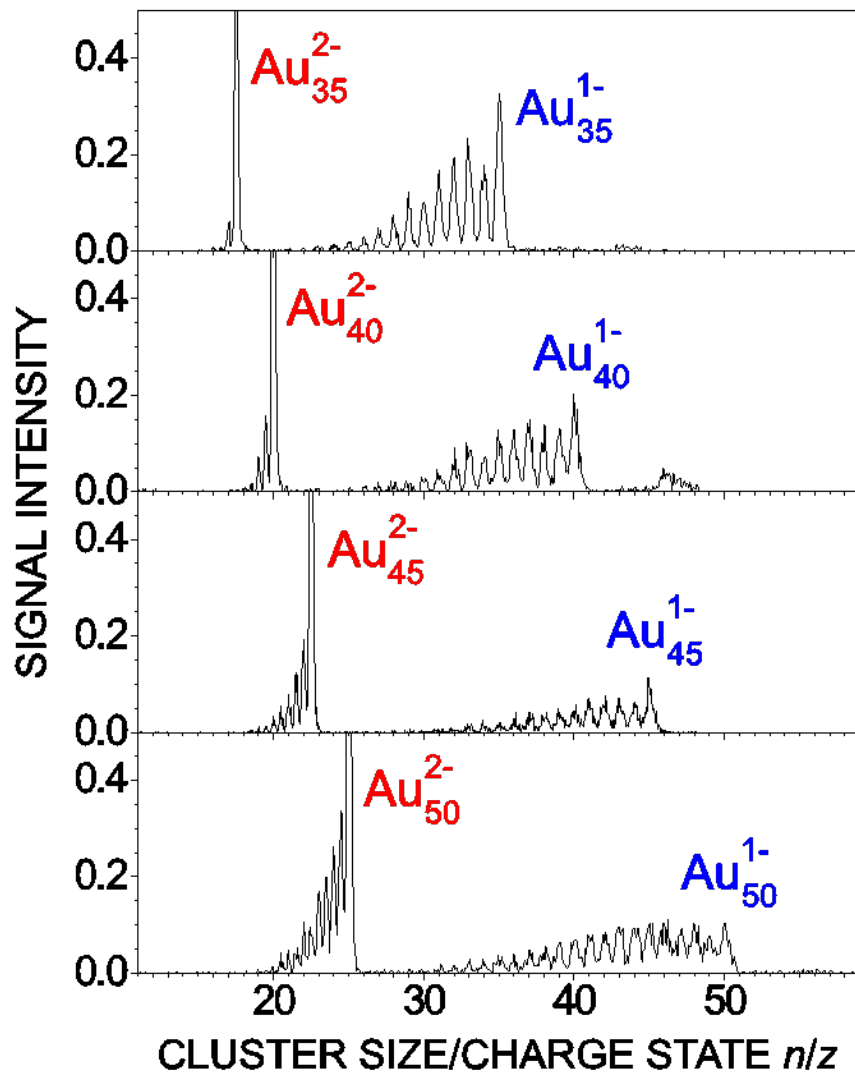
Herlert et al.  
IJMS 2004

# Photoexcitation of dianions

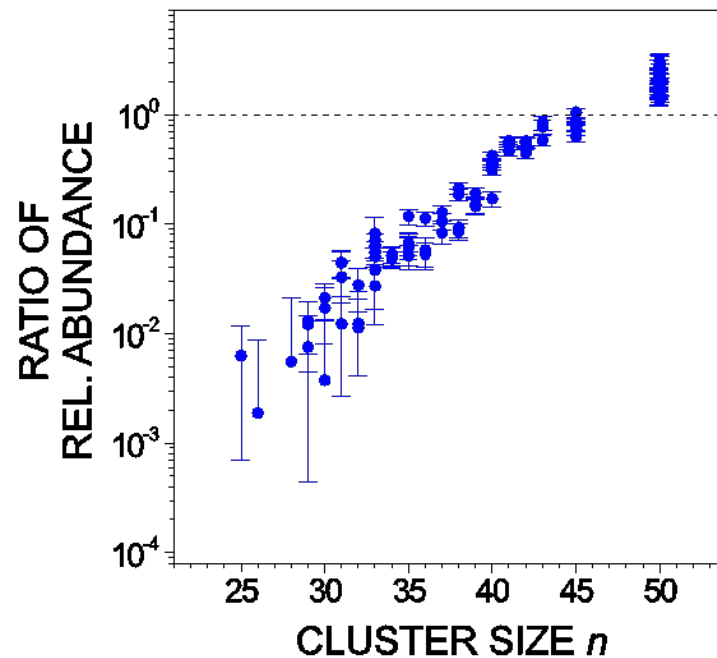
10 ns pulse,  $\lambda=355\text{nm}$   
 $E=1\text{mJ}$



# Photoabsorption of dianions



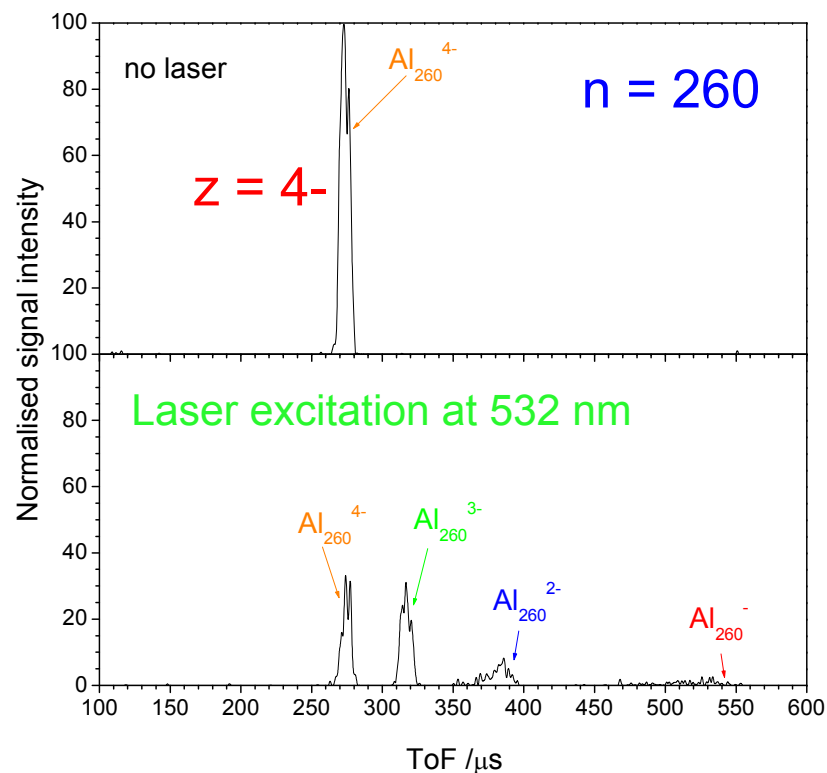
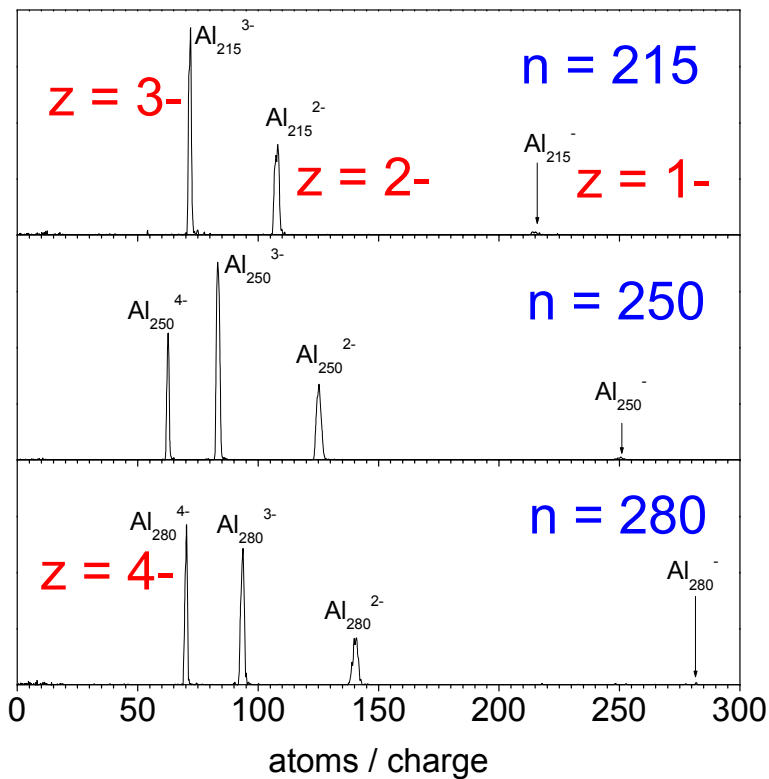
branching ratio  
of decay pathways  
(monomer vs.  
electron emission)



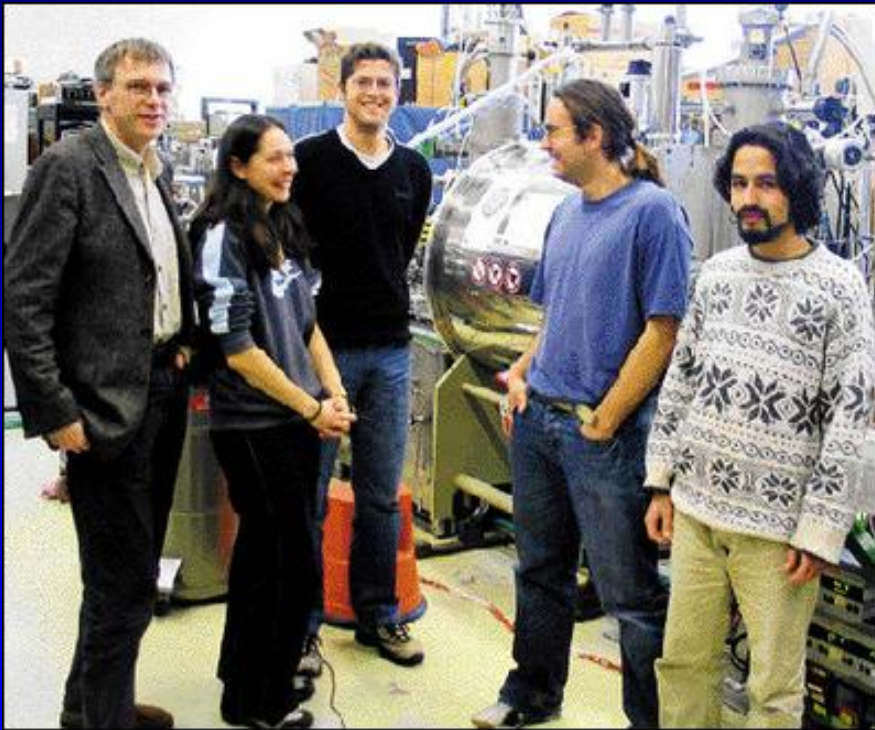
# Tetra-(quad-)anionic aluminum clusters

## production

## photoexcitation



# Current Ion Trappers at Greifswald (and at CERN and GSI)



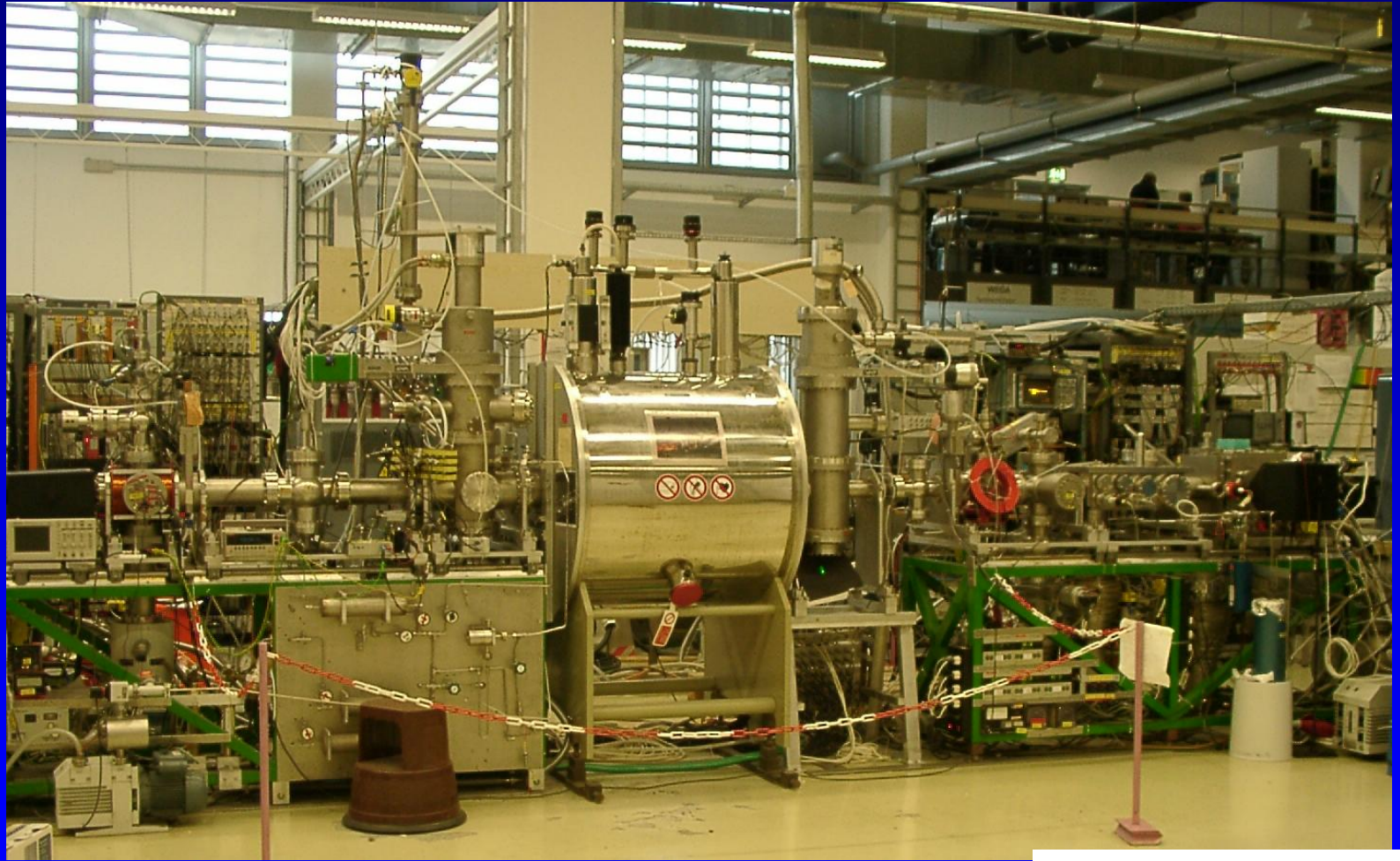
M. Arndt (Paul trap)  
S. Bandelow (Paul trap)  
Ch. Droese (SHIPTRAP/GSI)  
F. Martinez (ClusterTrap)  
Dr. G. Marx (almost all)  
M. Rosenbusch (ISOLTRAP/CERN)  
L. S.  
A. Vass(ClusterTrap)  
B. F. Wienholtz (just started)  
R. Wolf (ISOLTRAP/CERN)  
F. Ziegler (ClusterTrap)



Thanks also to  
DFG, BMBF, EU, ... Ch. Breitenfeldt, S. Gierke, S. Knaur

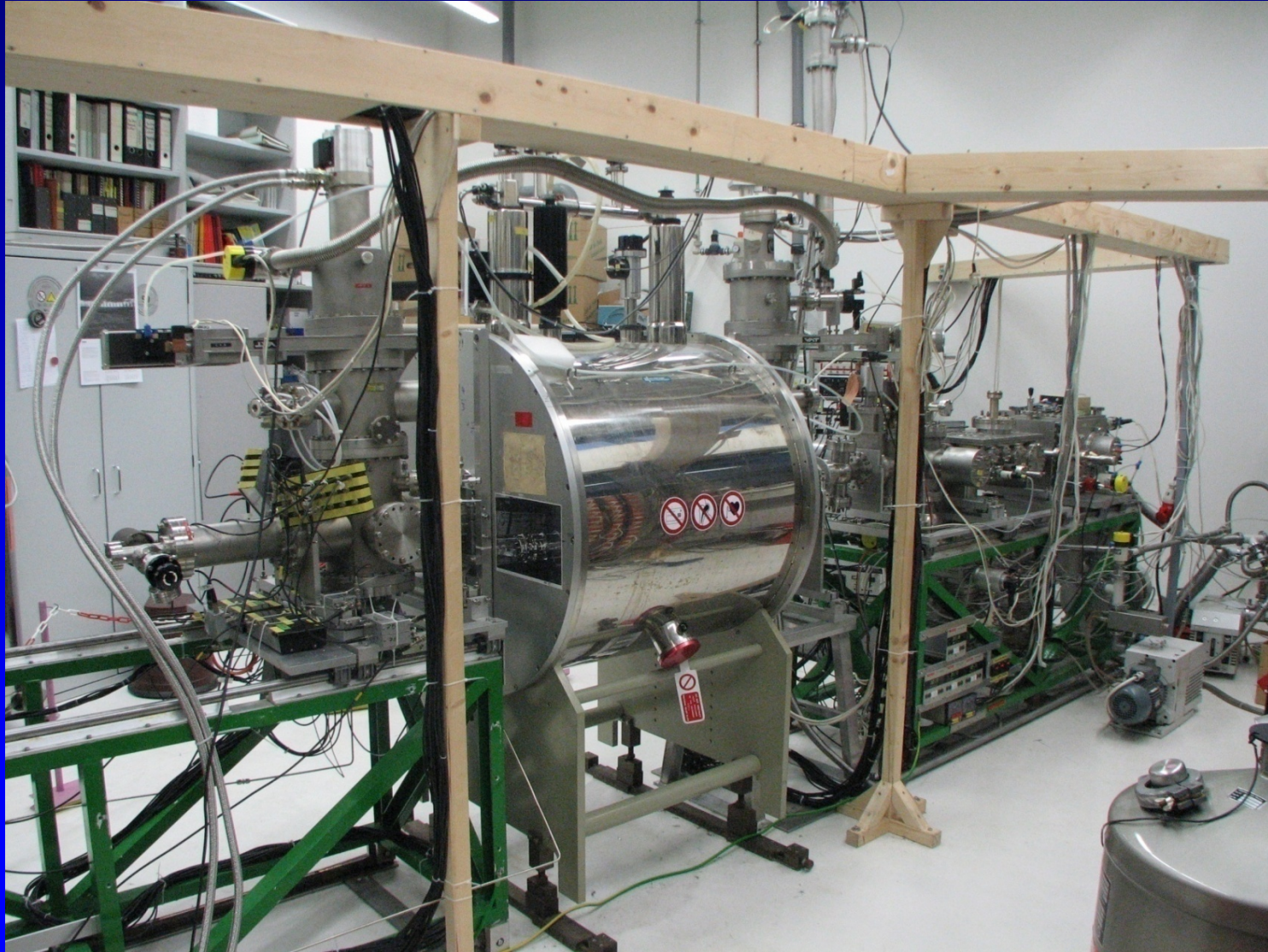
Diploma/Master students:

# We have moved from

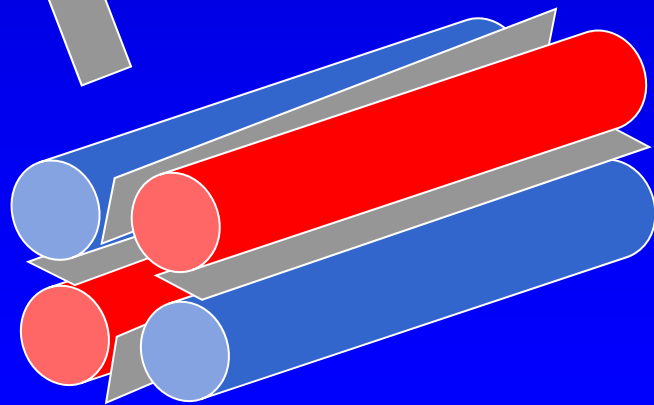
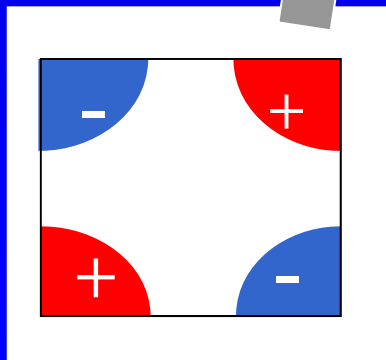
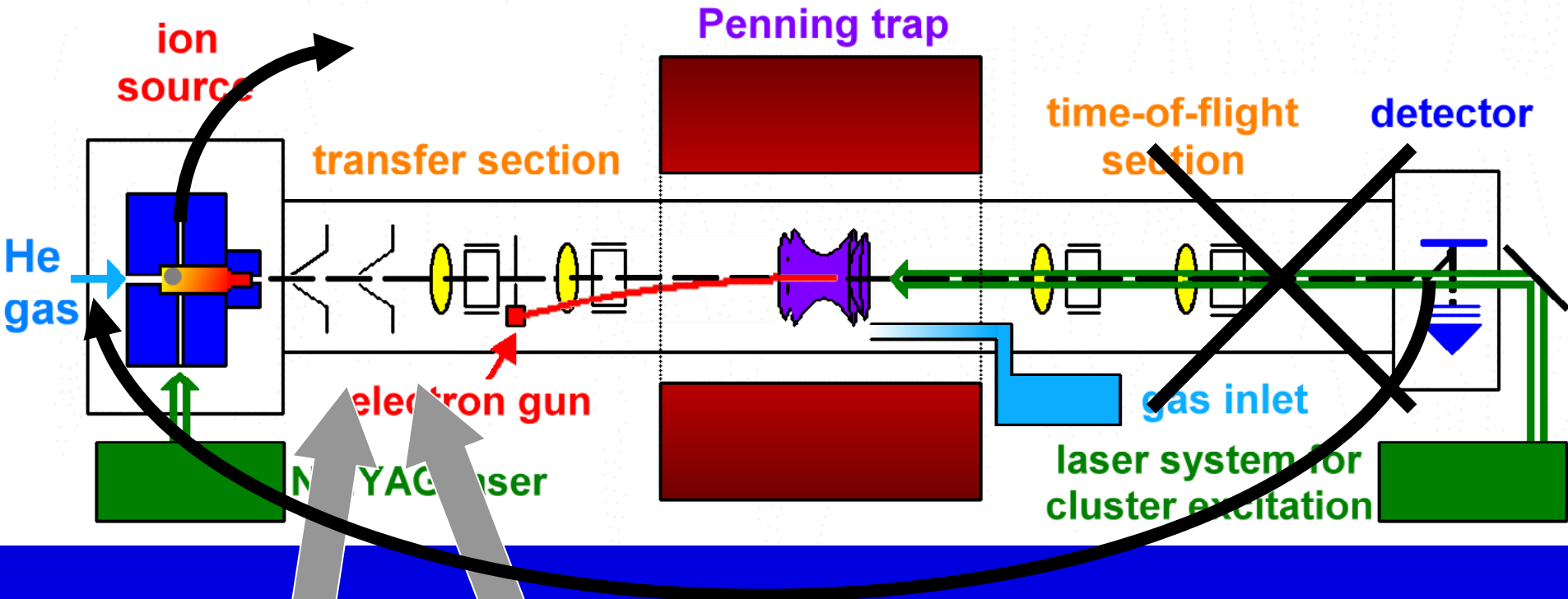
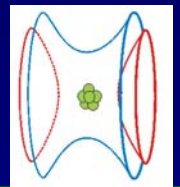


Max-Planck-Institut  
für Plasmaphysik

We have moved to the new building  
of the Inst. of Physics



# Current modifications



under way i.e.  
„construction site“



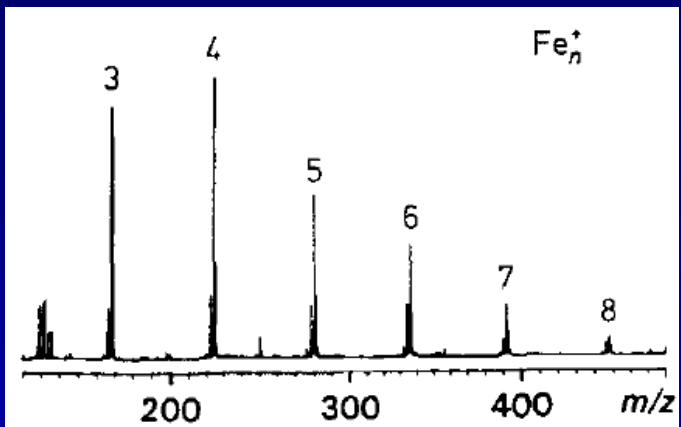
## Overview

# Other traps and applications

## ClusterTrap

clusters? why? how? what?

Other cluster-storage devices



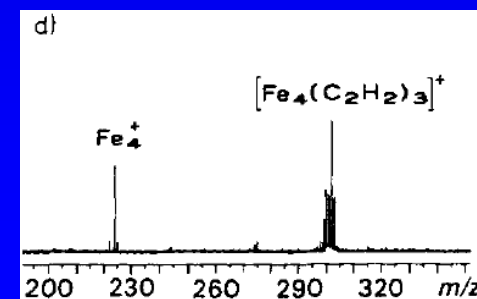
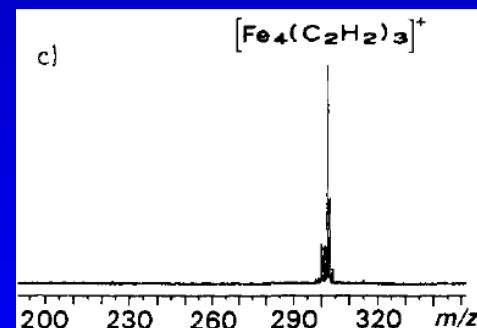
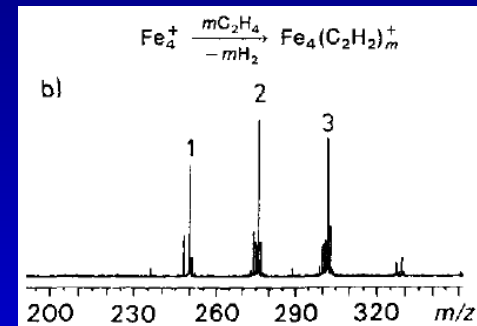
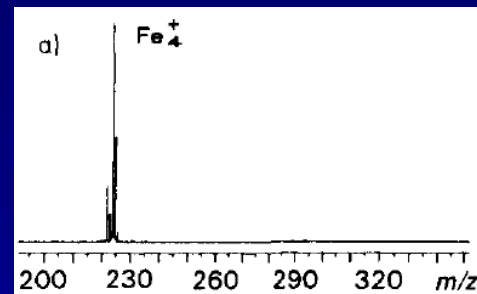
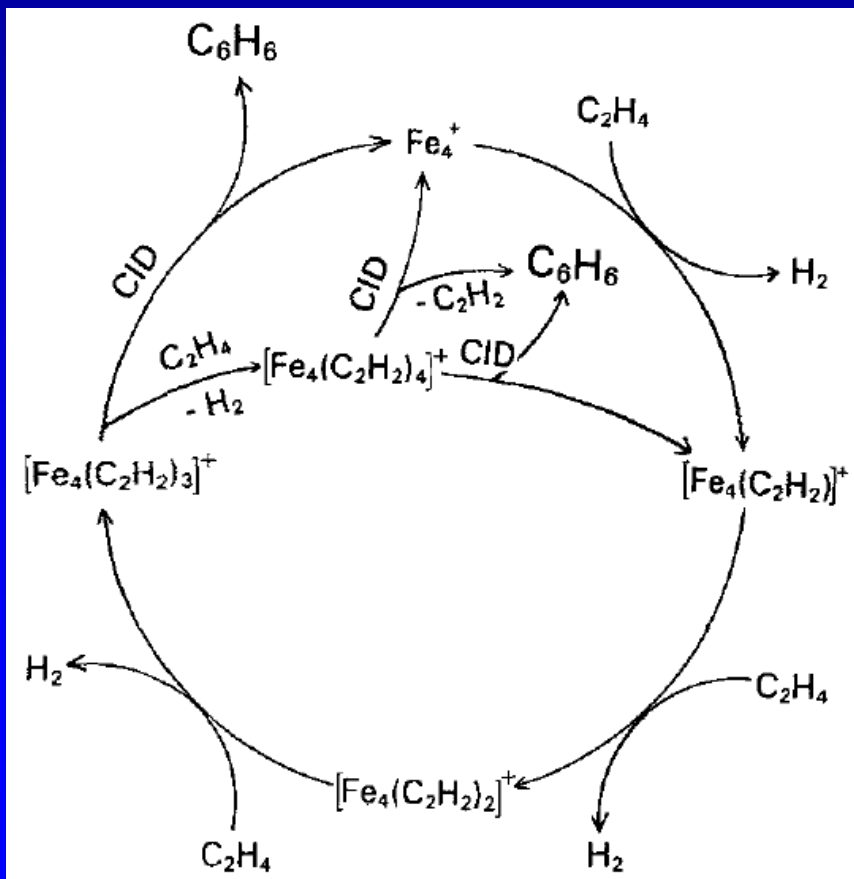
# multi-step reactions

growth of benzene from ethylene on iron tetramers

Schnabel et al. (Iron)

J. Chem., 1991

Angew. Chem., 1992



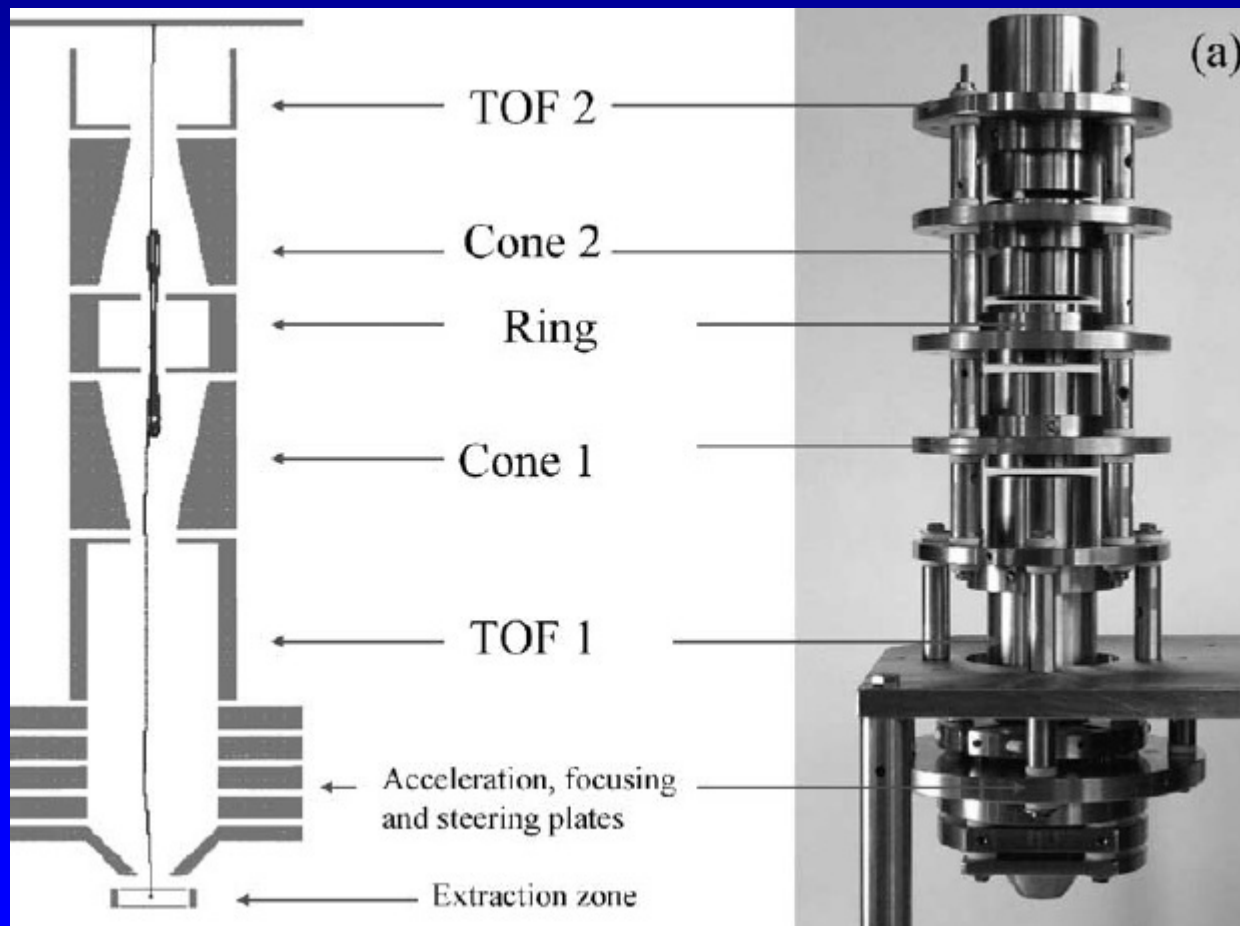
repeated selection and further reaction

two [!] cycles such as shown

⇒ catalysis research

Use of other types of traps:

# Electrostatic ion beam traps (detection of neutral products)



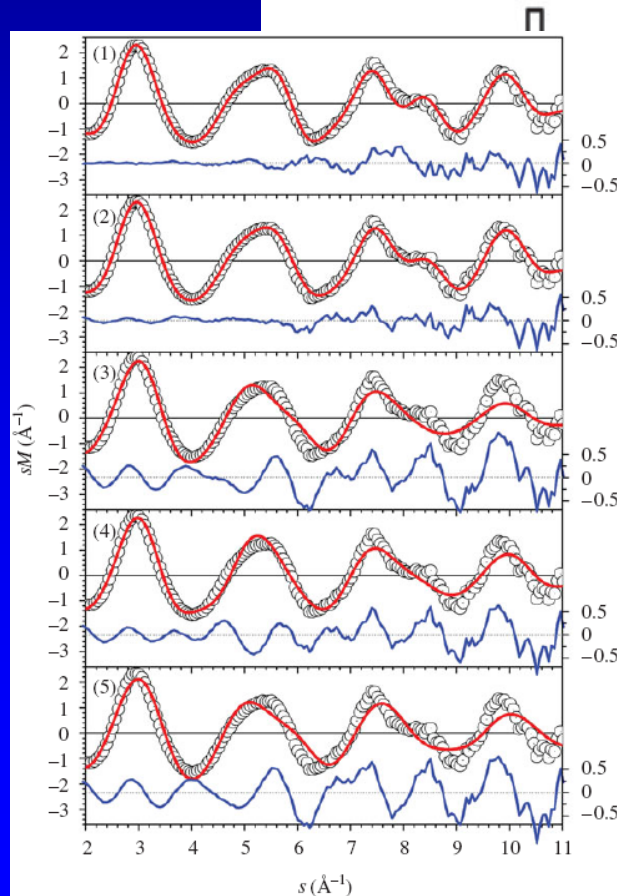
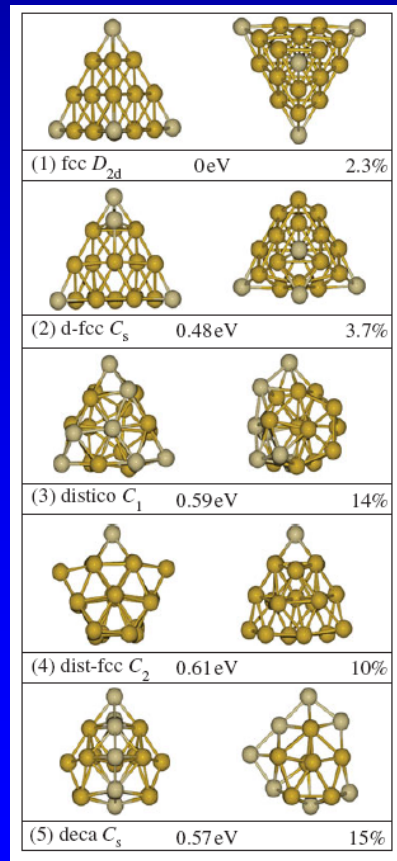
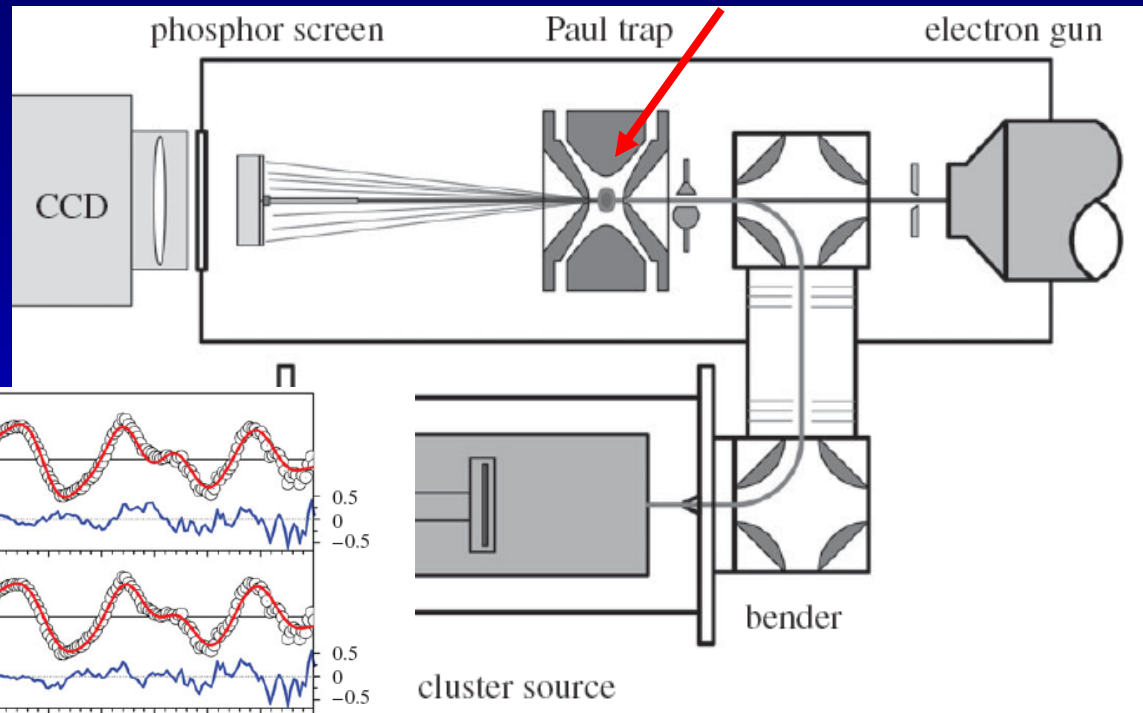
„Cone Trap“

Bernard et al.  
NIM B, 2003  
Trapping of  $C_{60}^{3+}$

Inspired by  
Zajfman & Co.

# Use of more exotic probes: Trapped ion electron diffraction

## Paul trap



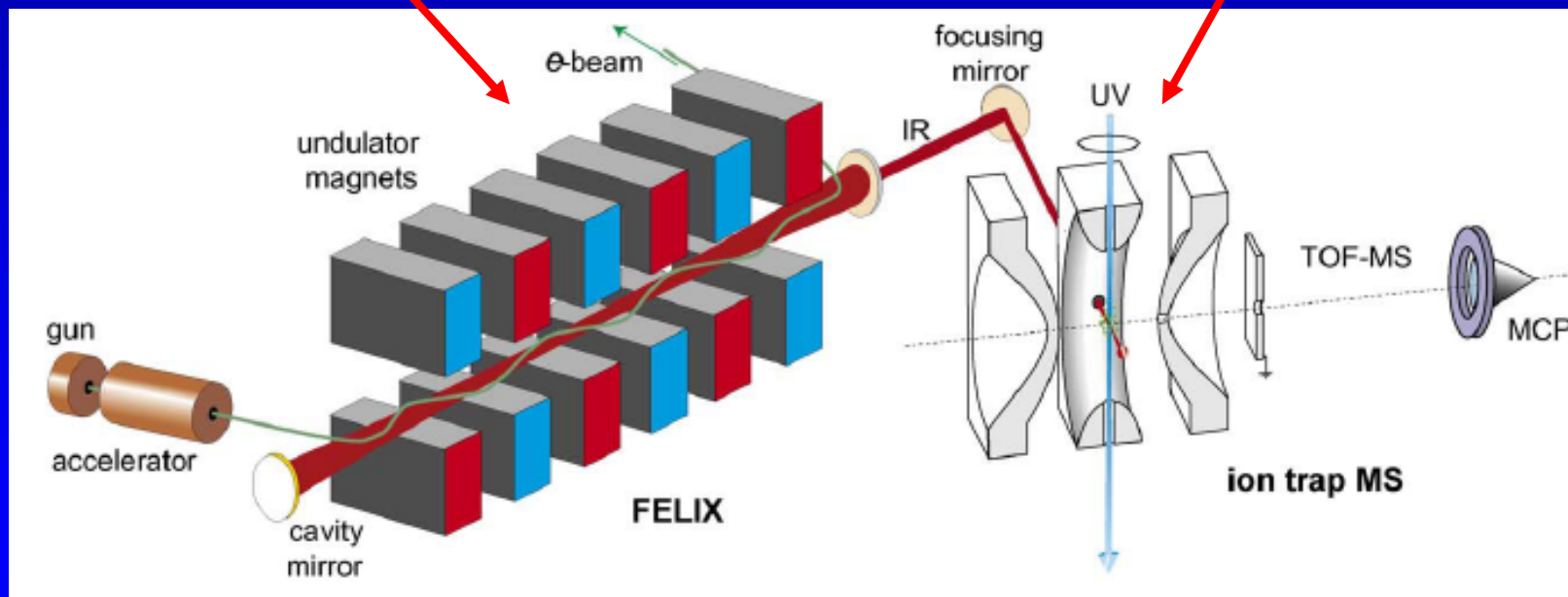
Schooß et al. (Kappes)  
Phil. Trans. Royal Soc.  
2010

based on  
J.H. Parks & Co  
Maier-Borst et al., PRA 1999  
Krückeberg et al., PRL 2000

# IR-MPI (infrared multiple photon dissociation) spectroscopy of mass-selected clusters (etc.)

IR-FEL at FOM  
(Nieuwegein)

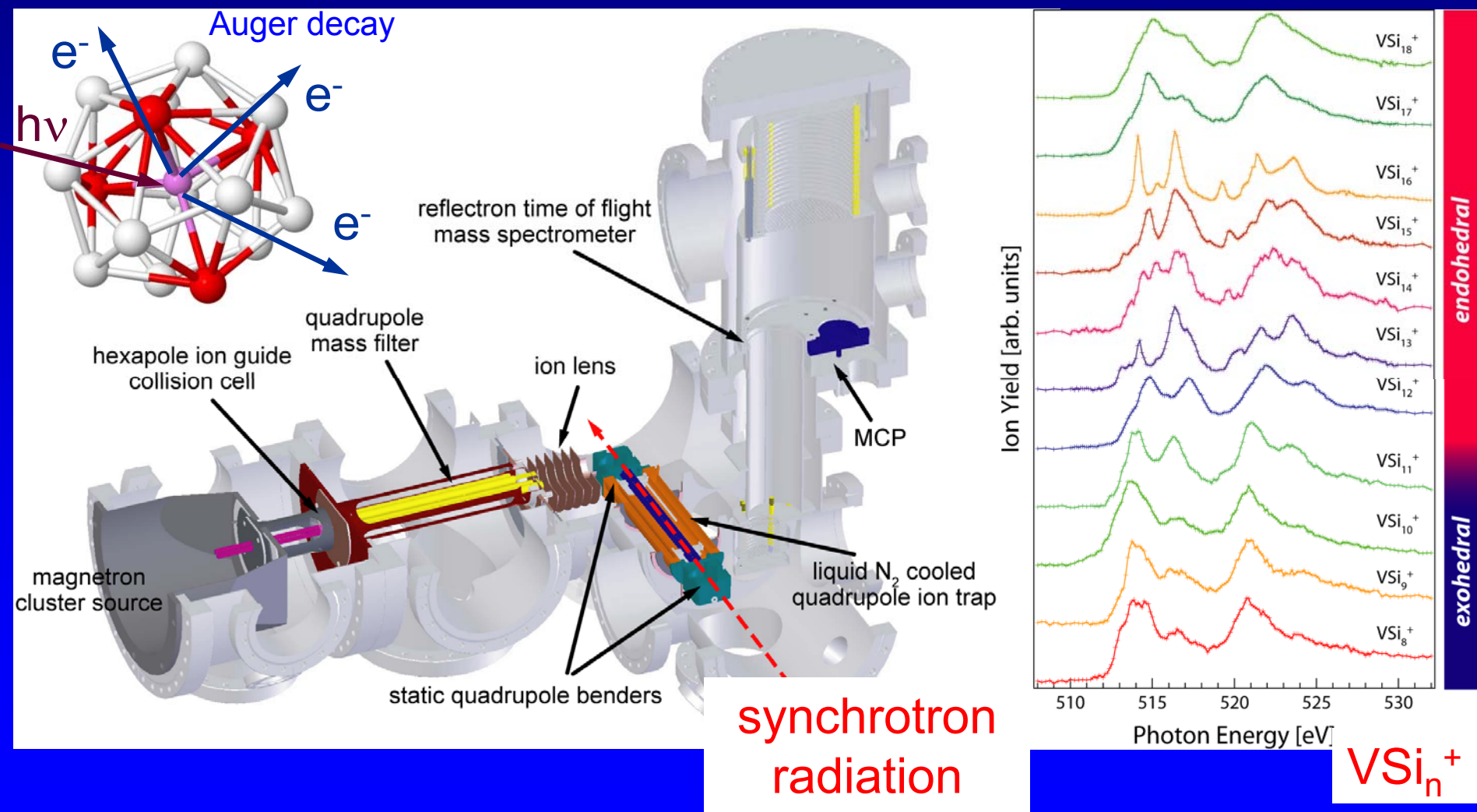
coupled to 3D rf trap  
or rather the other way



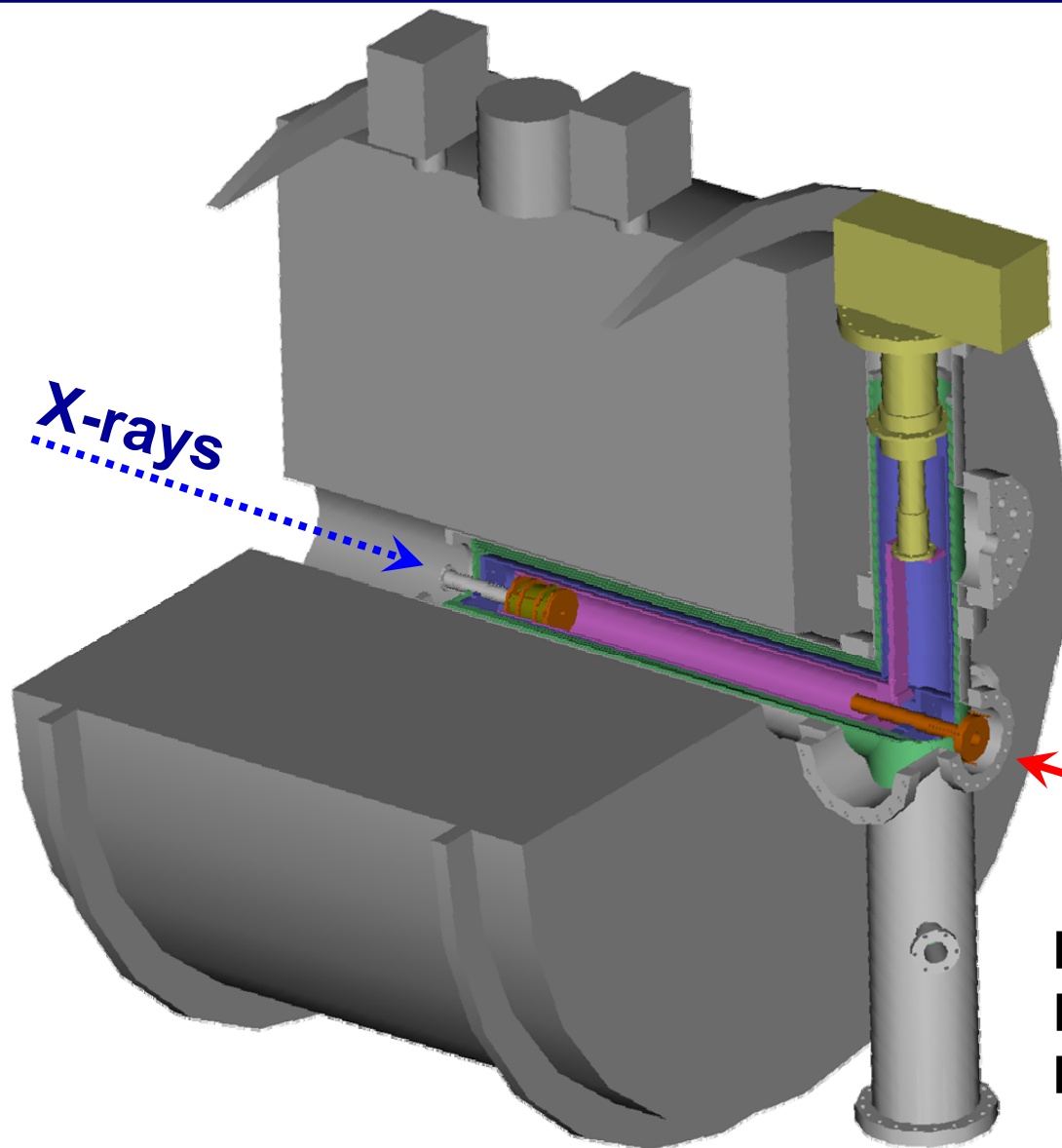
Oomens et al. (von Helden, Meijer) IJMS 2006

# X-ray spectroscopy on size-selected clusters in an ion trap (at BESSY/Berlin)

Lau & Co.  
PRL 101, 2008  
PRB 79, 2009  
JPhysB 42, 2009  
PRA 79, 2009



A novel concept for the storage of cold ions (20 K)  
within an FT-ICR spectrometer



**XMCD**  
**x-ray absorption**  
**magnetic dichroism**

- 100 K Ron Heeren
- 100 K Martin Beyer
- 100 K Evan Williams
- 30 K Christine Joblin
- 16 K FRITZ prototype
- 16 K GAMBIT prototype

**metal cluster ions**

Niedner-Schatteburg  
DPG (AMOP) meeting  
March 2010

## Overview

# Other traps and applications

## ClusterTrap

clusters? why? how? what?

## Other cluster-storage devices

**The End**

**Thanks for your attention !**