Low-energy interactions of electrons and atomic clusters in ion traps, recent results and possible further developments

Lutz Schweikhard
Institute of Physics, Univ. Greifswald
https://physik.uni-greifswald.de/ag-schweikhard/

Menu:

- ClusterTrap setup
- (previous experiments)
- Electron bath for dianion and polyanion production
- Decay channels of, e.g., dianionic Au clusters
- Recent studies: Pb clusters are different
- Outlook? Suggestions from / discussion with you

First some basics: Ion trapping, Why/How?
other application: Precision MS of exotic nuclei
Why (ion) trapping?!?

Precision needs Time!
(accuracy, resolving power)

\[ \Delta t \cdot \Delta \nu > 1 \]
\[ \Delta t \cdot \Delta E > \hbar \]

Storage

Resolving Power

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How to keep charged particles at rest („arrested“) in free space?

(Note: For now we forget about storage rings and alike.)

- Electrostatic trapping not possible due to Laplace: $\Delta \phi = 0$

- Electric radiofrequency fields
  - Quadrupolar potential: Paul trap, rf trap, QUISTOR, „ion trap“

- Static electric and magnetic fields
  - Penning trap
  - ICR cell (ion cyclotron resonance)
  - FT-ICR MS, FTMS
Penning trap
(Ion Cyclotron Resonance (ICR) Trap)

Paul trap
(Radiofrequency (RF) Ion Trap)

trapping motion
cyclotron motion
magnetron motion

\[ \omega_c = \frac{q}{m} B \]

strong B-field \( \Rightarrow \) supercond. magnet

upper mass limit, but no lower mass limit

no B-field but RF field

no mass limit, but small mass range

micro motion (like "quiver motion")

macro motion

Nobel prize 1989 for Hans Dehmelt and Wolfgang Paul

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2-D rf trapping

Radio-Frequency Mass Filter (RFQ)

Stability diagram

DC

AC

m/z dependent “stability“ of ion motion

Ideally: hyperbolic surfaces

Animation: F. Herfurth

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From 2-D to 3-D? the „easy“ solution: linear quadrupole ion trap

- Injection: 0 V, +5 V, +15 V
- Storage: +15 V, +5 V, +15 V
- Ejection: +15 V, +5 V, -10 V

\[ U(t) \]
“Paul trap”, also just called “ion trap”

“Paul [...] described an ‘ion trap’ [...] in 1960. It was modified to a useful mass spectrometer by Stafford et al. [...] at the Finnigan Company.”

de Hoffmann/Stroobant, 2011

From Nobel lecture:

From 2-D to 3-D?

The „real“ thing: quadrupole ion trap

1989

photo of macroscopic Al particles

Wuerker et al. (1959)

1989

stability diagram
Now static fields only

The Penning trap

Omegatron (late 1940s)
(vacuum gauge)

J.R. Pierce, 1954, book on "Theory and design of electron beams"

trapping motion
cyclotron motion
magnetron motion
=> all modes

\[ \omega_c = \frac{q}{m} B \]
Confinement

Axial harmonic potential

Radial confinement

B-field

The Penning trap

Confinement The Penning trap
Equations of motion

The Penning trap

Just Newton with Lorentz force:

$$\vec{F} = m\ddot{\vec{r}} = -q\nabla \Phi(\vec{r}) + q\vec{v} \times \vec{B}$$

=> axial oscillation

$$\frac{qU_0}{md_0^2} \cdot z + m\ddot{z} = 0$$

$$\omega_z = \sqrt{\frac{qU_0}{md_0^2}}$$

=> radial oscillation

substitution: $u = x + iy$

$$\omega_c = \frac{e_0 B}{m}$$

$$i\omega_c \dot{u} - \frac{\omega_z^2}{2} u + \ddot{u} = 0$$

$$u(t) = u_0 e^{-i\omega t}$$

$$\omega_+ = \frac{\omega_c}{2} + \sqrt{\frac{\omega_c^2}{4} - \frac{\omega_z^2}{2}}$$

$$\omega_- = \frac{\omega_c}{2} - \sqrt{\frac{\omega_c^2}{4} - \frac{\omega_z^2}{2}}$$

z-frequenzy, trapping frequency

modified or reduced cyclotron frequency

magnetron frequency
\[ \omega_{\pm} = \frac{\omega_c}{2} \pm \sqrt{\left( \frac{\omega_c}{2} \right)^2 - \frac{\omega_z^2}{2}} \]

**Relations between eigenfrequencies**

- ISOLTRAP, SHIPTRAP, ...

- "Invariance theorem"

\[ \omega_{\pm} + \omega_{-} = \omega_c \]

\[ \omega_{\pm} \omega_{-} = \frac{\omega_z^2}{2} \]

\[ 2 \frac{\omega_{\pm}}{\omega_z} = \frac{\omega_z}{\omega_{-}} \]

\[ \omega_{-} \approx \frac{\omega_z^2}{2\omega_{\pm}} \]

Relation of ideal trap; does also hold for
- tilded axis and
- radial asymmetry (\( x^2 - y^2 \), i.e. ellip. term).

(Brown and Gabrielse PRA 1982)
**Electrode configurations**

**Hyperbolical Penning trap**

\[ z_0 = r_0 / \sqrt{2} \] is NOT the best choice (Van Dyck)

**Cylindrical Penning trap**

**Axial Potential**
Some further configurations (as of 1992)

Penning trap


T – trapping
E – excitation
D – detection
Relations between eigenfrequencies, part 2

Penning trap

“critical mass“
maximal $m/q$

$$
\omega_{\pm} = \frac{\omega_c}{2} \pm \sqrt{\left(\frac{\omega_c}{2}\right)^2 - \frac{\omega_z^2}{2}}
$$

$$
\frac{\omega_c^2}{4} > \frac{\omega_z^2}{2}
$$

$$
\frac{m}{q} \langle \frac{B^2 d_0^2}{2U_0} \rangle
$$

L.S. et al., IJMSIP (1995)

e.g. $m/q$ or trapping voltage
Instability by „motional resonance“ („non-linear resonance“)

L.S. et al., IJMSIP (1995)

Many further instabilities were found and investigated by Werth et al.

Fig. 8. Measured trapping efficiency for gold cluster anions, Au$^{100}$, and trapping periods of 40 ms as a function of trapping voltage.

Closed ion trajectories
Energy of harmonic oscillators:

\[ E = \hbar \omega_+(n_+ + 1/2) + \hbar \omega_z(n_z + 1/2) - \hbar \omega_-(n_- + 1/2) \]

amplitudes:

\[ <\rho> \sim \sqrt{n + \frac{1}{2}} \]

usually cooling: quantum number \( n \to 0 \)

but

magnetron motion is un-/metastable!
Fourier-Transform Ion-Cyclotron-Resonance Mass Spectrometry

Marshall, Comisarow, 1974: FT-ICR MS

Penning trap for analytical mass spectrometry

Application in Analytical Mass Spectr. Penning trap = FT-ICR MS

after broad-band excitation:
transient in time domain = FT => freq. domain

\[ \omega_c = \frac{q}{m} B \]

\[ m = \frac{B}{q} \omega_c \]

\[ \Delta m = 0.02176 \text{ u} \]

\[ \frac{1}{\Delta m} = 45.964 \text{ / u} \]

mass = 44610 u
Application in precision MS for nuclear physics

ISOLTRAP/CERN

2017-07-10, NNP, Appleton
ISOLDE/CERN delivers a
• continuous ion beam
  ⇒ (1) RFQ buncher
• of a mixture of isobaric species
  ⇒ (2) Preparation Penning trap
before forwarding for MS at the
• Measurement Penning trap

⇒ Triple-Trap System
Magnetron excitation
↓
Quadrupolar excitation
↓
Ejection from trap
↓
Radial to axial energy conversion B-field gradient
↓
Time-of-flight detection
↓
Reload trap

Segmented ring electrode

Time of flight

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Example: $^{85}\text{Rb}^+$ (900ms excitation duration)
Example: $^{85}\text{Rb}$ (900ms excitation duration)
ISOLDE/CERN delivers a
• continuous ion beam
  => (1) RFQ buncher
• of a mixture of isobaric species
  => (2) Preparation Penning trap
before forwarding for MS at the
• Measurement Penning trap

=> Triple-Trap System
ISOLDE/CERN delivers a
- continuous ion beam
  => (1) RFQ buncher
- of a mixture of isobaric species
  => (2) MR-ToF MS
- Centering
  => (3) Preparation Penning trap before forwarding for MS at the
- Measurement Penning trap

=> unique 4-Trap System
ISOLDE/CERN delivers a
• continuous ion beam
  => (1) RFQ buncher
• of a mixture of isobaric species
  => (2) MR-ToF MS
• Centering
  => (3) Preparation Penning trap before forwarding for MS at the
• Measurement Penning trap

Which allowed a precision mass measurement of Zn-82

Multi-Reflection Time-of-Flight Mass Separator

ISOLTRAP/CERN precision MS for nuclear physics
ISOLDE/CERN delivers a continuous ion beam
• RFQ buncher
• of a mixture of isobaric species
• MR-ToF MS
• Centering
• Preparation Penning trap before forwarding for MS at the
• Measurement Penning trap

Which allowed a precision mass measurement of Zn-82

neutron-star crust

Multi-Reflection Time-of-Flight Mass Separator

81\text{Zn}^{51}

351\text{ms (5/2)}

M = 46200 (6)

B = 100%

B = 5\%

82\text{Zn}^{52}

200\text{ms (5/2)}

M = 42610 (300#)

B = 2%

B = 90\%

83\text{Zn}^{53}

100\text{ms (5/2)}

M = 36740 (500#)

B = 90%
In search for the "island of stability" of superheavy elements
First Direct Mass Measurements above Uranium
Direct Mapping of Nuclear Shell Effects

Production yield of $^{256}\text{Lr}$
just 2 nuclei/minute
(at about 40MeV kinetic energy!)

M. Block et al., Nature 463, 785 (2010)
E. Minaya Ramirez et al., Science 337, 1207 (2012)
Spatial detection with delay-line detector

time-of-flight detection

MCP

charge collection fingers

serpentine delay

MCP active area
=> Improvement by a factor 5 in uncertainty and a factor 40 in resolution or by more than an order of magnitude in reduction of measurement time.

Not covered:

- Precision mass measurements of $^3$He vs. $^3$H
- Precision mass measurements of $e^+$ vs. $e^-$
- Precision mass measurements of antiproton proton

- Precision measurements of g-factor of (bound) electron
- … of g-factor of positron
- Precision measurements of g-factor of proton
- … and antiproton
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- Outlook? Suggestions from / discussion with you

First some basics:  Ion (charged-particle) trapping, Why/How?
other application: Precision MS of exotic nuclei
Experimental setup of ClusterTrap @ Greifswald

before the move to the new building of the Inst. of Physics
Experimental setup of ClusterTrap @ Greifswald

before the move to the new building of the Inst. of Physics
Cluster Trap setup: moved from IPP building to new institute building

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ClusterTrap setup: replaced of 5-Tesla magnet by 12-T magnet
ClusterTrap setup:

Overview

- 12Tesla superconducting magnet
- Cluster ion source
- Nd:YAG laser
- He gas
- Radio frequency trap 1
- Transfer & time-of-flight section
- Quadrupole ion deflector
- Time-of-flight section
- Penning trap: electron attachment
- Superconducting magnet
- Electron source
- Detector 1
- Detector 2
- Detector 3
- Gas inlet
- Ion optical lens & deflector
- Laser for photoexcitation

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**ClusterTrap**

What is it good for?

**MS^n** is most easily realized in trapping devices (provided the products are not lost after the interactions!)

**Interaction**
- Atoms
- Molecules
- Electrons
- Photons
- Clusters
- Ions

**Partners**

**Reactions**
- Dissociation (evaporation, fission)
- Ionization
- Recombination
- Electron attachment
- Adsorption
- Radiative cooling
- Fusion

... and ...

Reviews:
- S. Becker et al., RSI, 1995
- L. Schweikhard et al., Physica Scripta, 1995

It’s time for a new review!

For an exp. distinction betw. geometric and electronic effects look at both cluster size and charge-state dependence

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CAPTURE
ClusterTrap

**typical experimental sequence**

**SELECTION**

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INTERACTION
(e.g. electron bombardment)
RE-ACTION
(e.g. ionization and dissociation)
EJECTION
for ToF mass analysis
ClusterTrap  
electron bombardment of gold-cluster cations

time-of-flight spectra:

(a) \(16^+\)  
(b)  
(c) \(20^+\)  
(d) \(20^{2+}\)

ION SIGNAL

CLUSTER SIZE/CHARGE STATE \([n/z]\)

CAPTURE  
ACCUMULATION  
SELECTION  
ELECTRON BOMBARDMENT

A. Herlert et al.,  
CID of product ions: => decay channels

capture/accumulation and electron bombardment

1. selection

CID

2. selection

CID

CID after first selection

Krückeberg et al. ZPhysD (1997)
observation of both ELECTRONIC and GEOMETRIC shells

Krückeberg et al. (1999)
ClusterTrap multi-photoexcitation of singly charged Ag-clusters

ION SIGNAL [ARB. UNITS]

3 9 21 41 49 59 55

electronic shell closings

Ag$^+$

55

geometric shell closing

Cluster Trap

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ClusterTrap

delayed photodissociation

Time range from microseconds to (almost) seconds

\[ \lambda = 710 \text{ nm} \quad \lambda = 780 \text{ nm} \]

Walther et al., Z. Phys. D., 1996
Lindinger et al., Z. Phys. D., 1997
i.e. pump – probe at up to tens of milliseconds

=> investigation of radiative cooling

C. Walther et al., PRL (1999)
Attachment of methanol as sensor molecule for IR-Photodetachment Spectroscopy

Rousseau et al., CPL (1998)  
detachment energies: Vogel et al., JCP (2002)

ClusterTrap

some „chemistry“

Capture and Adsorption

$\text{Au}_6^+(\text{CH}_3\text{OH})_m$

$m = 0$

1

2

Selection

$\text{Au}_6^+(\text{CH}_3\text{OH})_2$

Desorption

$\text{Au}_6^+(\text{CH}_3\text{OH})_1$

Ion Intensity [arb. units]

Time of Flight [μs]

Resonance of the CO-stretching mode of $\text{Au}_9^+\text{CH}_3\text{OH}$

Transition from planar to 3D structures

Theory

Experiment

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

- Electron-impact ionisation for cationic clusters (as shown in previous examples)
- Electron attachment for anionic clusters
ClusterTrap
dianion production

CAPTURE

(a)

SIGNAL INTENSITY

CLUSTER SIZE/CHARGE STATE $n/z$
Dianion production

Cluster Trap

ACCUMULATION

(a)

(b)

SIGNAL INTENSITY

CLUSTER SIZE/CHARGE STATE n/z

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ClusterTrap dianion production

SIZE SELECTION

(a)

(b)

(c) \(\text{Au}_{27}^{1-}\)

HORIZONTAL SIGNAL INTENSITY

CLUSTER SIZE/CHARGE STATE \(n/z\)

2017-07-10, NNP, Appleton
Simultaneous storage of clusters, $m_{\text{cluster}} \approx 5000 \text{ u}$ and electrons, $m_e \approx 1/2000 \text{ u}$

Herlert et al., Physica Scripta (1999)
ClusterTrap  
magic numbers, higher (neg.) charges, appearance sizes

Martinez et al., EPJD (2013)  „Quantum capacitors“  Herlert et al., EPJ D (2001)

Martinez et al., JCP (2015)

Bandelow et al., to be published
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Simultaneous storage of clusters, $m_{\text{cluster}} \approx 5000 \text{ u}$ and electrons, $m_e \approx 1/2000 \text{ u}$

Herlert et al., Physica Scripta (1999)

Note: No decay during application of electron beam and subsequent electron bath
Size dependent branching ratio of decay pathways: monomer evaporation vs. electron emission (followed by monomer evaporation) as expected:

Qualitative explanation of the size dependence

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Dianion production and cluster decay during “electron bath”

Lead is different:

\[ Pb_n^- + e^- \rightarrow Pb_m^- + Pb_{n-m}^- + e^- \]

\[ Pb_{2n}^2^- \rightarrow Pb_{n}^- \rightarrow Pb_{n}^3^- \]

\[ Pb_{2n}^2^- + e^- \rightarrow Pb_m^- + Pb_{n-m}^- + e^- \]
So far (earlier meas. on Au, Ag, Cu, Al, and several others):
- No dissociation during e\(^-\)-beam application and e\(^-\)-attachment
- Upon photoexcitation either e\(^-\)-emission (from small dianionic clusters)
  or dissociation by neutral monomer evaporation

**Lead is different:**

**Photoexcitation spectra**

- **mono-cations**
- **mono-anions**
Photoexcitation of lead clusters

mono-cations

$Pb_n^+ + h\nu \rightarrow Pb_m^+ + Pb_{n-m}^+$

mono-anions

$Pb_n^- + h\nu \rightarrow Pb_m^- + Pb_{n-m}^-$

ClusterTrap

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Disentanglement of decay pathways by time-resolved measurements of delayed dissociation
Work in progress!

Note, not shown:
Photon-energy dependence of decay and growth times!

ClusterTrap

Lead is different
Dianion production and cluster decay during "electron bath"

**Lead is different:**

\[ Pb_n^- + e^- \rightarrow Pb_m^- + Pb_{n-m}^- + e^- \]

\[ Pb_{n-1}^- \rightarrow Pb_{n-2}^2^- \rightarrow Pb_{n-3}^3^- \]

\[ Pb_{n-2}^2^- + e^- \rightarrow Pb_{m-1}^- + Pb_{n-m}^- + e^- \]
$n^2^- \Rightarrow (n-10)^- + 10^-$

Fission ???

Lead is different
Photoexcitation of mono-anionic lead clusters

\[ \text{Pb}_{35}^{2-}, \text{Pb}_{34}^{-}, \text{Pb}_{33}^{-}, \text{Pb}_{35}^{2-}-\text{Pb}_{25}^{-}, \text{Pb}_{10}^{-} \]

⇒ strong evidence for photo-fission of di-anionic metal clusters

Herlert, NJP 2012

Unusually!
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for the work at ClusterTrap: Dr. Gerrit Marx and many students over the years, in particular Alexander Herlert (PhD 2003), Noelle Walsh (2008), Franklin Martinez (2012) [plus Masters students]

Current students at ClusterTrap: Steffi Bandelow, Stephan König, Markus Wolfram [Alexander Jankowski]

… ISOLTRAP and SHIPTRAP collaborations