lundi 25 avril 2016

DES IONS ATOMIQUES AUX NANOPARTICULES DE HAUTE ÉNERGIE POUR SONDER LA SURFACE ET OBTENIR UNE IMAGE IONIQUE.

MEV PARTICLES,

HUGE IMPACT,

SOFT DESORPTION

S. Della-Negra

Institut de Physique Nucléaire d'Orsay, UMR 8608

CNRS-IN2P3, Univ. Paris-Sud, F-91406Orsay Cedex

(dellaneg@ipno.in2p3.fr)

Unité mixte de recherche
CNRS-IN2P3
Université Paris-Sud 11

91406 Orsay cedex
Tél. : +33 1 69 15 73 40
Fax : +33 1 69 15 64 70
http://ipnweb.in2p3.fr

lundi 25 avril 2016

DAWN OF THE BIO SURFACE ANALYSIS ...

5 MARCH 1976

SCIENCE, VOL. 191

Californium-252 Plasma Desorption Mass Spectroscopy

Nuclear particles are used to probe biomolecules.

R. D. Macfarlane and D. F. Torgerson

DAWN OF THE BIO SURFACE ANALYSIS ...

5 MARCH 1976

SCIENCE, VOL. 191

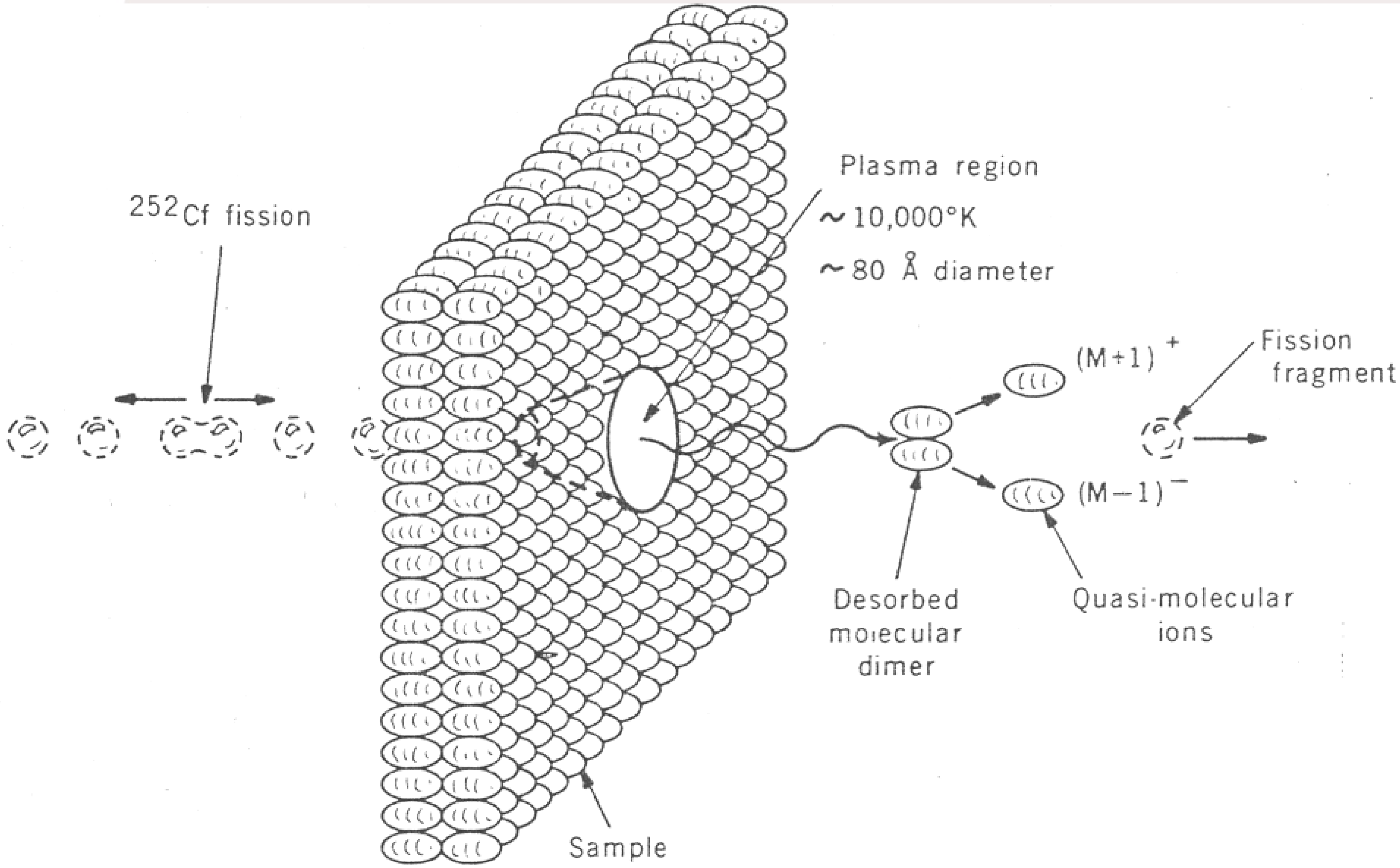
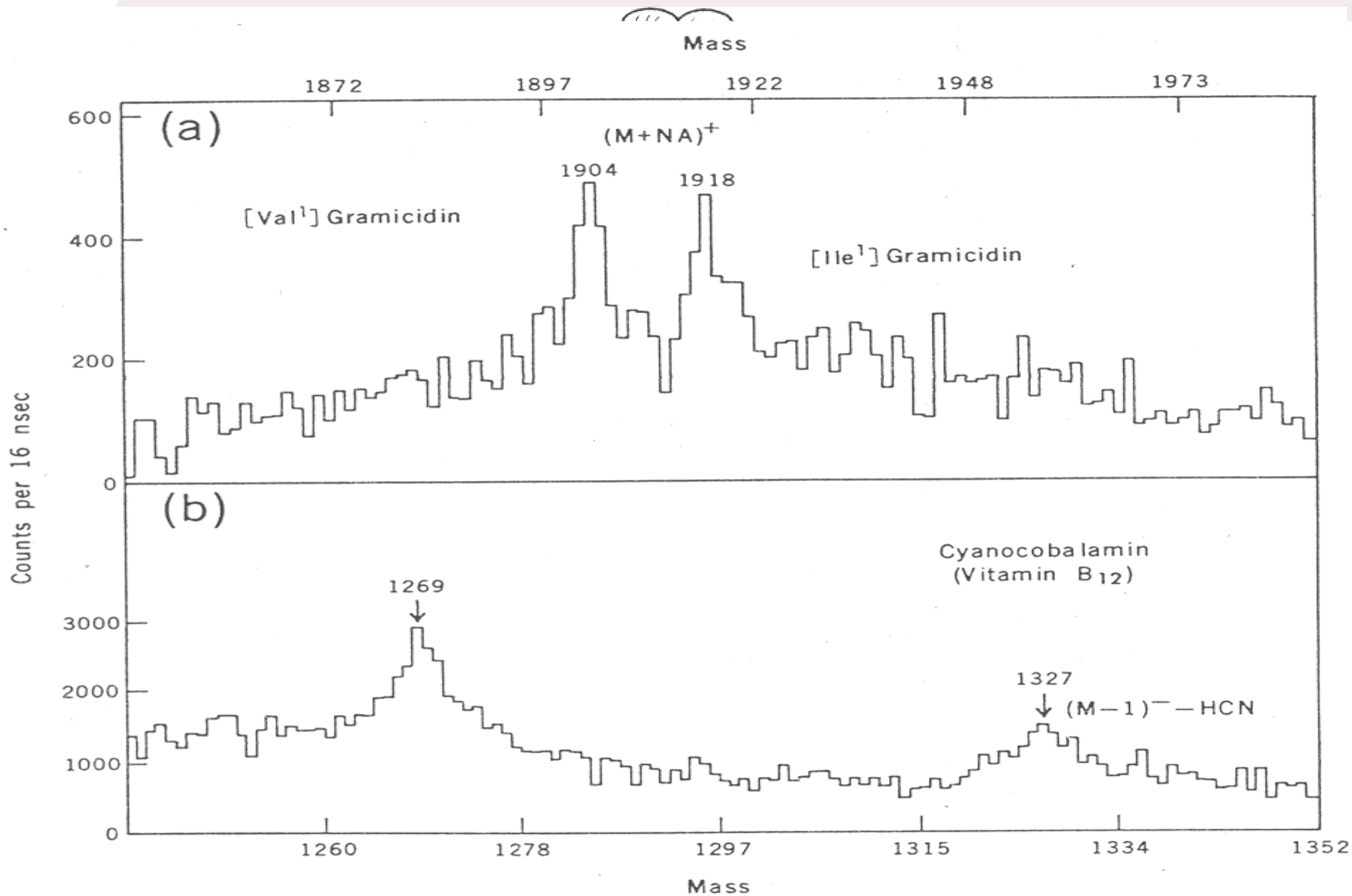


Fig. 2. Interaction of nuclear fission fragments with surface molecules. The large energy deposition produces a localized "hot spot," resulting in volatilization. Results show that for some molecules, such as amino acids, ion-pair formation takes place by proton transfer within a desorbed dimer.

DAWN OF THE BIO SURFACE ANALYSIS ...

5 MARCH 1976

SCIENCE, VOL. 191



such as amino acids, ion-pair formation takes place by proton transfer within a desorbed dimer.

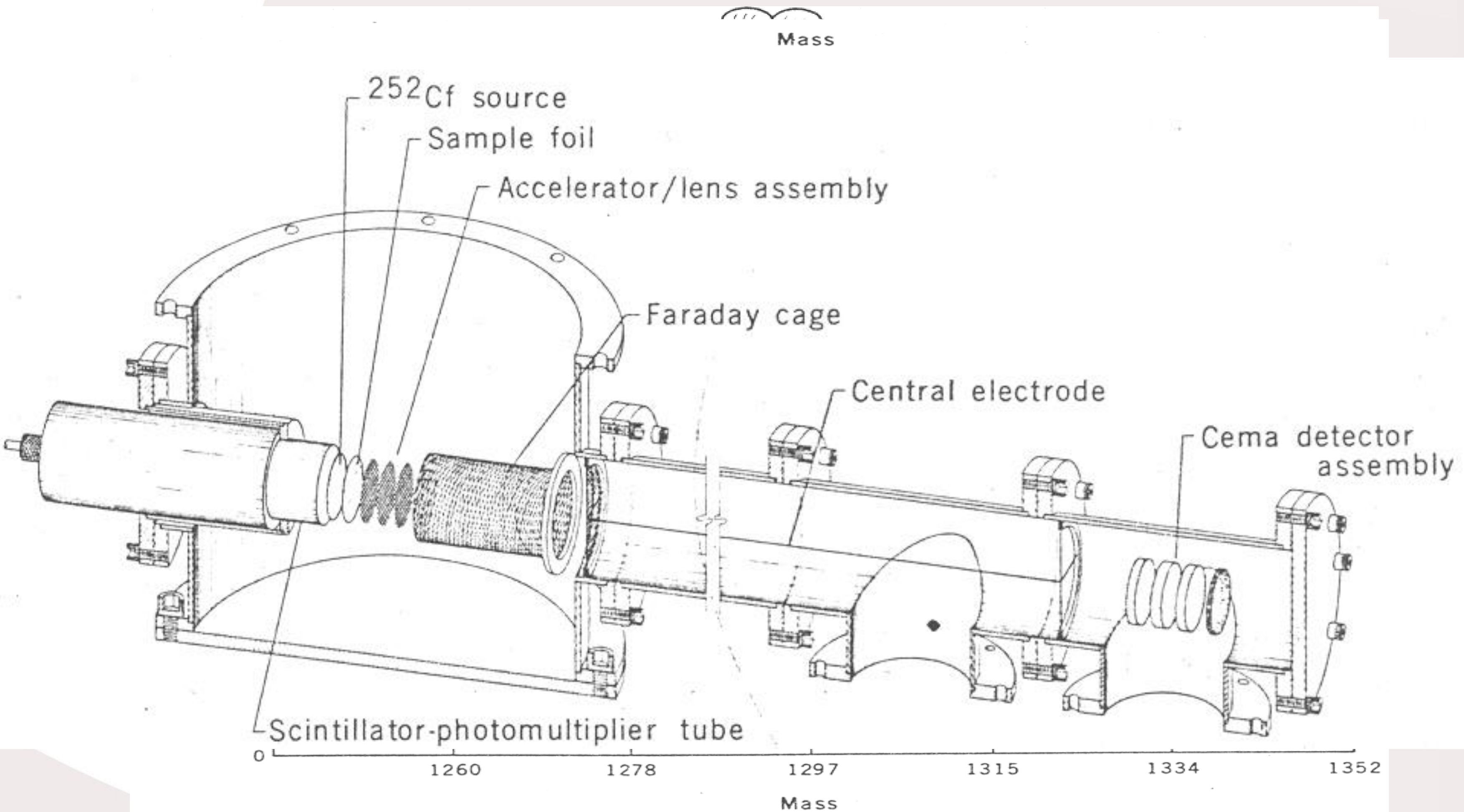
INSTITUT DE PHYSIQUE NUCLÉAIRE
ORSAY

lundi 25 avril 2016

DAWN OF THE BIO SURFACE ANALYSIS ...

5 MARCH 1976

SCIENCE, VOL. 191

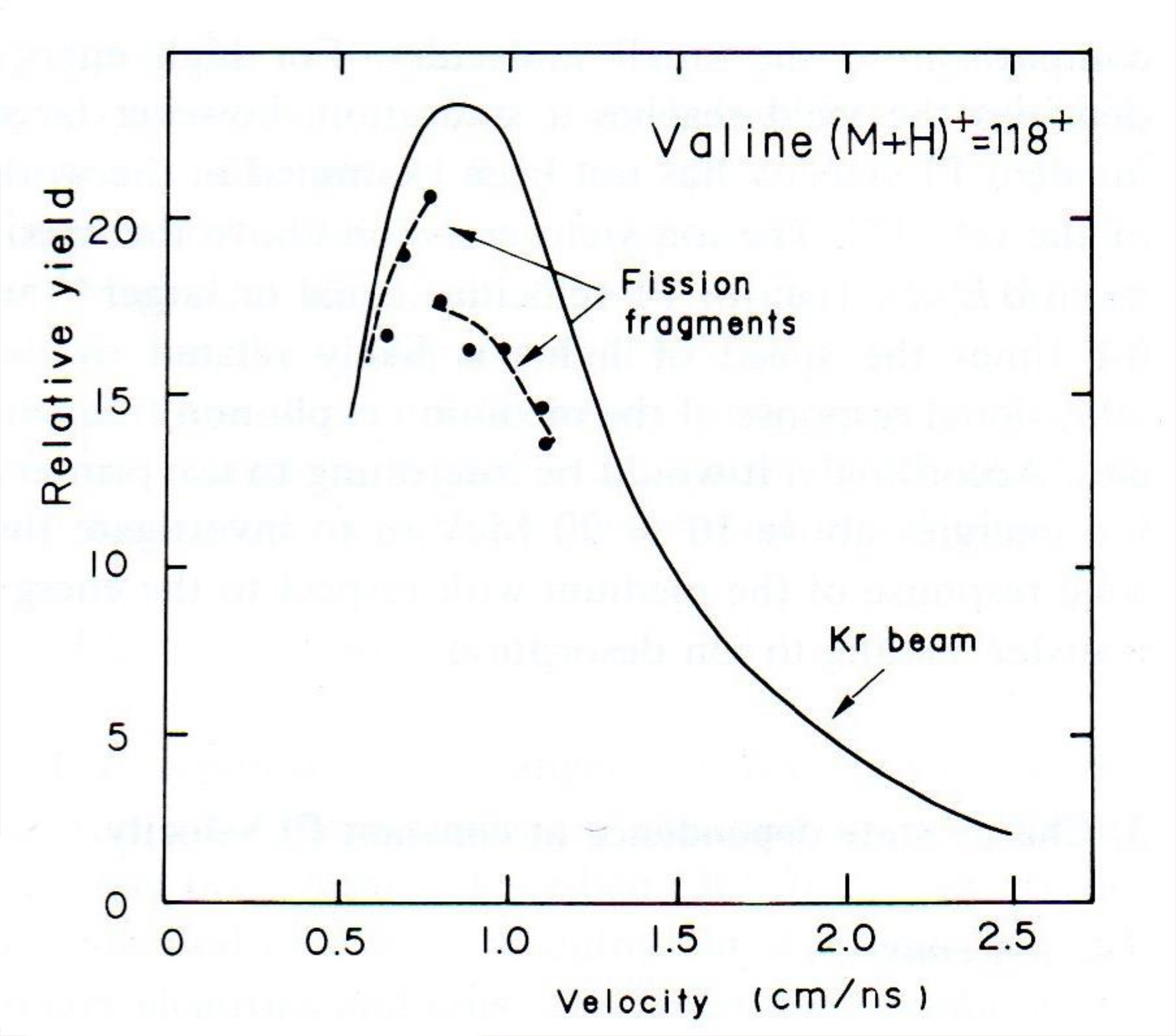


such as amino acids, ion-pair formation takes place by proton transfer within a desorbed dimer.

^{252}Cf F. F. & SWIFT ATOMIC IONS

lundi 25 avril 2016

0.5 MeV/u
=
1 cm/ns



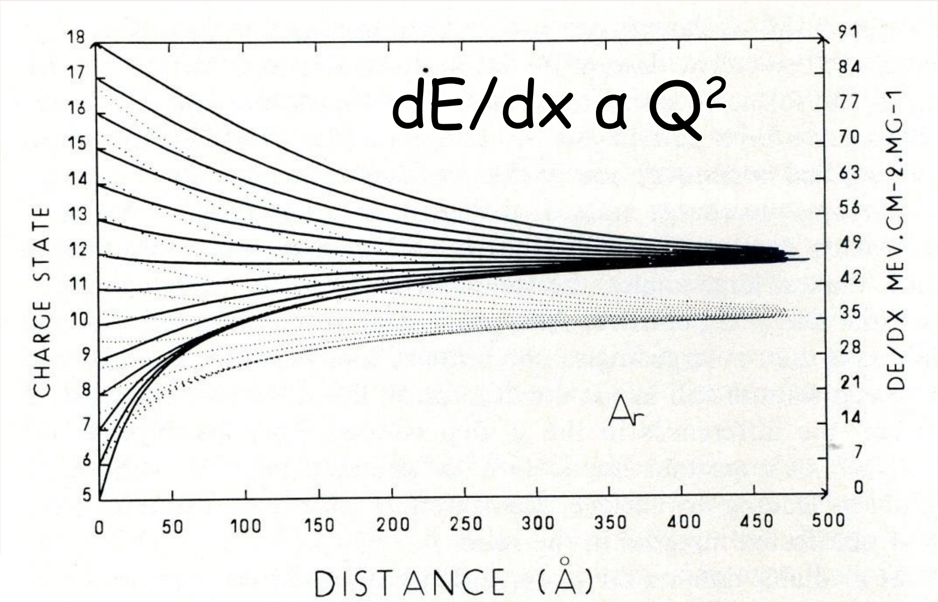
HIGH ENERGY ATOMIC IONS

Accelerator Facilities

Advantage : To control all Solid-particle interaction parameters

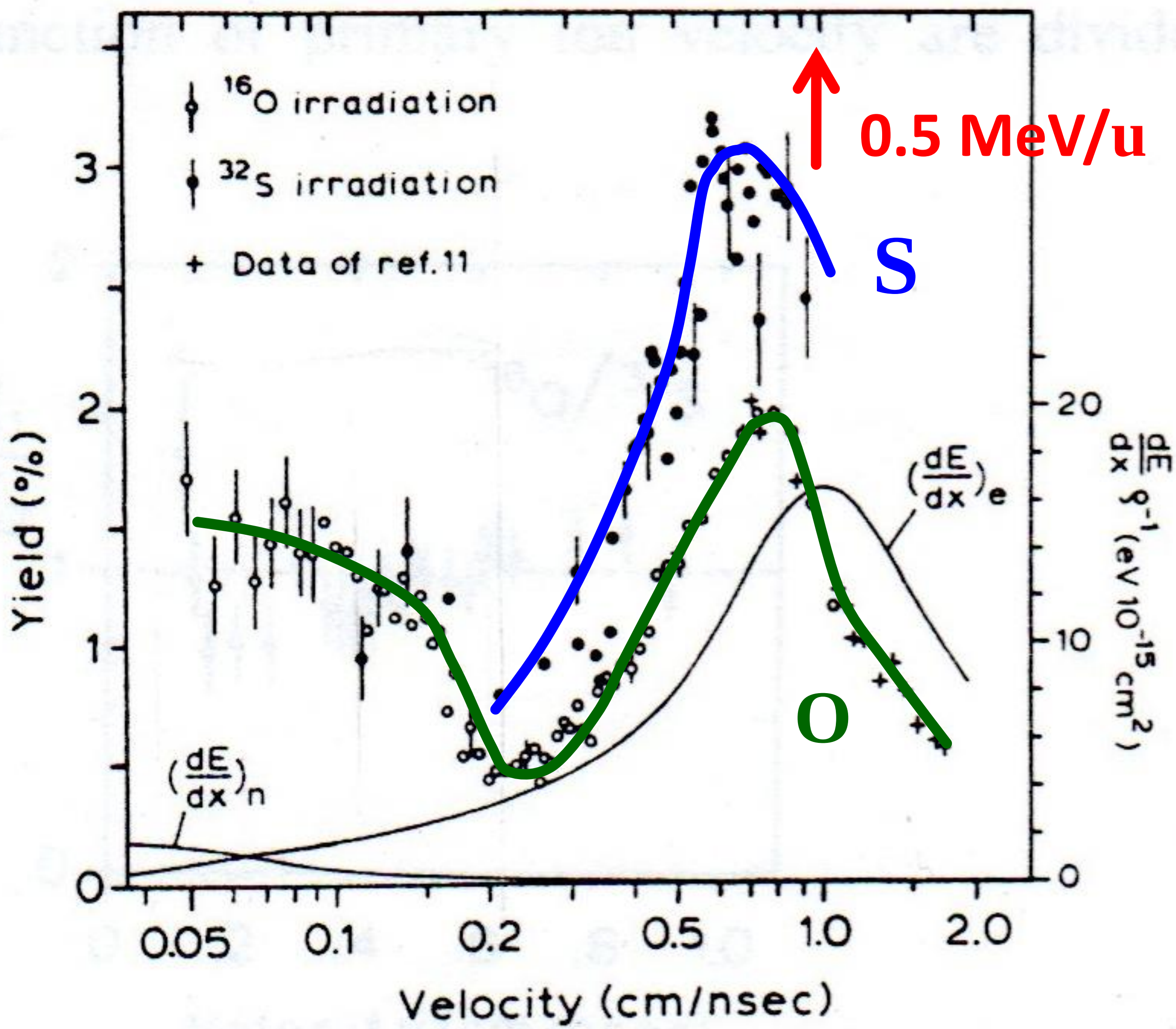
1. The energy deposited in the solids versus the energy loss measurment, dE/dx (V) = f(sample thickness)
2. The energy density versus the projectile velocity (δ electron range gives the radius of the initial track).
3. The projectile charge state permits to modify the deposited energy near the surface and to probe the emission depth

Q (V) = f(sample thickness)

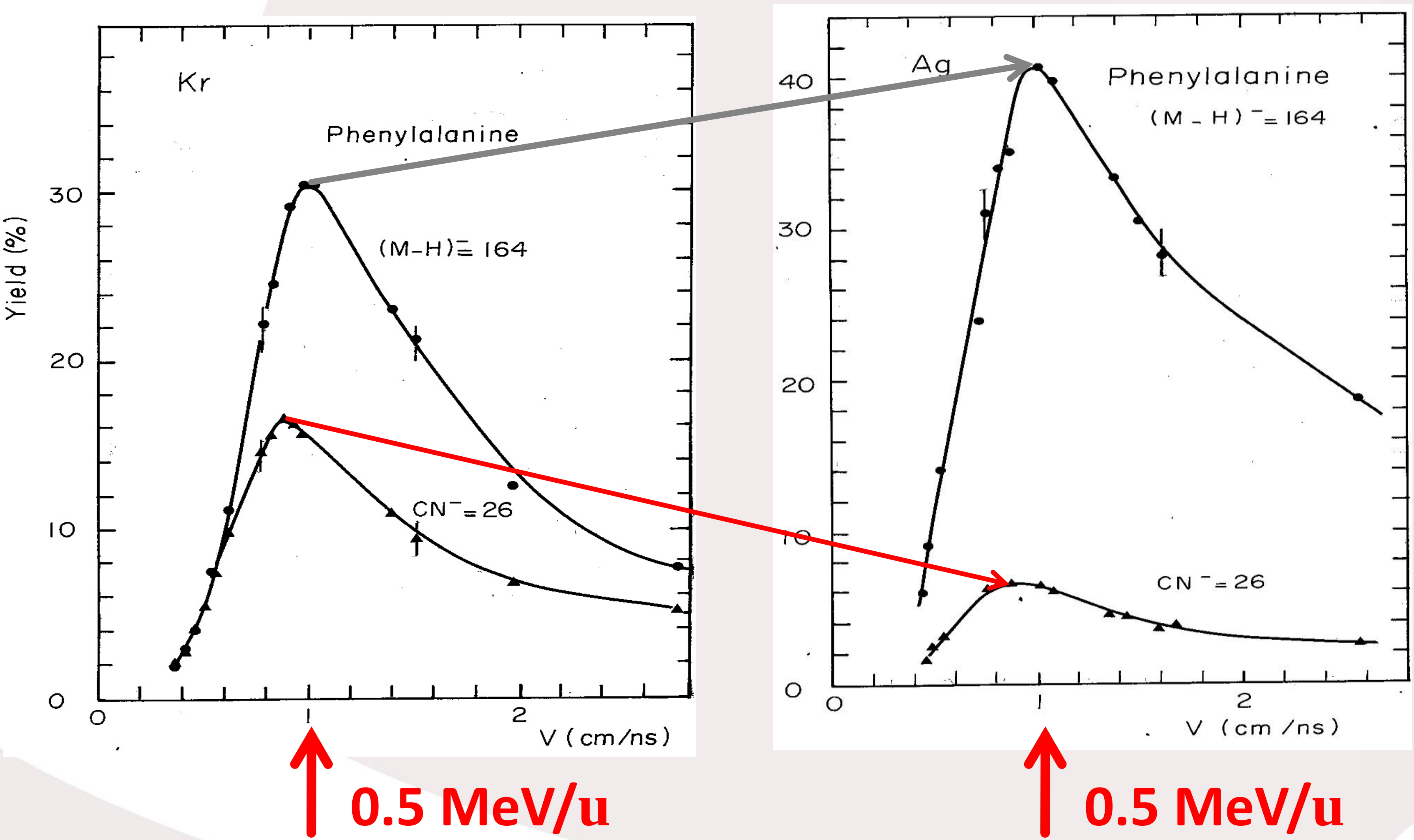


lundi 25 avril 2016

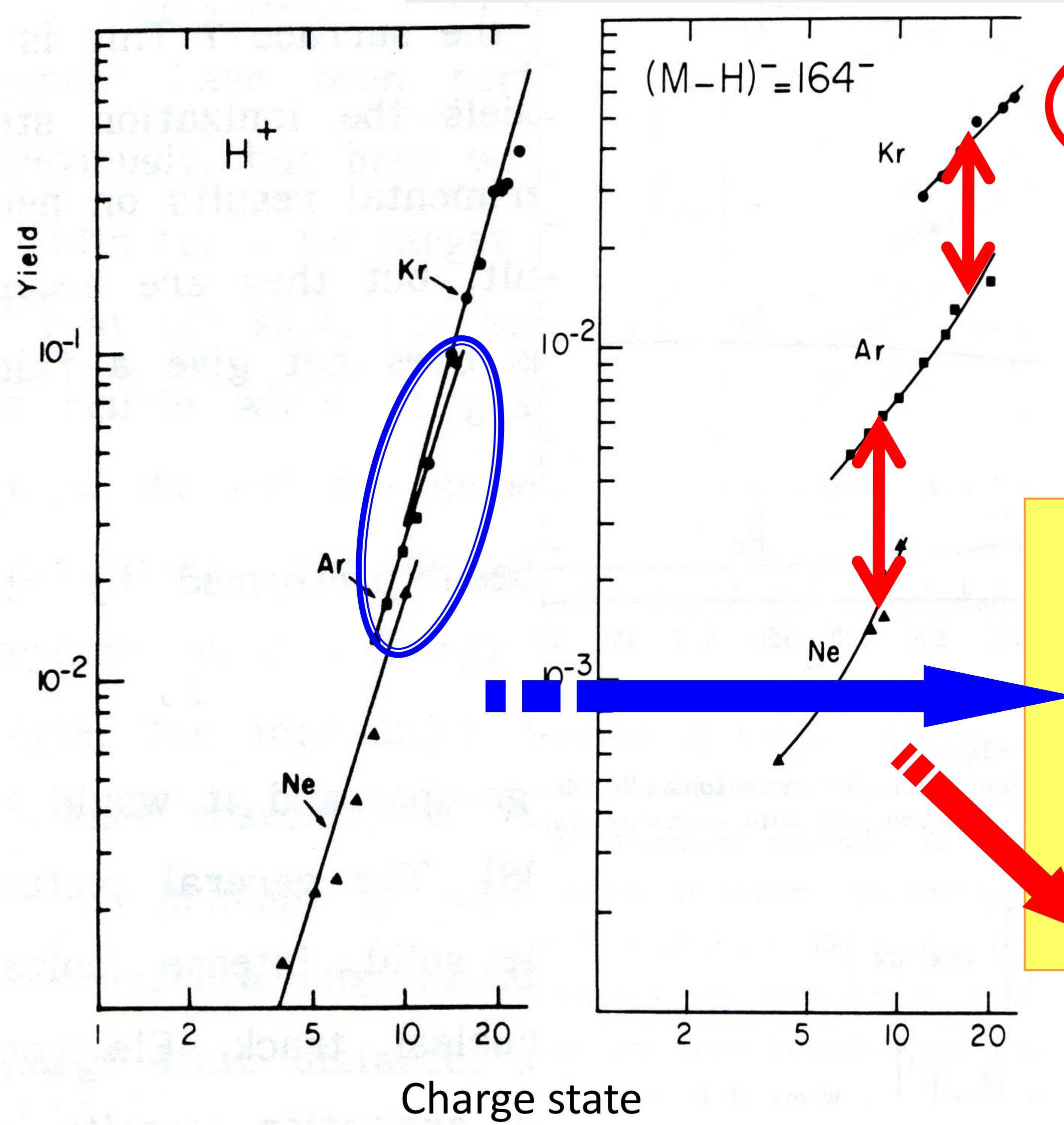
HIGH ENERGY ATOMIC IONS,

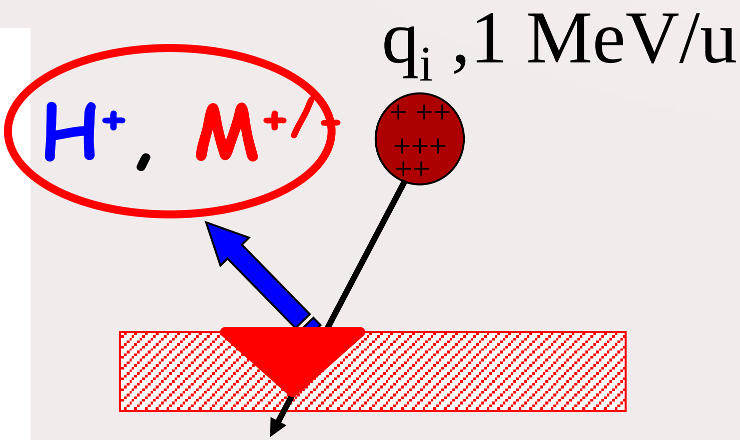


SECONDARY ION YIELD VERSUS PROJECTILE AND VELOCITY



EMISSION DEPENDENCE ON INCIDENT CHARGE STATE



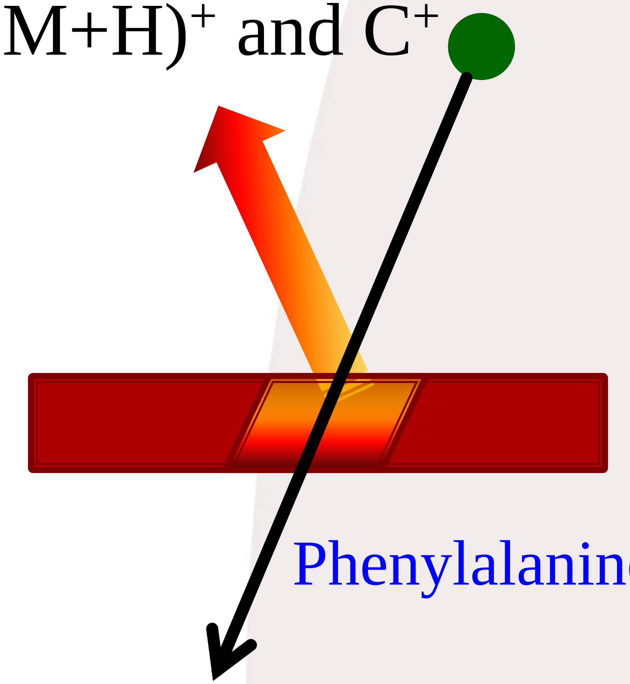


H+ emission independent of the projectile
Surface interaction < 1nm
And
molecular ion emission: NO
Volume of interaction
Depth ~10-20 nm

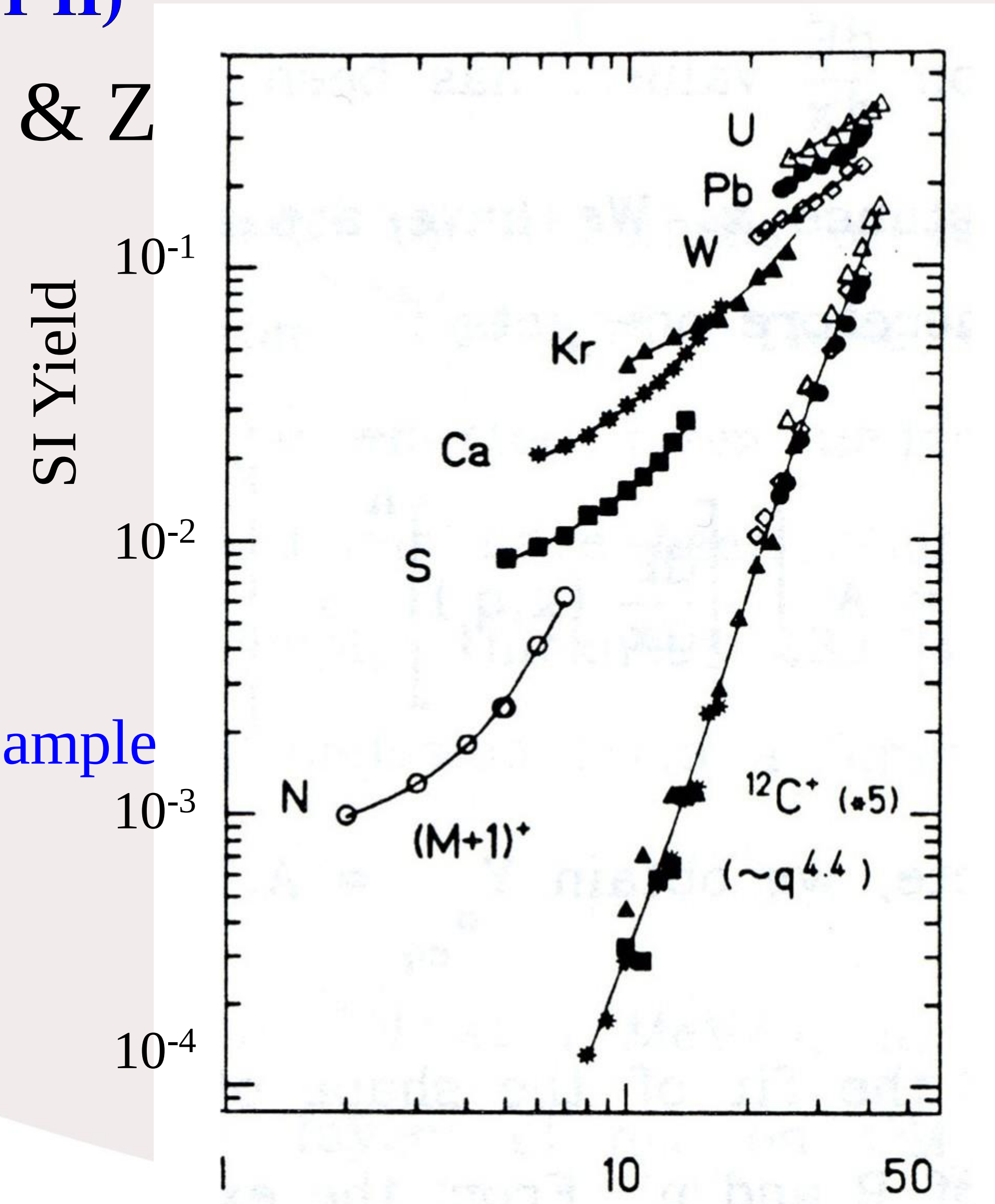
INFLUENCE OF THE INCIDENT CHARGE STATE (PART II)

PI : q, M & Z

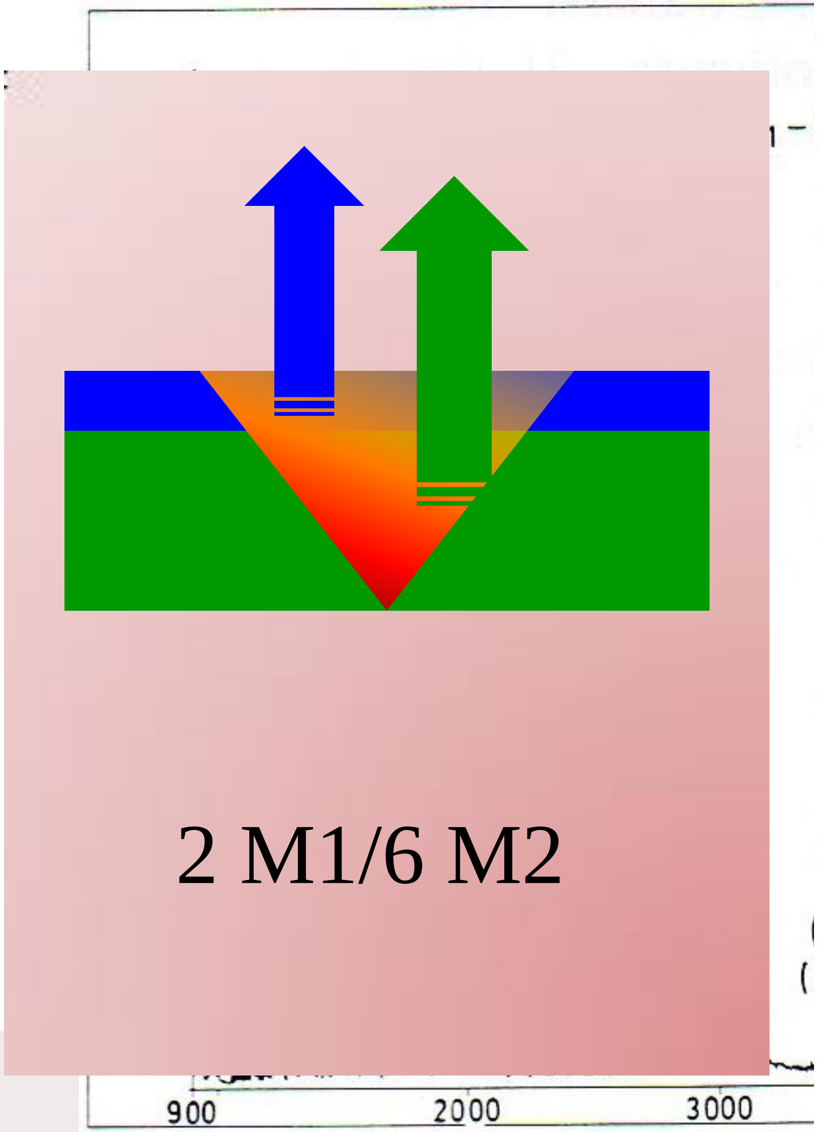
$(M+H)^+$ and C^+

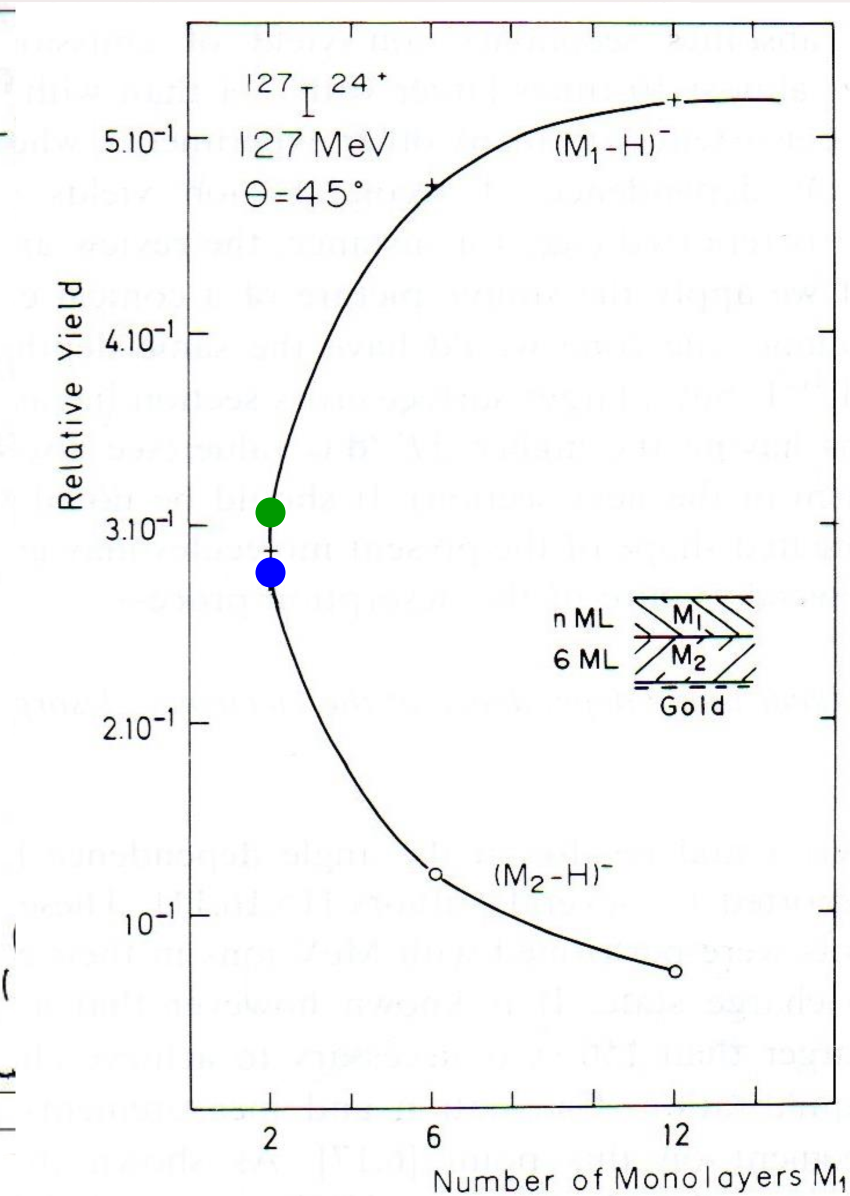


Phenylalanine Sample



EMISSION DEPTH





HIGH ENERGY ATOMIC IONS FROM MEV TO GEV

•The maximum SI yield is reached around 0.5 Mev/u (1 cm/ns)

-The studies of the projectile velocity and the energy loss in the matter demonstrate that the energy density in the track is the main parameter. SI yield ~ $\int(dE/dx)^2$

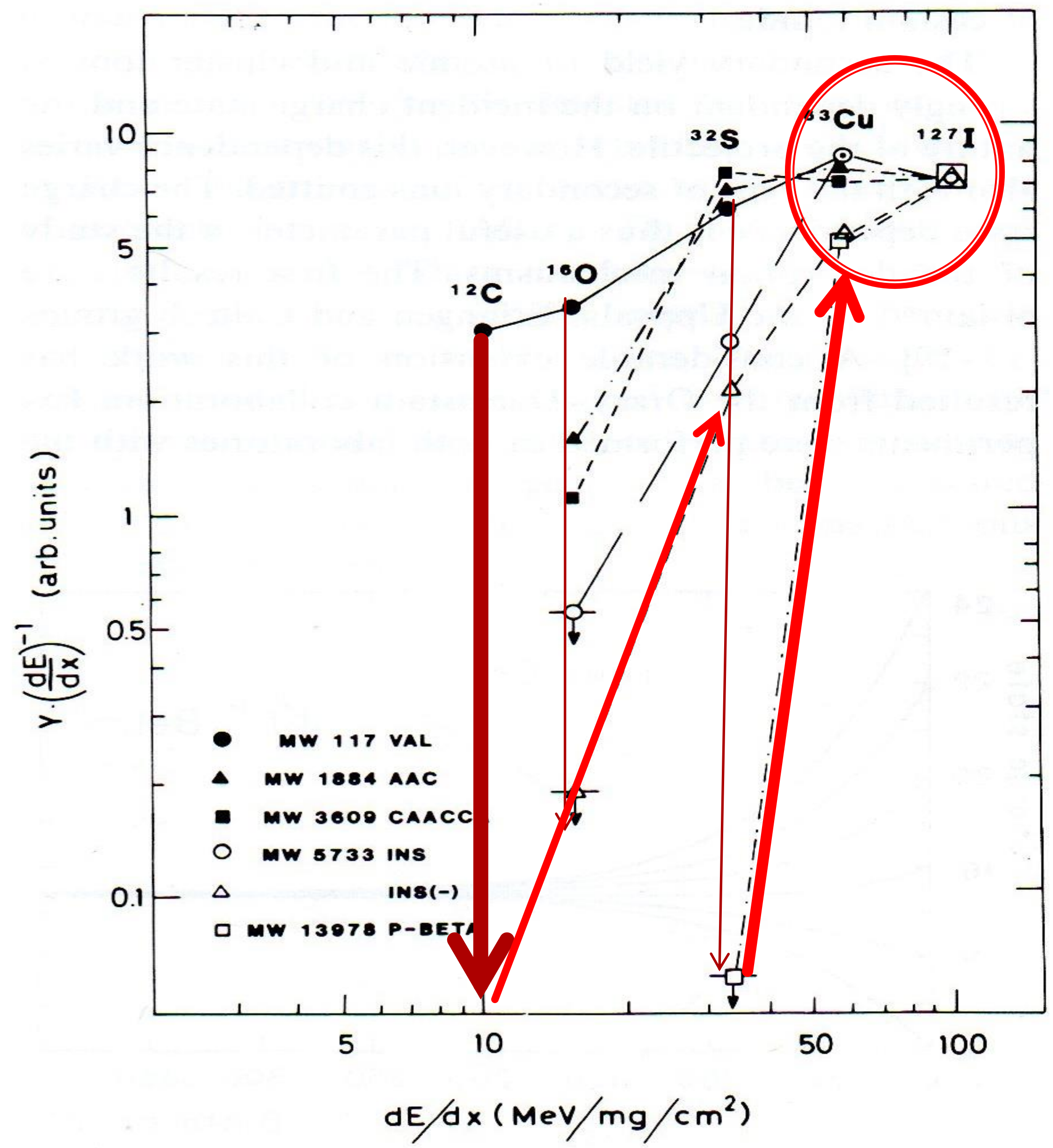
-The knowledge of the charge state evolution inside the solid and thus of the energy loss permits to probe the energized volume taking part in the ionic emission

•H^+ and C^+ ions are emitted from the zone of impact in a time of about 10^{-15}sec and the emission depth is around 1 nm;

•On the contrary the molecular and cluster ion emission are emitted from the deep layers. The volume of interaction depth is between 10 and 20 nm and the maximum depth for the ionic emission is 10 nm.

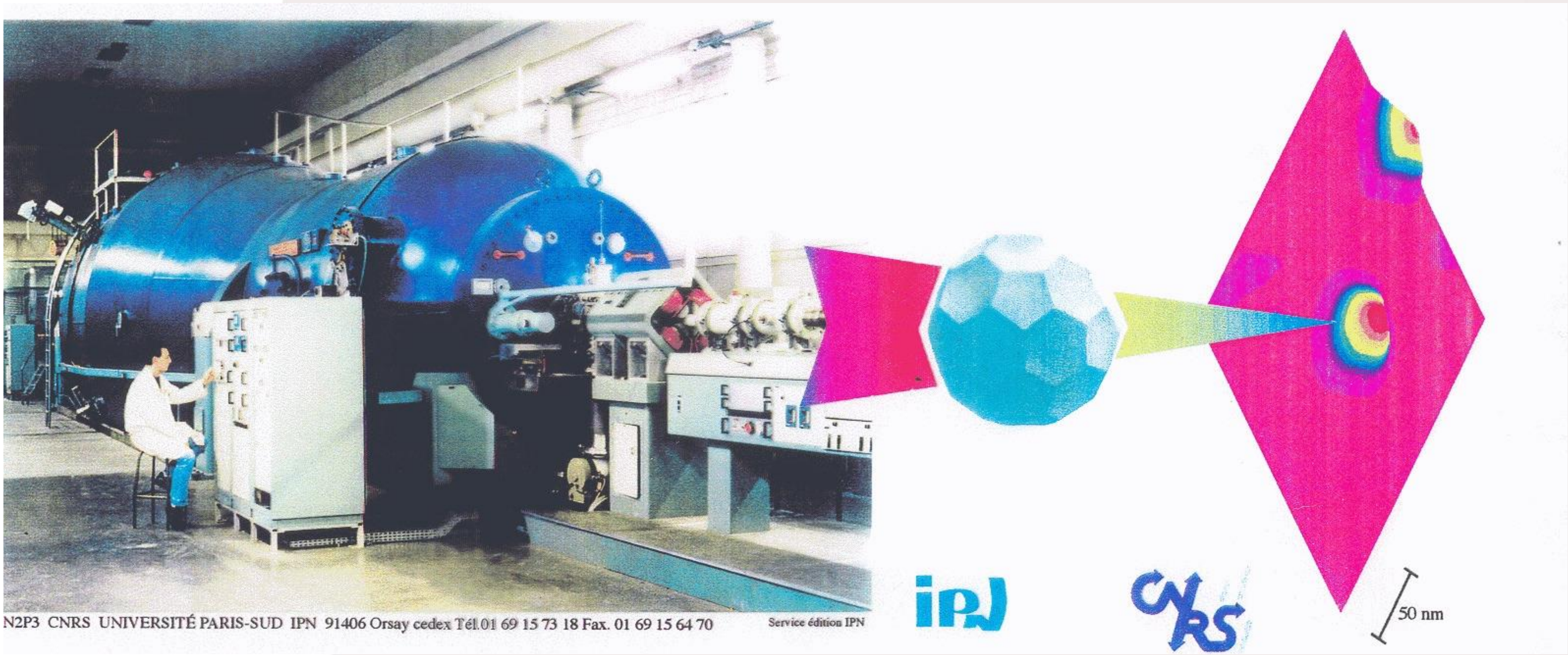
THE RÔLE OF THE SAMPLE (MOLECULAR WEIGHT)

lundi 25 avril 2016



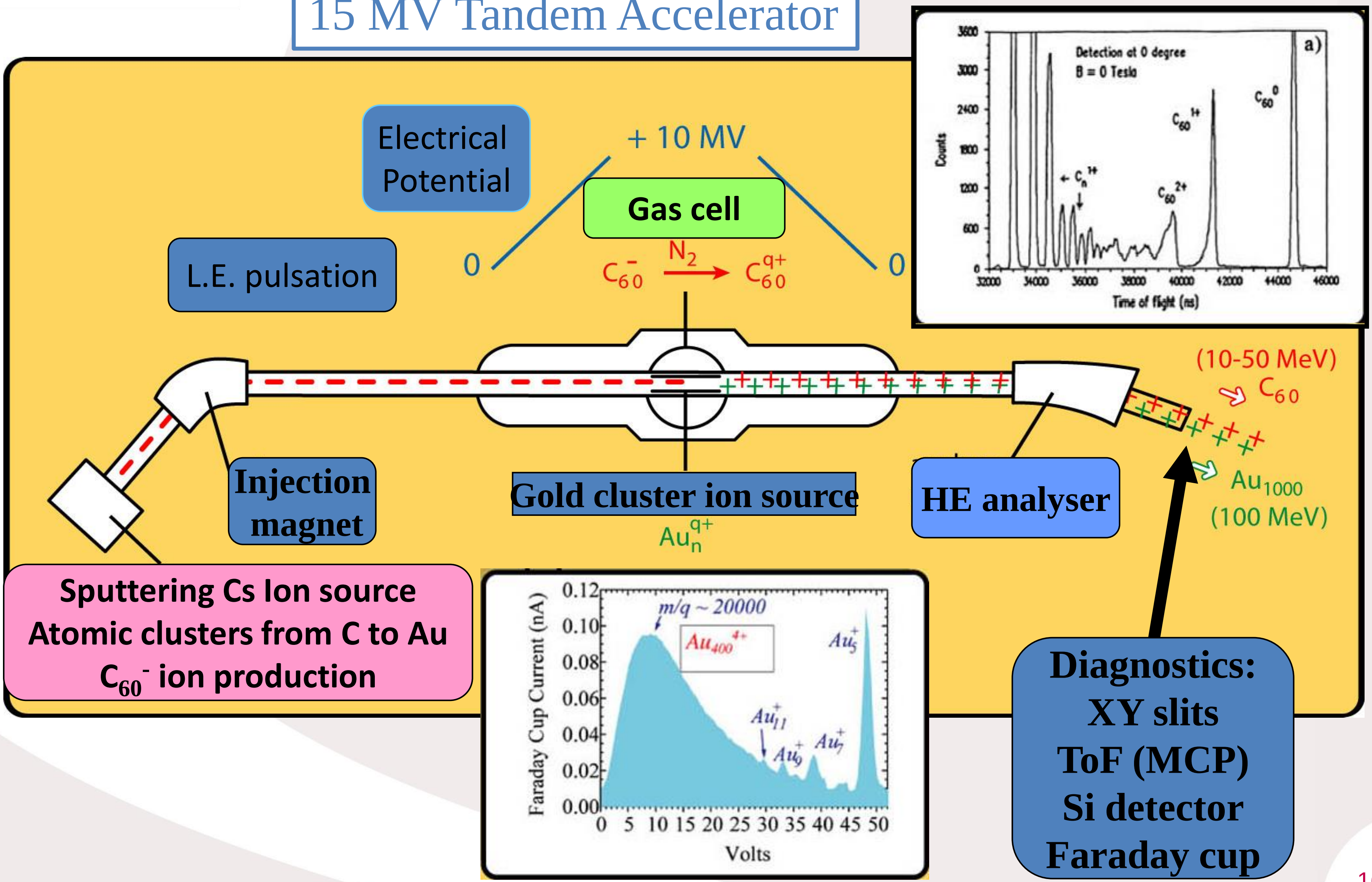
POLYATOMIC MEV ION SOURCE !!!

lundi 25 avril 2016



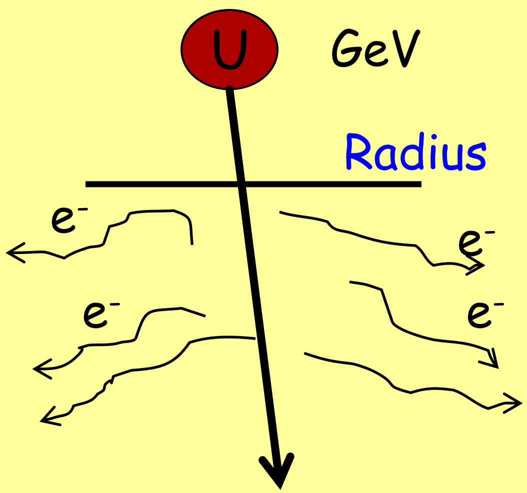
Orion project (1990-1993)

15 MV Tandem Accelerator



THE ENERGY DENSITY IN THE TRACK

U ions at 1 GeV → dE/dx 4 keV/Å



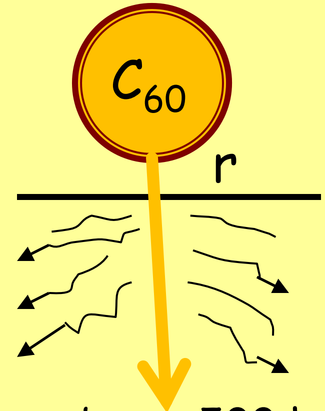
Large range of electrons (R>100nm)

Large volume of transient energy deposition

SMALL DENSITY

C_{60} at 30 MeV → dE/dx> 4 keV/Å

dE/dx (C_n) = n dE/dx (C_1)



Each carbon = 500 keV

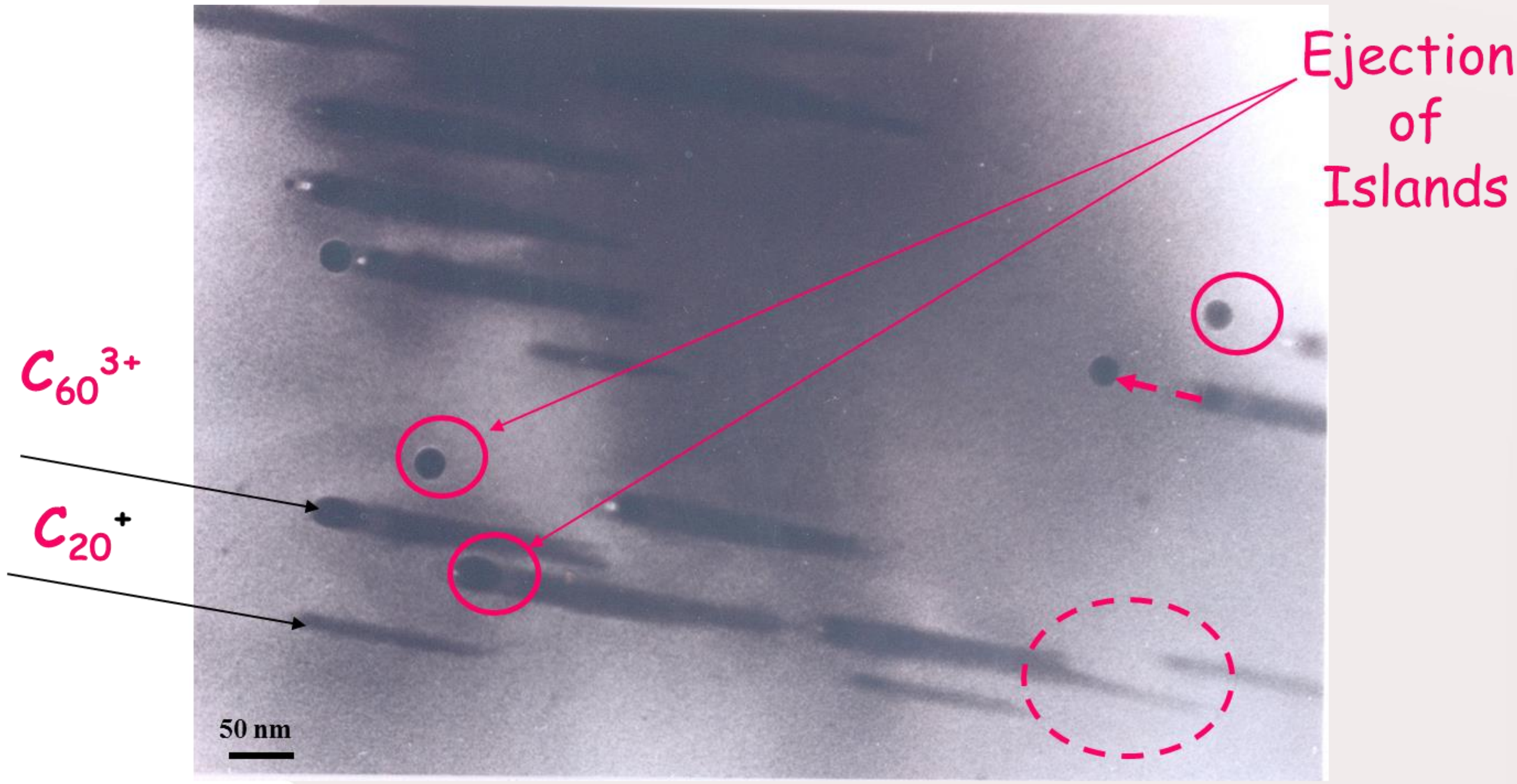
small range of electrons (r~ nm)

Small volume of transient energy deposition

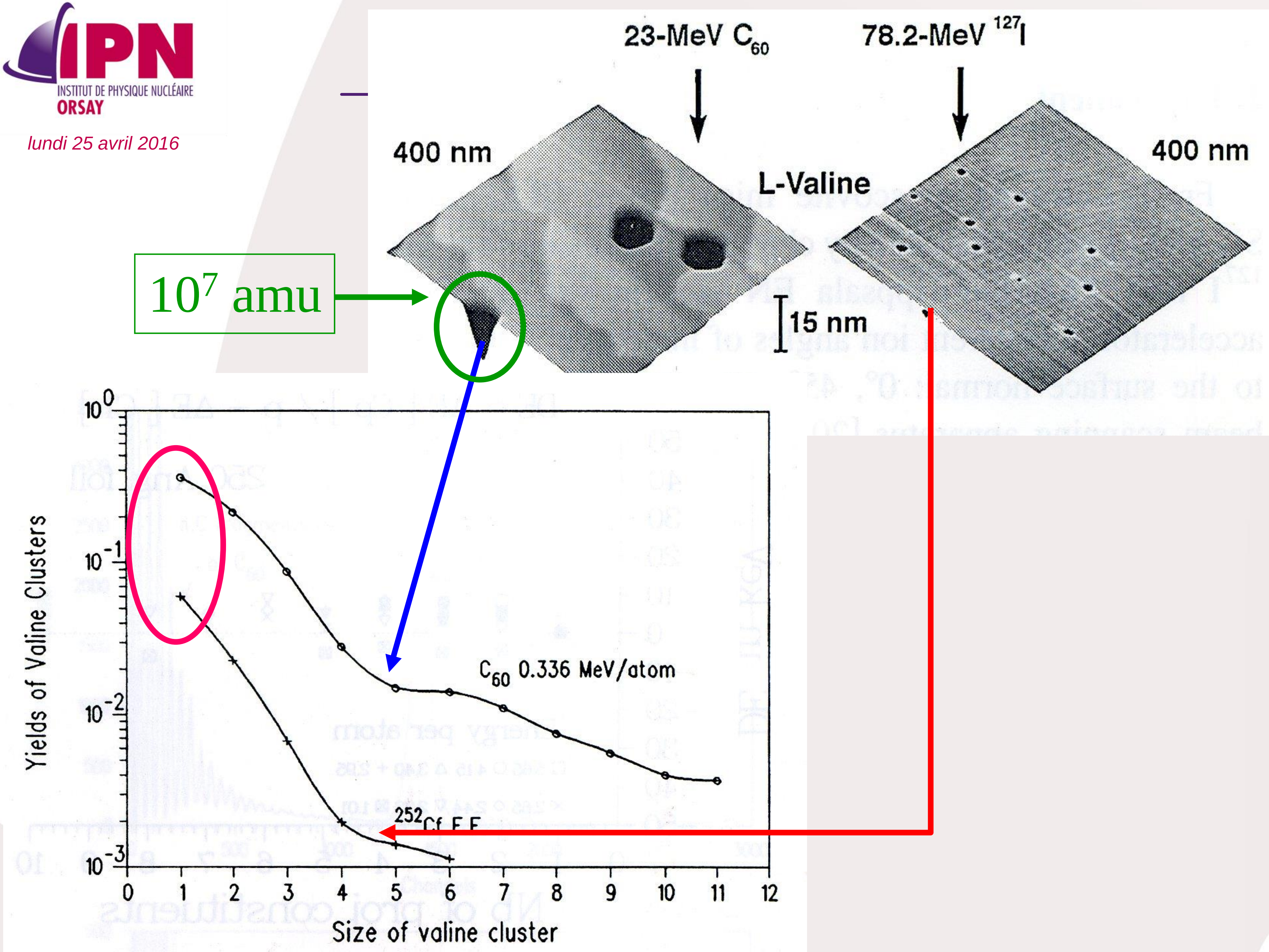
LARGE DENSITY

FAST CLUSTER IONS : A UNIQUE WAY TO DEPOSIT A LARGE VOLUMIC ENERGY DENSITY IN A SOLID

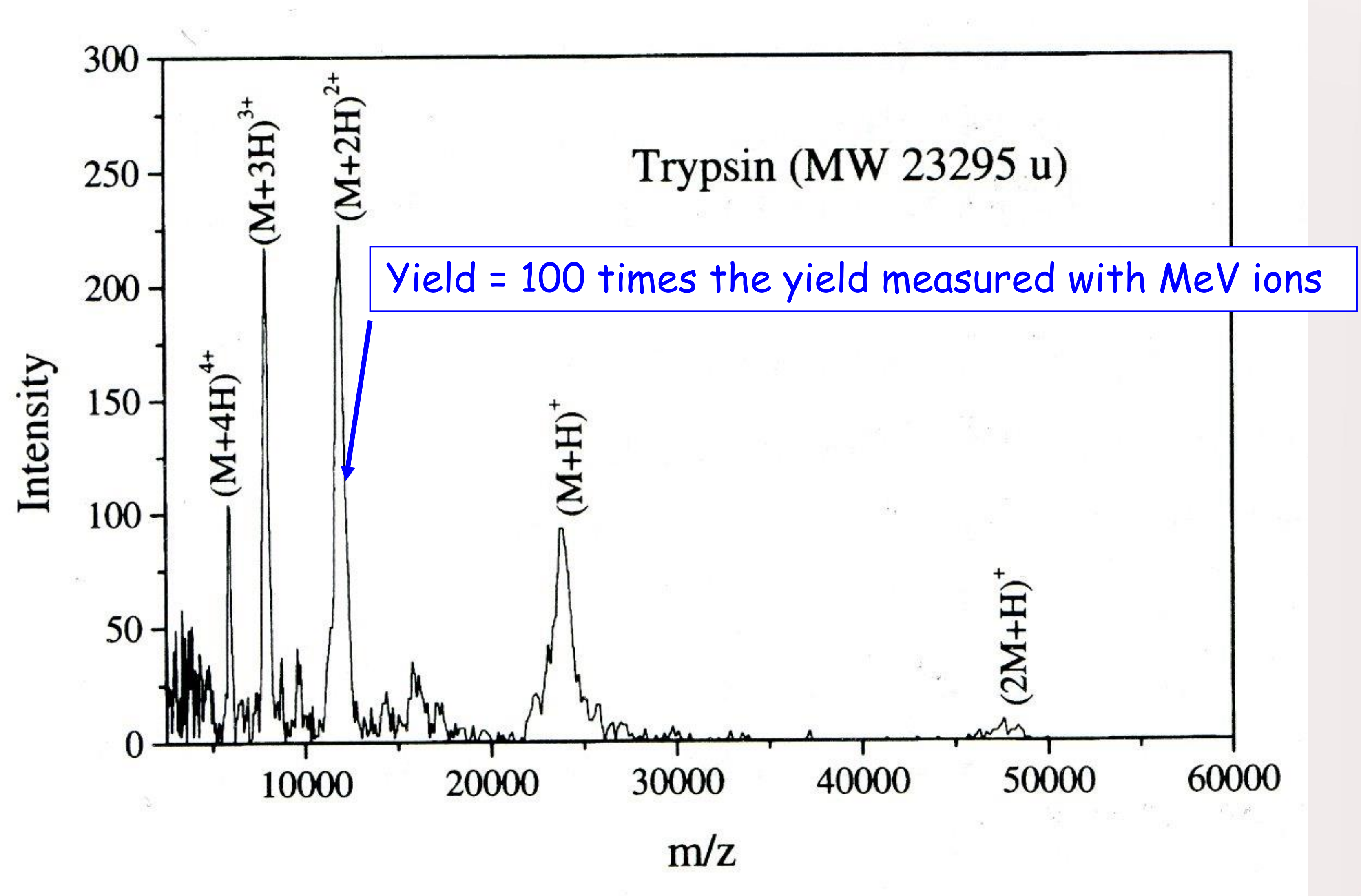
TRACKS IN YIG ($Y_3Fe_5O_{12}$)



Straggling effect


23-MeV C60
78.2-MeV 127I
400 nm
L-Valine
400 nm
15 nm
10^7 amu
Yields of Valine Clusters
C60 0.336 MeV/atom
252Cf F.F.
Size of valine cluster

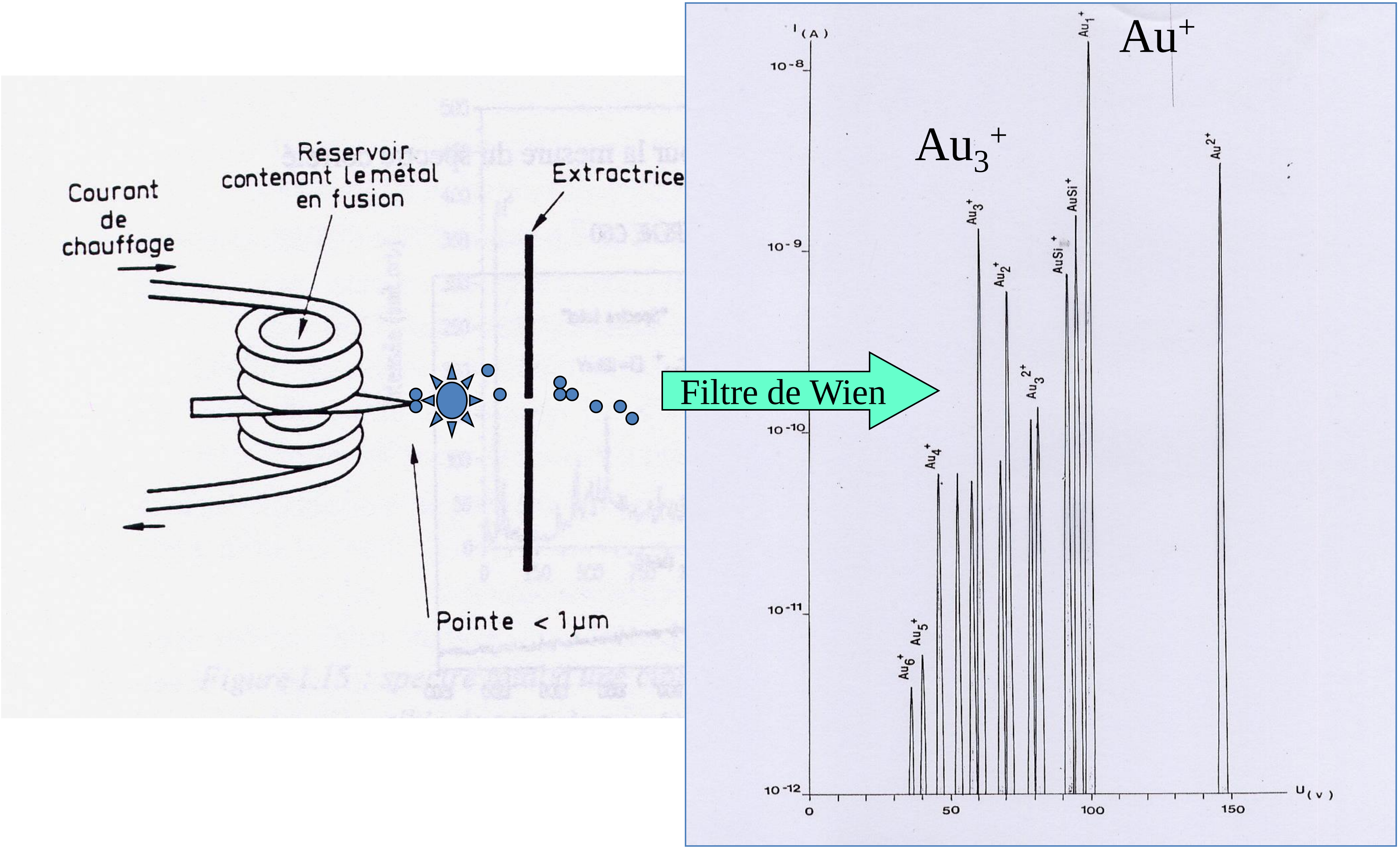
DESORPTION OF LARGE BIOMOLÉCULES



Gold cluster beams

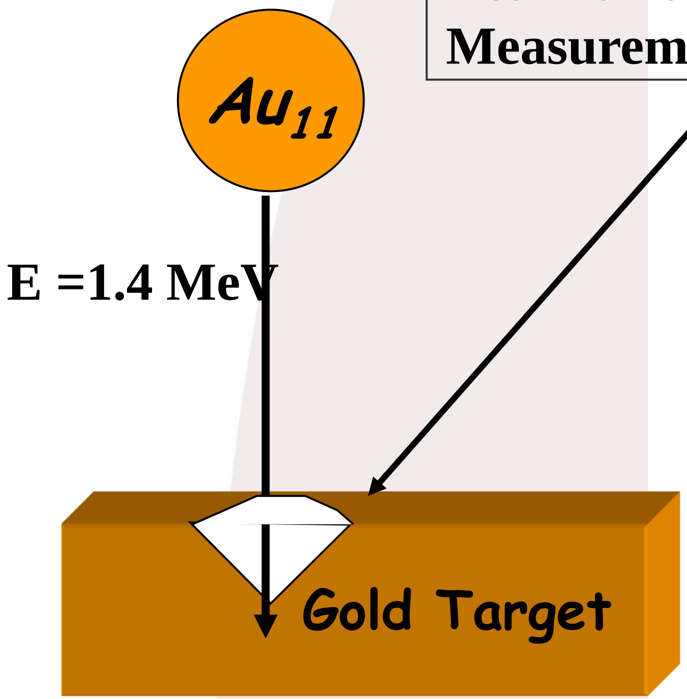
Nuclear stopping Power
Elastic collisions

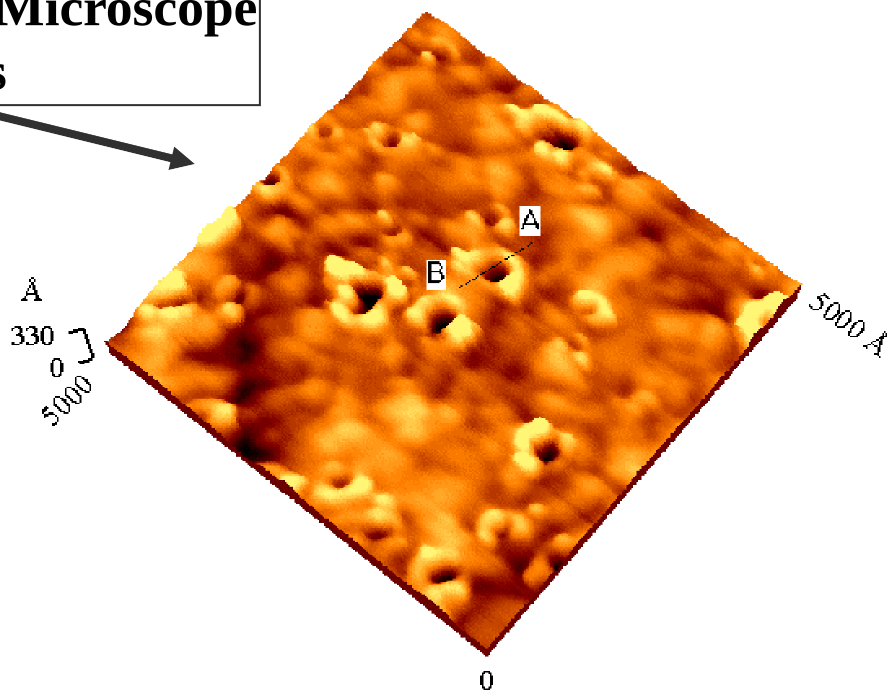
L.M.I.S. (Liquid Metal Ion Source)



GOLD CLUSTER IN THE MEV RANGE

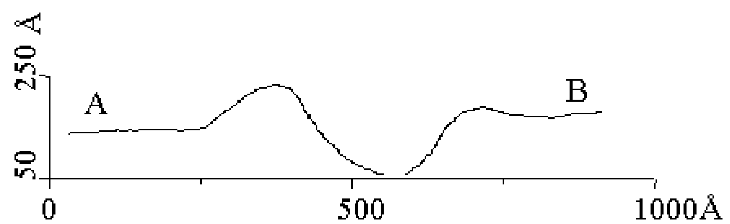
Atomic Force Microscope Measurements



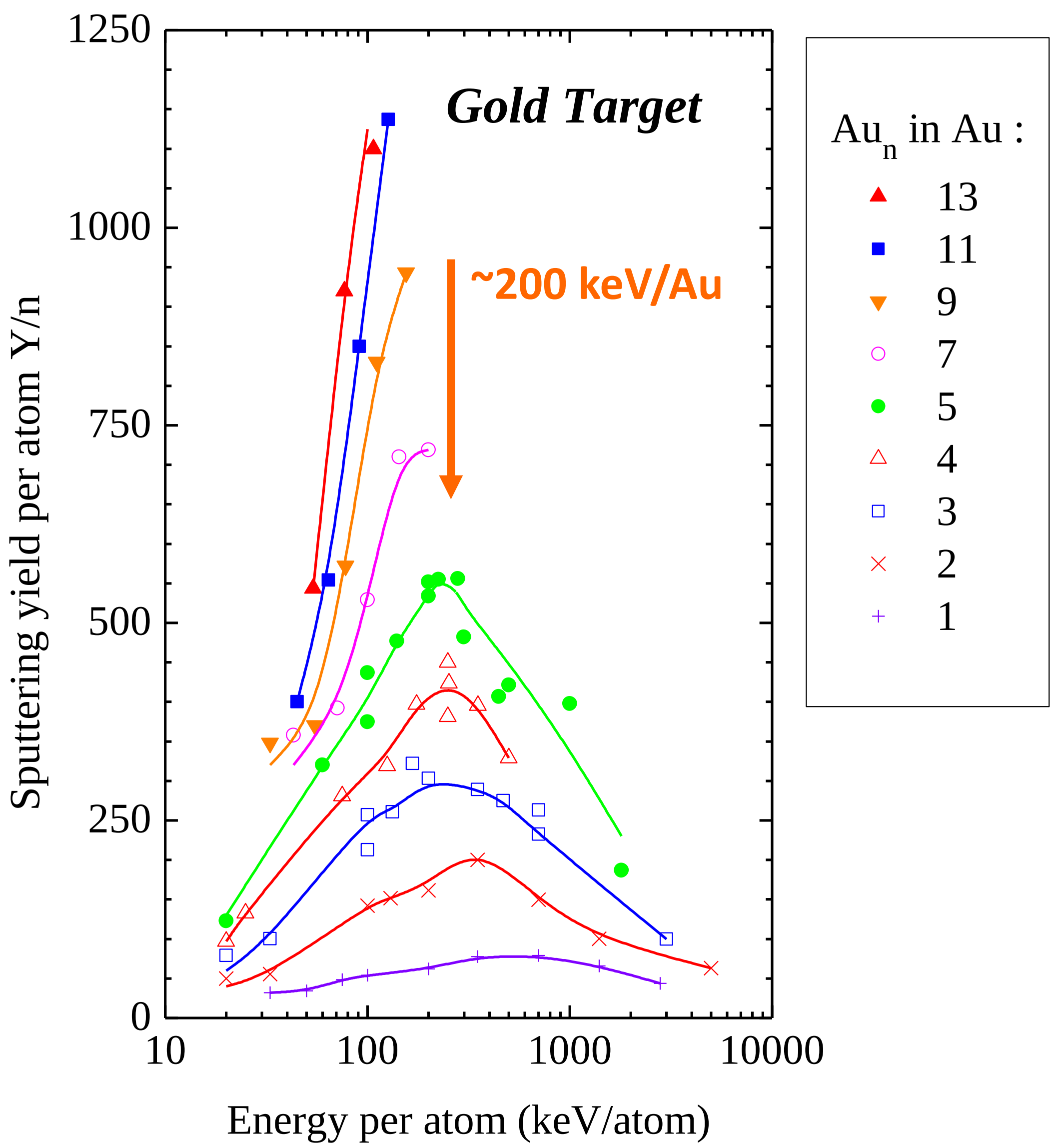


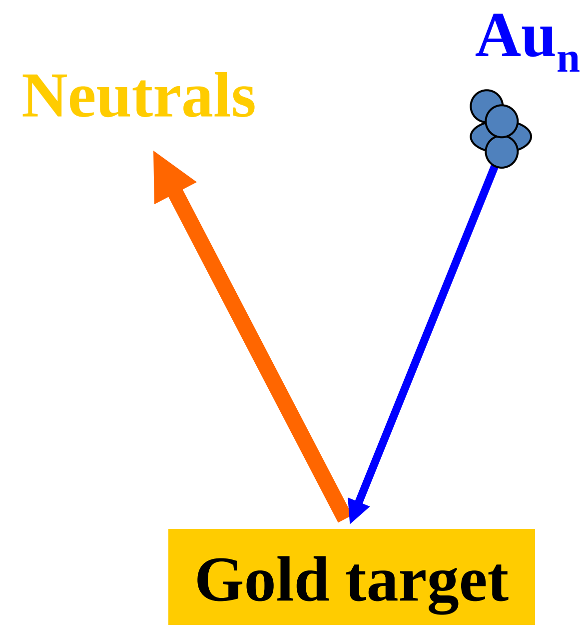
Range = 120 Å

$(dE/dx)_{nuc}$ = 100 keV/nm



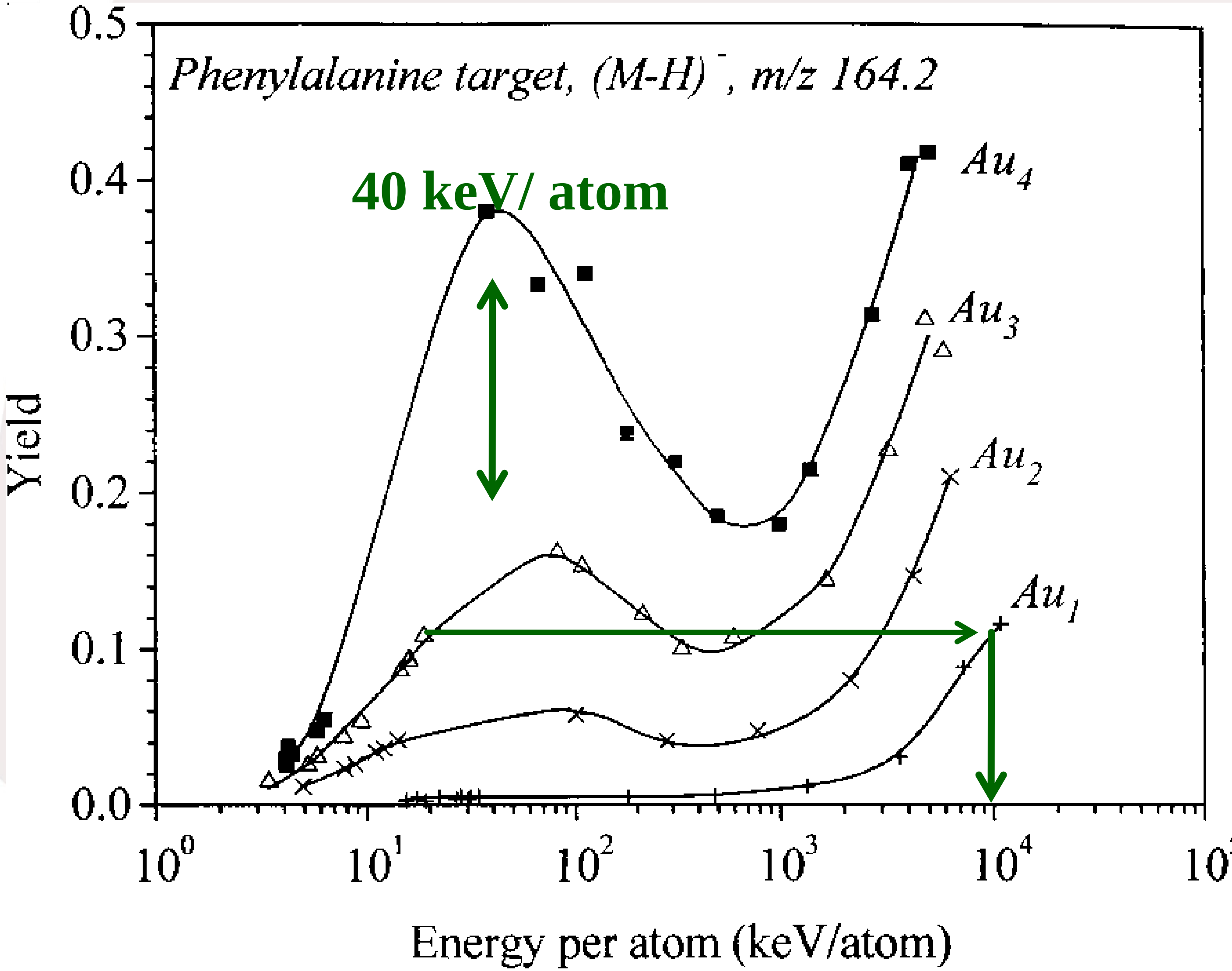
GOLD CLUSTER IMPACT ON METALLIC SURFACE



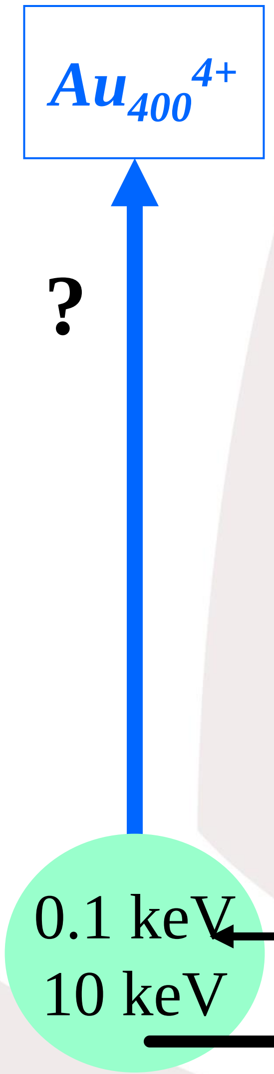


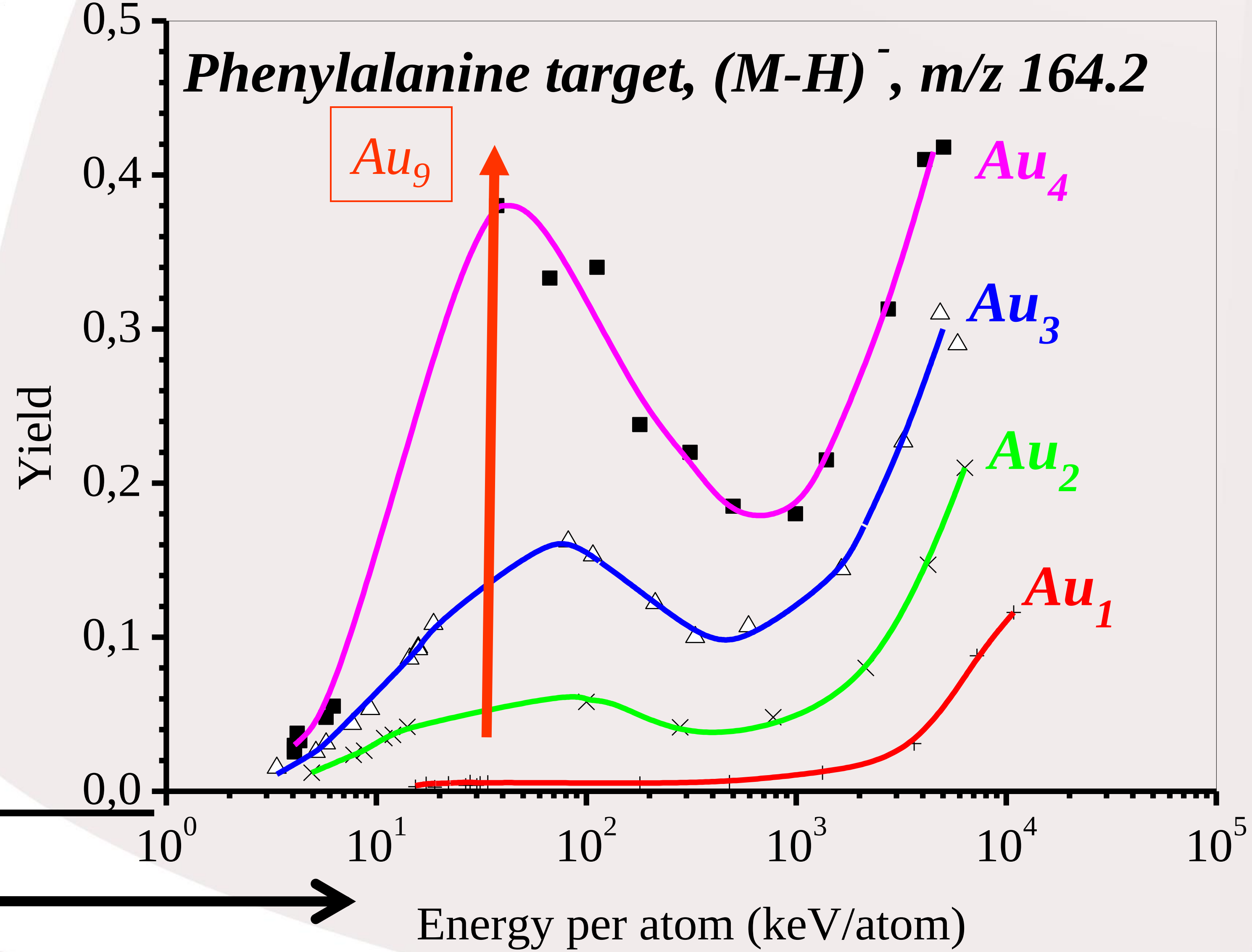
Phys. Rev. Lett. **80** (1998) 5433.
Phys. Rev. B **65** (2002) 144106

GOLD CLUSTERS IN THE MEV RANGE



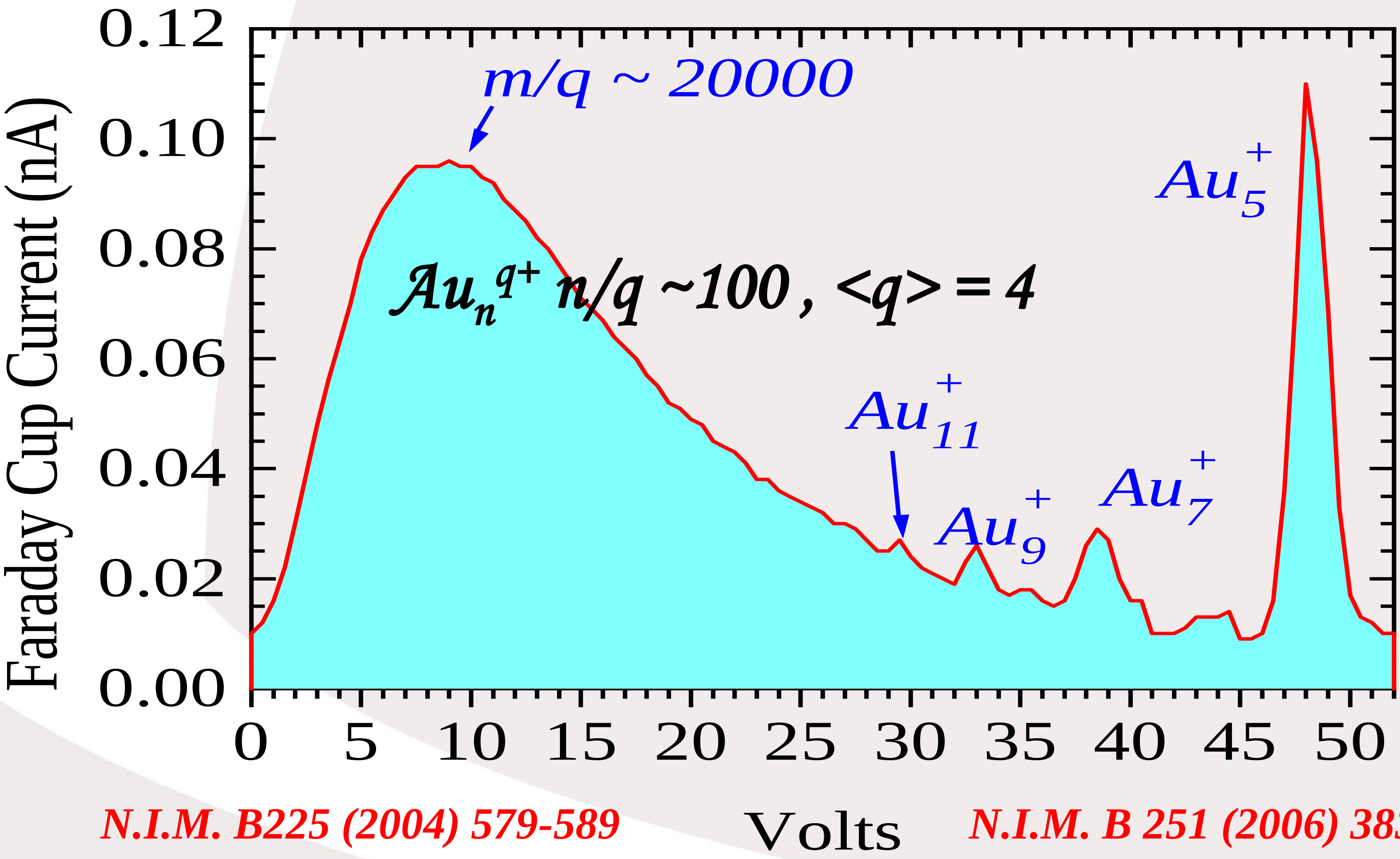
GOLD CLUSTER IN THE MEV RANGE





Phys. Rev. A 63 (2001) 22902.

MASSIVE CLUSTERS OR NANODROPLETS



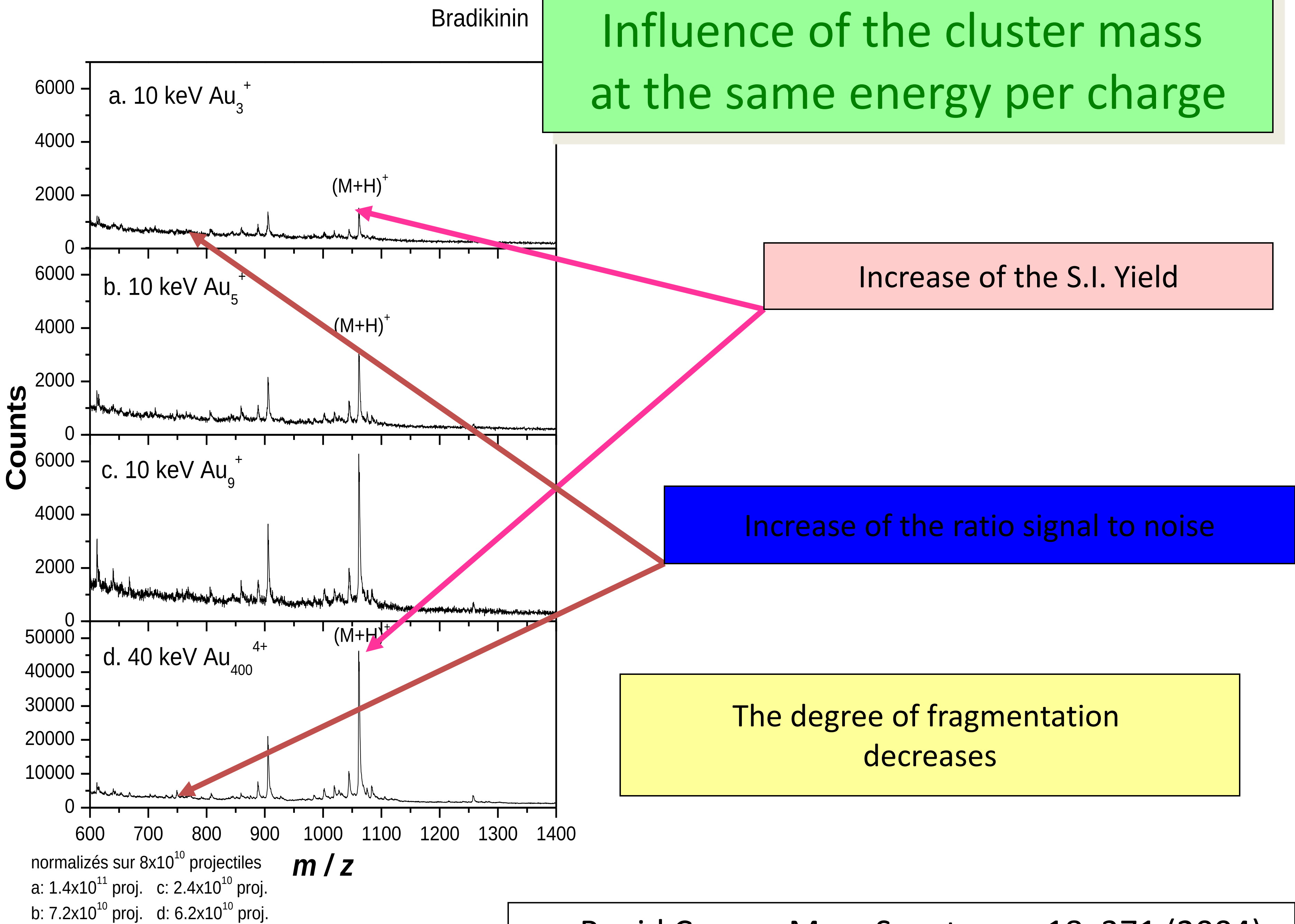
N.I.M. B225 (2004) 579-589

N.I.M. B 251 (2006) 383-389

Gold nanoparticle beams

From 10 to 4000 qkeV

Influence of the cluster mass at the same energy per charge

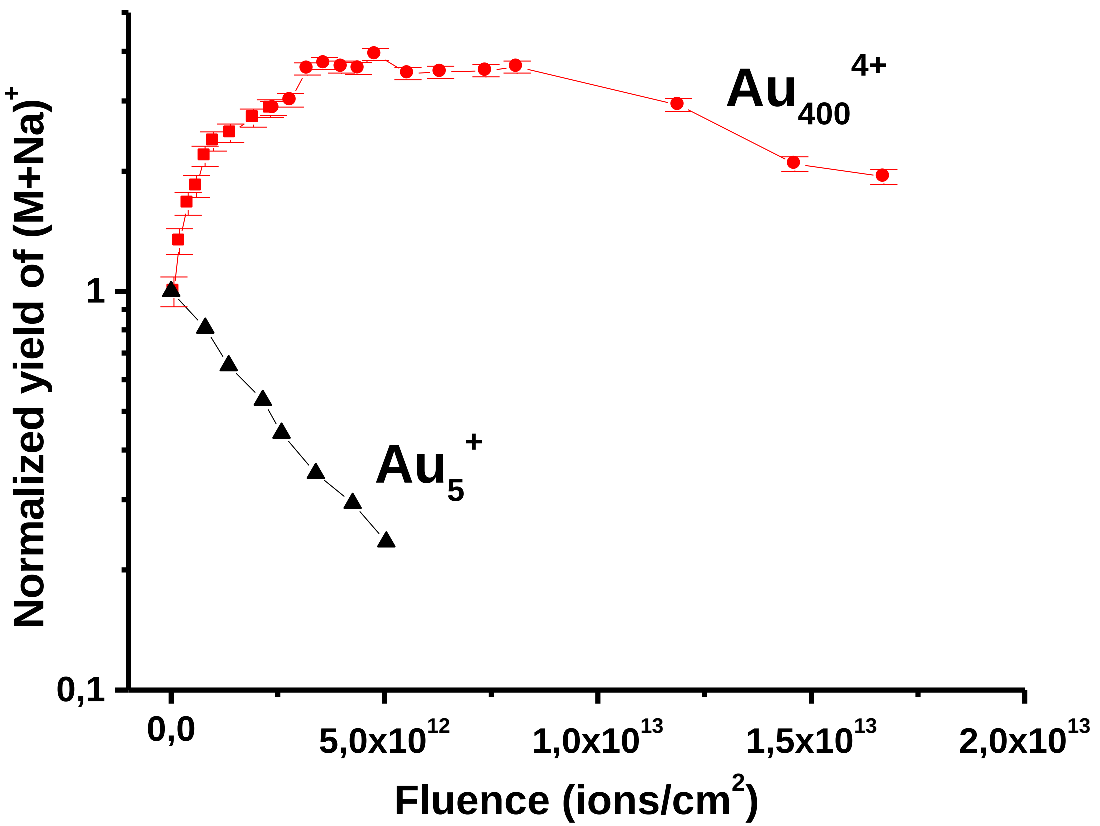


The degree of fragmentation decreases

Rapid Comm. Mass Spectrom., 18, 371 (2004)

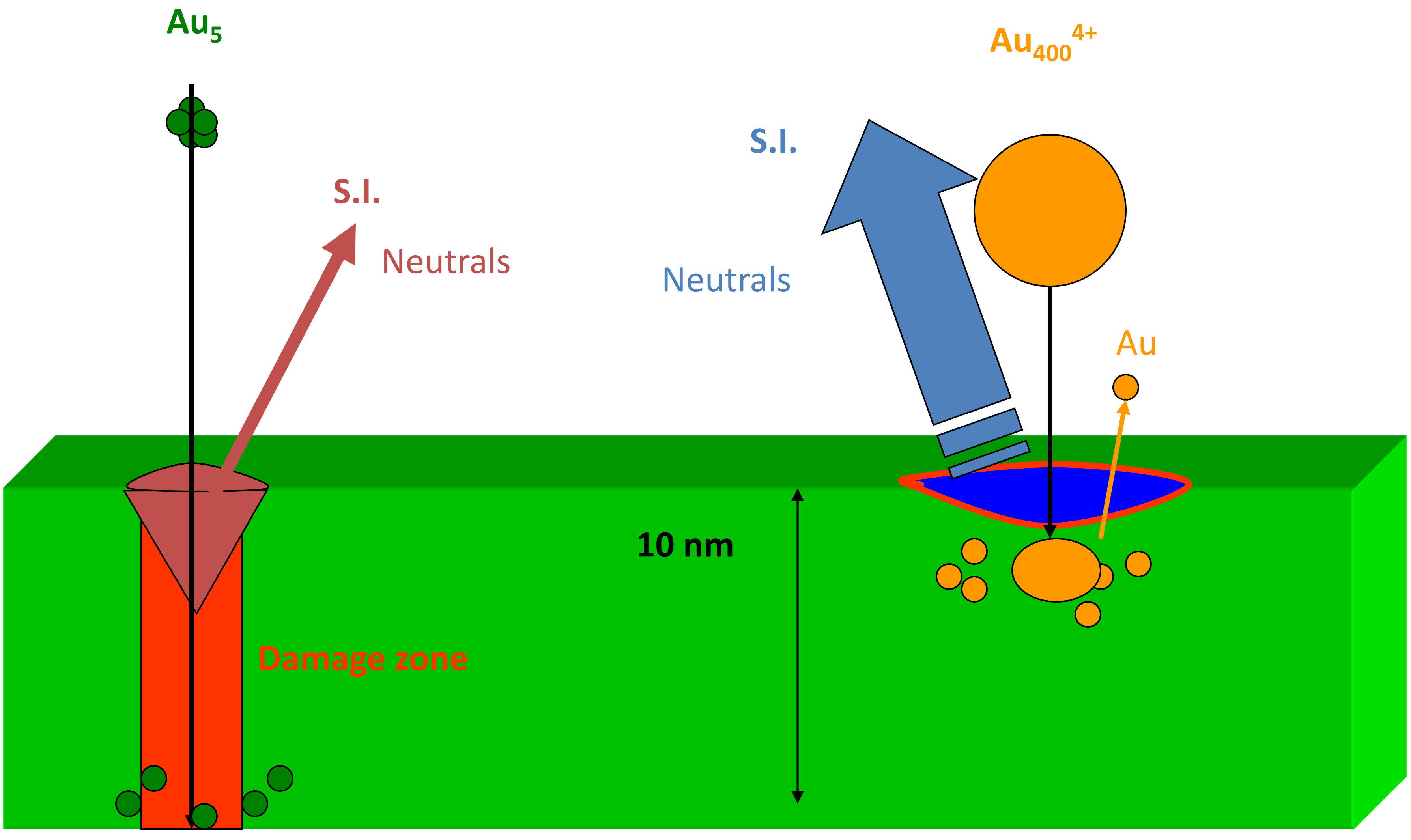
Au_{400} projectiles are not destructive for bio-organic samples !

Gramicidin S $(M+Na)^+$ ion yield as a function of fluence of 40 keV Au_{400}^{4+} and 10 keV Au_5^+ projectiles



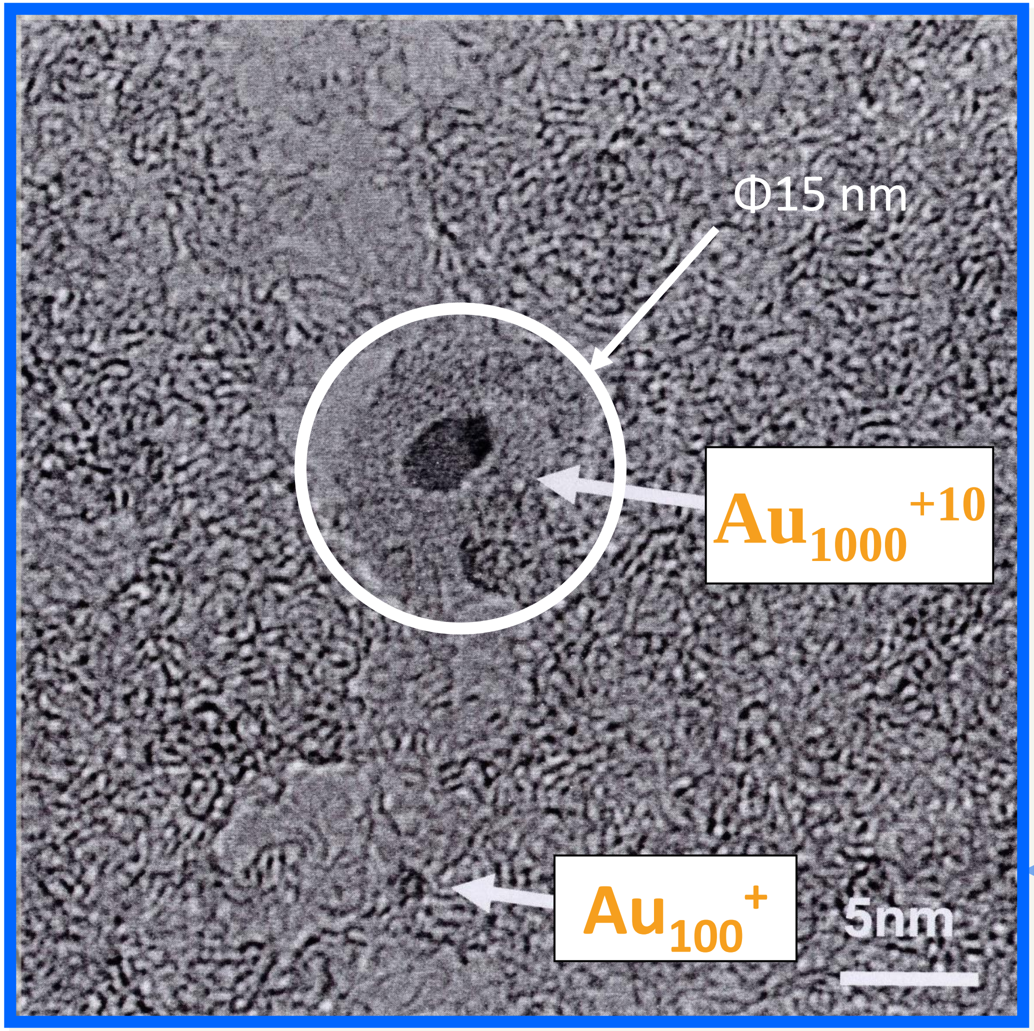
Rapid Comm. Mass Spectrom., 18, 371 (2004) 371

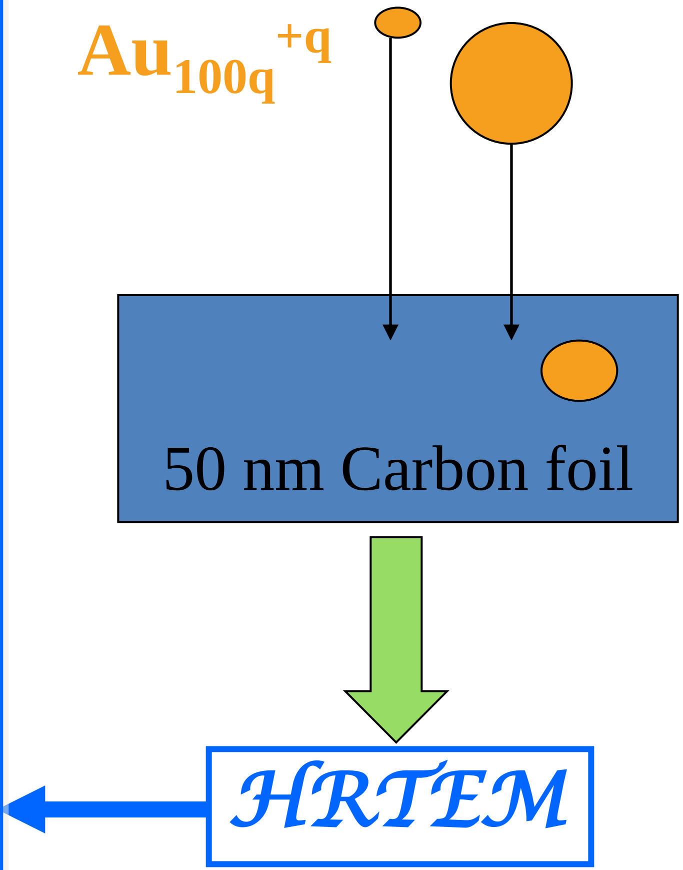
Differences between Au_5 and Au_{400}



Massive Gold Cluster on Carbon film

Int. Journal of Mass Spect., 275 (2008) 86-90





Conclusions

- 75 % of the projectile final state is a :

Nano-crystal >>>>Coherent Motion

- Large range – 14 nm< R < 17 nm

S. J. Carroll, et al, Phys Rev Lett, **84** (2000) 2654-2657.

C. Anders, H. M. Urbassek, Nucl. Instrum. Meth. B 228 (2005) 57.

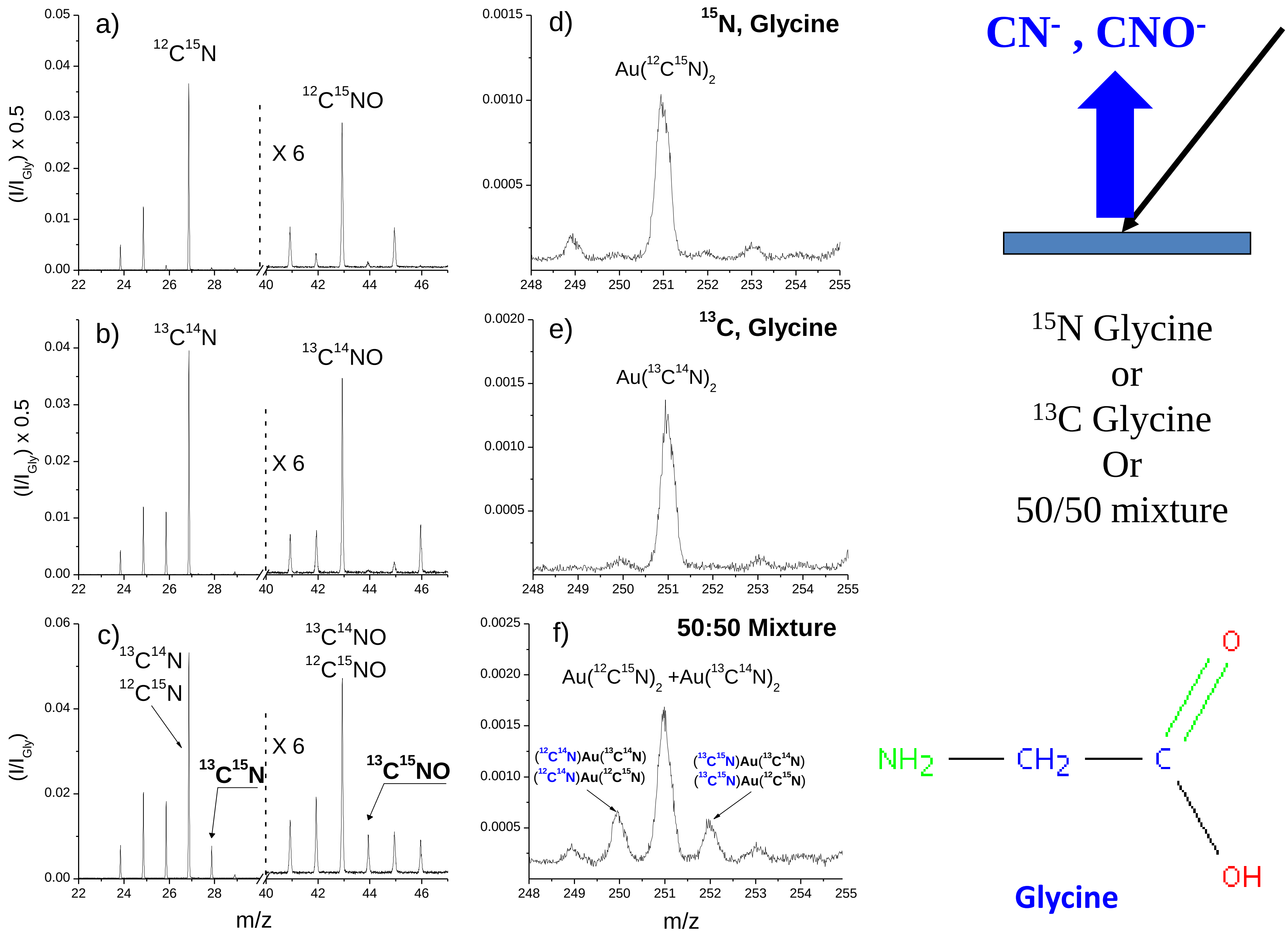
clearing the way effect

Hydrodynamic regime

Friction ?

-temperature, pressure ?

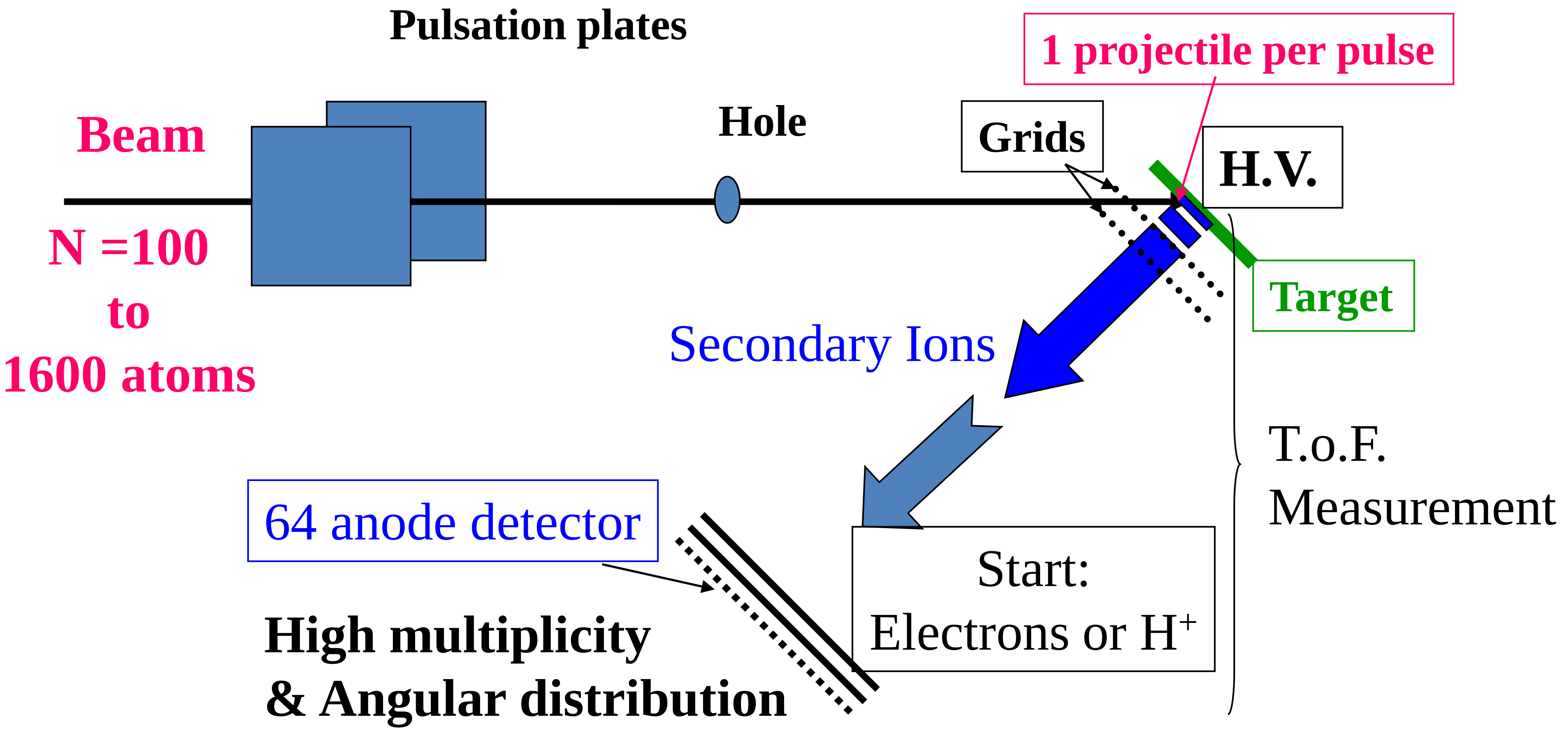
-atom and electron stripping processes ?



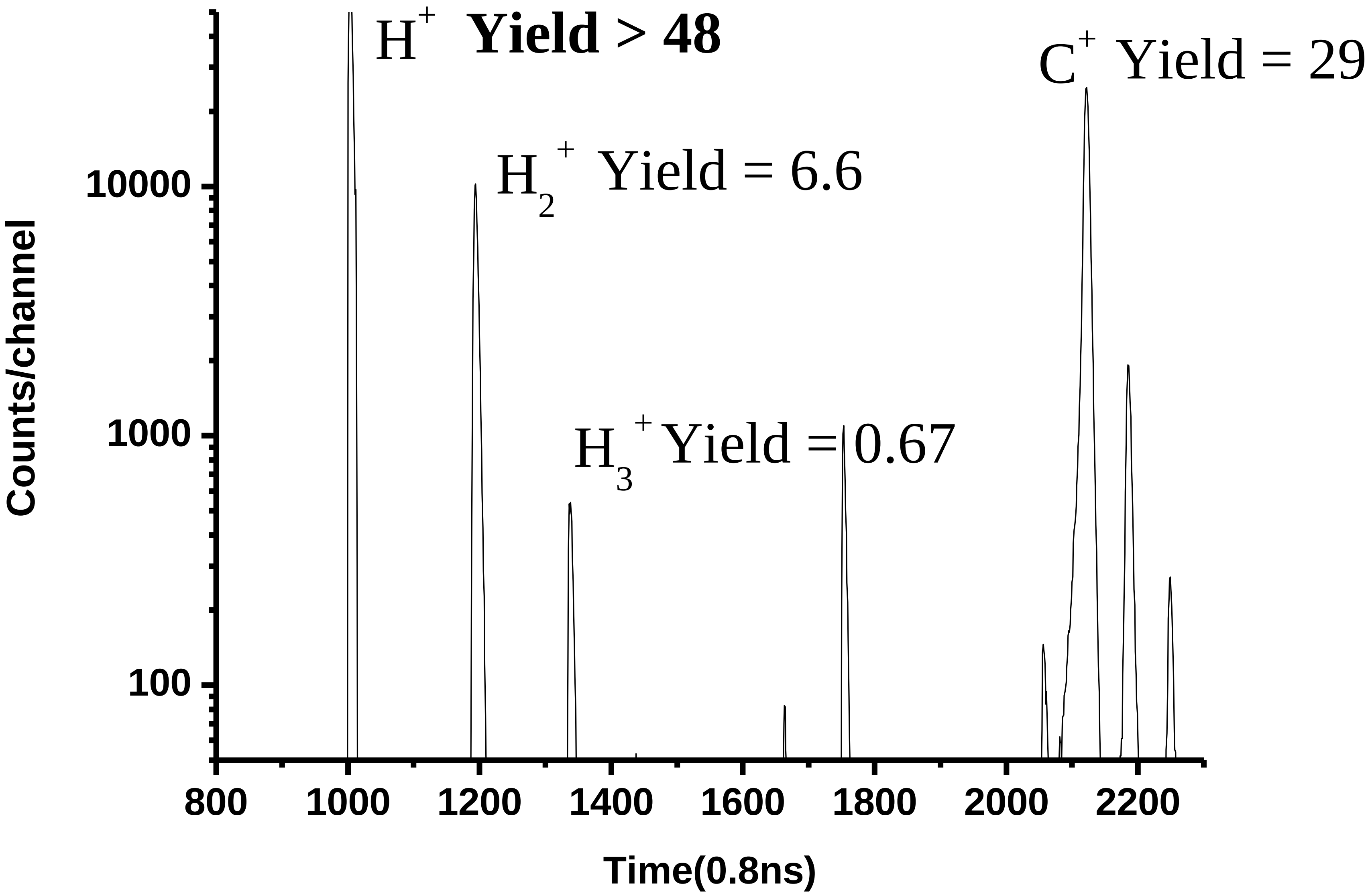
a)
12C15N
12C15NO
X 6
(I/IGly) x 0.5
b)
13C14N
13C14NO
X 6
(I/IGly) x 0.5
c)
13C14N
12C15N
13C15N
13C14NO
12C15NO
13C15NO
X 6
(I/IGly)
m/z
d)
15N, Glycine
Au(12C15N)2
e)
13C, Glycine
Au(13C14N)2
f)
50:50 Mixture
Au(12C15N)2 +Au(13C14N)2
(12C14N)Au(13C14N)
(12C14N)Au(12C15N)
(13C15N)Au(13C14N)
(13C15N)Au(12C15N)
m/z
CN- , CNO-
15N Glycine
or
13C Glycine
Or
50/50 mixture
NH2
CH2
C
O
OH
Glycine

Cluster Impact @ High Energy
From 200 to 4000 qkeV

Targets : Glycine (^{13}C and ^{15}N), guanine, fulleren, lipidA and gold



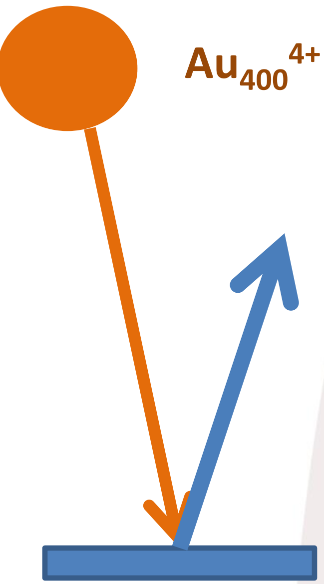
C_{60} Target (thickness: 200 nm), Au_{100q}^{q+} projectiles @ 2 qMeV



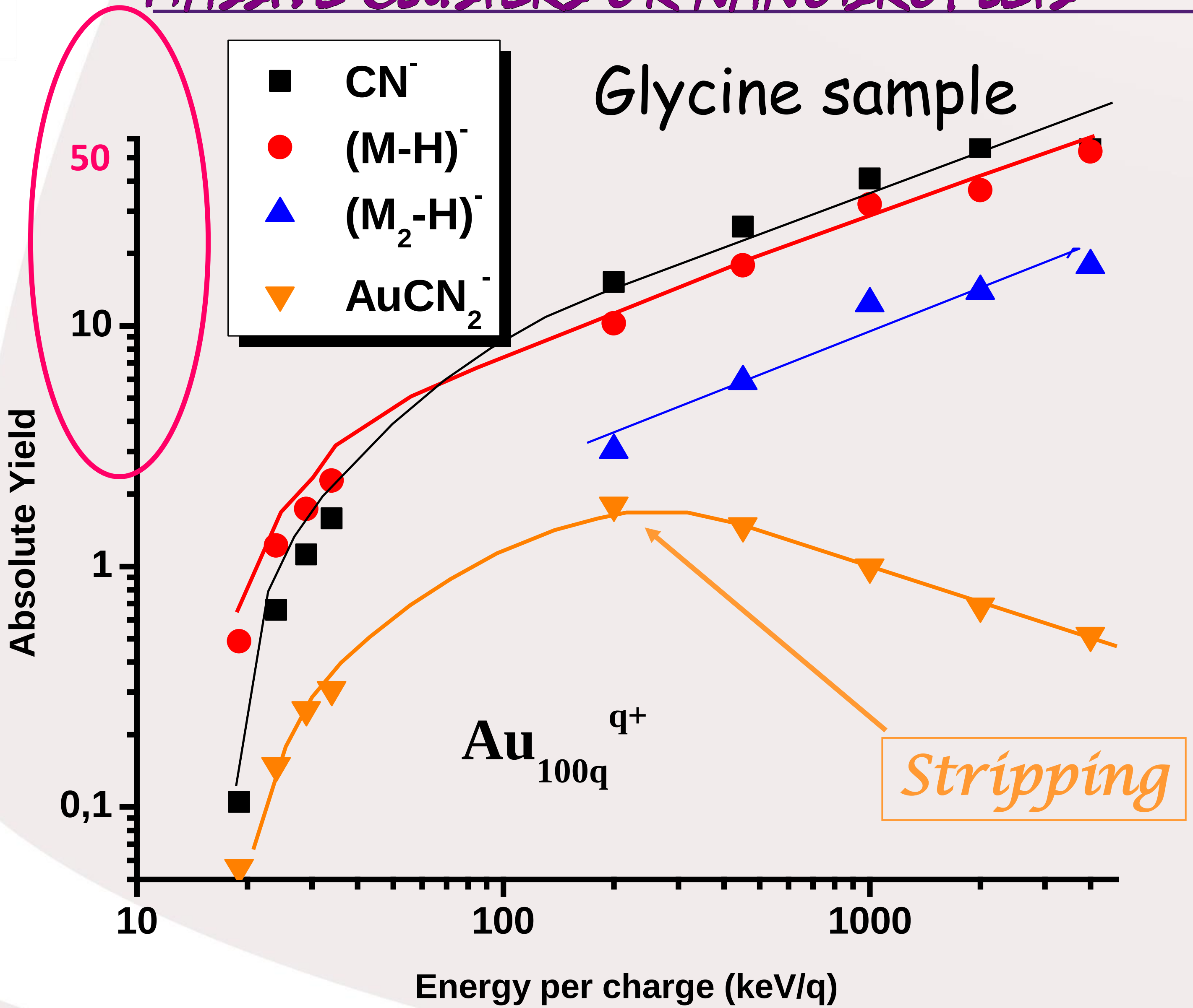
Electronic stripping, electronic friction

MASSIVE CLUSTERS OR NANODROPLETS

lundi 25 avril 2016

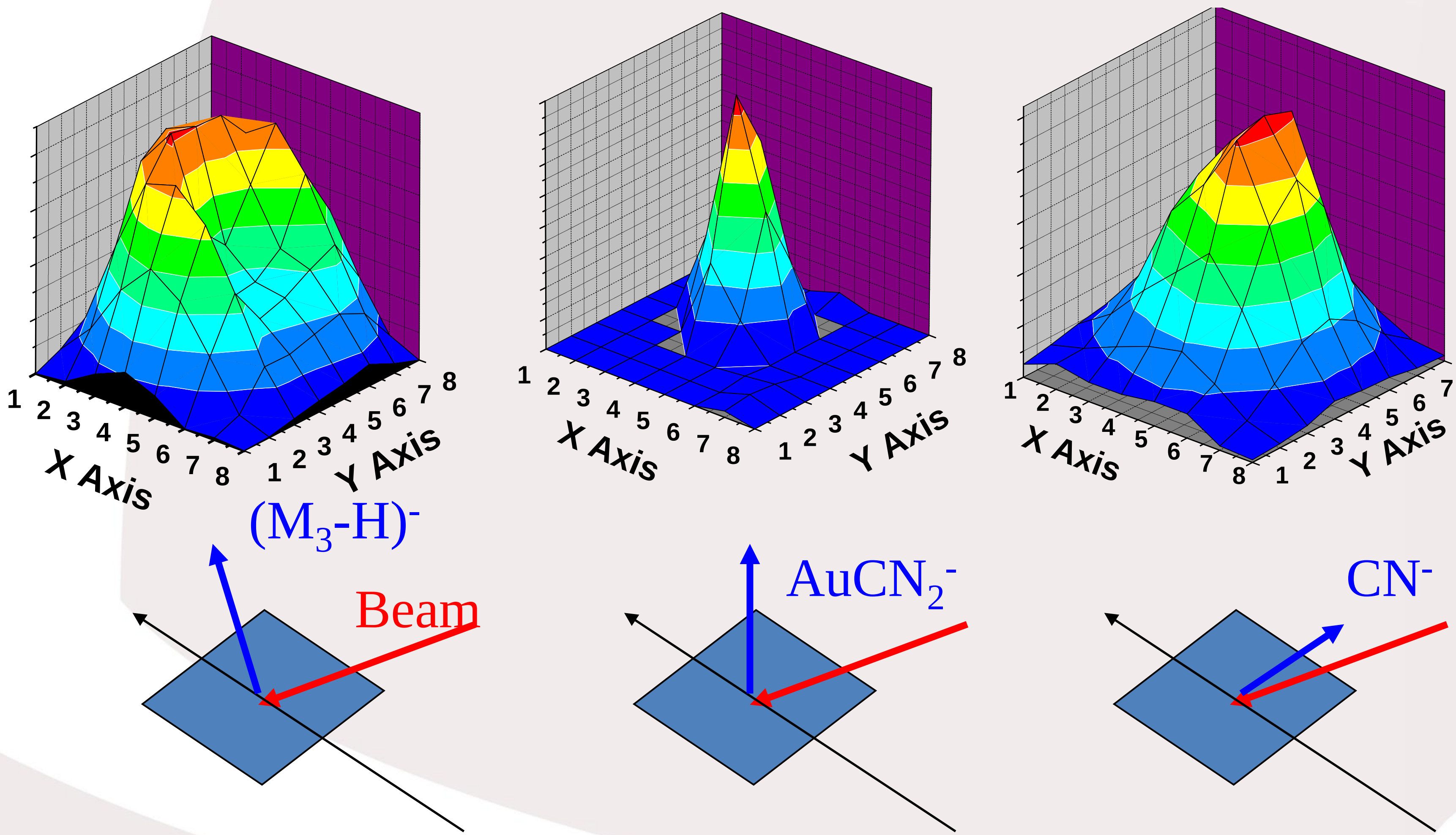


Glycine sample



MASSIVE CLUSTERS OR NANODROPLETS

Radial Velocity Distribution



Conclusions

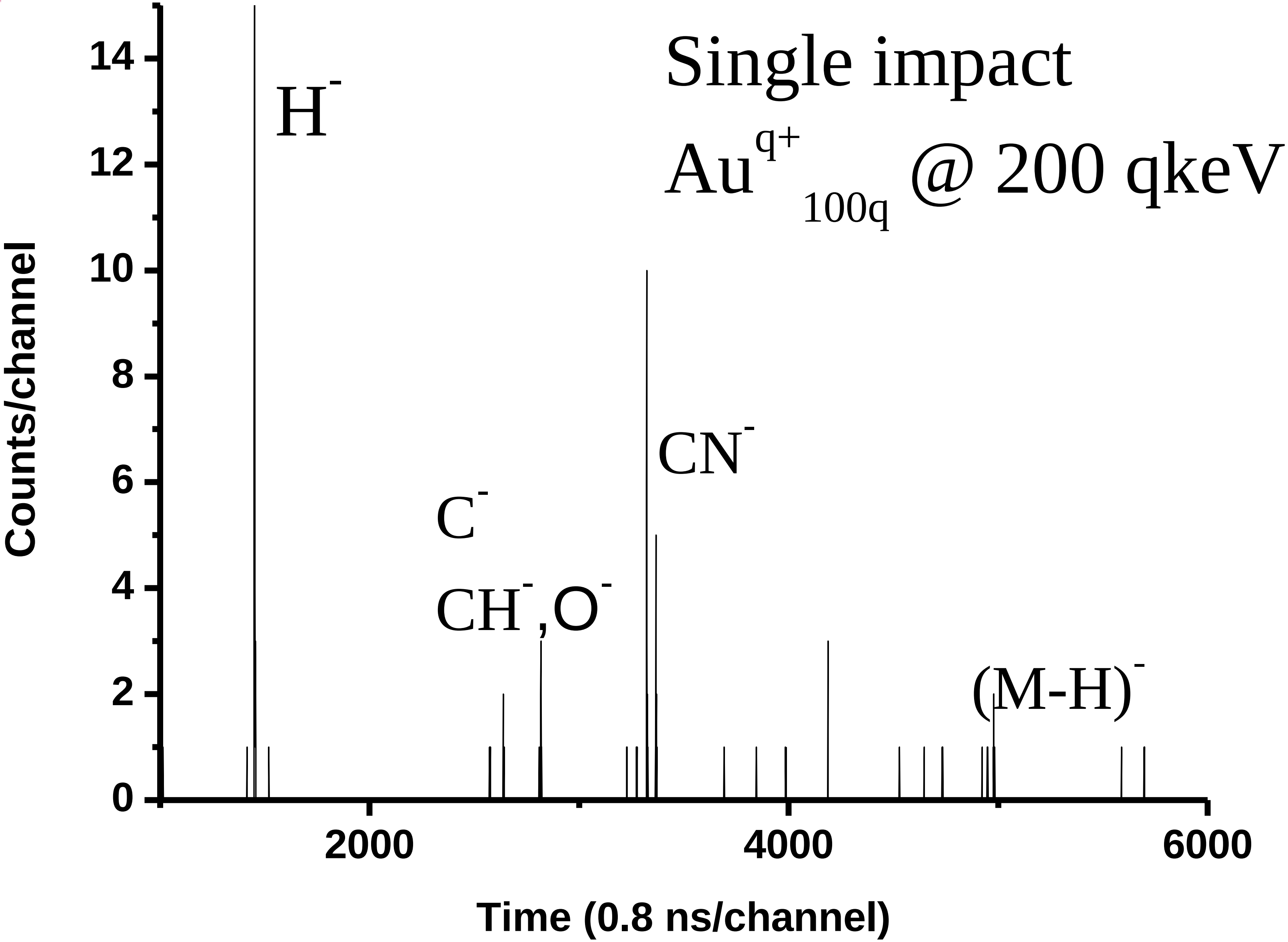
- With a “reasonable” energy of about a hundred keV per charge **the massive projectiles induce emission rates of several tens to hundreds of ions per impact**.

- The ion emission yields reach large values for bio molecules, for example the molecular ion yield is 30 % for lipid A (MW ~1300-1800 u). There is an increase of almost a factor 50 with respect to Au9 at 200 keV for complex molecules like lipid A.

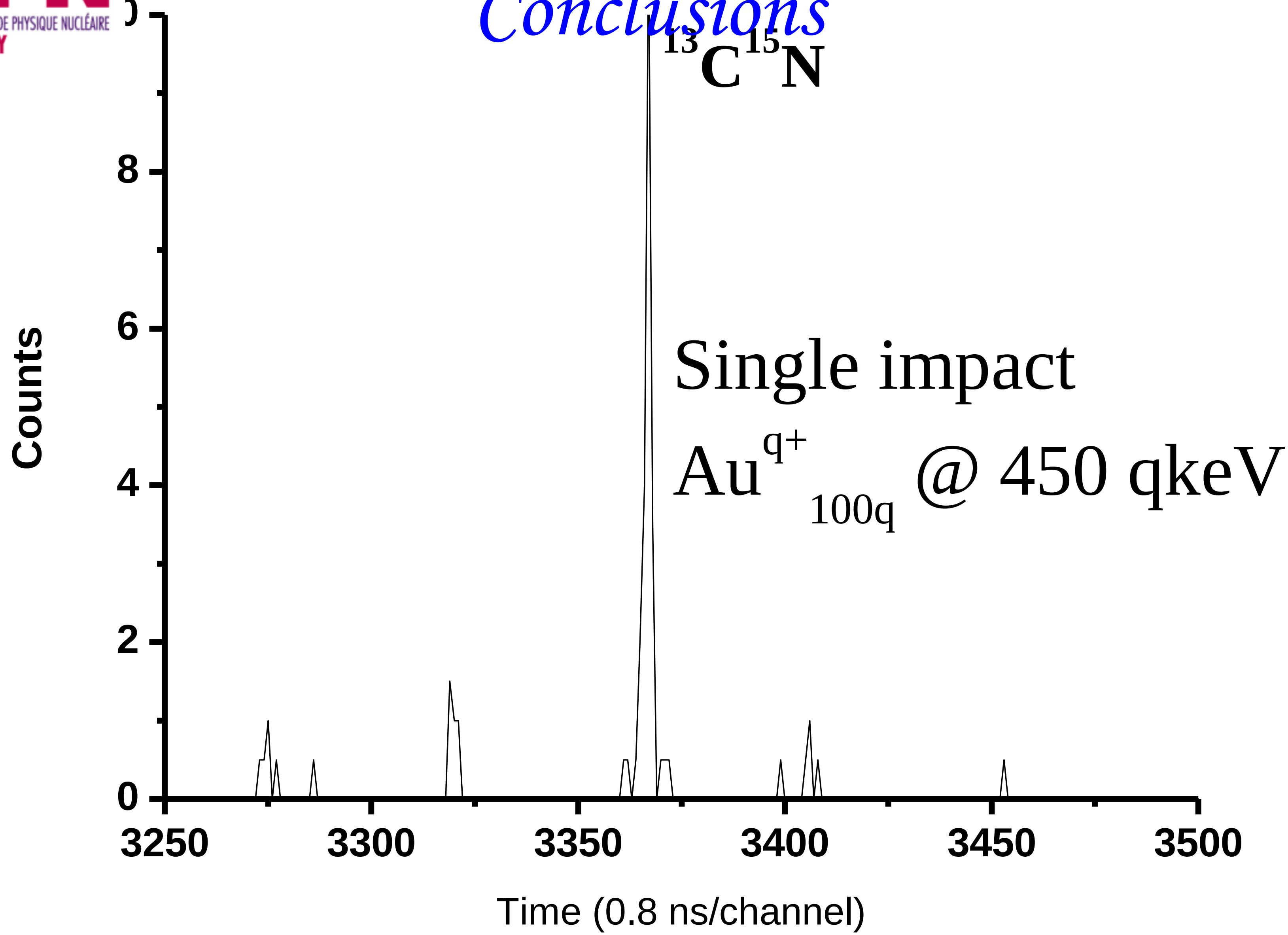
- It is possible to obtain a **Time of Flight spectrum with only one impact** and thus corresponding to **a surface of approximately 100 nm^2 and a volume of 10^3 nm^3**. These spectra permit to characterize light molecules (MW~ a few hundreds) with their fragments and intact molecular ion peaks.

The availability of massive clusters at 150 keV with the Pegase project (Grant CHE-0750377)..**and the future Andromeda Project in the MeV range opens promising prospects for probing nano-domains.**

Conclusions



Conclusions



The Pegase project

project financed by NSF (Grant CHE-0750377)

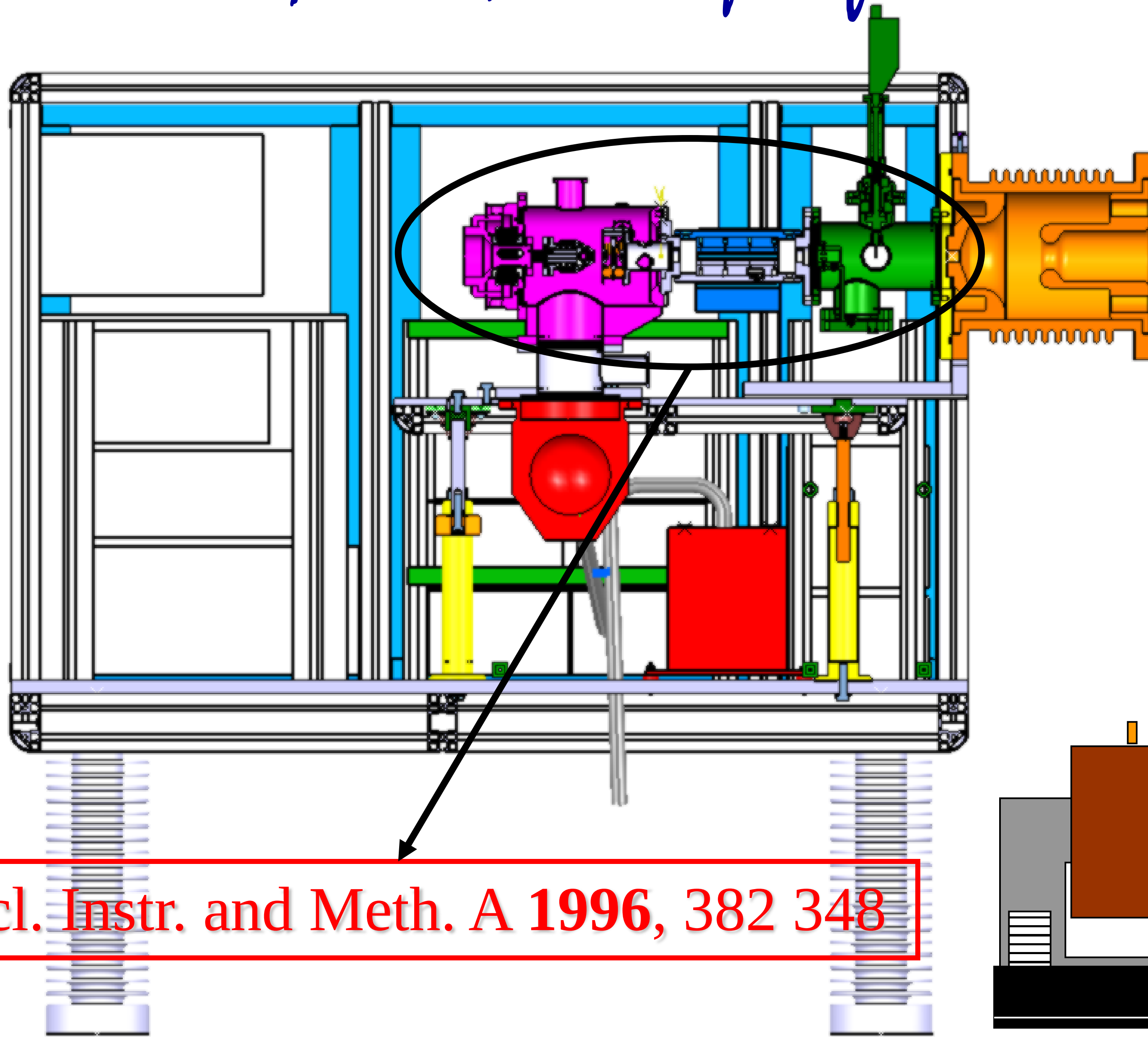
IPNOrsay

S. Della-Negra,
J. Arianer, J. Depauw,

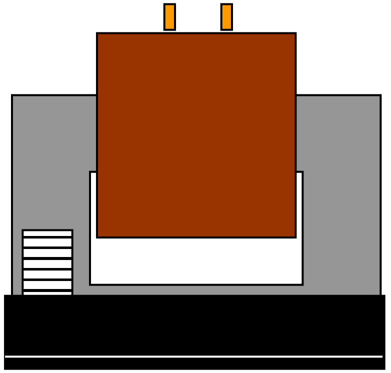
Texas A&M U

S.V. Verkhoturov, E.A. Schweikert

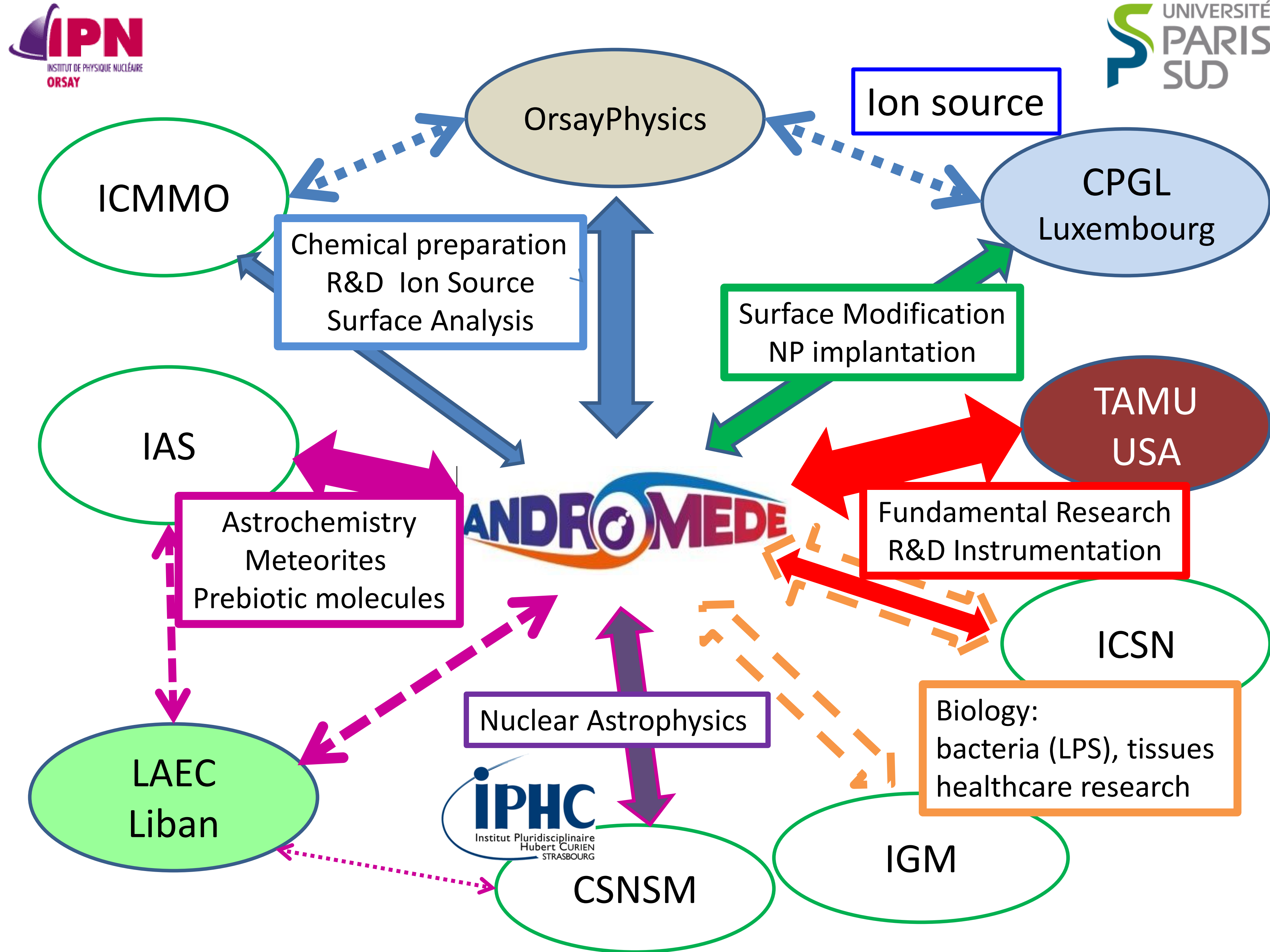
PEGASE: 130 kV platform



Nucl. Instr. and Meth. A **1996**, 382 348




Andromède
De la nucléosynthèse à la chimie prébiotique
IPN
INSTITUT DE PHYSIQUE NUCLÉAIRE
ORSAY
IGM
Institut de Génétique et Microbiologie
UNIVERSITÉ PARIS SUD
ICMMO
INVESTISSEMENTS D'AVENIR
ORSAY PHYSICS
TESCAN ORSAY HOLDING
TEXAS A&M UNIVERSITY
IAS
Institut d'Astrophysique Spatiale
Orsay
CSNSM


IPN
INSTITUT DE PHYSIQUE NUCLÉAIRE
ORSAY
UNIVERSITÉ PARIS SUD
OrsayPhysics
Ion source
ICMMO
CPGL
Luxembourg
Chemical preparation
R&D Ion Source
Surface Analysis
Surface Modification
NP implantation
IAS
TAMU
USA
ANDROMEDE
Astrochemistry
Meteorites
Prebiotic molecules
Fundamental Research
R&D Instrumentation
ICSN
Nuclear Astrophysics
Biology:
bacteria (LPS), tissues
healthcare research
LAEC
Liban
IPHC
Institut Pluridisciplinaire
Hubert Curien
Strasbourg
CSNSM
IGM

Work supported by the EQUIPEX program – Ministère de la recherche, CNRS-IN2P3 and Université Paris Sud XI (ANR-10-EQPX-23)

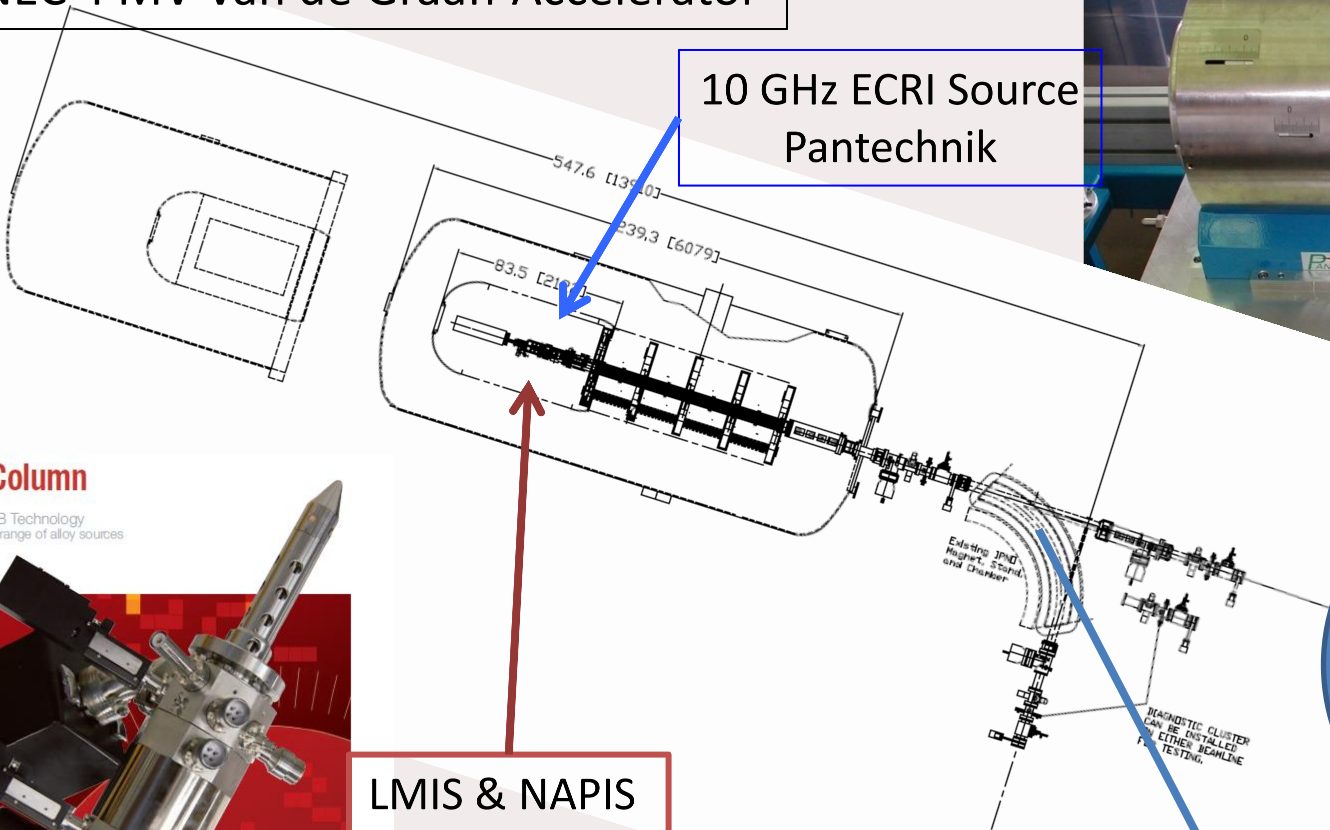
The goal of Andromeda is to create a new instrument for the analysis by mass spectrometry of nano-fields and objects present on a surface with a spatial resolution of ~ 20 nm

Moreover this instrument will permit the surface analysis at the ambient pressure and therefore the mass spectrometry analysis of native hydrated biological surfaces. This project is a very efficient alternative to the Secondary Ion Mass Spectrometry, SIMS. Molecular information (mass and structure) will be obtained from the impact of a Nano-Particle accelerated in the MeV range by a 1 to 4 MV single stage electrostatic accelerator

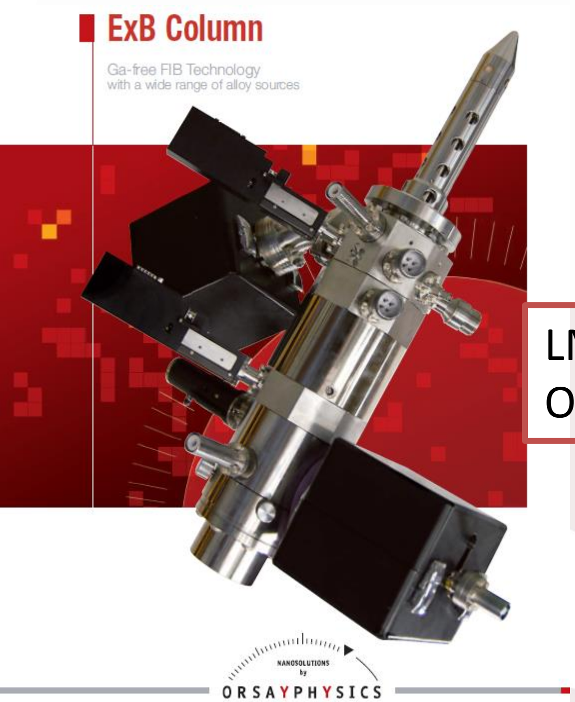
IPN
INSTITUT DE PHYSIQUE NUCLÉAIRE
ORSAY

ANDROMEDE

NEC 4 MV Van de Graaff Accelerator



10 GHz ECRI Source
Pantechnik



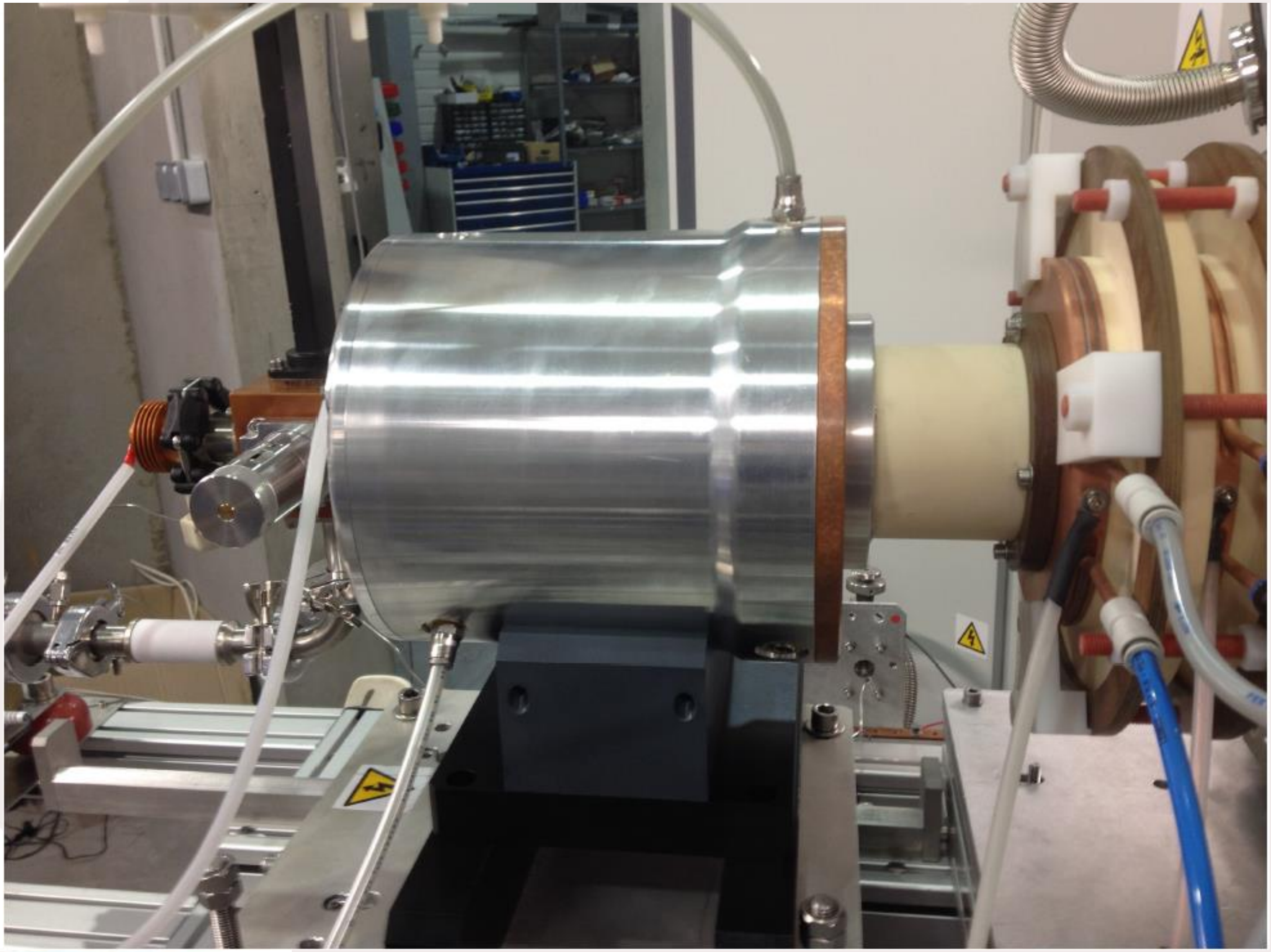
LMIS & NAPIS
OrsayPhysics

nuclear astrophysics
research

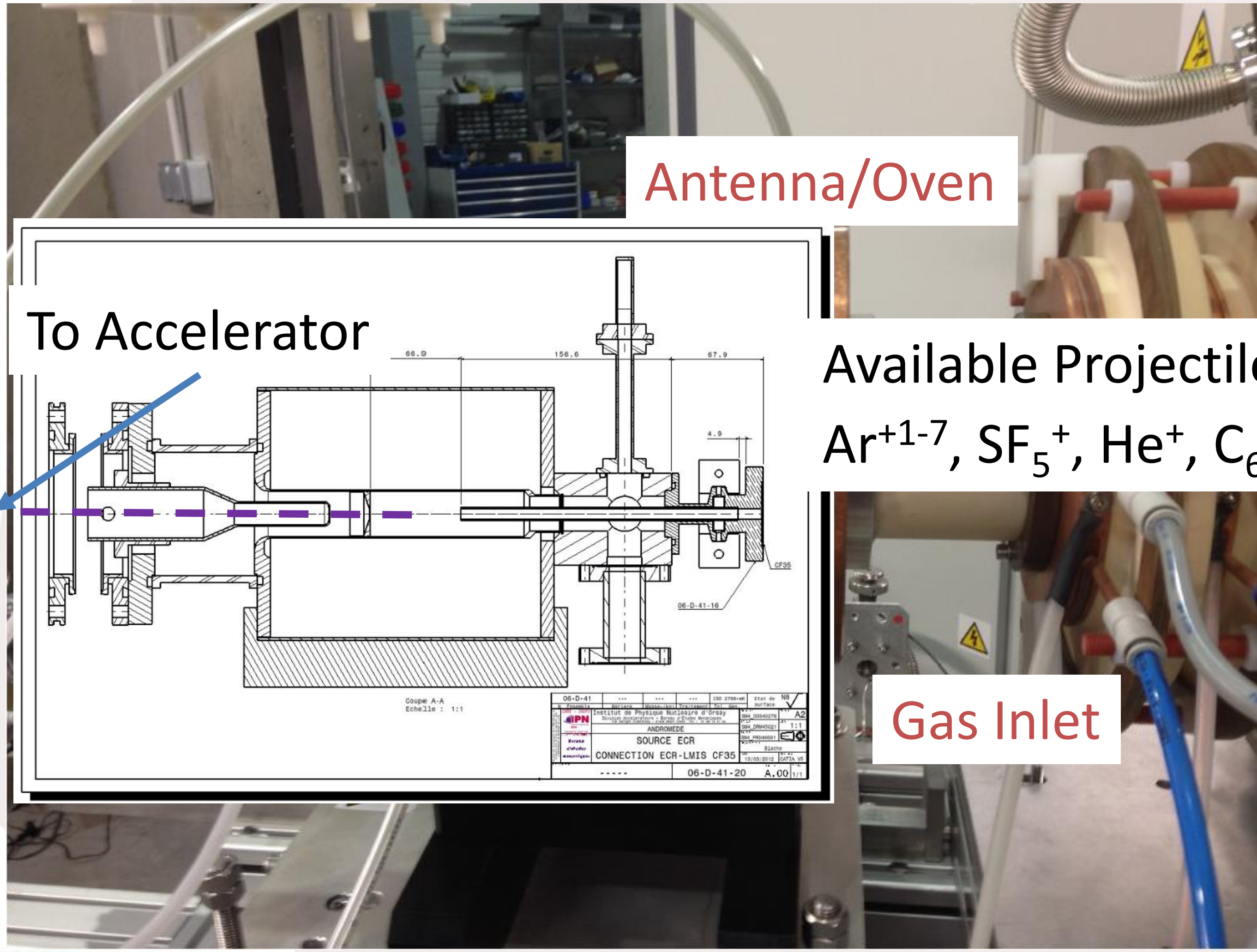
Cluster
MeV-SIMS
&
Material
modification

μ-IBA

MICROGAN POUR NEC



MICROGAN POUR NEC



Beam Direction

Available Projectiles:

$Ar^{+1\text{-}7}$, SF_5^+, He^+, $C_{60}^{+1\text{-}3}$ etc.

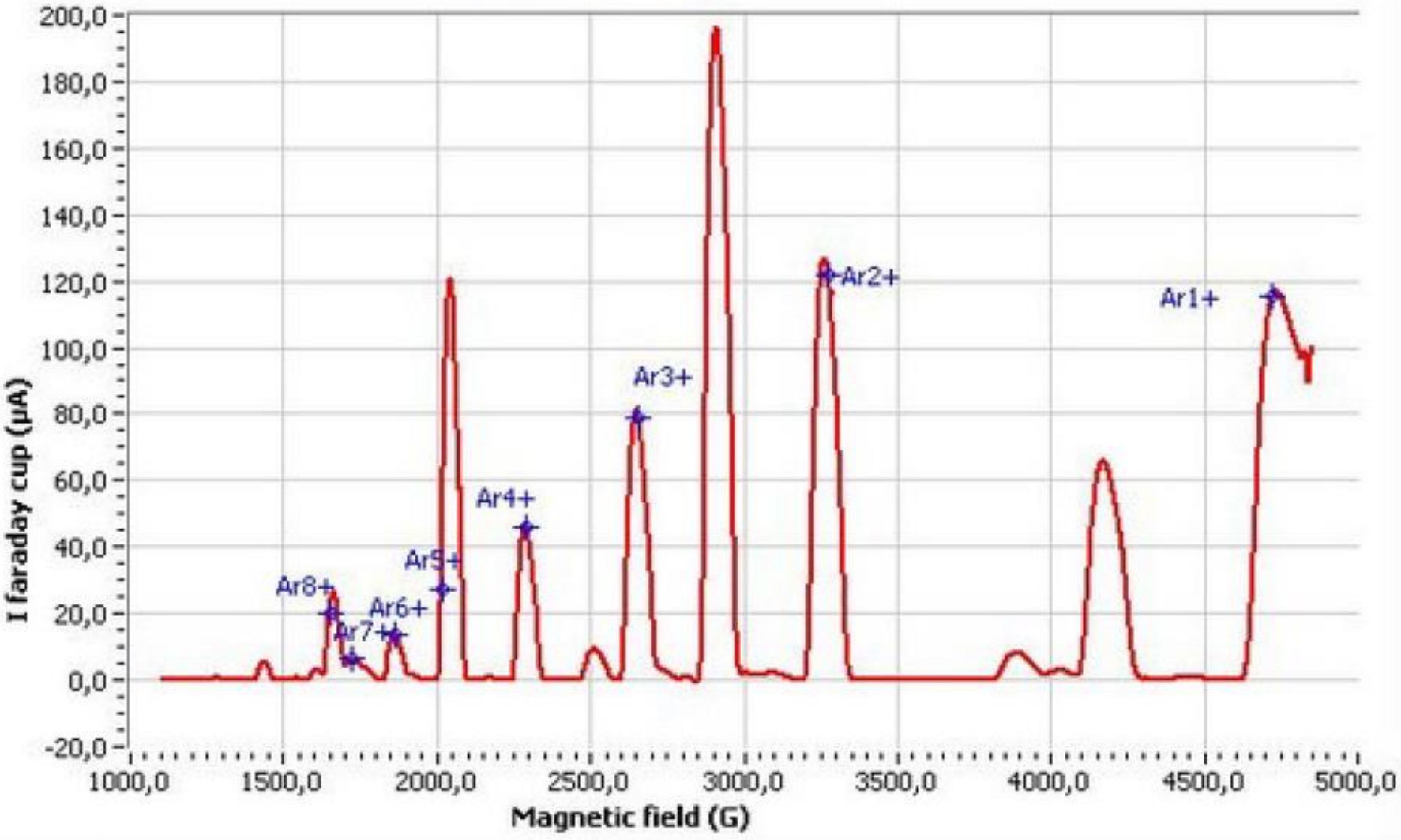


Illustration 12: Ar spectra with oxygen gas support

Argon

S. Della Negra – E. Cottereau – V. Poux

MICROGAN POUR NEC

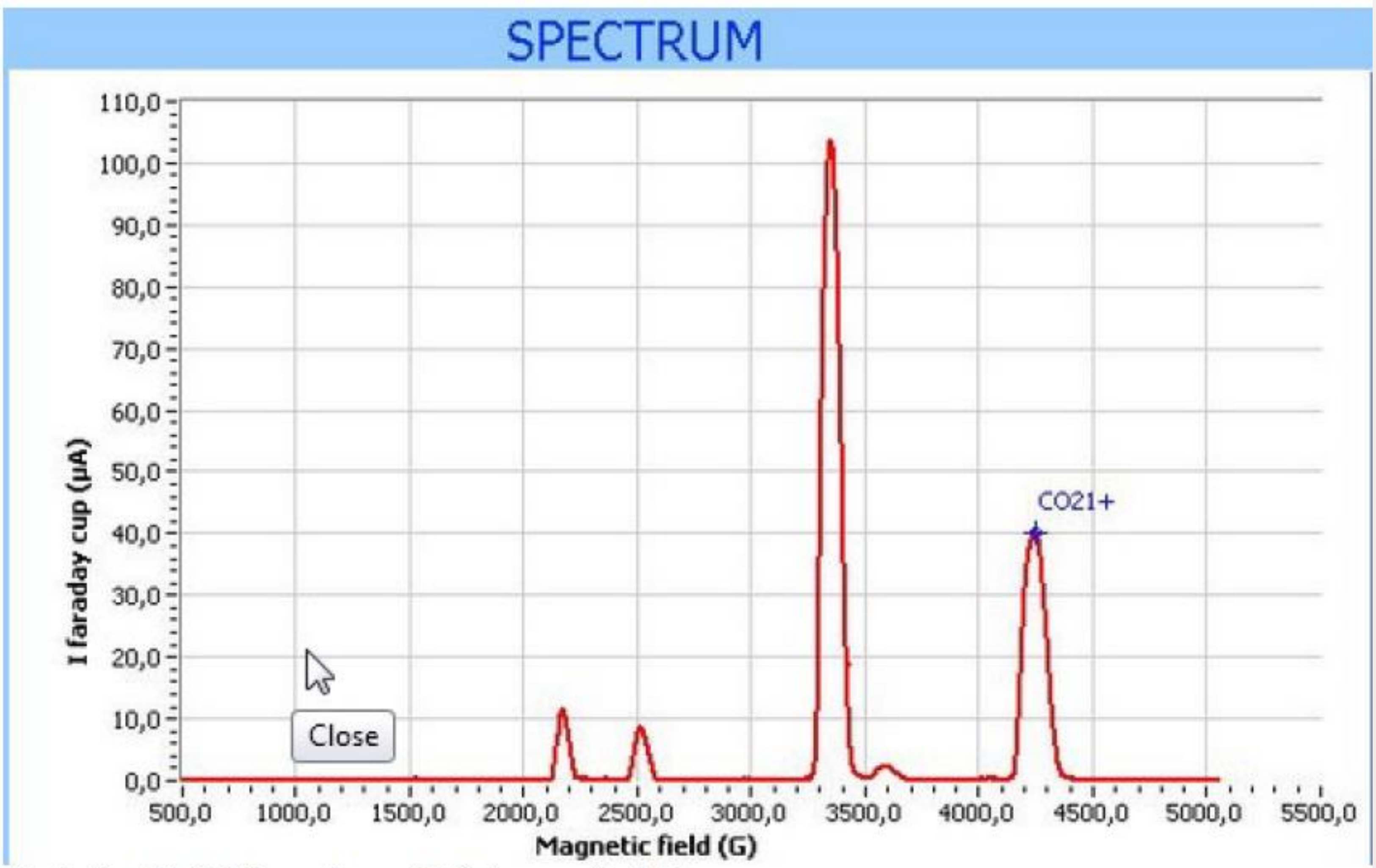


Illustration 21: CO_2^+ spectrum with flat magnetic field

MICROGAN POUR NEC

Four de la source ECR Microgan

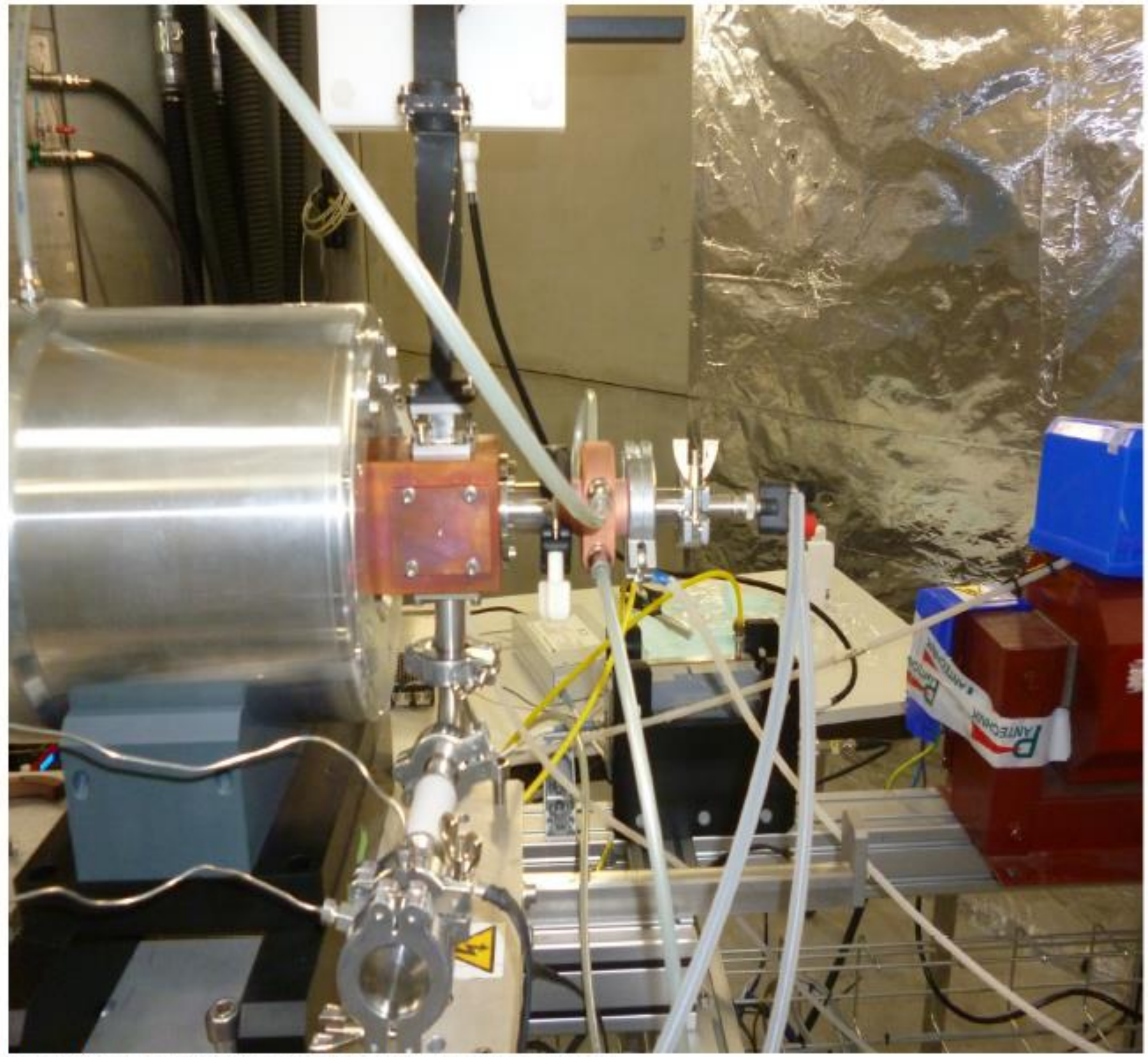
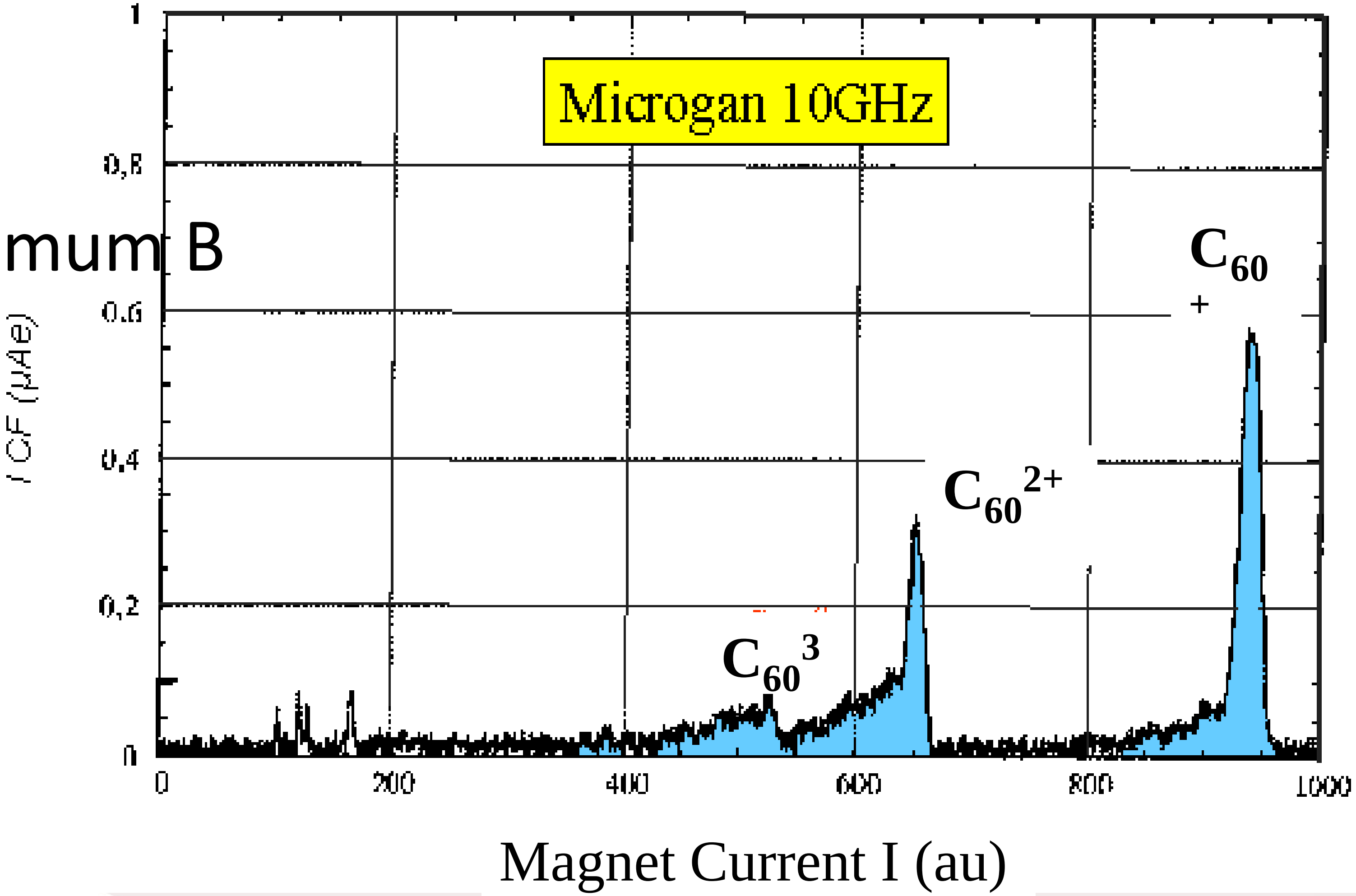
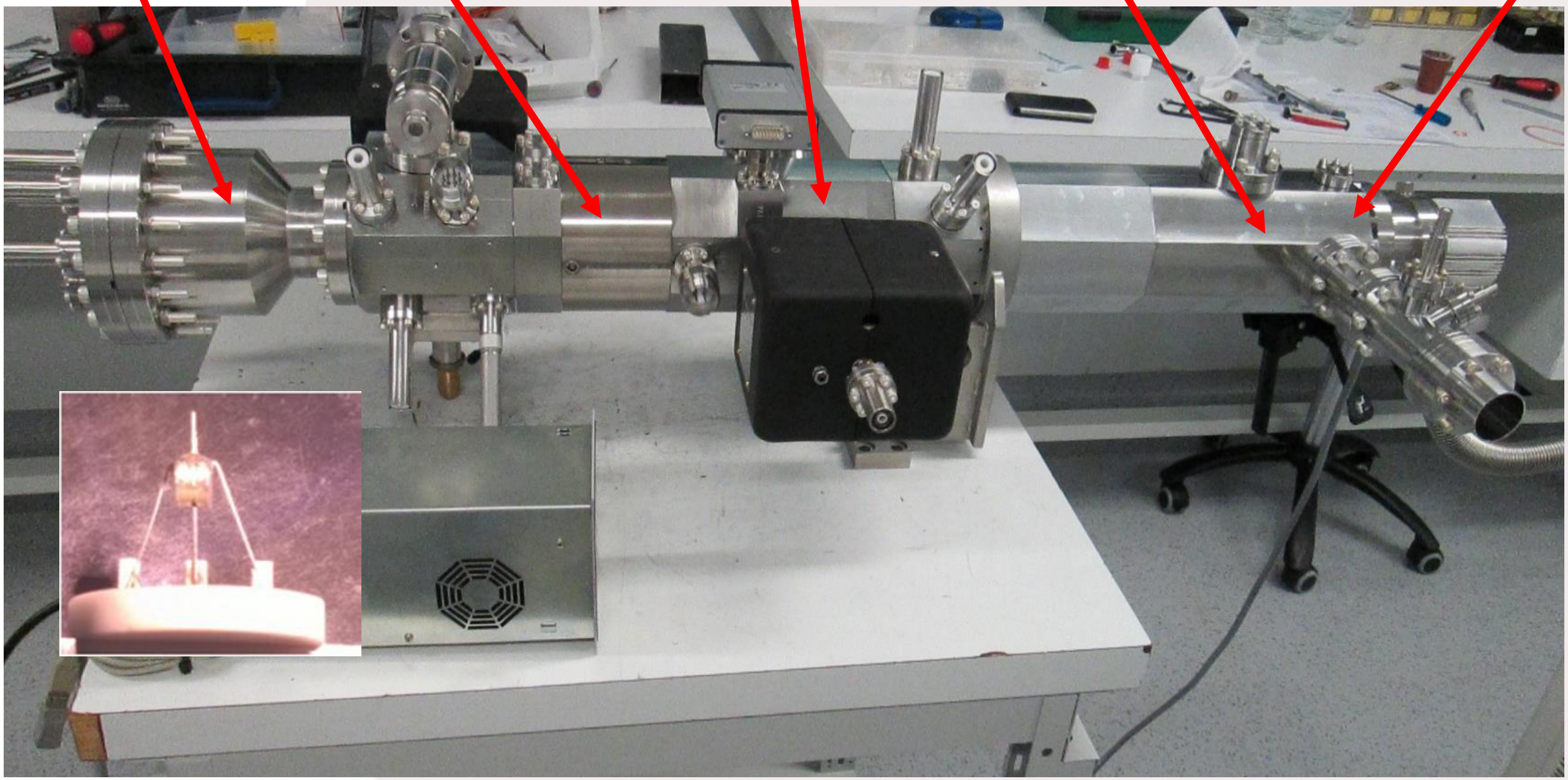


Illustration 2: Oven system with source body

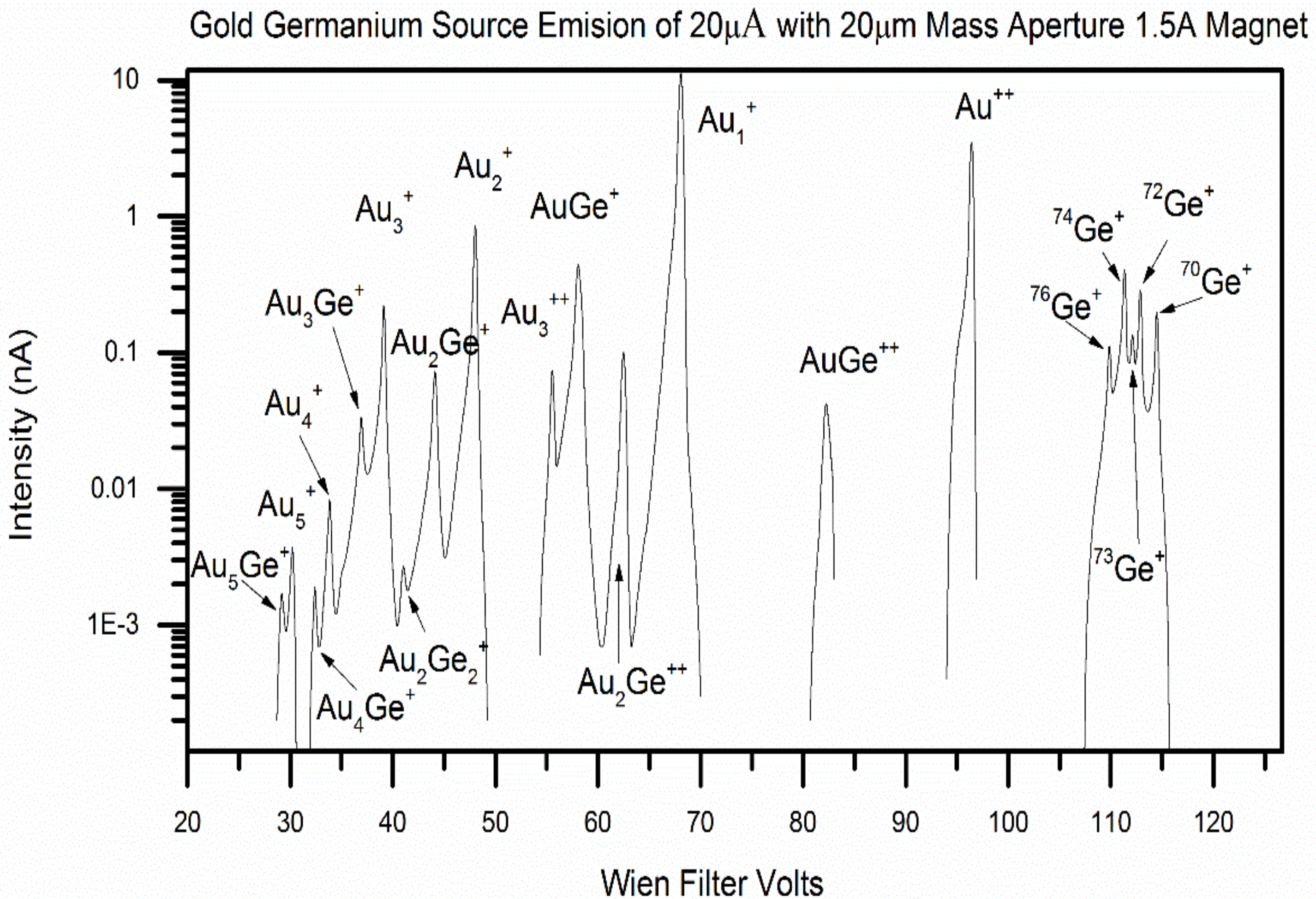
Sans Minimum B

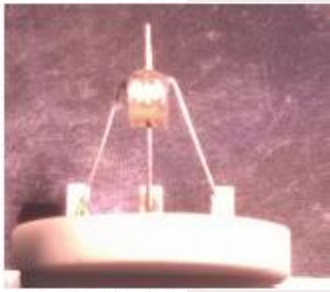


ANDRO-NEC D'ORSAYPHYSICS

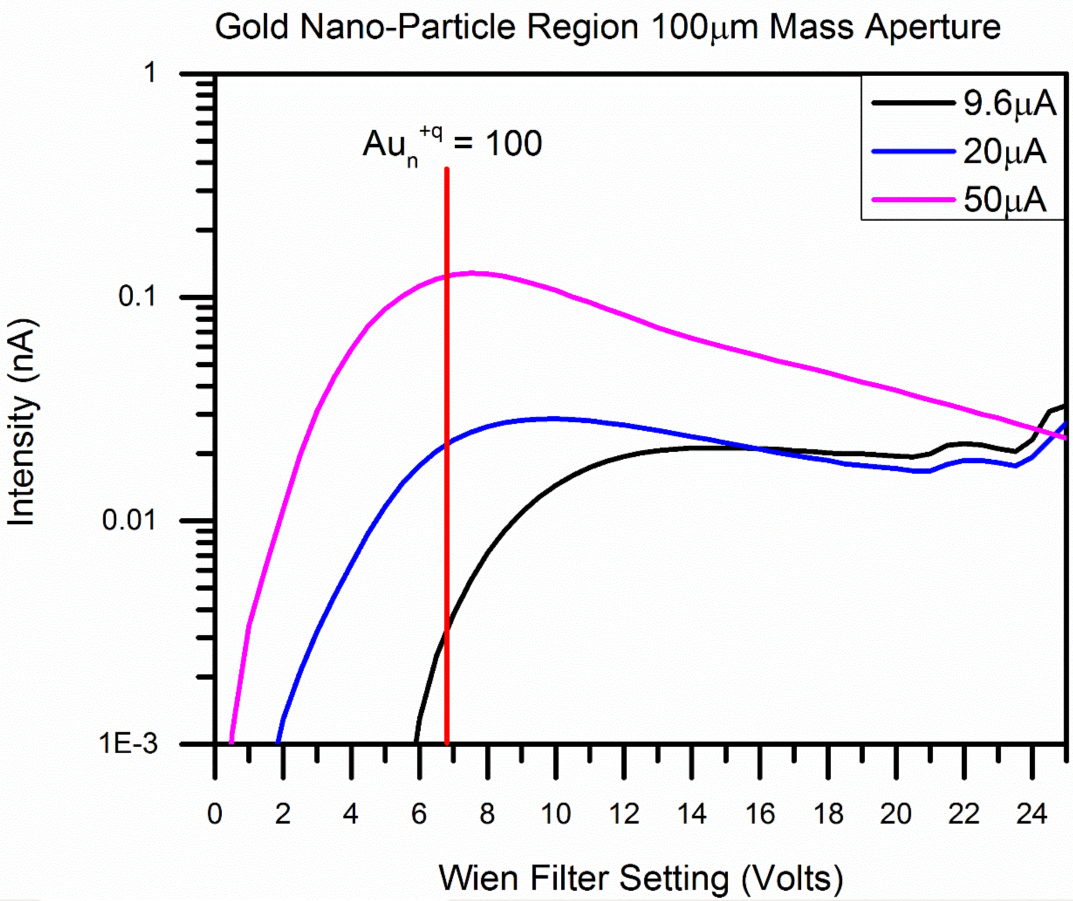


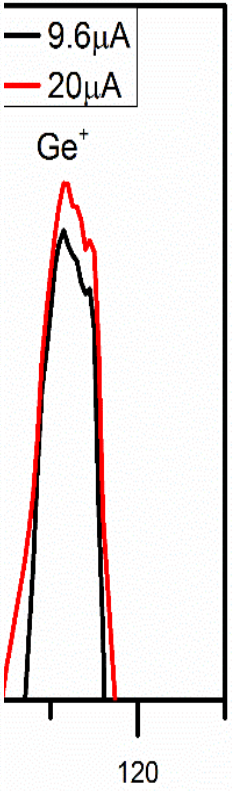
ANDRO-NEC D'ORSAYPHYSICS

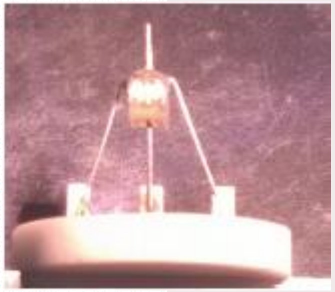




ANDRO-NEC D'ORSAYPHYSICS







Accélérateur, ligne de faisceau et sources d'ions

Unité mixte de recherche
CNRS-IN2P3
Université Paris-Sud 11

91406 Orsay cedex
Tél. : +33 1 69 15 73 40
Fax : +33 1 69 15 64 70
http://ipnweb.in2p3.fr

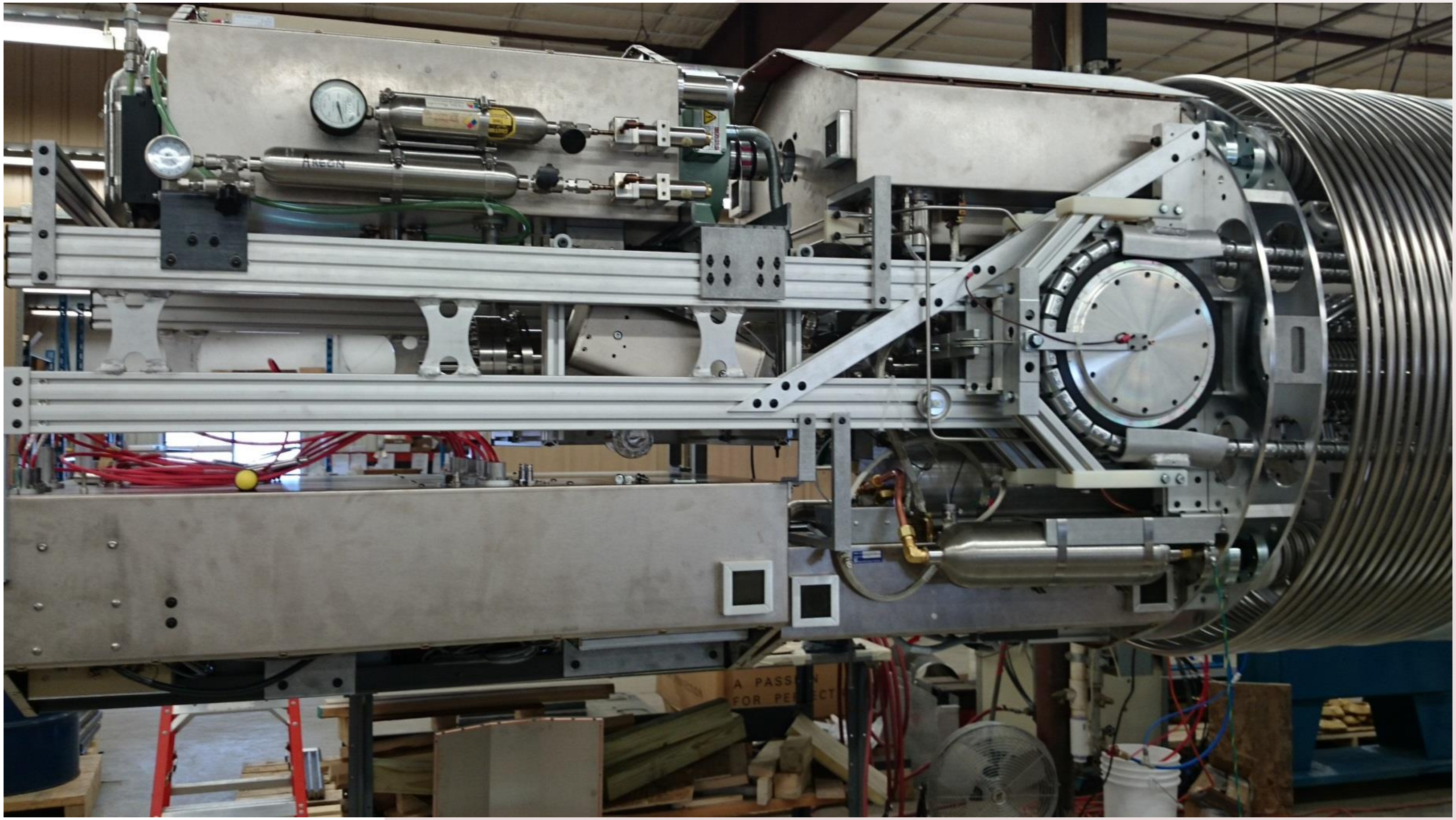
ANDROMEDE
RECEPTION DE L'ACCÉLÉRATEUR CHEZ NEC

Terminal HE

ANDROMEDE
RECEPTION DE L'ACCÉLÉRATEUR CHEZ NEC

IPN
INSTITUT DE PHYSIQUE NUCLÉAIRE
ORSAY

ANDROMEDE



Source LMIS ANDRO-NEC d'Orsay Physics TH

ANDROMEDE
RECEPTION DE L'ACCÉLÉRATEUR CHEZ NEC

ANDROMEDE PROJECT, FROM DREAM TO REALITY.

lundi 25 avril 2016

WHY ATOMIC MEV IONS ?

1-The accelerators are available (electrostatic accelerator from 1 to 4 MV) for: IBA (MeV Ion Beam Analysis) techniques, ranging from PIXE (Particle Induced X-ray Emission) and PIGE (Particle Induced Gamma-ray Emission) to RBS (Rutherford Backscattering Spectroscopy), IBIC (Ion Beam Induced Charge) and IBIL (Ion Beam Induced Luminescence). And also AMS (Accelerator Mass Spectrometry)

2-It is possible to extract MeV ions into air through a thin window.

3-A conventional scanning microprobe using a heavy ion can be used to produce MeV-SIMS maps of molecular material.

4-simultaneous PIXE, RBS and SIMS measurements can be made using the same ion beam providing complementary measurements of the sample.

Joint IAEA-SPIRIT-Japan Technical Meeting on Development and Utilization of MeV-SIMS

IAEA
Division of Physical and Chemical Sciences
Physics Section

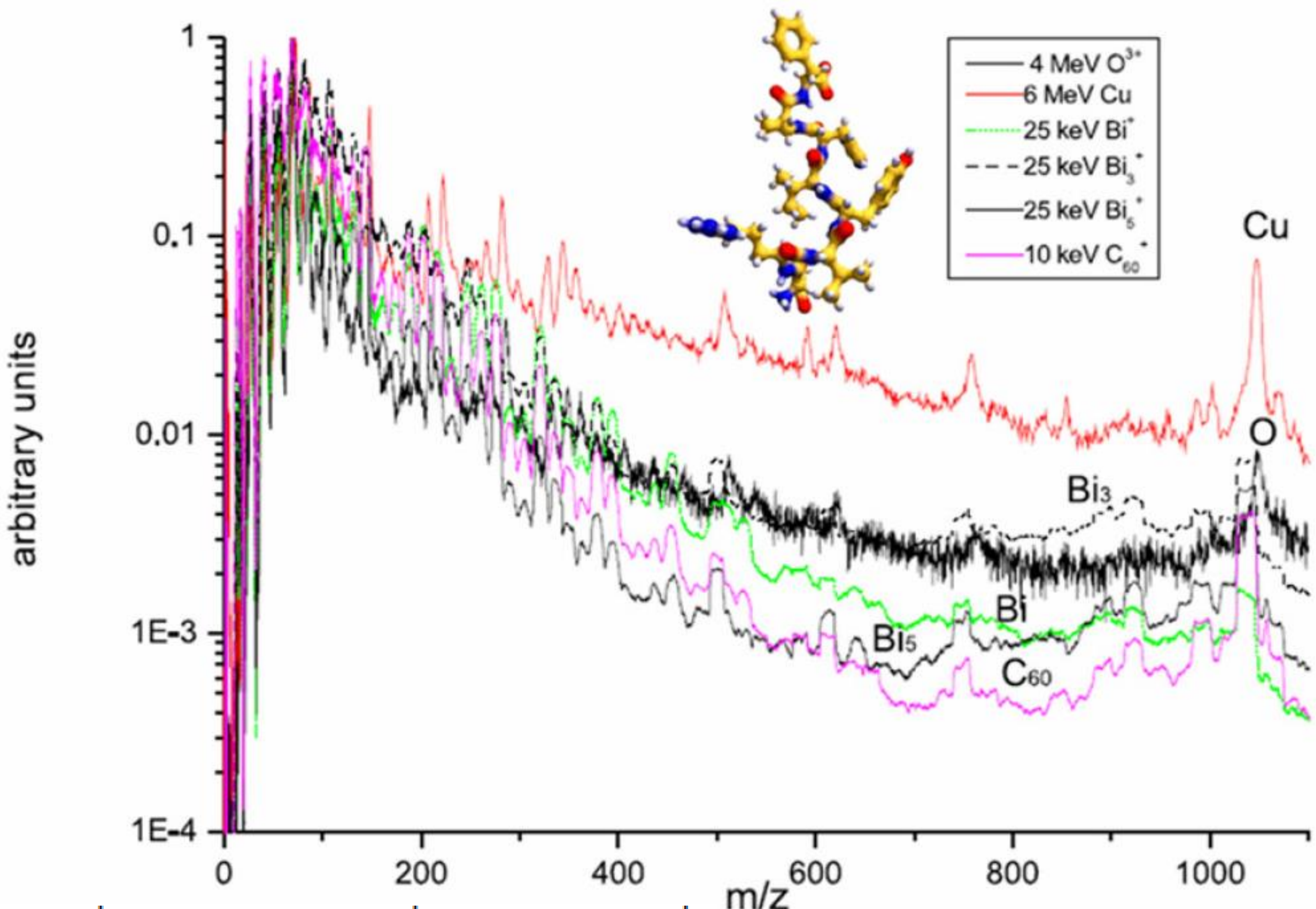
IAEA

COMPARISON SIMS KEV & SIMS MEV

lundi 25 avril 2016

SIMS XVII, Toronto

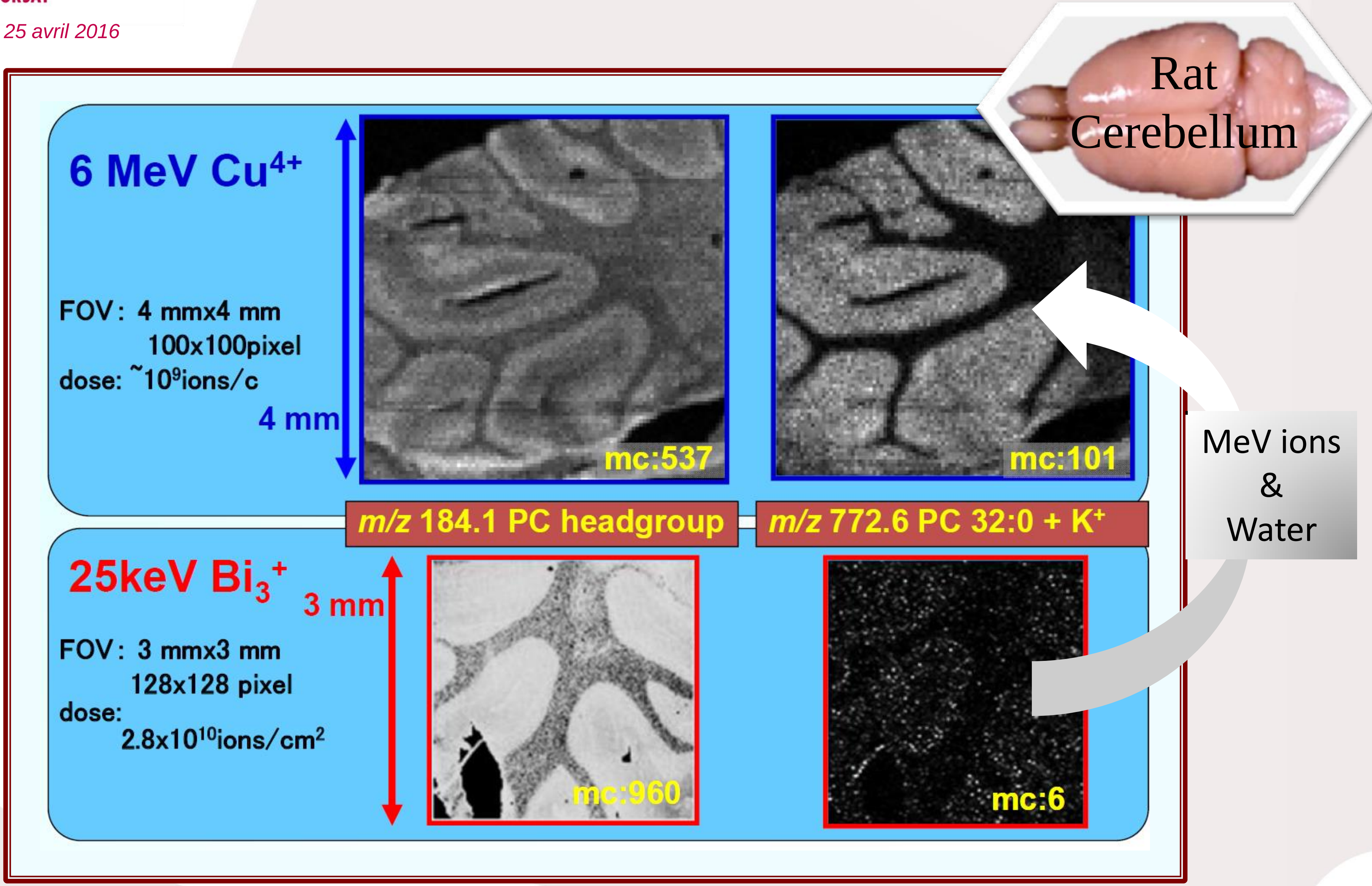
The Secondary Ion Mass Spectra of Angiotensin II using various primary ions and energies



Brian N. Jones[a*], Jiro Matsuo[b,c], Yoshihiko Nakata[d], Hideaki Yamada[d], John Watts[e], Steven Hinder[e], Vladimir Palitsin[a] and Roger Webb[a]

Surf. Interface Anal. **2011**, *43*, 249–252

COMPARISON KEV CLUSTER-SIMS & MEV-SIMS

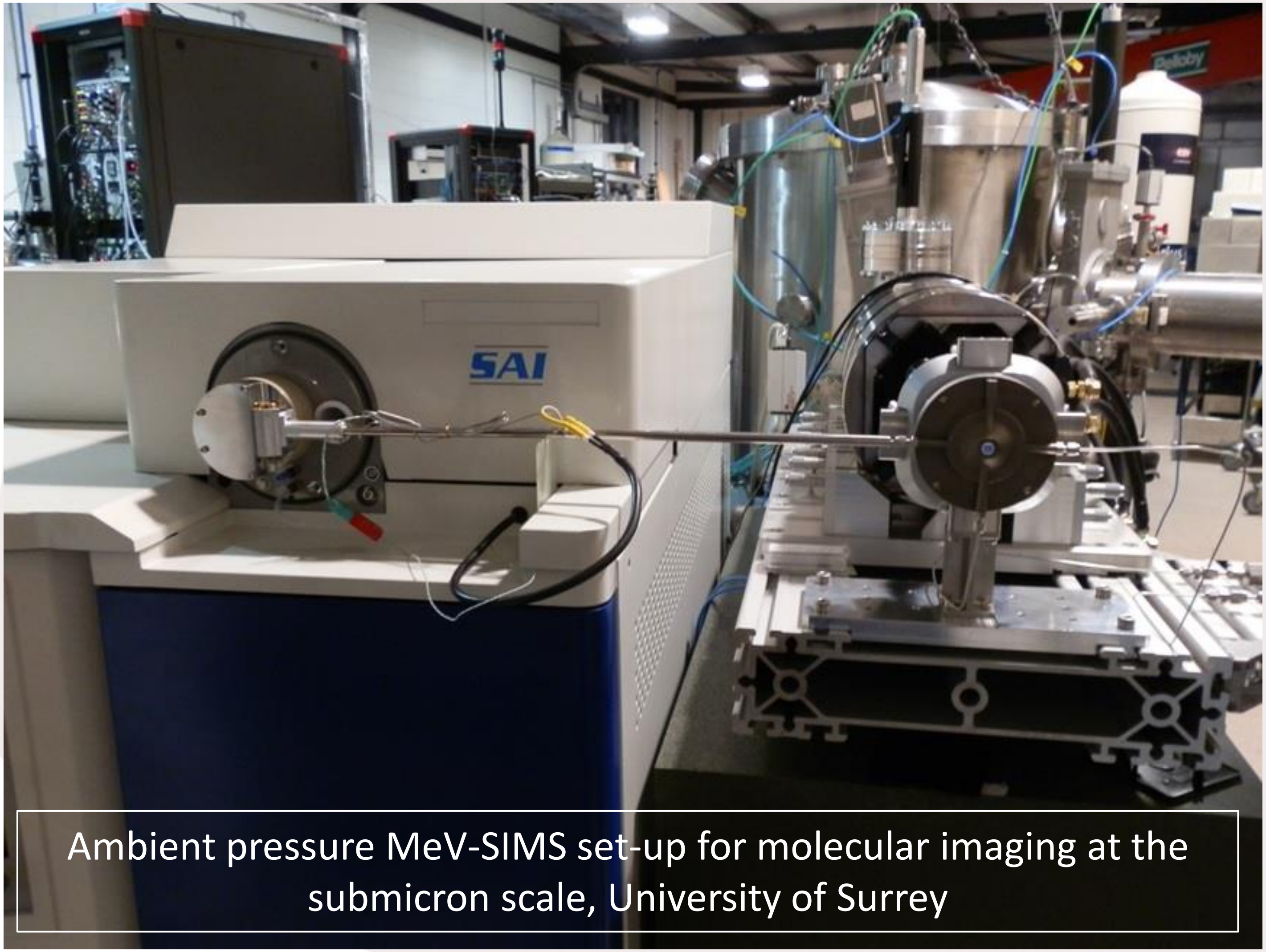


T Seki et al NIM B. Volume 332, 2014, Pages 326–329

IPN
INSTITUT DE PHYSIQUE NUCLÉAIRE
ORSAY

lundi 25 avril 2016

AMBIENT PRESSURE MEV-SIMS



Ambient pressure MeV-SIMS set-up for molecular imaging at the submicron scale, University of Surrey

https://nucleus.iaea.org/sites/accelerators

FORENSIC ANALYSIS AT SURREY

Dr Melanie Bailey
Department of Chemistry, University of Surrey, Guildford, UK

For fingerprint:
SIMS : high resolution imaging in situ, relative quantification, depth profiling
MeV SIMS : similar to SIMS, + in air analysis

GSR :
PIXE + MeV SIMS could give enhanced discrimination of GSR particles from different sources or for Pb-free ammunition
PIXE can solve isomeric interferences with SIMS
MeV SIMS : in air analysis is possible :

General conclusion
MeV SIMS could be useful in forensic science for applications where molecular imaging in air analysis is necessary
Deposition sequences
Fingerprint imaging
Chemical profiling of fingerprints
Gunshot residue analysis (GSR)

MJ.Bailey, B.N.Jones, S.Hinder, J.Watts, S.Bleay & R.P.Webb, Nucl. Instrum. & Meths. B, 268(11), 1929-1932, (2010)
N.J.Bright, R.P.Webb, S.Bleay, S.Hinder, N.I.Ward, J.F.Watts, K.J.Kirkby & M.J.Bailey, Anal. Chem., 84(9), 4083-4087, (2012)

Information	MALDI MS	SIMS	Ambient MS	NanoSIMS	MeV SIMS	LA-ICP-MS
Spatial resolution	10 μm	> 200 nm for organics	> 50 μm. Sub-micron in development.	50 nm	1 μm	> 100 μm
Size molecules detected	Up to ~ 150 kDa (large proteins)	Up to ~ 2 kDa (small peptides)	Up to ~ 50 kDa (medium proteins)	elemental	Up to ~ 10 kDa (large peptides)	elemental
3D ability	To be developed	Yes (5 nm depth resolution)	Potential to be developed	Yes	Potential to be developed	Some
Ambient and real time	Some (AP-MALDI)	×	✓	×	✓	×
Portable	Benchtop available	×	✓	×	×	×
Quantitative	With internal standards but difficult	Relative quantification	With internal standards	Can be with isotopic labelling	Unknown **Relative Quantification**	✓

G. Spoto and G. Grasso; spatially resolved mass spectrometry in the study of art and archeological objects, Trend in Analytical Chemistry, 2011, 30, 856-863

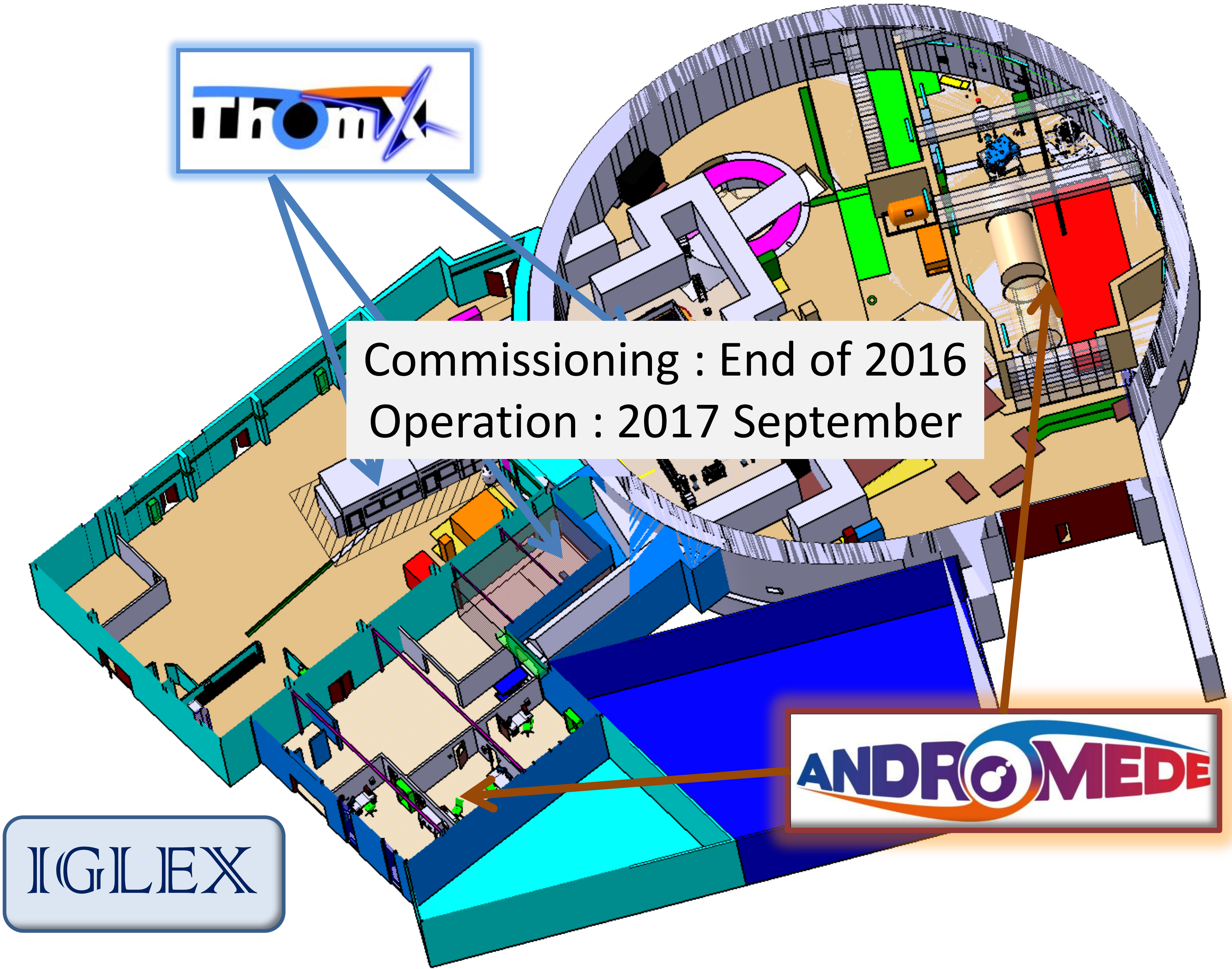
SUMMARY

High secondary ion yields are obtained with swift heavy ions in the MeV range. *MeV cluster beams are probably better*

Molecular imaging has been demonstrated with µm resolution by using heavy atomic ions. *Next step MeV cluster beams*

Heavy ion microprobe works at high pressure (a few tens to hundreds Pa) & permits to obtain ion imaging of tissues at the µm level. Natural matrix: the water is a good help for this analysis. *Next step : MeV nanoparticles in air without window*

Simultaneous complementary analysis under vacuum or in air with µ-IBA techniques (good quality images) give elemental composition and quantitative measurments.


ThomX
Commissioning : End of 2016
Operation : 2017 September
ANDROMEDE
IGLEX