

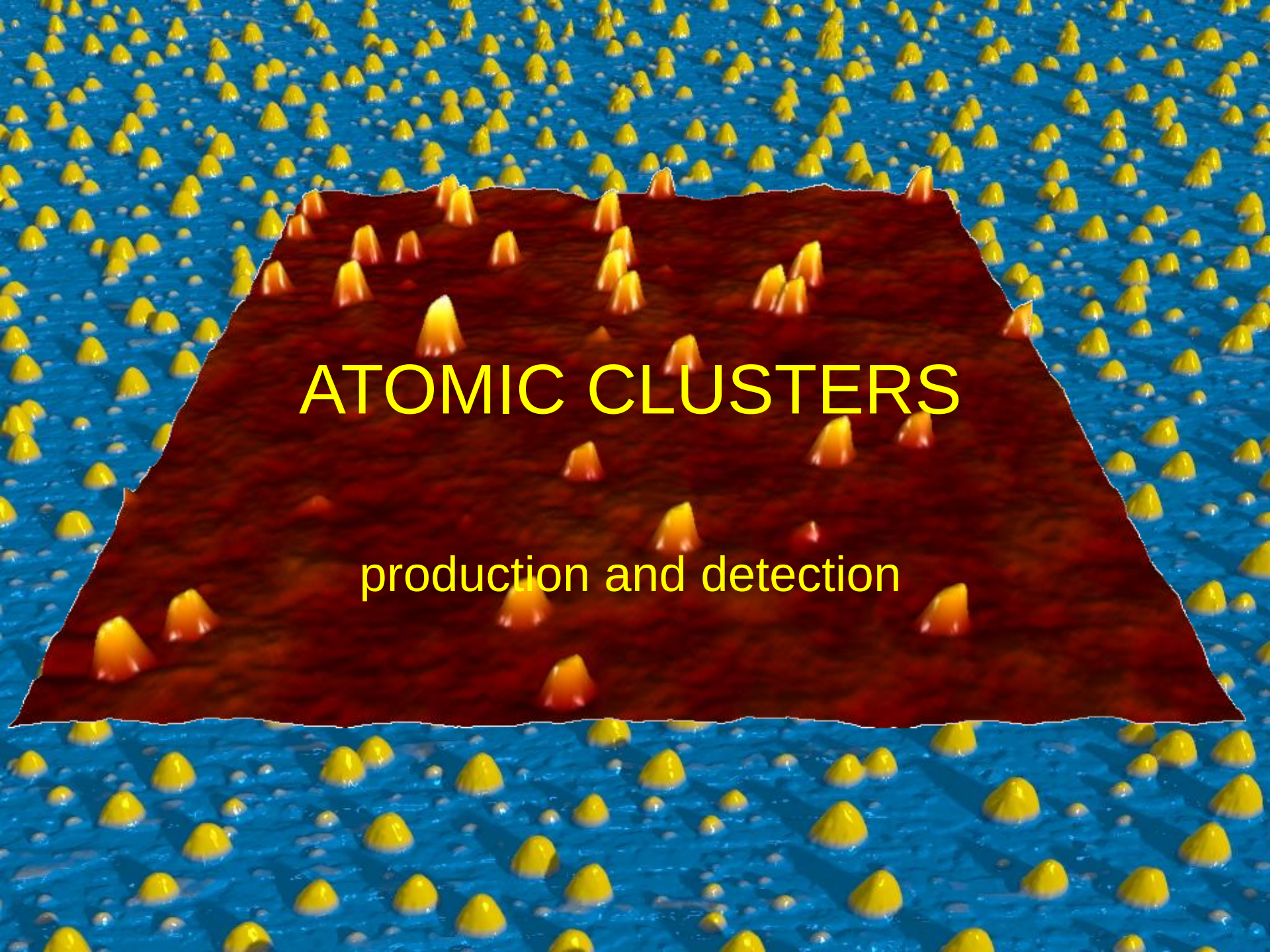
lecture 16.12.2010

we had so far:

- cluster physics: cluster production and detection

now:

- more details with respect to production and detection
- mass spectroscopy and cluster mass spectra

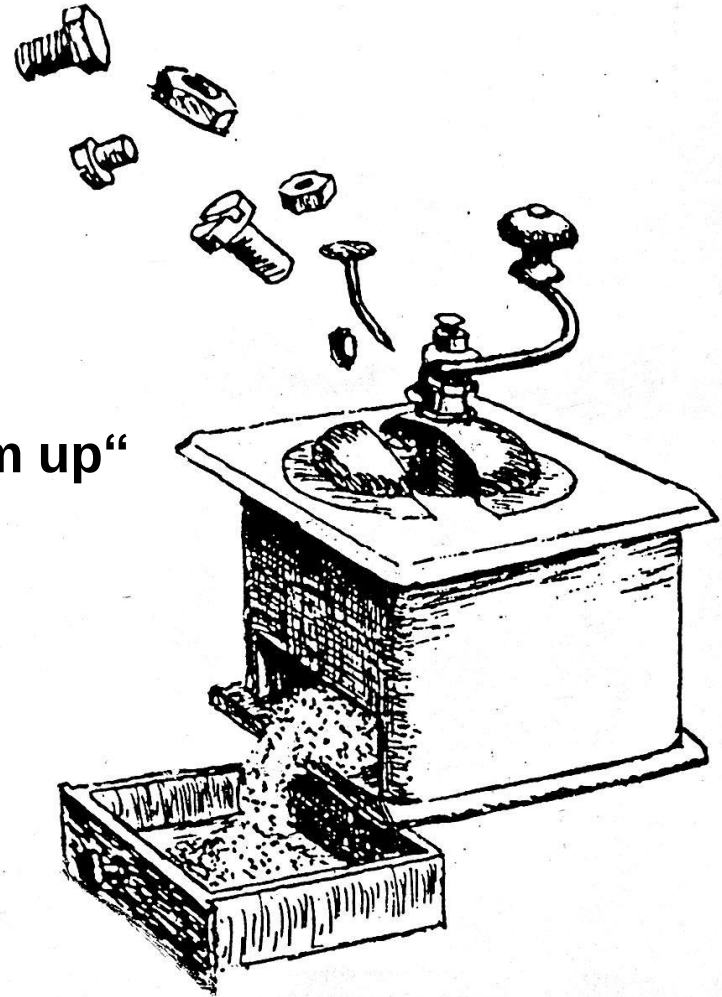
The image features a 3D visualization of a surface. A central rectangular region is colored dark red and has a textured, slightly uneven appearance. This red region is surrounded by a vast field of small, yellow, conical peaks that resemble a sea of dunes or a molecular lattice. The peaks are distributed across a blue base, which also has a textured surface. The overall effect is one of a microscopic or atomic-scale landscape.

ATOMIC CLUSTERS

production and detection

nanofabrication

- big → small: „top down“
- atoms → nanostructures: „bottom up“



cooling by adiabatic expansion

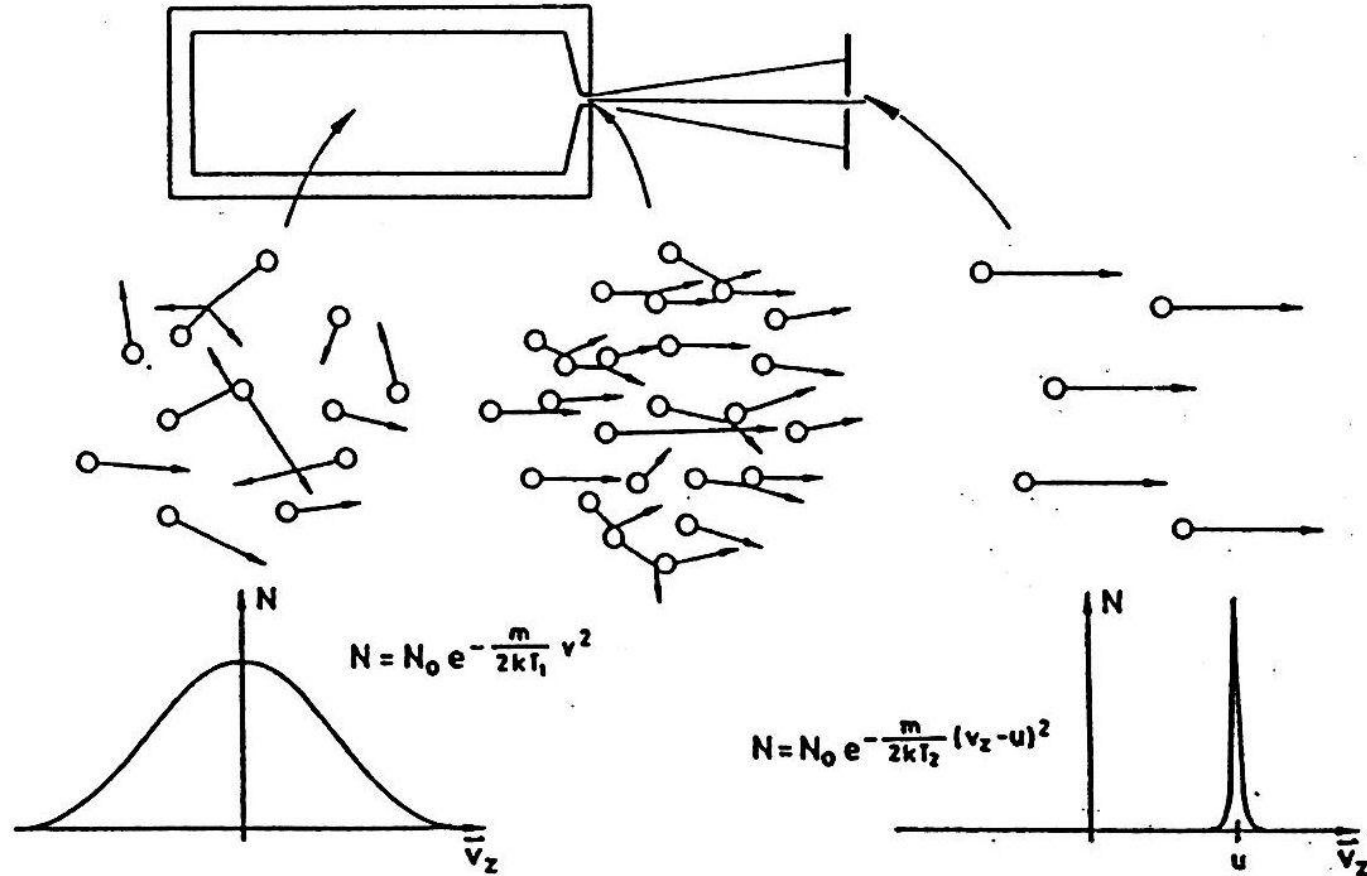
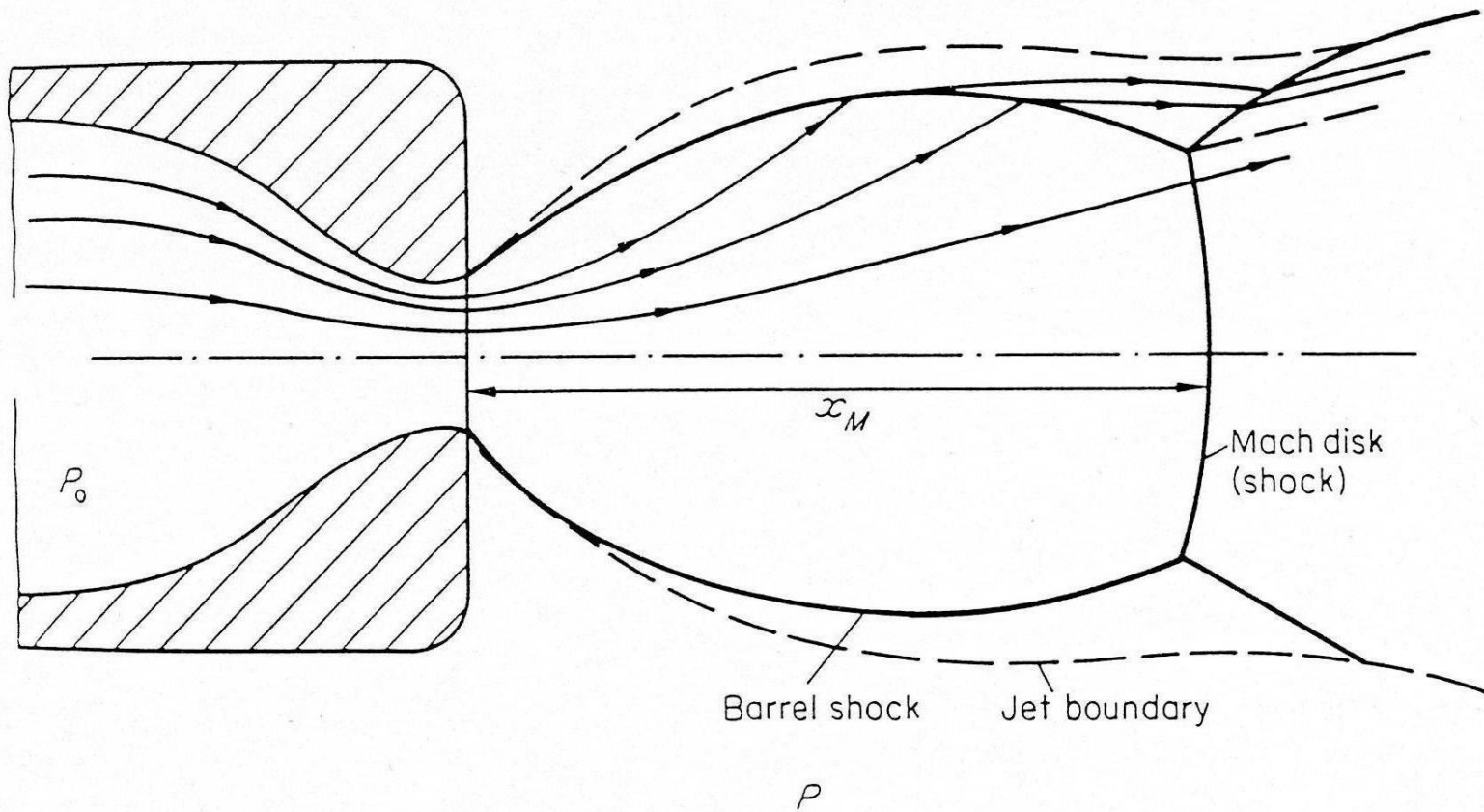
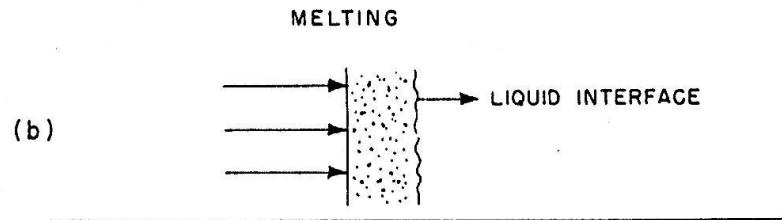
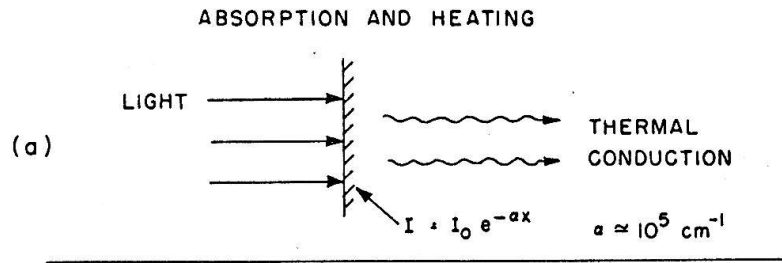


Fig. 8: Die mikroskopische Ursache für die Temperatureniedrigung und Clusterbildung bei der adiabatischen Expansion [13]. Im Ausgangsbehälter herrscht vor der Expansion thermisches Gleichgewicht. Die ungerichtete Geschwindigkeitsverteilung der Teilchen ist durch die Maxwellverteilung bestimmt. Bei der Expansion des Gases durch eine Düse kommt es durch Stöße mit den anderen Gasparkeln zur Abnahme der inneren Energie zu Gunsten der Expansionsgeschwindigkeit u . Die Relativgeschwindigkeit im kalten Molekularstrahl nimmt stark ab, wodurch die "kalten" Atome zu Clustern zusammenlagern.

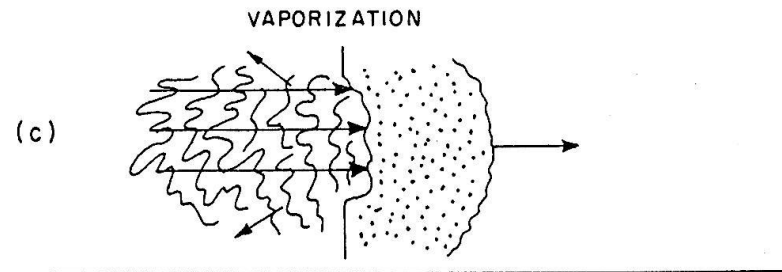
Supersonic jet expansion



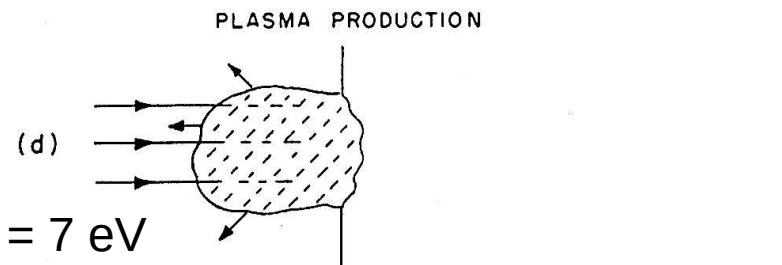
Laser – matter interaction



10^5 W/cm^2



$10^6\text{-}10^8 \text{ W/cm}^2$

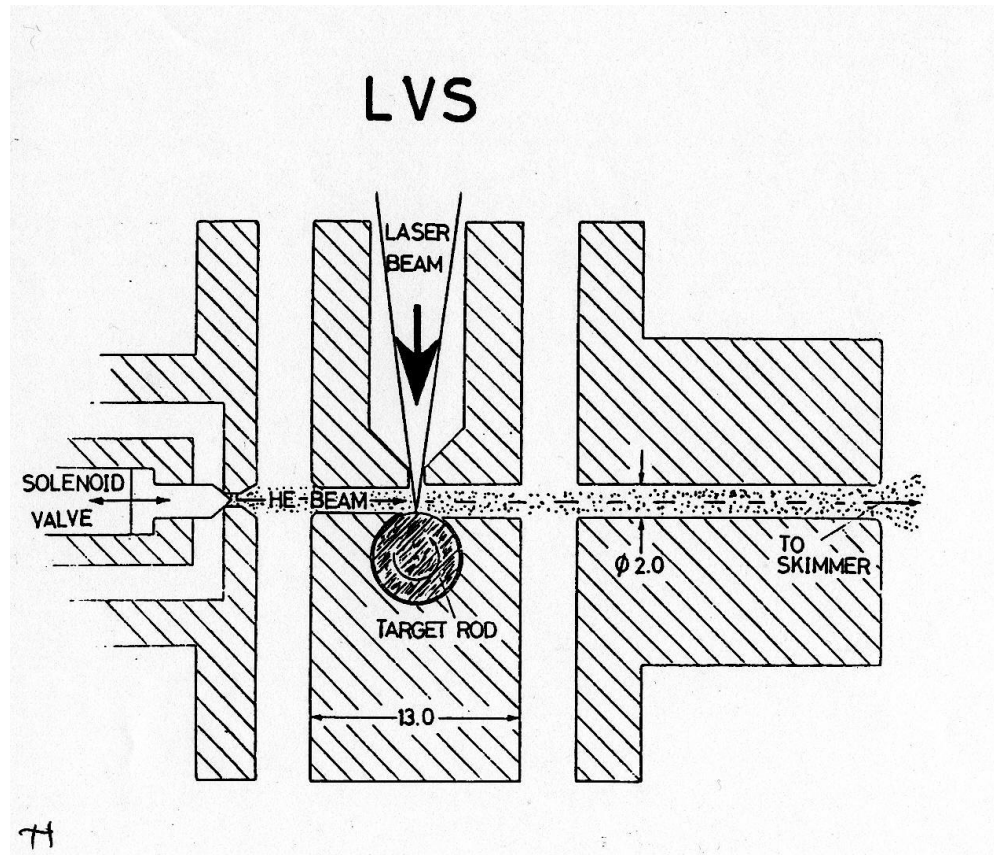


over 10^8 W/cm^2

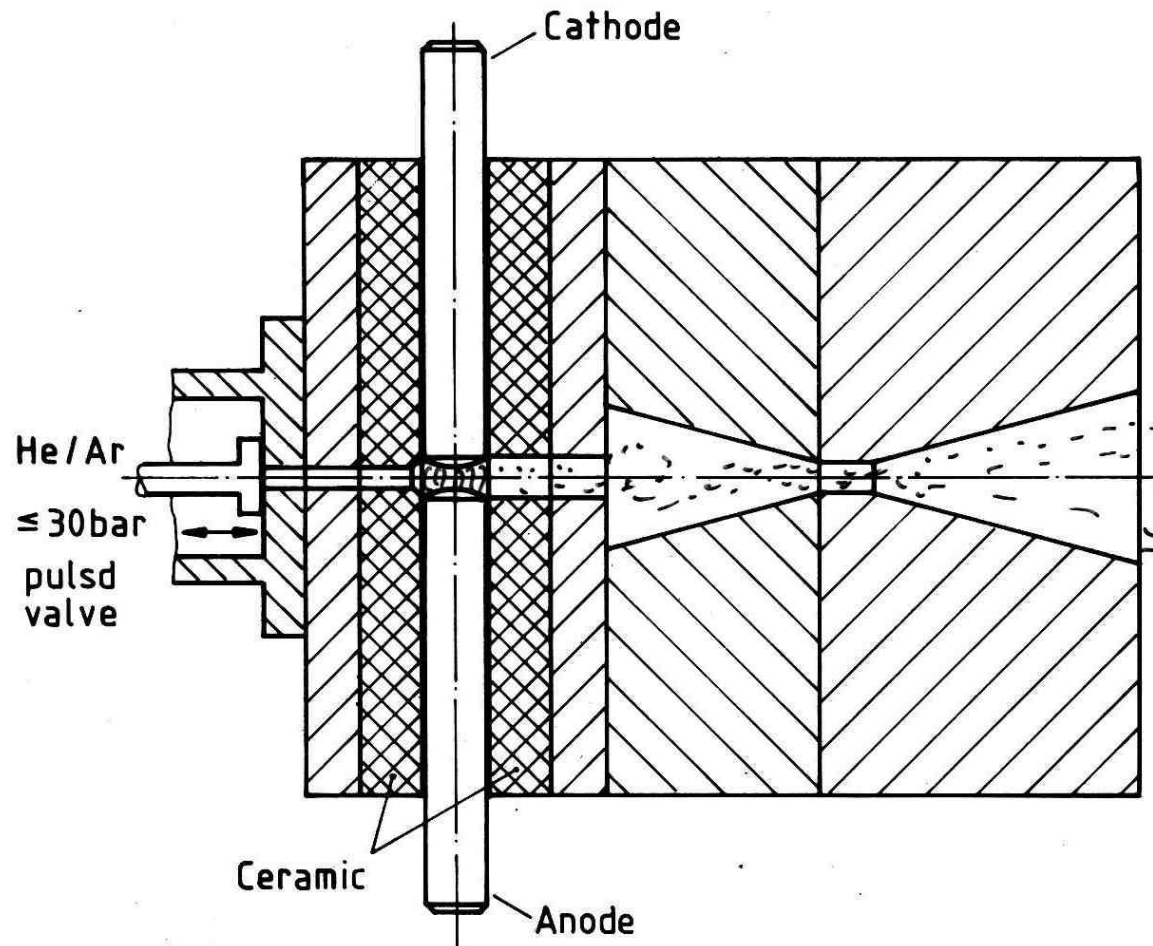
$E_{\text{kin}} (\text{Cu}^+) = 7 \text{ eV}$

Fig. 13-13 Schematic diagrams of physical processes occurring when a high-power laser beam strikes an absorbing surface.

Laser vaporization cluster source



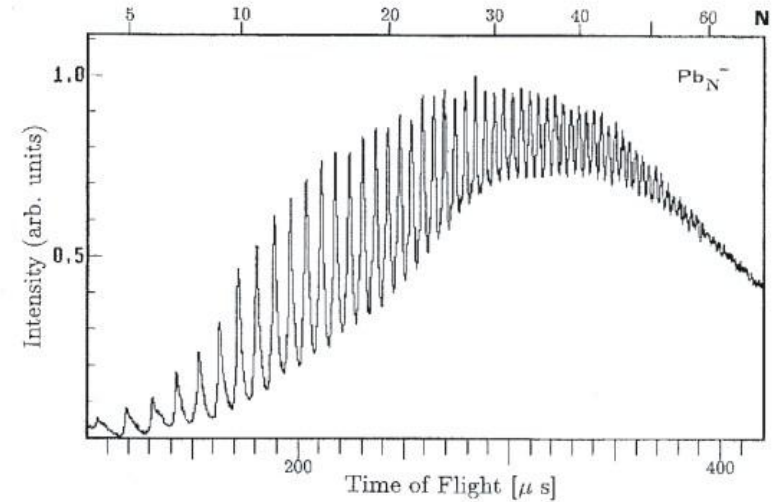
the pulsed arc cluster source



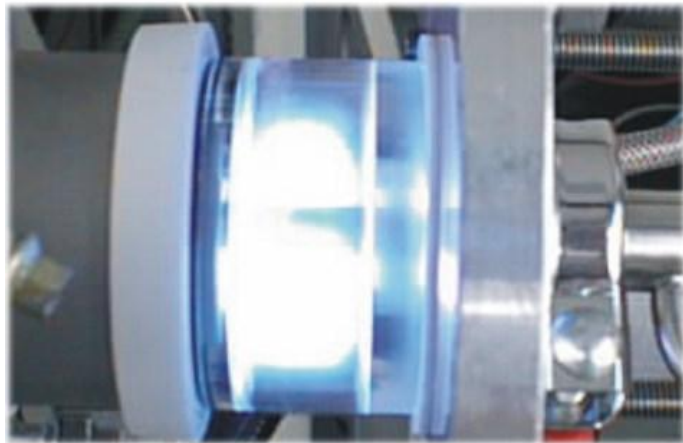
PACIS



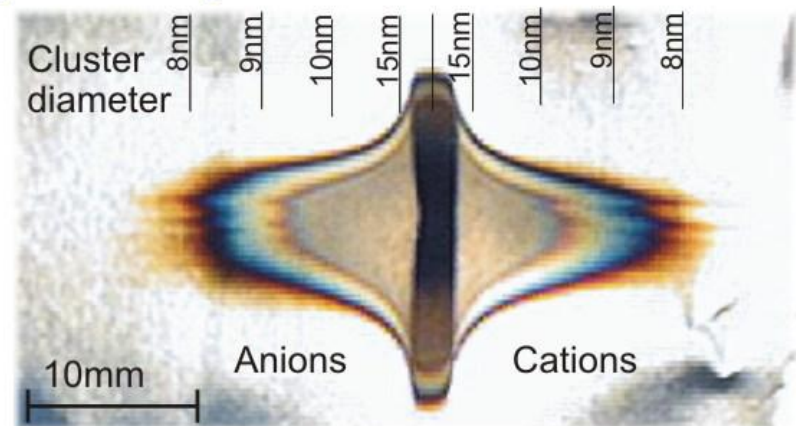
Siekmann/Ganteför



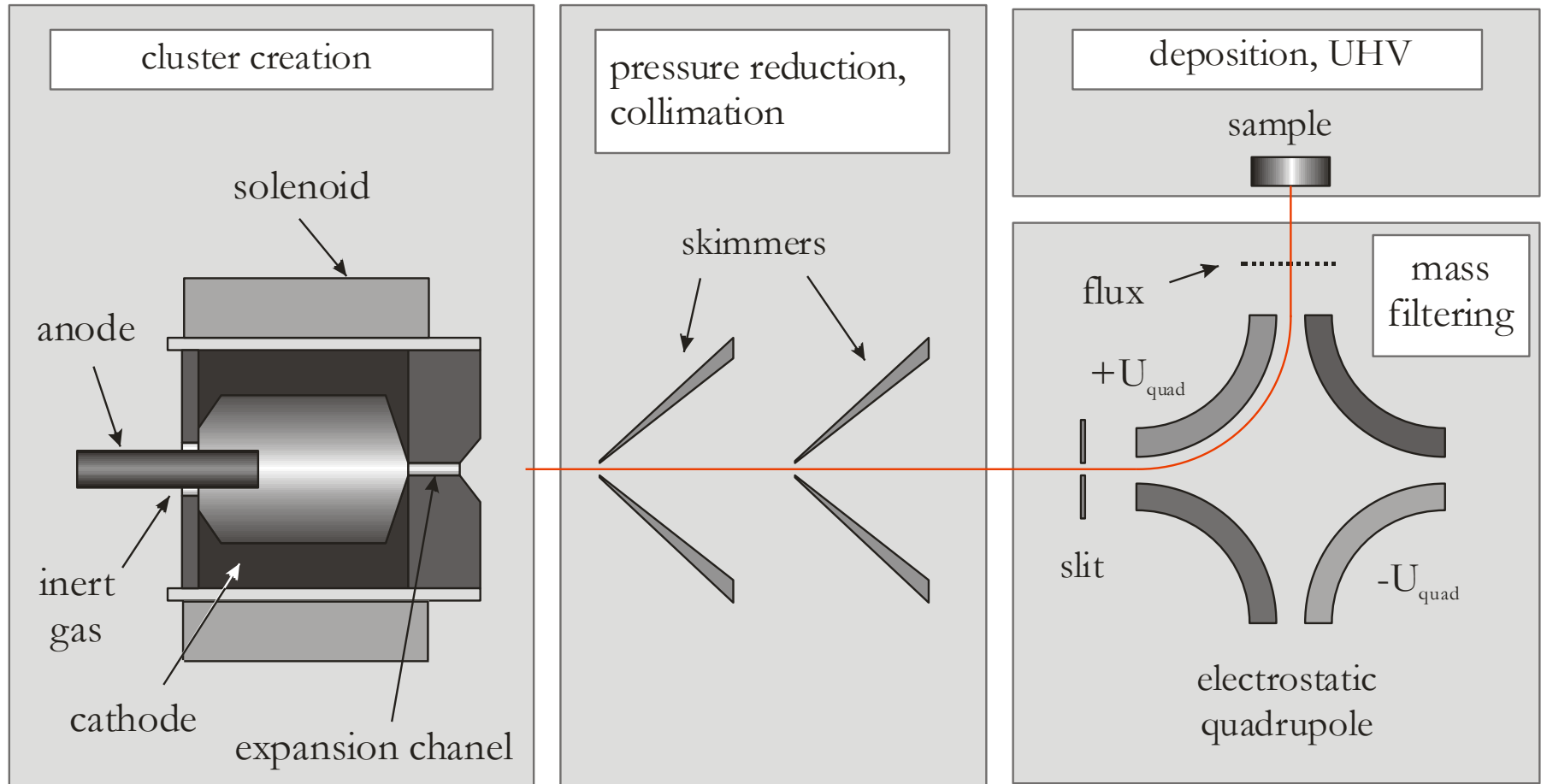
Arc cluster ion source (ACIS)



Klinkenberg/Mayer



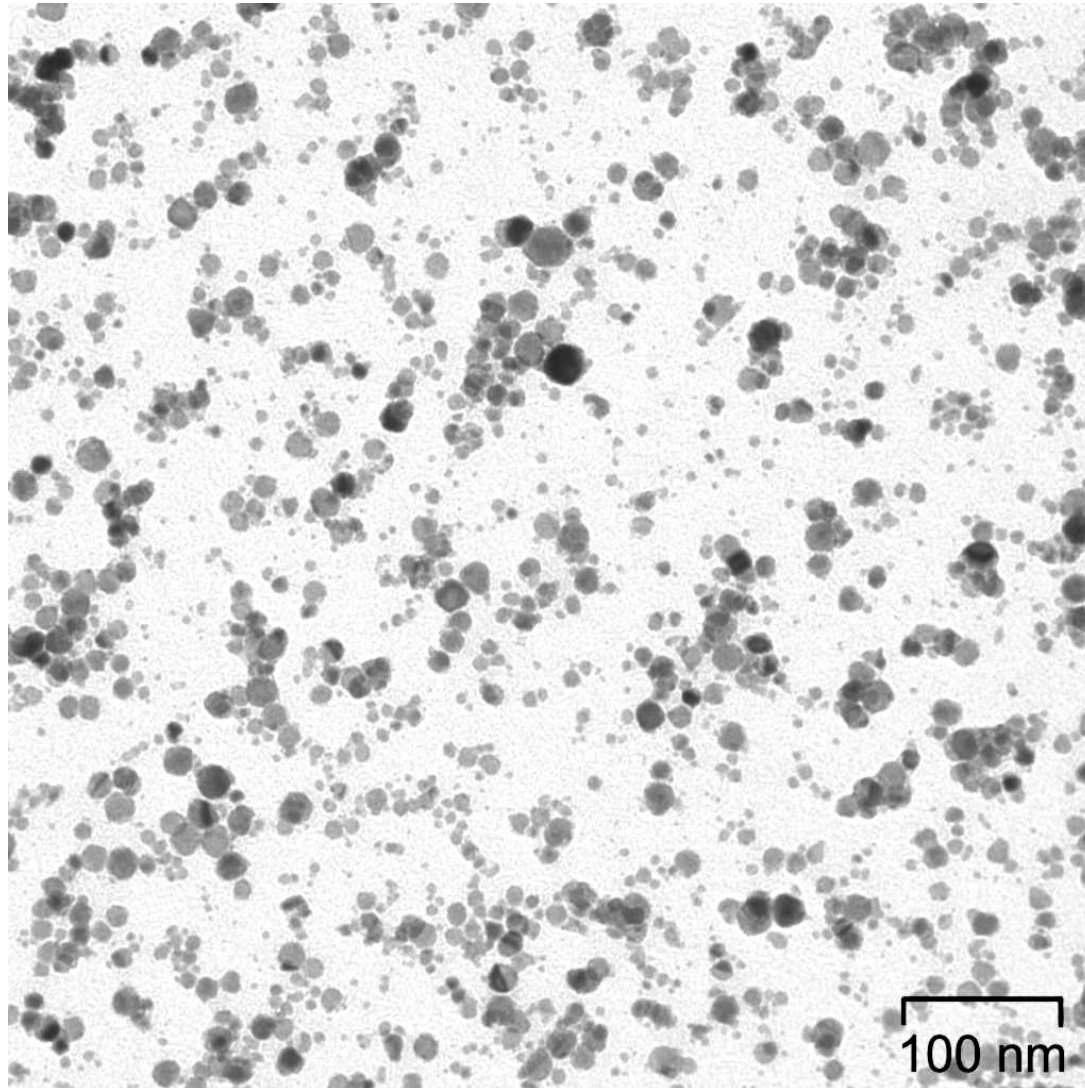
Arc Cluster Ion Source (ACIS)



Methling et al., EPJD 16, 173 (2001)

Cu_N from the ACIS

without mass filter

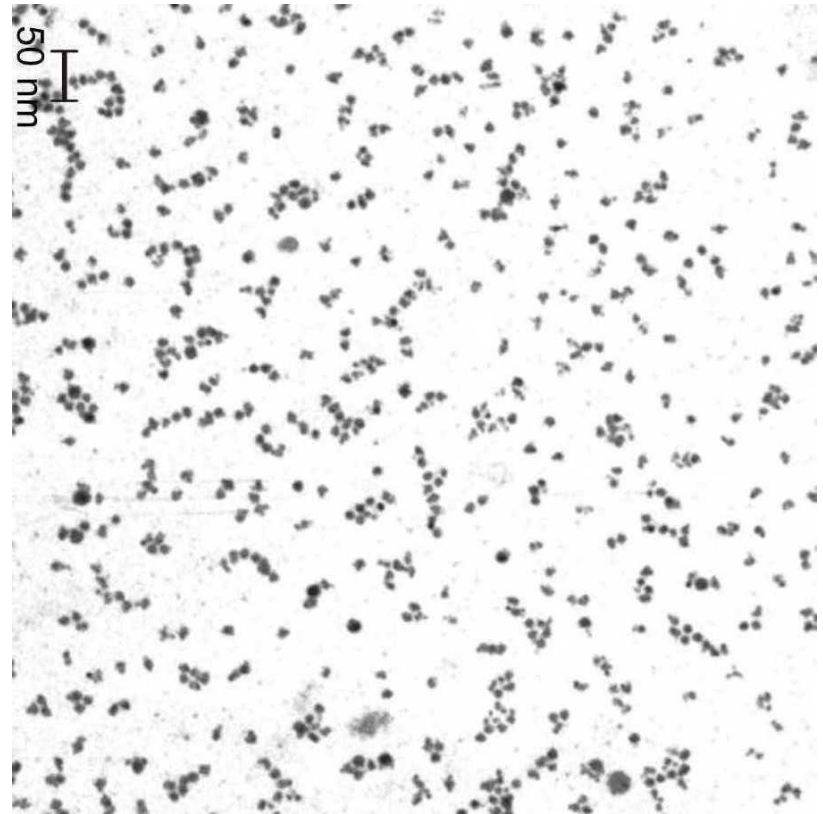
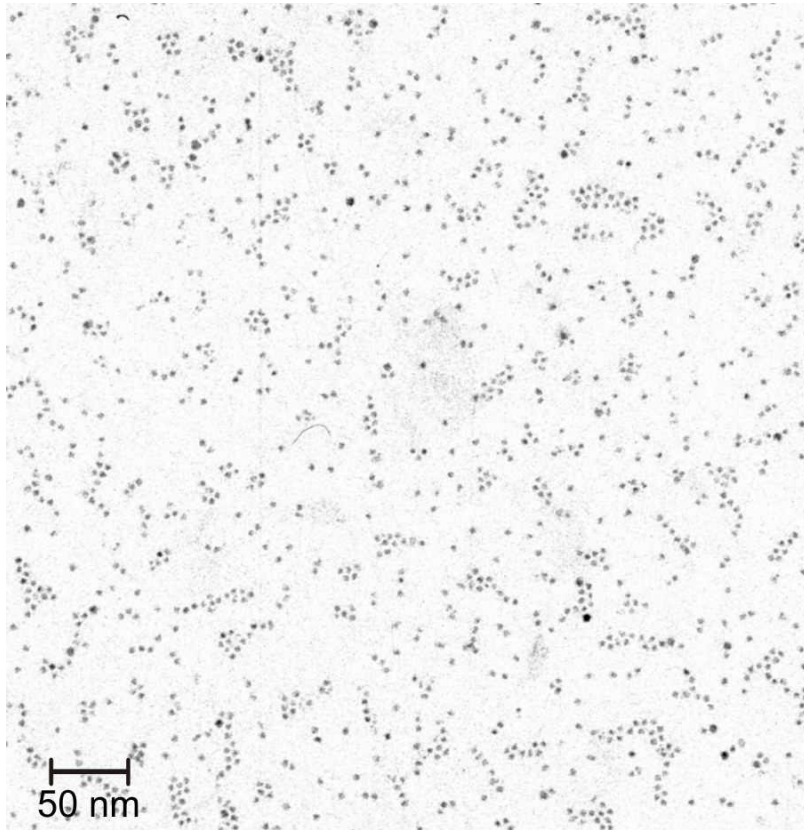


Cu_N from the ACIS

with mass filter

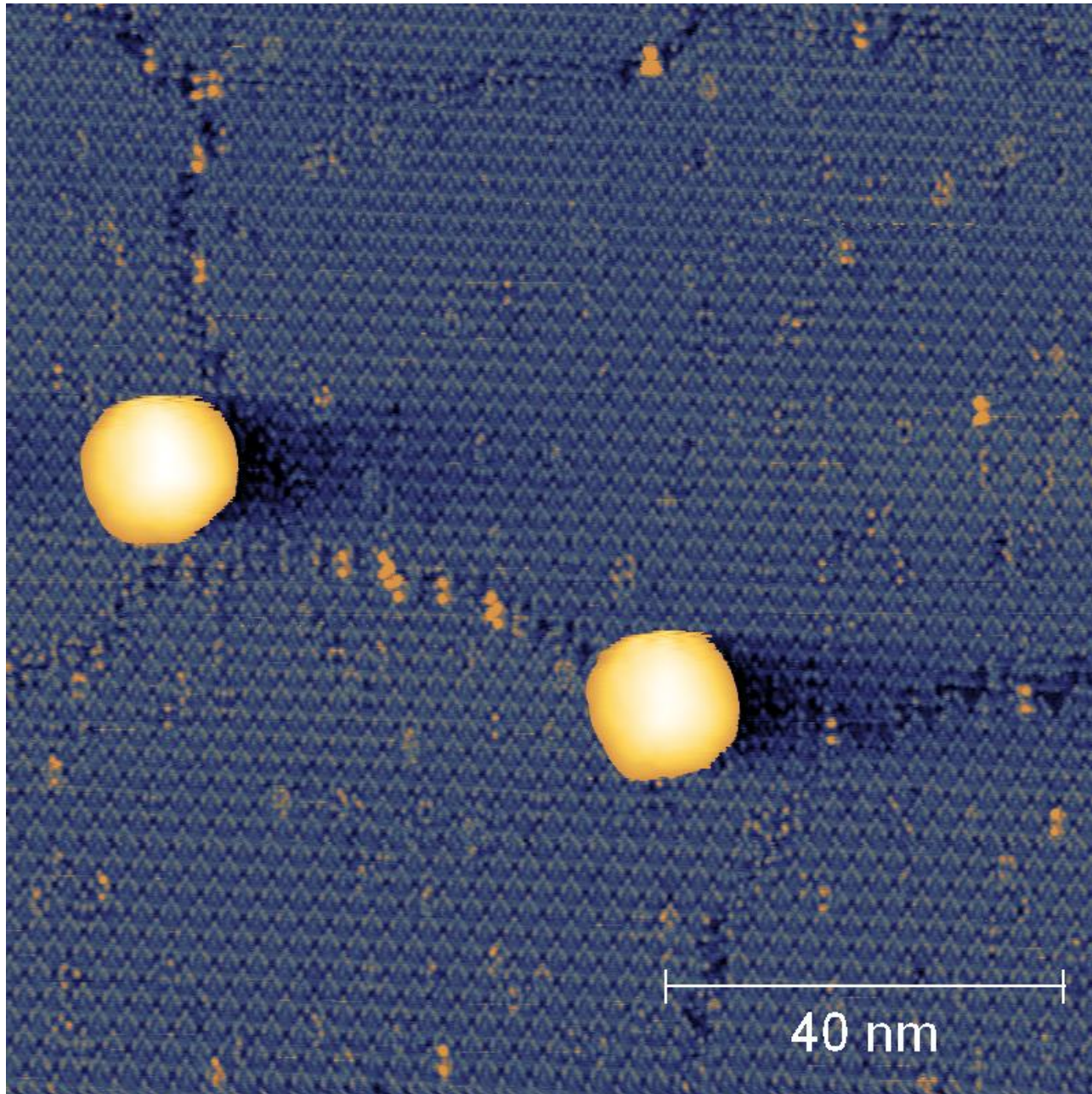
80 V

250 V

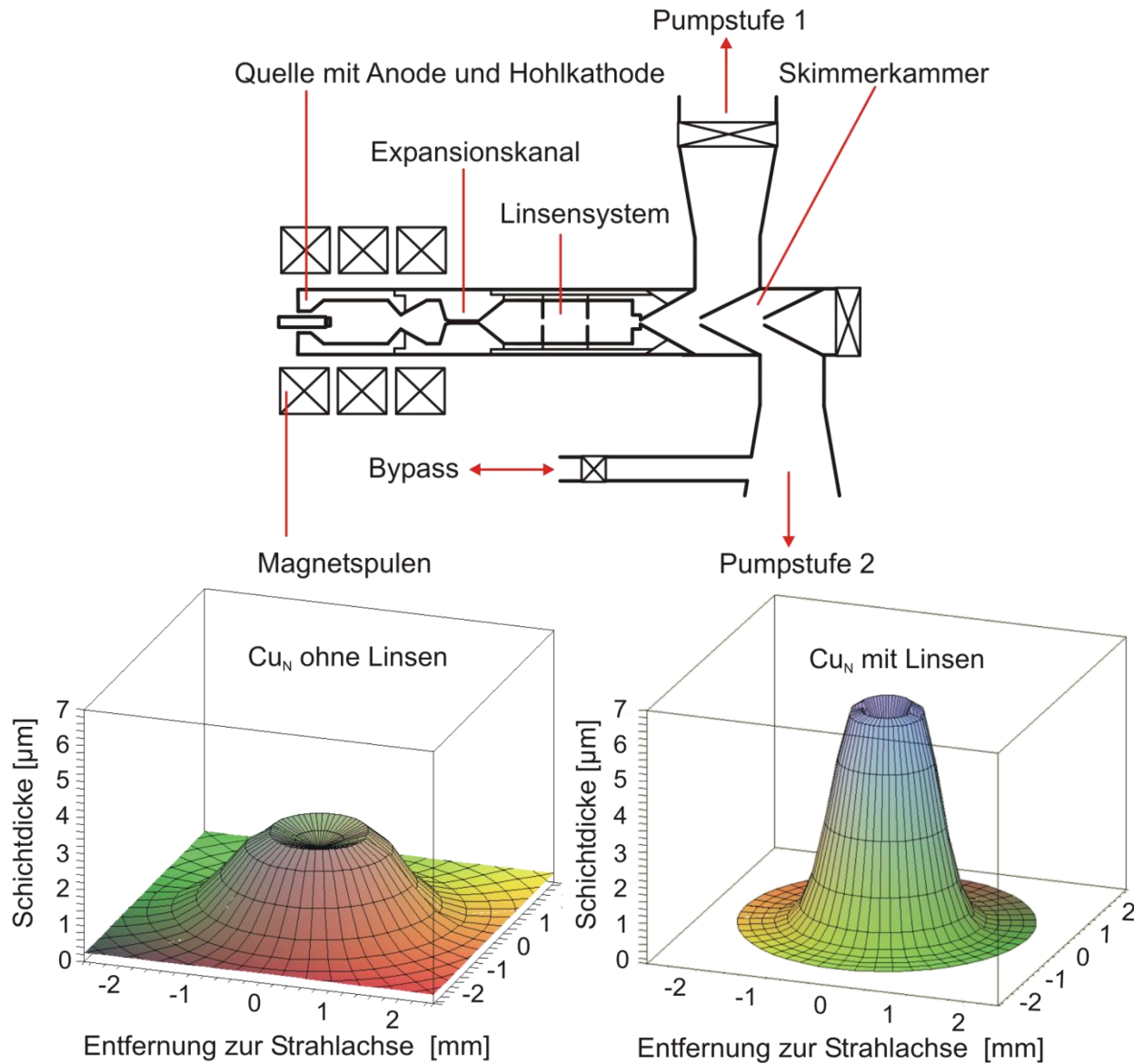


Ag_N on Si (111) from the ACIS

STM image
 $d_{\text{cluster}} = 2 \text{ nm}$



aerodynamic focussing



Sputtering (Zerstäuben)

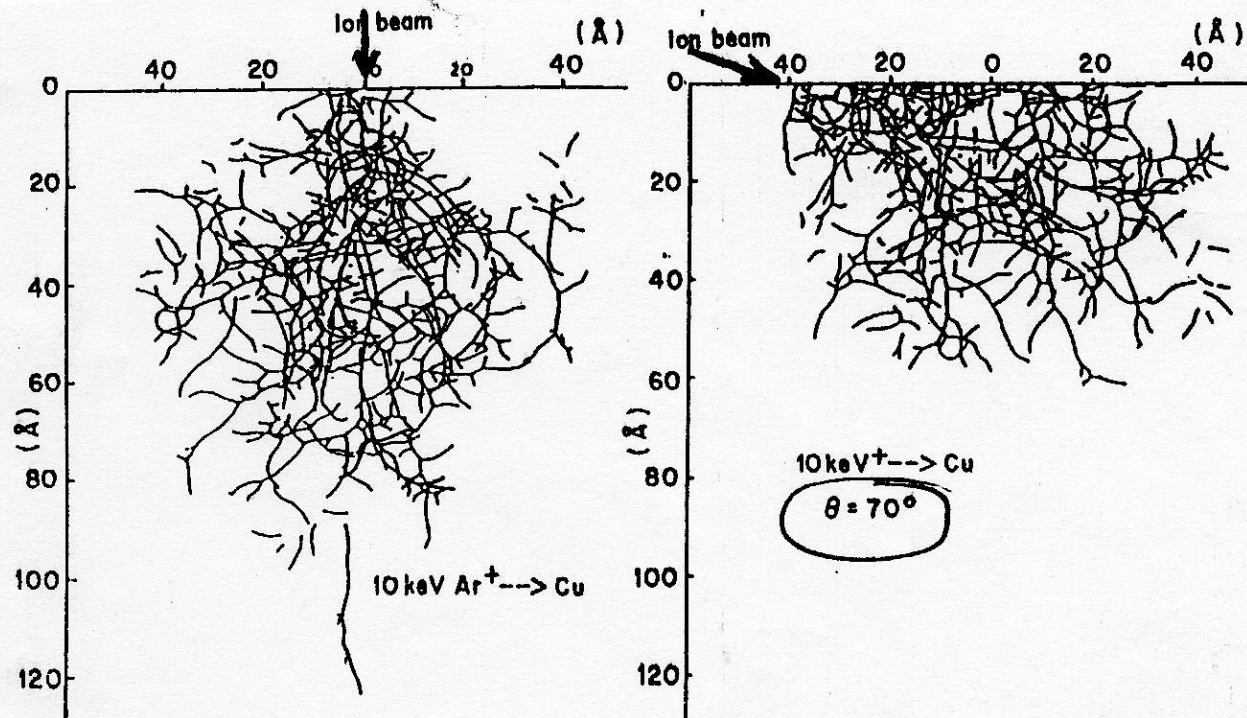
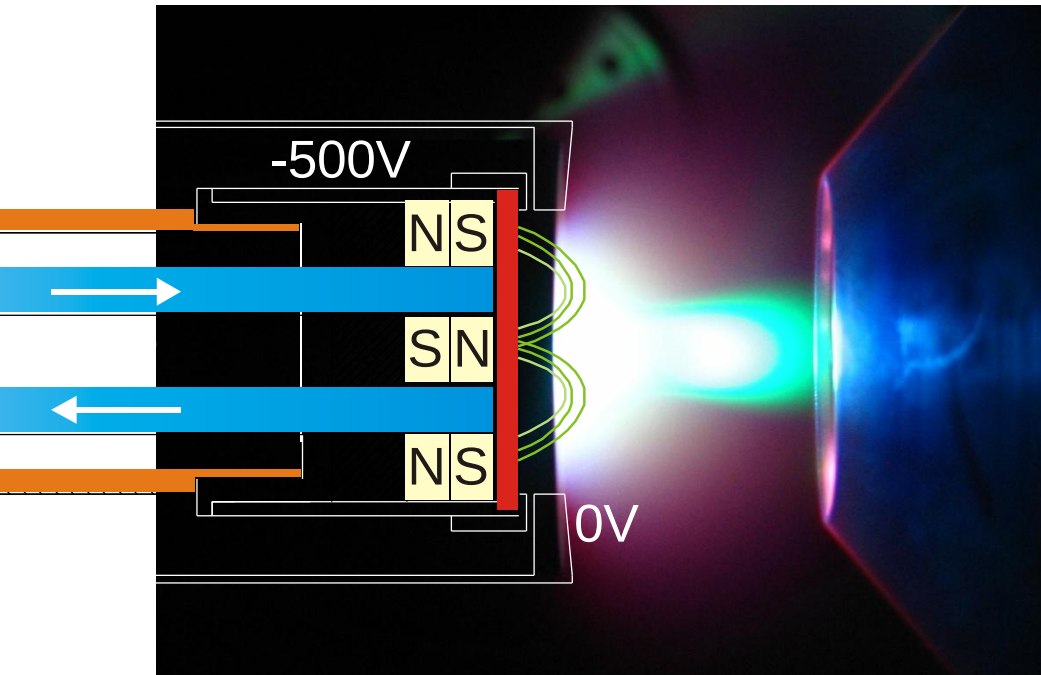


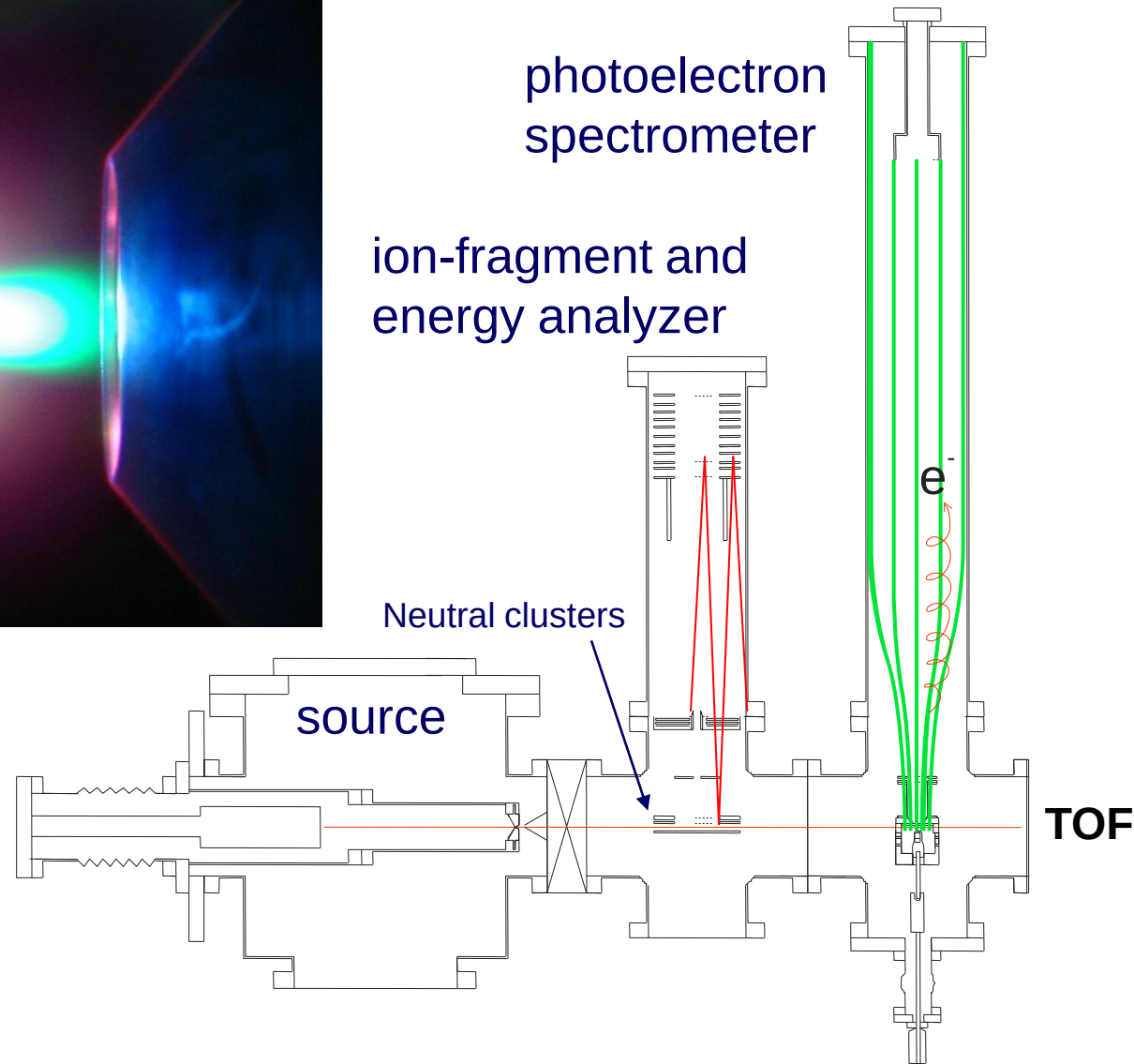
Fig. 1. Monte Carlo simulation of the trajectories of recoiling Cu atoms bombarded by 10 keV Ar⁺ ions at (a) normal incidence and (b) 70° (from ref. [5]).

The recoil trajectories are due to first-, second-, and higher-order collisions within the cascade. While the volume of the cascade caused by a single incident particle is quite large and extends nearly 100 Å into the solid, the area on the surface from which sputtered atoms are ejected about the impact site is only on the order of 40 Å in diameter.

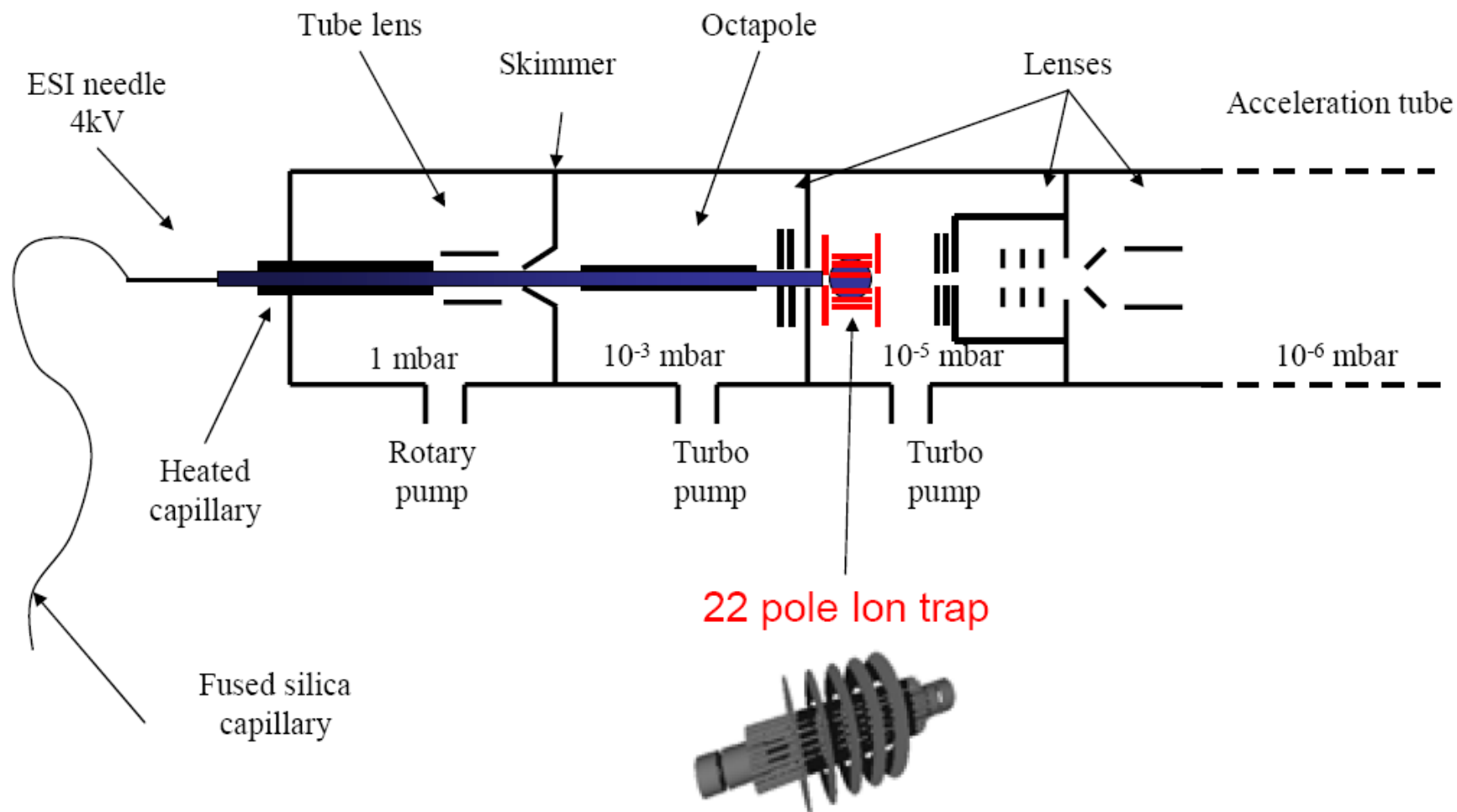
sputtering source



**Magnetron sputtering
(Haberland type)**



Electrospray Ion Source



M. Yamashita and J. B. Fenn, Electrospray ion source. Another variation on the free-jet theme, *J. Ph. Chem.* **88**, 4451 (1984)

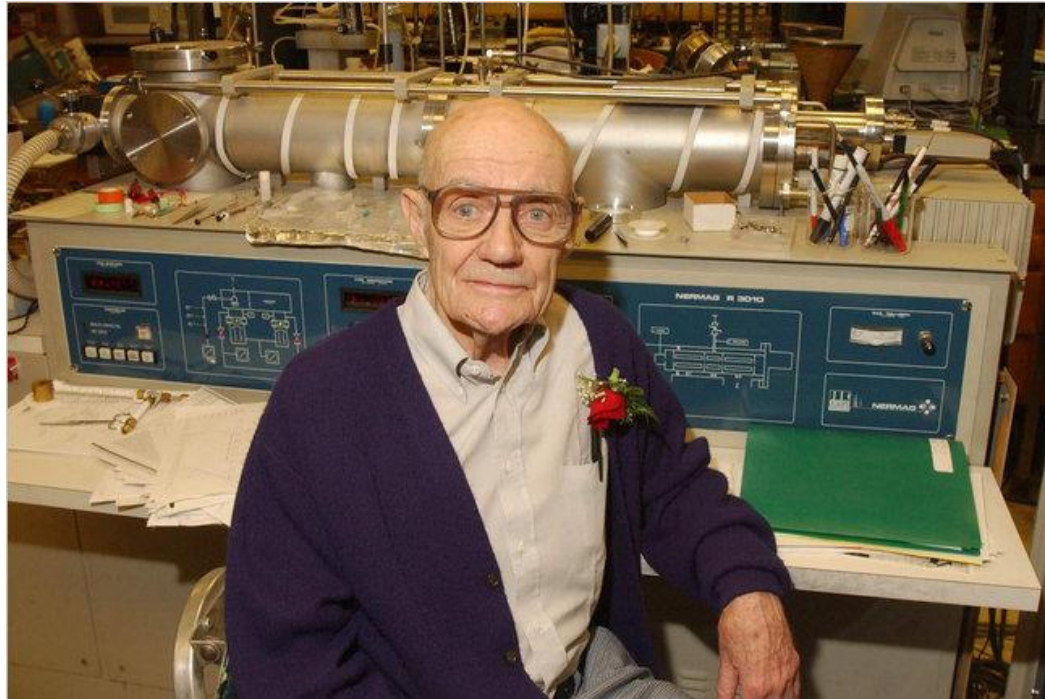
J. B. Fenn, *et al.* Electrospray ionization for mass spectrometry of large Biomolecules. *Science*. **246**, 64 (1989)

S. Brøndsted Nielsen *et al.*, Biomolecular ions in accelerators and storage rings, *J. Ph. B: At. Mol. Opt.Phys.* **37**, R25 (2004)

Prof. John Fenn, inventor of the electrospray ion source

Nobel price 2002

We learned to make elephants fly

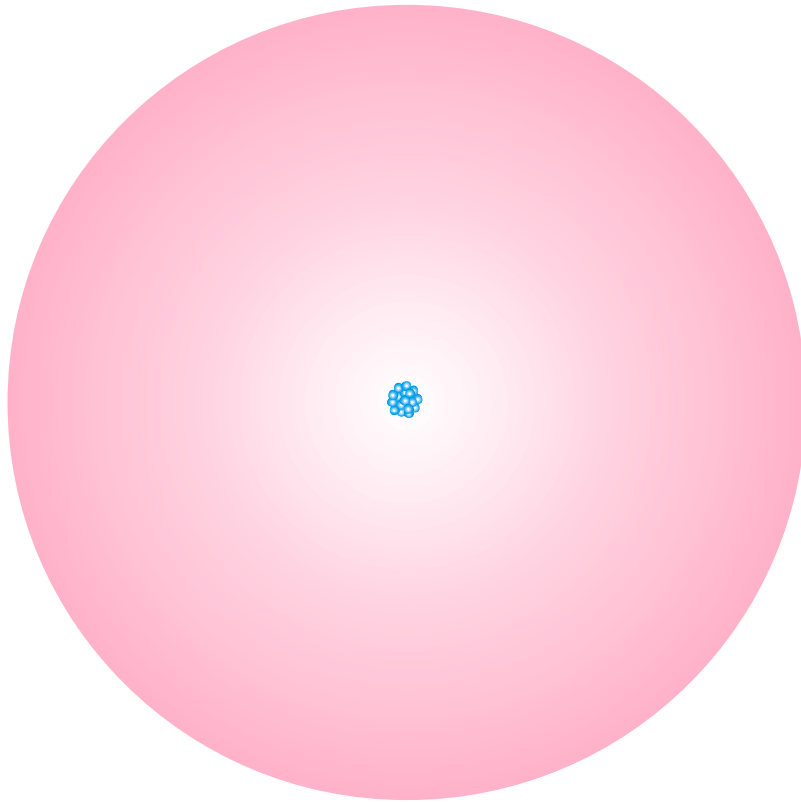


The New York Times 12.12.2010 Prof. Fenn died at the age of 93

Dr. Fenn personally patented it and then licensed the patent to a company he had co-founded. A federal judge ruled in 2005 that Dr. Fenn was guilty of “civil theft,” assigned the patent to Yale and ordered Dr. Fenn to pay Yale more than \$1 million. He appealed the ruling but lost.

Helium droplet pick-up source

atom pick-up in superfluid and 0.4 K cold helium droplets

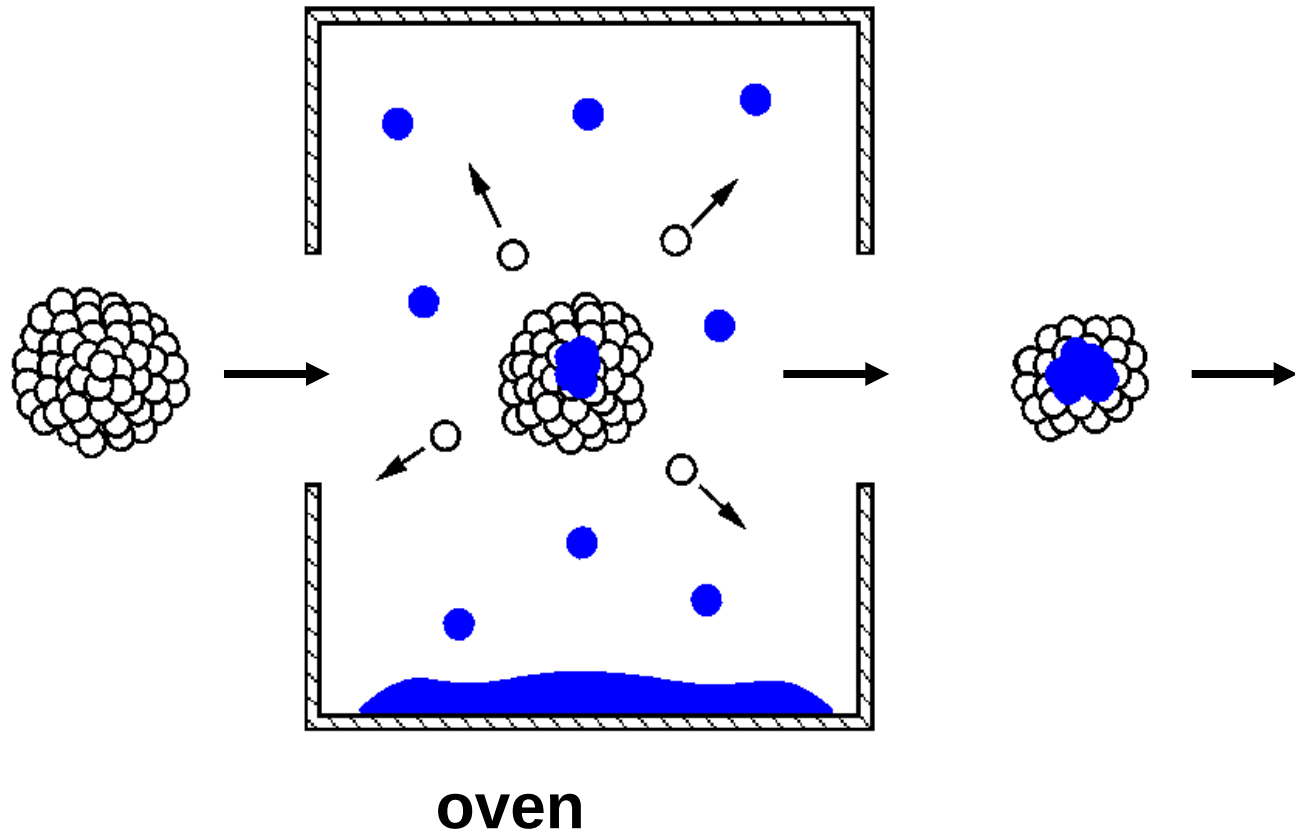


**Binding energy $\text{He}@ \text{He}_N = 7 \text{ K}$
1 eV BE > 1000 Atoms
stabilization at 0.375 K**

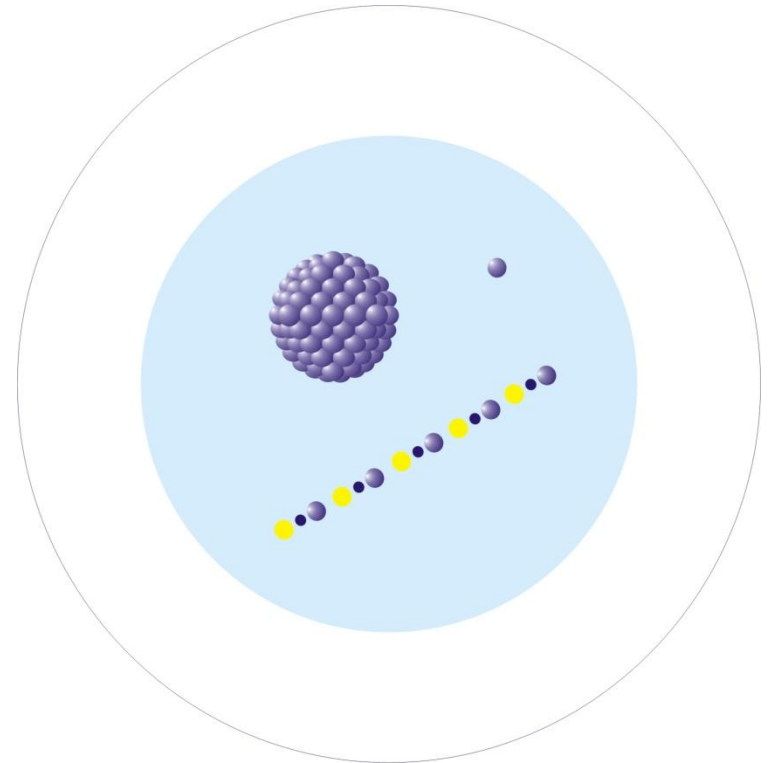
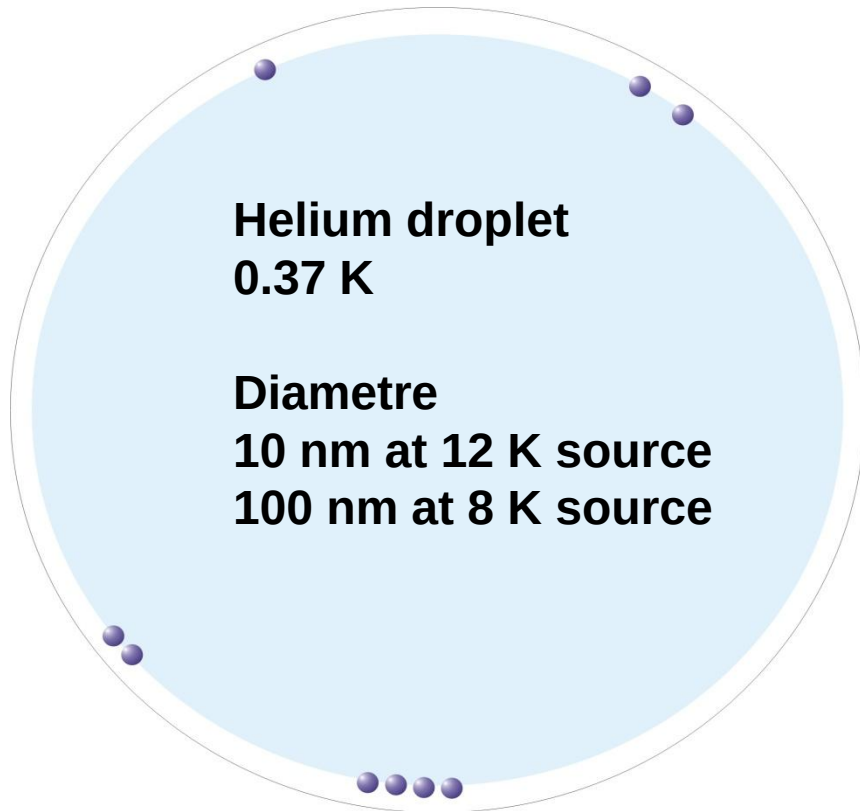
**Schematics of a Ag_{147}
silver cluster inside a
Helium droplet with
 10^6 atoms**

low-temperature physics

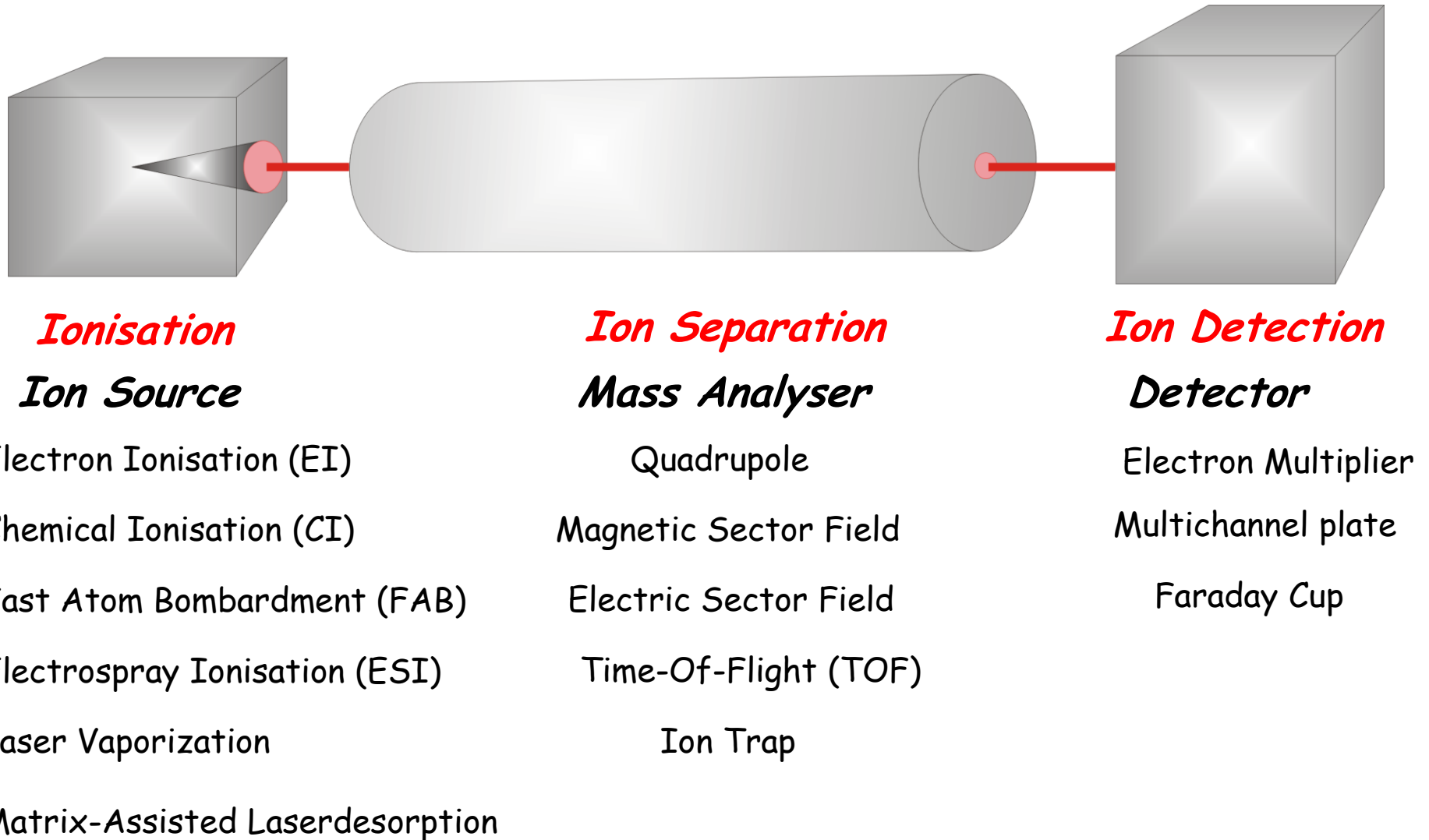
atom pick-up in Helium droplets



exotic systems in and on He droplets



How to see the clusters - Components of a mass spectrometer



Warum m/q und nicht m ?

- elektrische und magnetische Felder:
 $F = q(E + v \times B)$
 - Trägheit:
 $F = ma$
- ➔ $a = q/m (E + v \times B)$
(Ionen mit m/q haben identische Flugbahnen)

Alle Massenspektrometer bestimmen m/q eines Ions.

Time-of-flight mass spectrometer

What if the ions are formed in different locations?

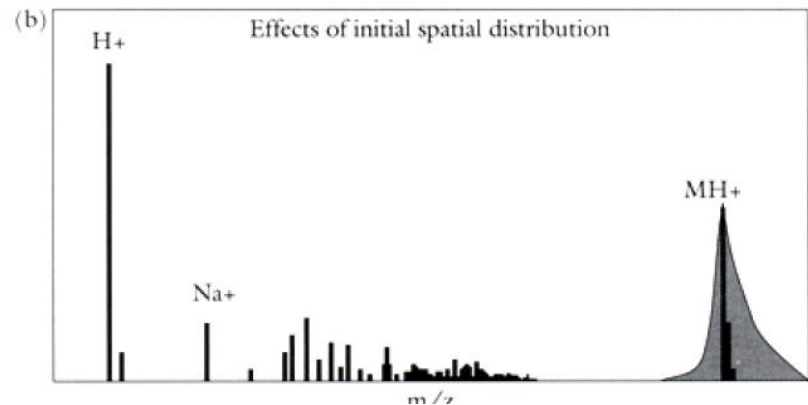
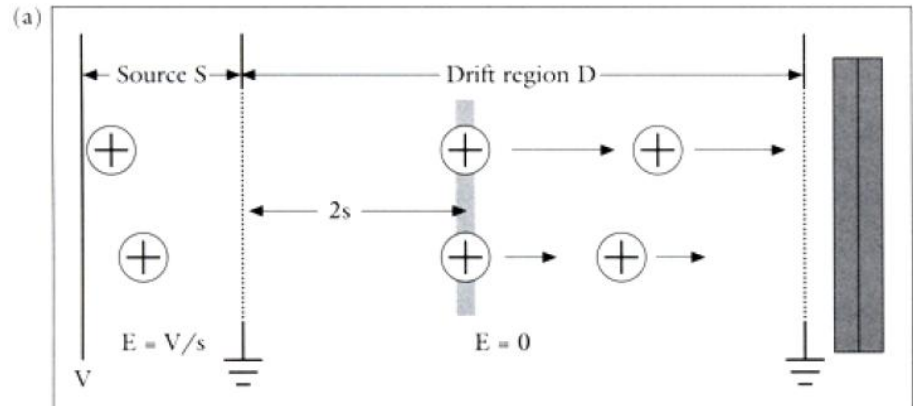
Ions leave the source with energies eEs' dependent upon their location

$$t = \left(\frac{m}{2eEs'} \right)^{1/2} [2s' + D]$$

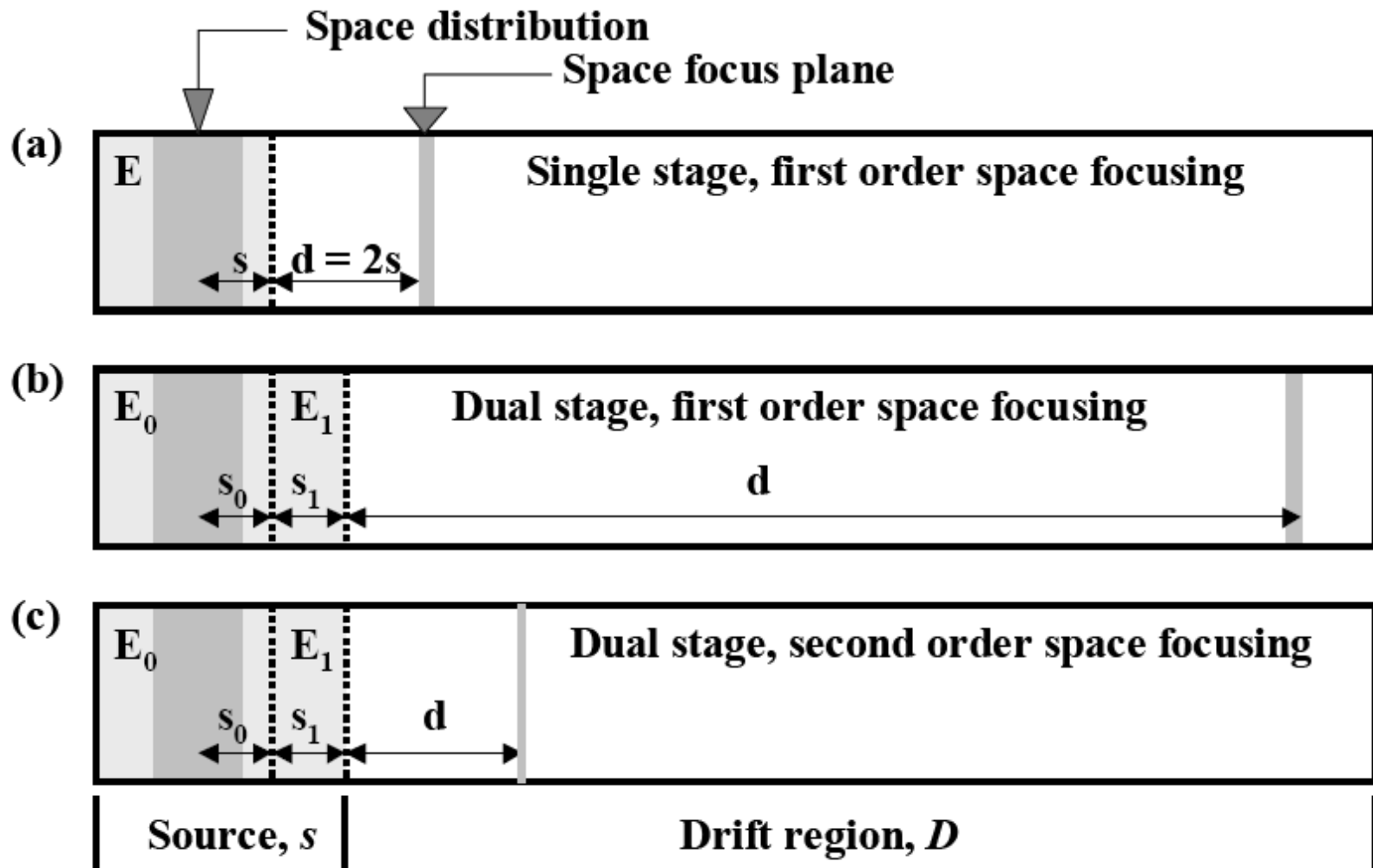
where $s' = s - \Delta s$

How is the effect of an initial spatial distribution improved?

- thin sample
- detector at $D = 2s$
- dual-stage extraction to move the space-focus plane

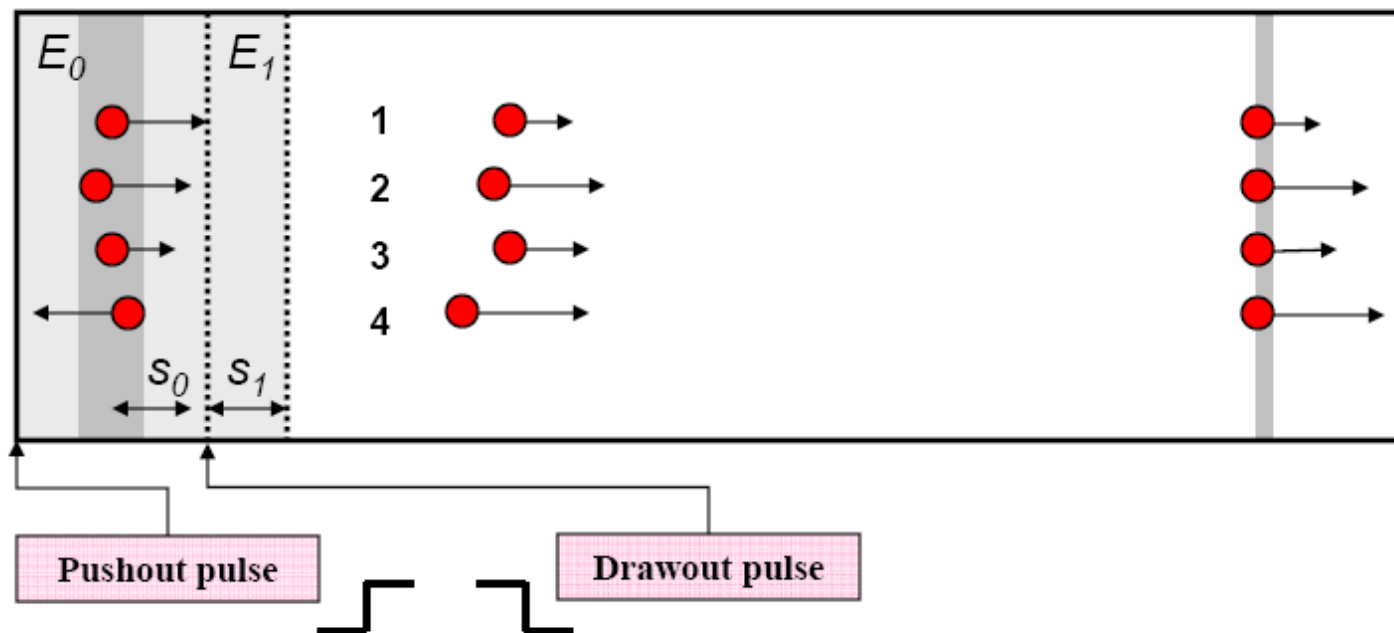


The *space-focus plane*



Time-lag focusing

Wiley, W.C.; McLaren, I.H., **Rev. Sci. Instrument.** **26** (1955) 1150-1157.



Ions differing in initial position in the source, initial kinetic energies and different directions of their initial velocities are focused in the Wiley-McLaren TOF mass spectrometer.

Time of flight (TOF) mass spectrometry

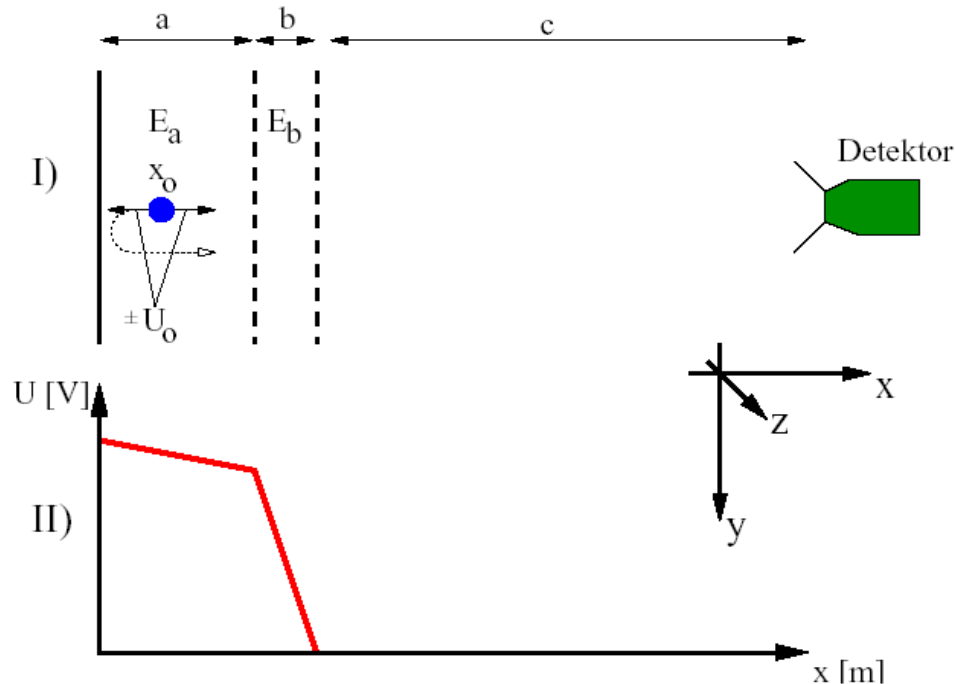


Abbildung 3.7: Feldverlauf und Spannungen im TOF

I) Aufbau eines 2-stufigen TOF. In den Bereichen a und b werden die Teilchen ausgehend von ihrem Startort x_0 durch die Felder E_a und E_b beschleunigt. Ist ihre Anfangsenergie U_0 entgegen dem Feldgradienten gerichtet, wird das Teilchen umgelenkt (gepunktete Linie). Bei hinreichend großen Werten von U_0 ist dies als Aufspaltung der Massenlinien im Spektrum zu beobachten. Nach einer feldfreien Driftstrecke c treffen die Ionen auf den Detektor und werden dort nachgewiesen. Die Geschwindigkeit aus der Überschall-Expansion wird in die Simulation nicht einbezogen, da sie senkrecht auf dem Vektor der Beschleunigungsrichtung steht und somit keinen Einfluß auf die Flugzeit hat. Lediglich die Transmission (s. Kap. 3.4.3) wird durch sie beeinflusst. **II)** Spannungsverlauf im TOF.

Time-of flight (TOF) mass spectrometry

$$x(t) = x_0 + v_0 \times t + \frac{b_a}{2} \times t^2 \quad (3.3)$$

mit der Anfangs-Geschwindigkeit v_0 und der Beschleunigung b_a , die sich folgendermaßen durch die Anfangsenergie U_0 und die Feldstärke E_a ersetzen lassen:

$$v_0 = \sqrt{\frac{2U_0}{m}}, \quad b_a = \frac{Ze}{m} E_a \quad (3.4)$$

$Ze \equiv q$ ist die auf dem Cluster akkumulierte Ladung. Die Z -fache Aufladung mit $Z > 1$ wird nur bei der Wechselwirkung der Teilchen mit intensiven Laserstrahlen beobachtet. Als Lösung ergeben sich für die drei Bereiche folgende Gleichungen:

$$t_a = \frac{\sqrt{2m}}{qE_a} \left[\sqrt{U_0 + q(a-x)E_a} \pm \sqrt{U_0} \right] \quad (3.5)$$

$$t_b = \frac{\sqrt{2m}}{qE_b} \left[\sqrt{U_0 + q(a-x)E_a + qbE_b} - \sqrt{U_0 + q(a-x)E_a} \right] \quad (3.6)$$

$$t_c = c \sqrt{\frac{m}{2(U_0 + q(a-x)E_a + qbE_b)}} \quad (3.7)$$

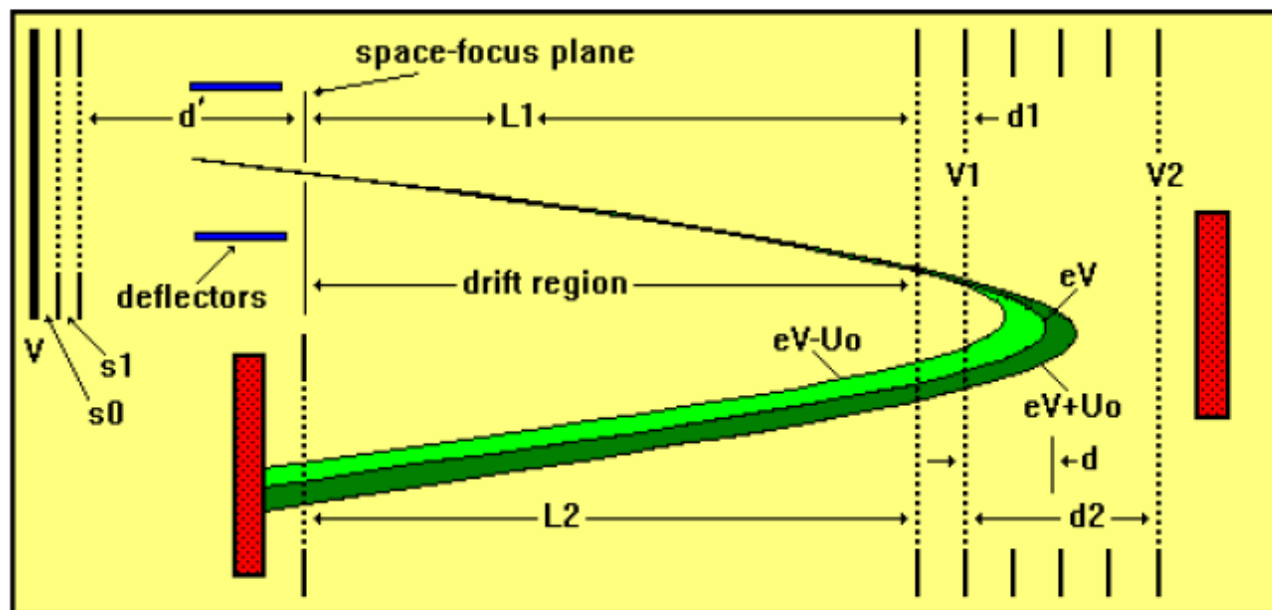
$$t_{gesamt} = t_a + t_b + t_c \quad (3.8)$$

Reflectrons improve mass resolution

Dual-stage reflectron

The original reflectron invented by Boris Mamyrin was a dual stage.

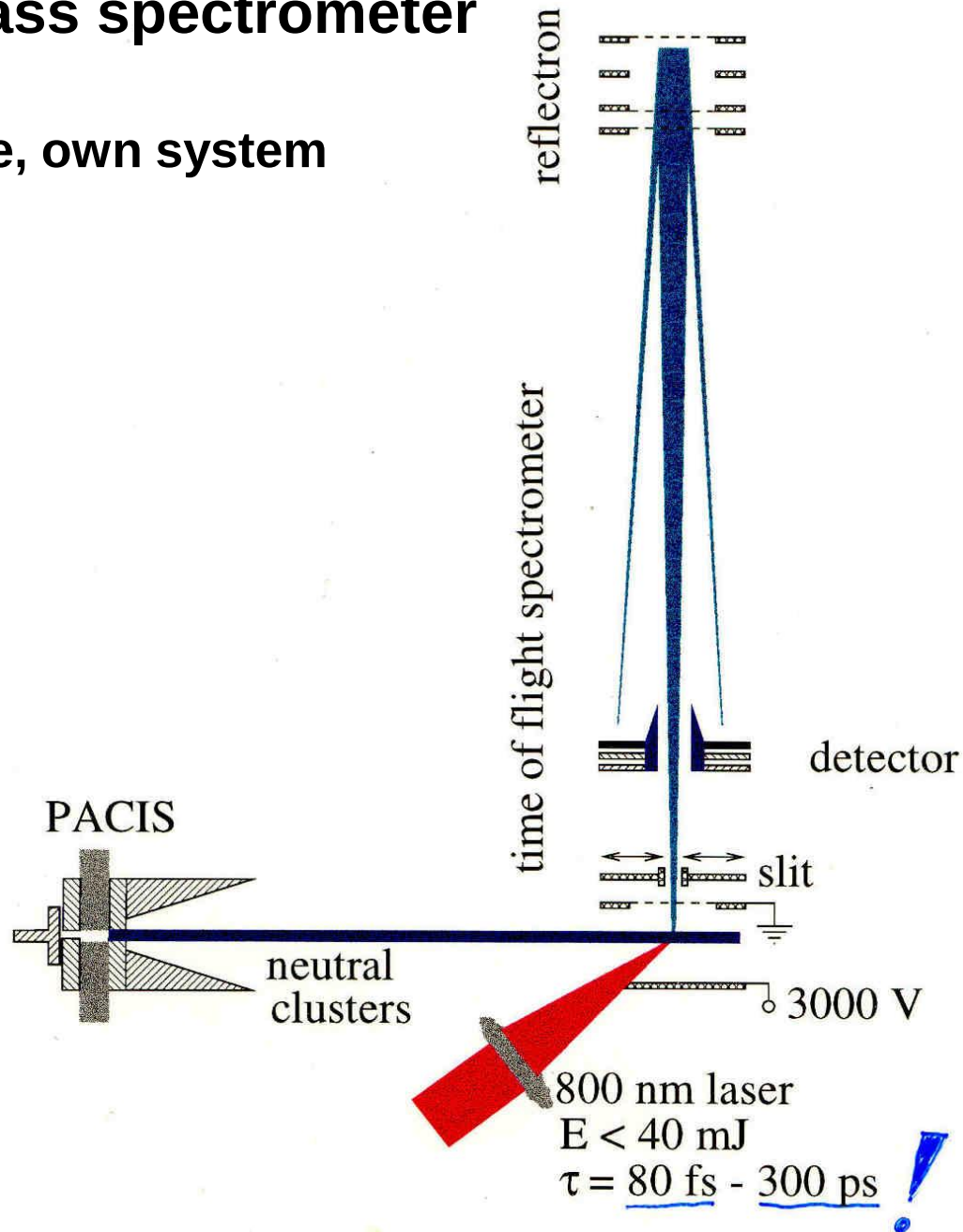
Mamyrin, B. A.; Karataev, V. I.; Shmikk, D. V.; Zagulin, V. A, *Mass reflectron. New nonmagnetic time-of-flight high-resolution mass spectrometer*. Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki (1973) 64, 82-89.



The dual stage reflectron can be designed to achieve second order focusing. In this case the reflectron depth is much smaller than the flight tube length.

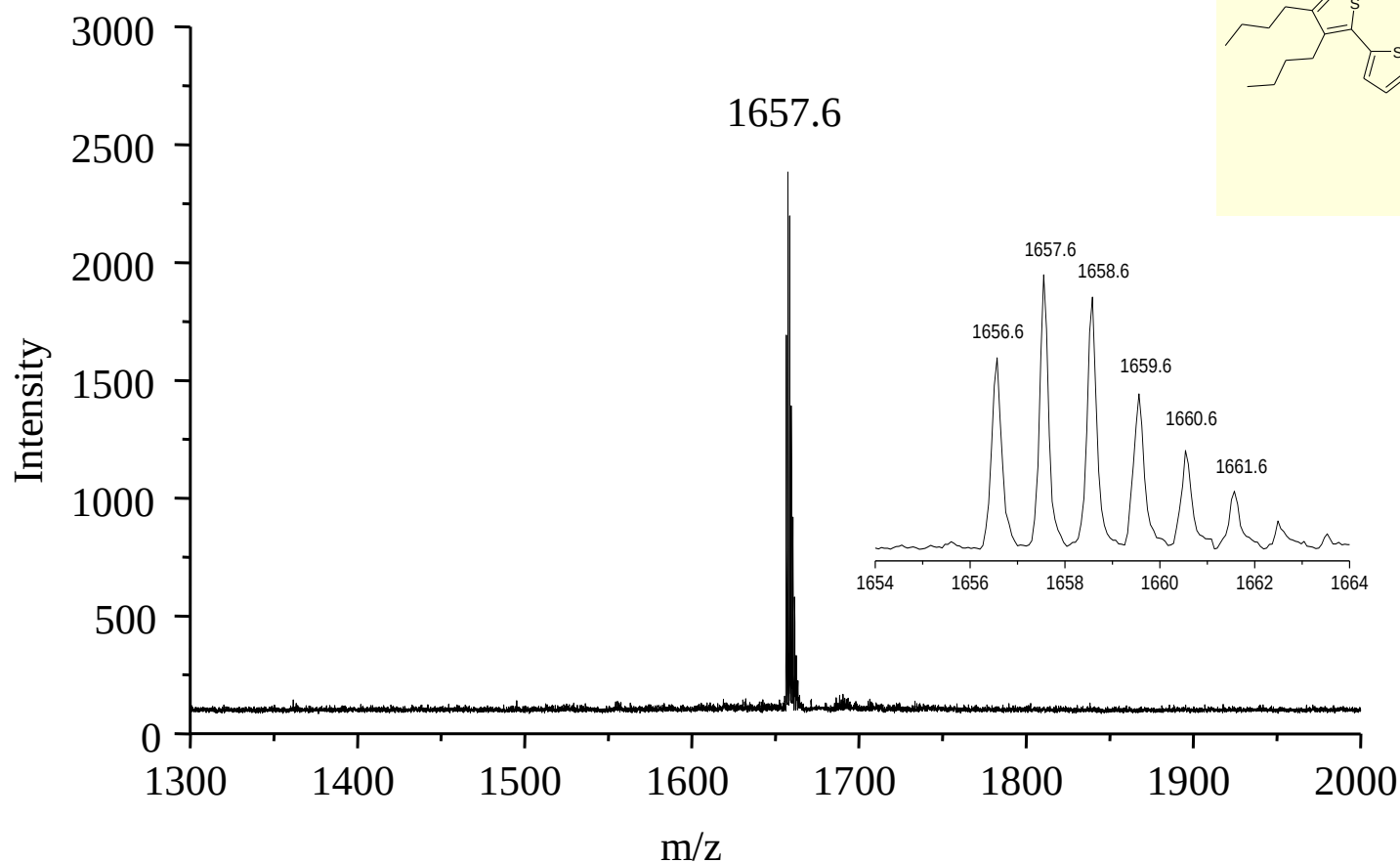
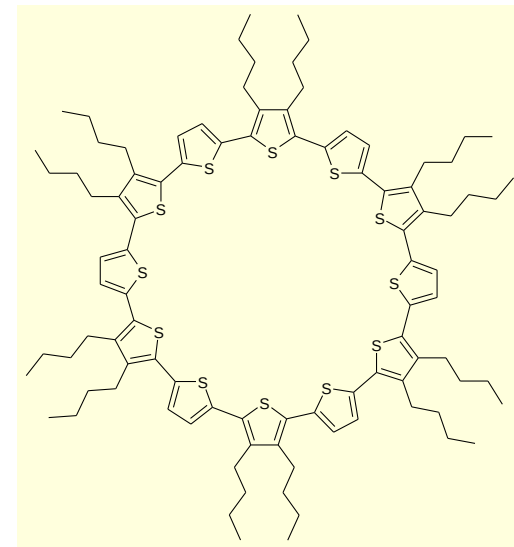
Time-of-flight mass spectrometer

here: reflectron-type, own system

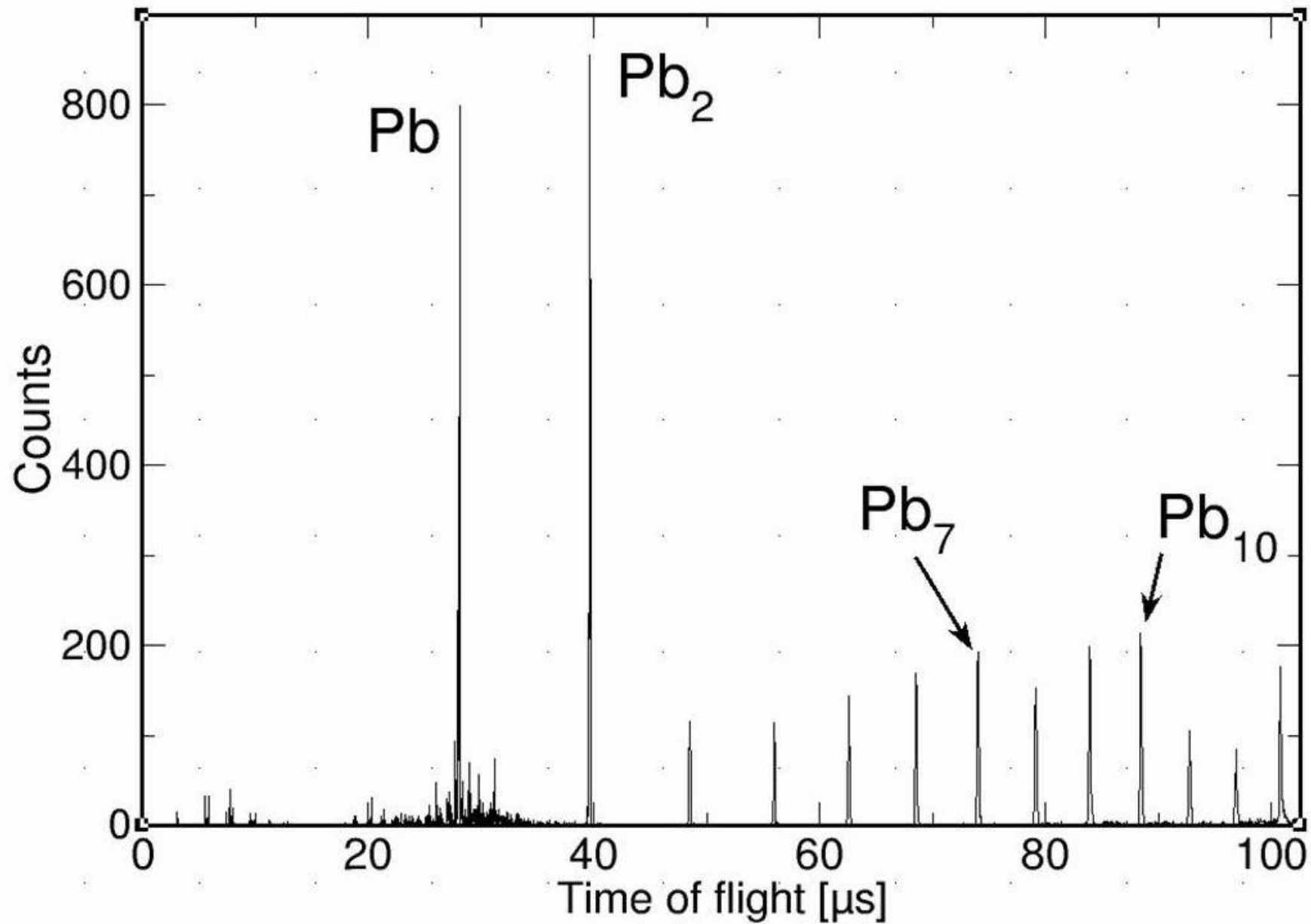


example: mass spectrum of Cyclothiophen

Cyclo[12]thiophen

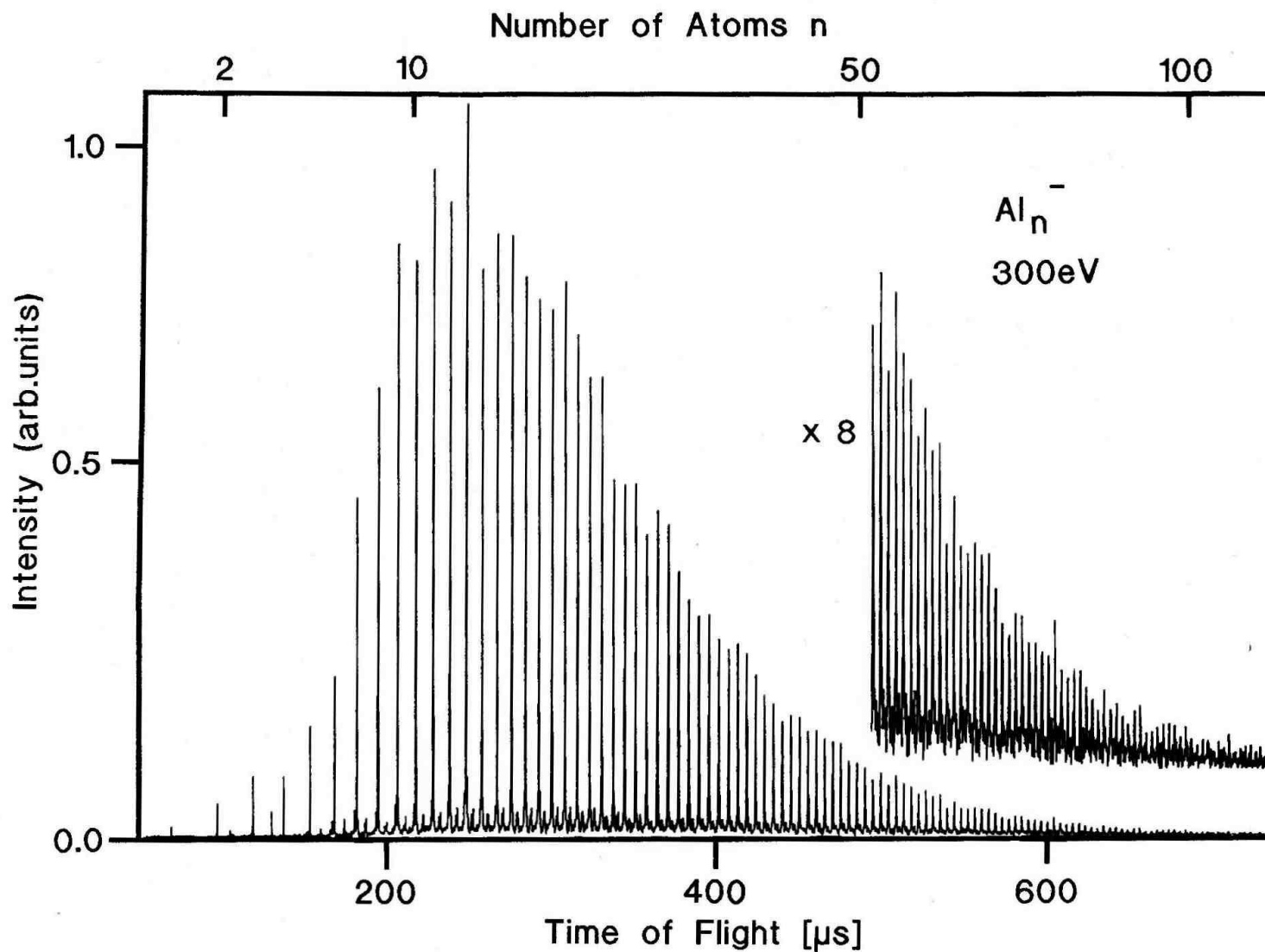


time-of-flight mass spectrum of Pb clusters



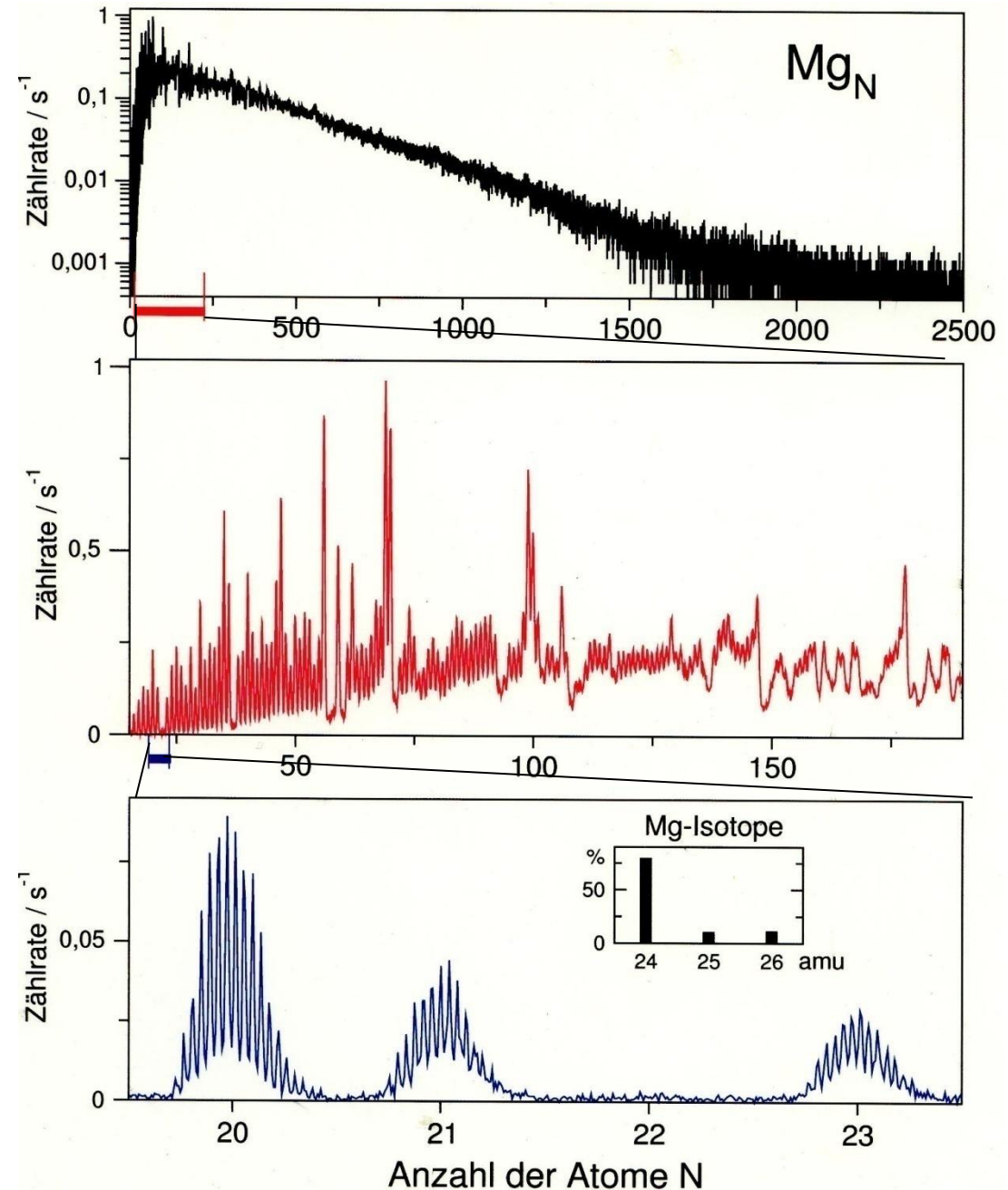
time-of-flight mass spectroscopy

negatively charged Al clusters



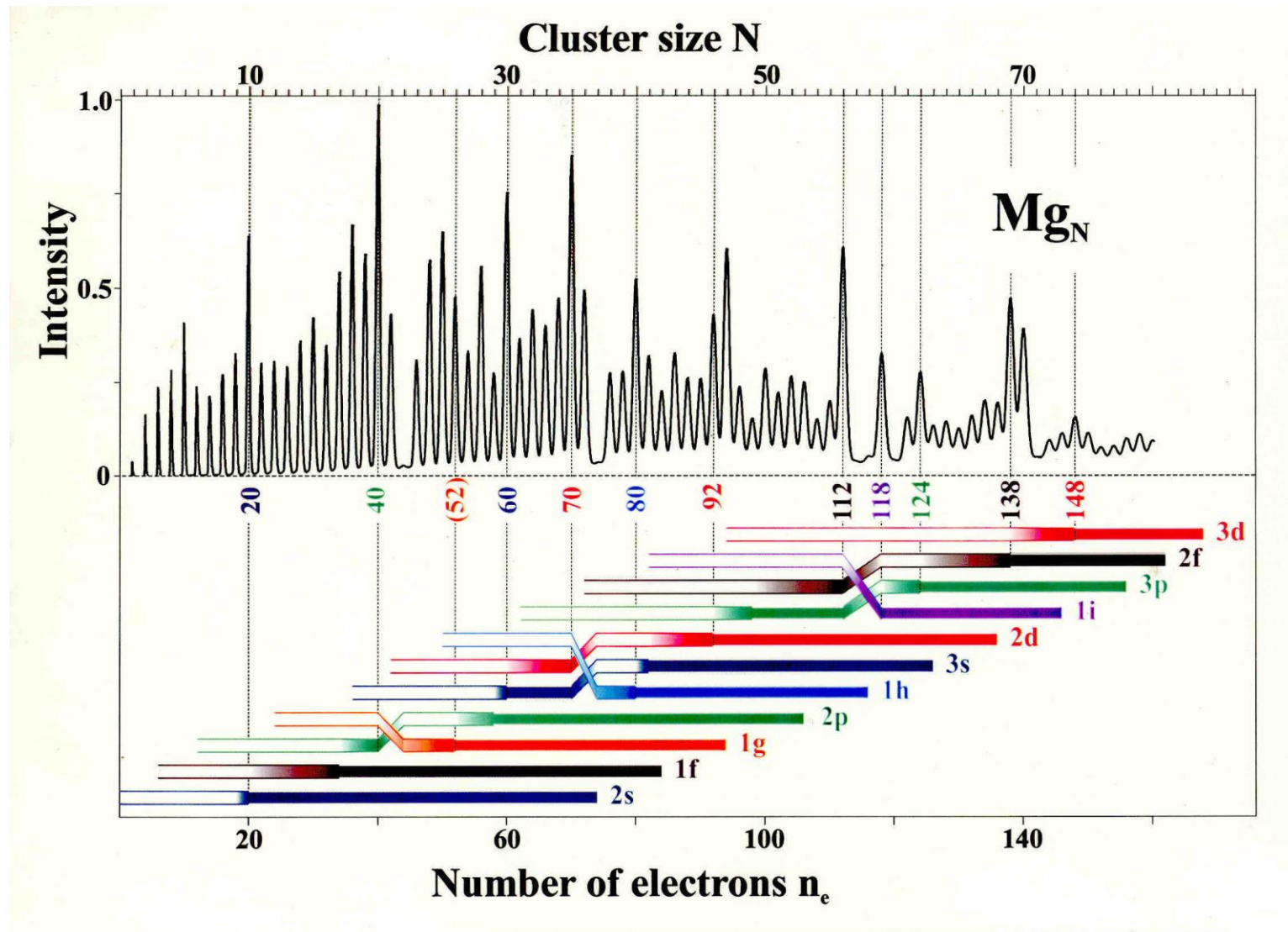
Mg_N grown in large He droplets

note changes in mass scale



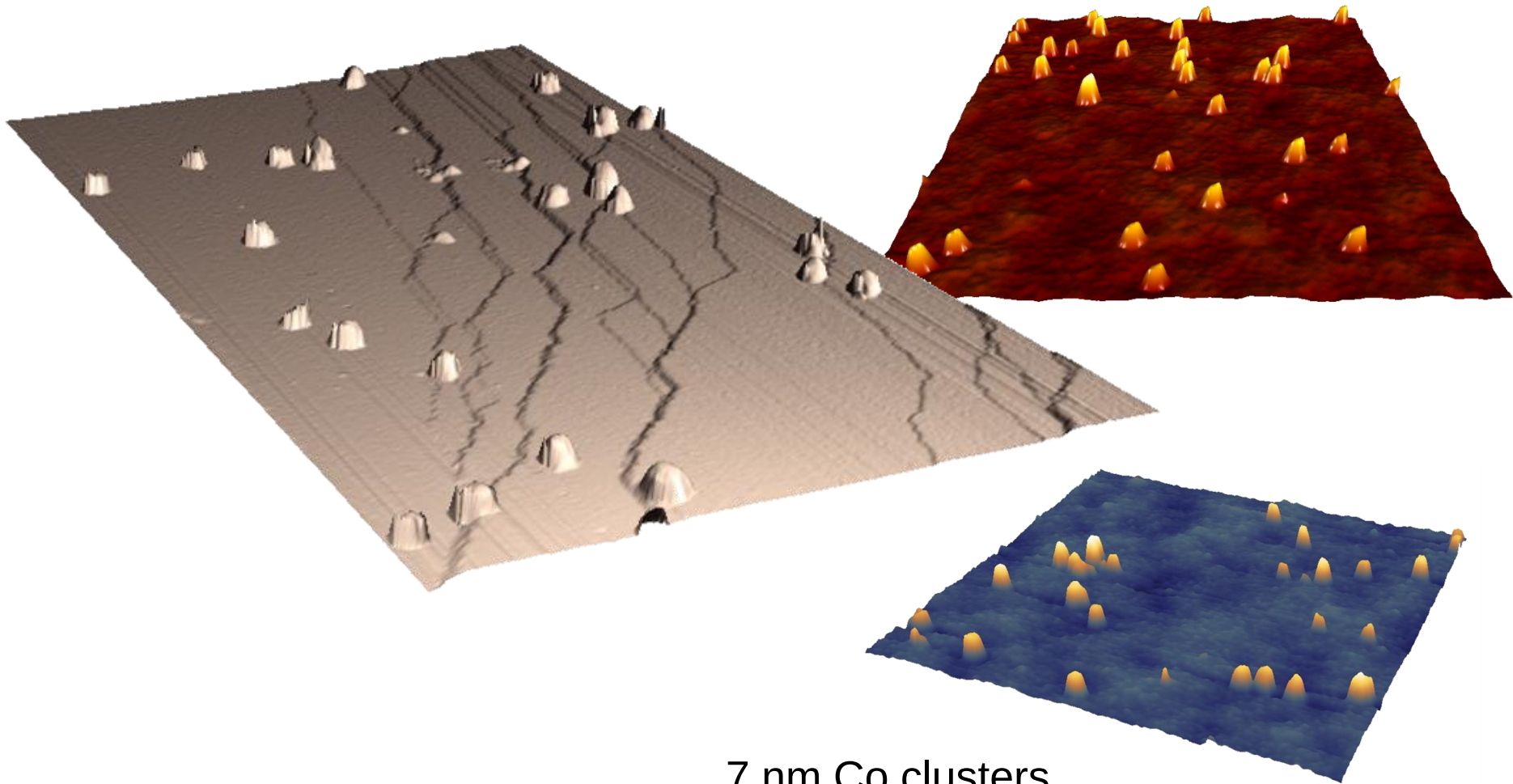
Th. Diederich, T. Döppner, Th. Fennel, J. Tiggesbäumker und K.-H. Meiwes-Broer
Phys. Rev. A **72**:023203, 2005

mass spectrum shows quantum effects



detection by microscopy

3 – 10 nm Cobalt particles



7 nm Co clusters