PIXE

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PIXE TALKS (I)

Morning Lectures will cover:-

PIXE Overview

- Ion - atom interactions
- Vacancy production
- ECPSSR K, L shell ionisation theory
- Ion transport

PIXE TALKS (II)

PIXE Systems

- PIXE end station designs
- Current measurement
- X-ray detection
- PIXE spectra, escape peaks
- PIXE electronics, pileup, sum peaks
- Filters and spectrum shaping
- Spectrum analysis, line shapes, backgrounds
- Peak areas to concentrations
- PIXE system calibrations
- X-ray detectors, efficiency

PIXE TALKS (III)

PIXE Analysis Methods

- DOPIXE Code,
- Peak areas,
- Elemental concentrations,
- Calibrations,
- For thin and thick samples.

PIXE

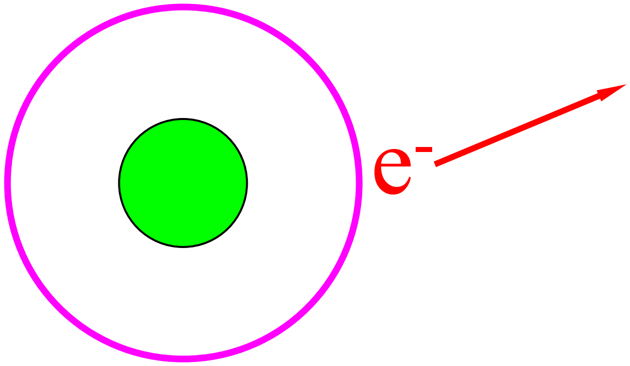
Particle Induced X-ray Emission -

PART I

An Overview - Ion-Atom Interactions with Matter

Question - *What is an ion?*

What is an ion ?



Atom

e^-

electron
ejected

proton -	H^+
alpha -	He^{2+}
gases -	Ne^+
metal -	Ti^{2+}

Ion Energy

E = q*V

for example for 12 MV acceleration voltage,

H^+ ion gives 12 MeV

Cl^{10+} ion gives 120 MeV

Ion Currents

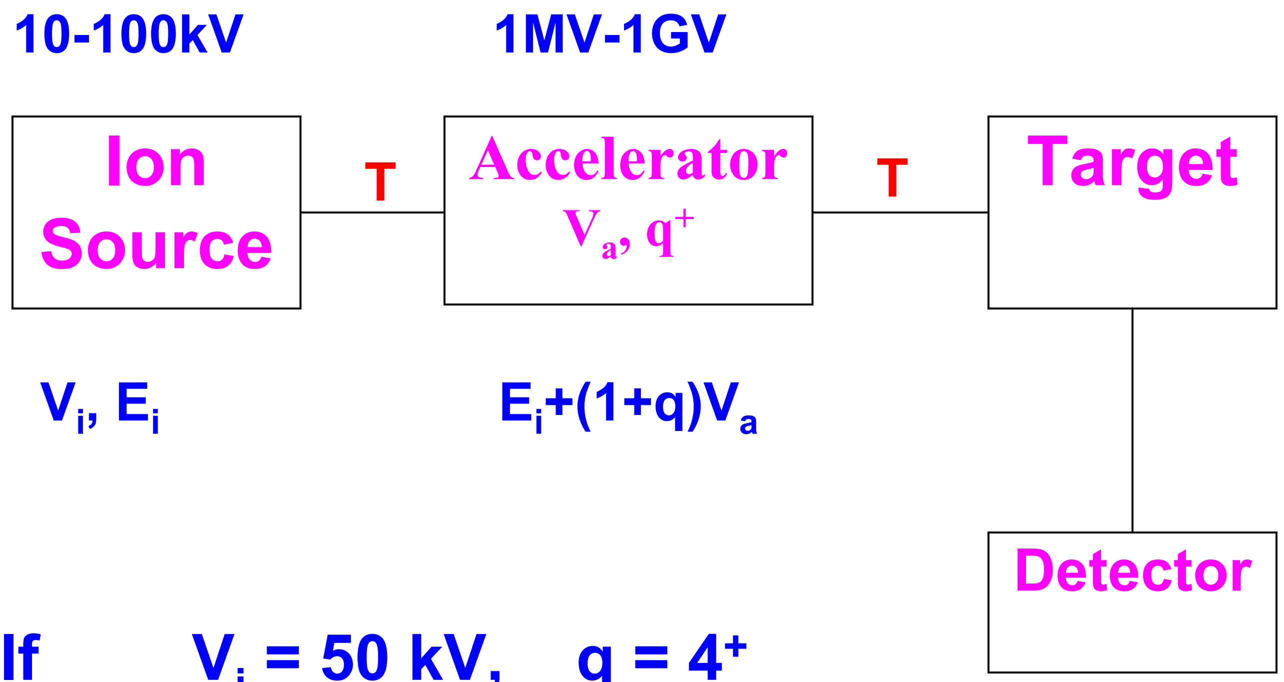
I = Q/t   Charge Q = qe

N/t = I/(qe) is number of ions/ sec

1 pA = 6×10^6 ions/sec (q=1)

100 µA = 6×10^{14} ions/sec (q=1)

Ion Acceleration & Transport



10-100kV

1MV-1GV

Ion Source

T

Accelerator

V_a, q^+

T

Target

V_i, E_i

$E_i+(1+q)V_a$

Detector

If $V_i = 50$ kV, $q = 4^+$

$V_a = 8$ MV

Then

$E_{target} = 40.05$ MeV

Power

P = I*V

For example, 1 μA of protons from a 3 MV accelerator will produce 3W of power in the target over the beam area.

Ion Velocity

$v = 1.384\times10^{9} * \mathrm{sqrt}(E/M)$ cm/s

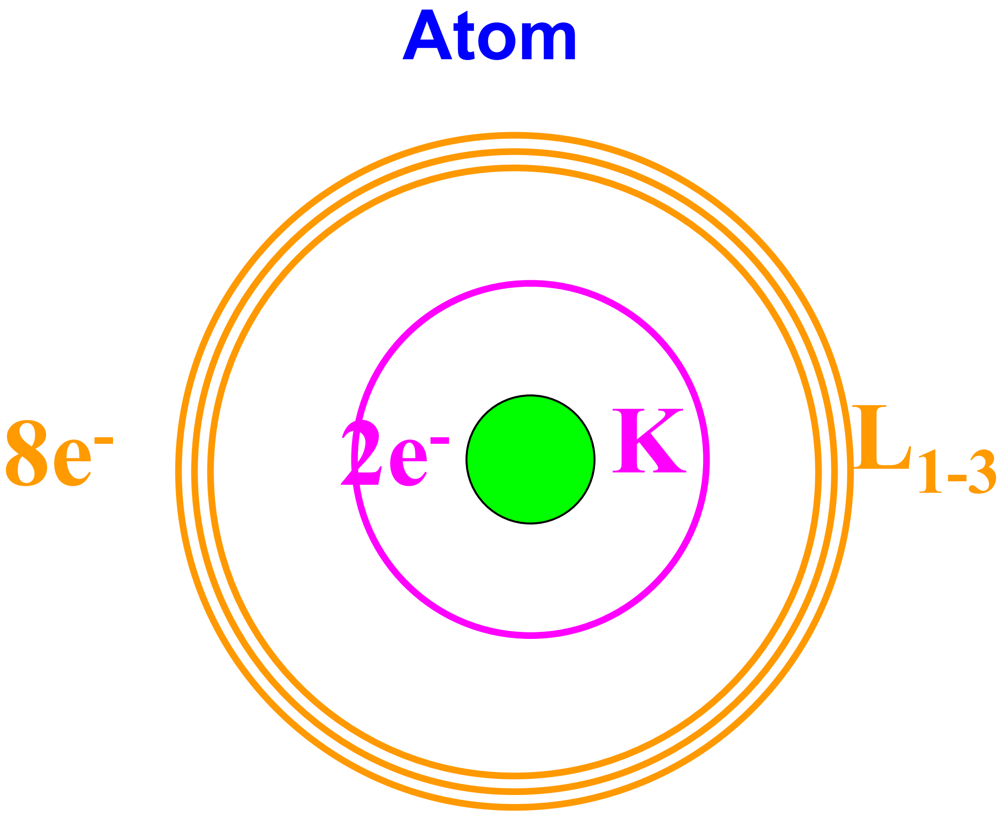
$(v/c) = 0.046 * \mathrm{sqrt}(E/M)$

where E in MeV and M in amu

1 MeV proton 4.6% of c

120 MeV ^{36}Cl ion 8.4% of c

What is an atom ?



Shell radius $a_n = 0.53(n^2/Z) \sim 0.5$ Å

Nuclear radius $R = R_0A^{1/3} \sim 10^{-5}$ Å

Electron Velocity

For atomic electrons,

$$(v/c) = Z/(137n)$$

where n is the principal quantum number.

For H K shell (v/c) = 0.7%

For Pb K shell (v/c) = 60%

So ion velocities from accelerators comparable with loosely bound electron velocities.

velocity matching !!

Atomic Sizes

Z	K Shell Radius Å	Atomic Radius Å
H	0.53	0.53
He	0.27	0.27
Cl	0.031	M 0.28
Pb	0.006	P 0.23

For H and He on Pb their K shells are outside the Pb atomic radius so the charge state is not important.

There are two distinct regions, inside/ outside the atom

Distance of closest approach d is small,

$$2d = 2Z_1Z_2/\{M_1M_2v^2/(M_1+M_2)\}$$

e.g. for 1 MeV protons on Au d = 0.002 Å

Time Scales

Atom	Energy (keV)	(v/c)	Lifetime (secs)
Si Kα	1.74	0.10	2.0×10^{-13}
Si Lα	0.12	0.036	1.6×10^{-10}
Pb Kα	75	0.60	1.1×10^{-17}
Pb Lα	10.6	0.28	1.6×10^{-16}

(i) Collision times < Lifetimes of states.

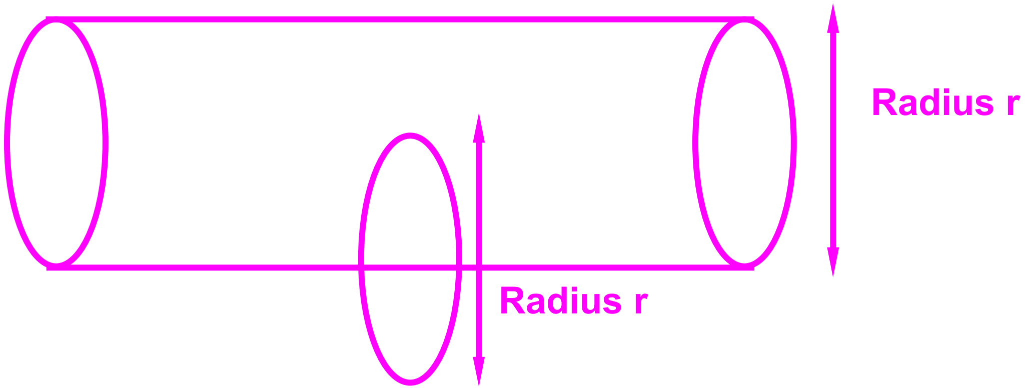
(ii) Max ionisation cross sections for velocity matching of removed electron and bombarding ion.

Ion	Energy (MeV)	(v/c)	Fly past Si (L) secs	Fly past Pb(L) secs
H^+	1.0	0.046	3×10^{-18}	4×10^{-19}
	3.0	0.080	2×10^{-18}	2×10^{-19}
He^+	1.0	0.023	7×10^{-18}	8×10^{-19}
	3.0	0.040	4×10^{-18}	5×10^{-19}

What is a cross section ?

It is an interaction area

Area cm^2 10^{-24} cm^2 = 1 barn



For the H atom,

Area = $\pi r^2 = \pi\ (0.5 \times 10^{-8})^2$ cm^2

= 7.9×10^{-17} cm^2

= 79 Mb

For the nucleus,

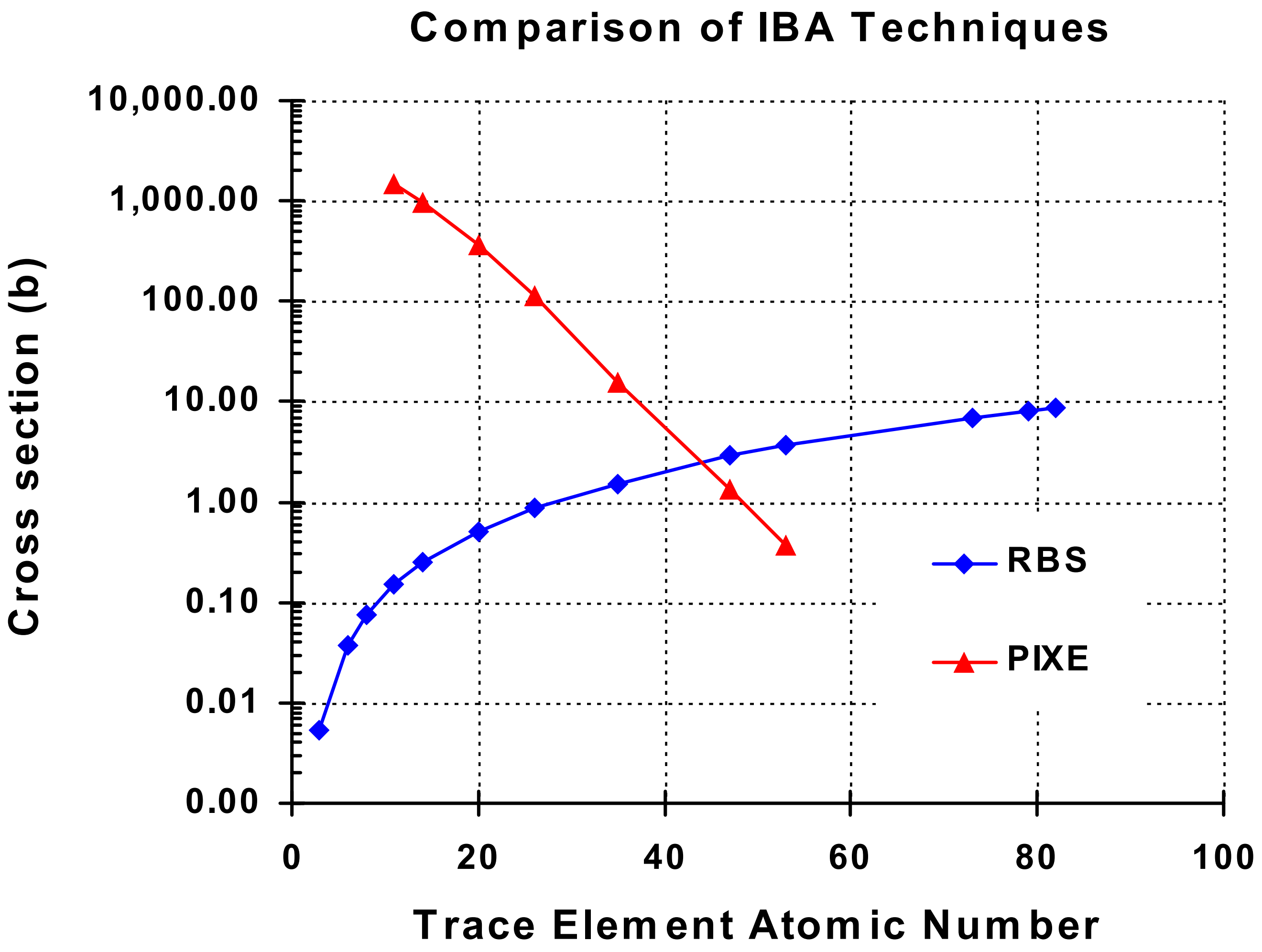
Area = $\pi r^2 = \pi\ (10^{-13})^2$ cm^2

= 3.1×10^{-26} cm^2

= 31 mb

9 orders of magnitude !

Ion-Atom Cross Sections



PIXE ideal for low Z elements

RBS ideal for heavy elements in a light matrix

How Far Does an Ion Travel ?

- Charged particles interact with matter through the electron cloud and the nucleus.

- The electron cloud acts as a drag force on the ion slowing it down and reducing its energy - this is called electronic stopping.

- Eventually the ion energy becomes low enough for the ion to have a reasonable chance of interacting directly with the target nucleus - this is called nuclear stopping.

- The range of an ion is the integral of the stopping power over all energy losses.

Proton in carbon,

Energy MeV	S_{total} keV/µm	$S_{electronic}$ keV/µm	$S_{nuclear}$ keV/µm
1	52.7	52.7	0.034
3	24.2	24.2	0.013

For alphas in carbon,

Energy MeV	S_{total} keV/µm	$S_{electronic}$ keV/µm	$S_{nuclear}$ keV/µm
1	427	427	0.47
3	248	248	0.18

Electronic stopping power is proportional to Z^2 for the same velocity ion.

The corresponding ranges are:

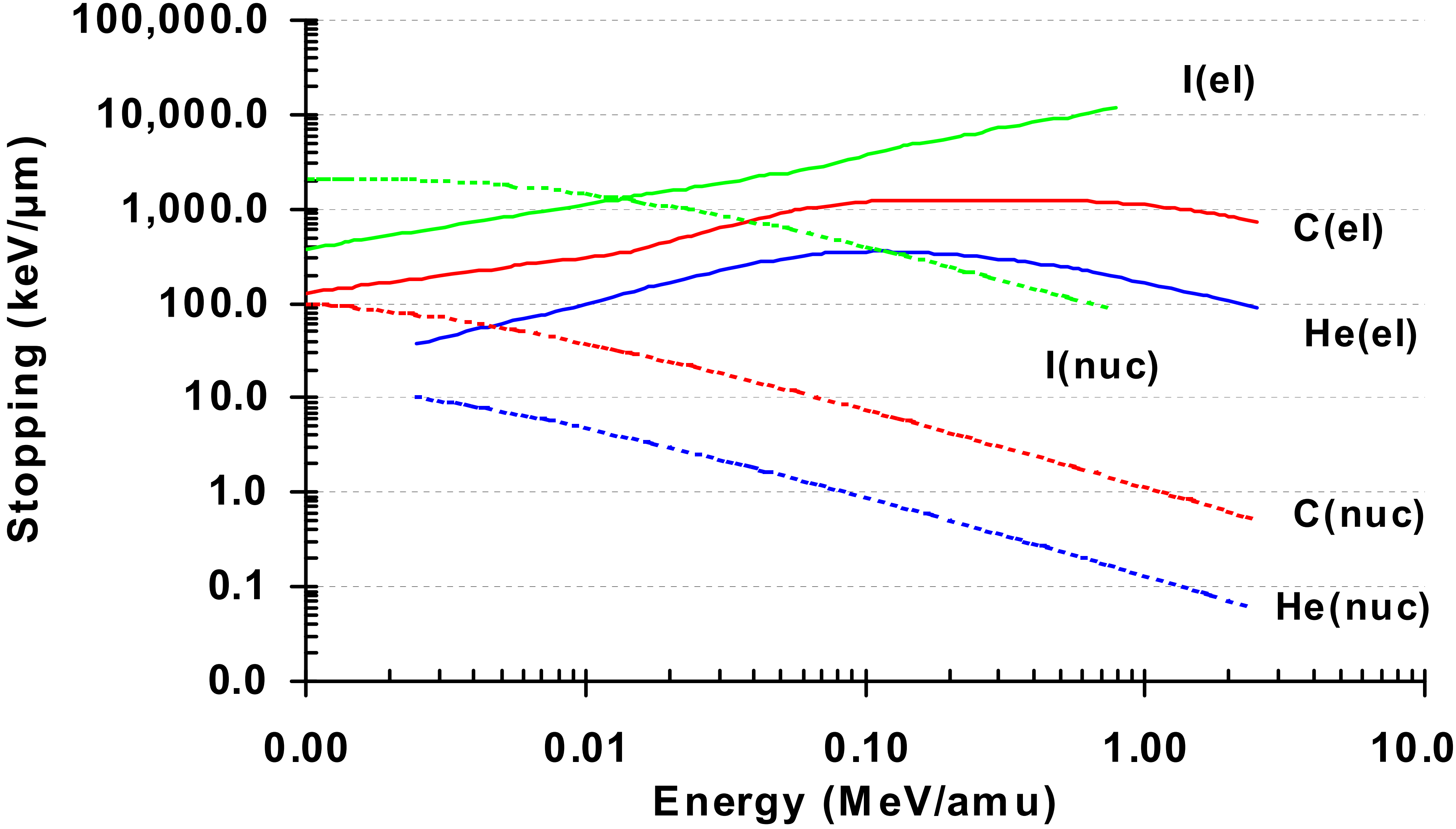
For protons in carbon,

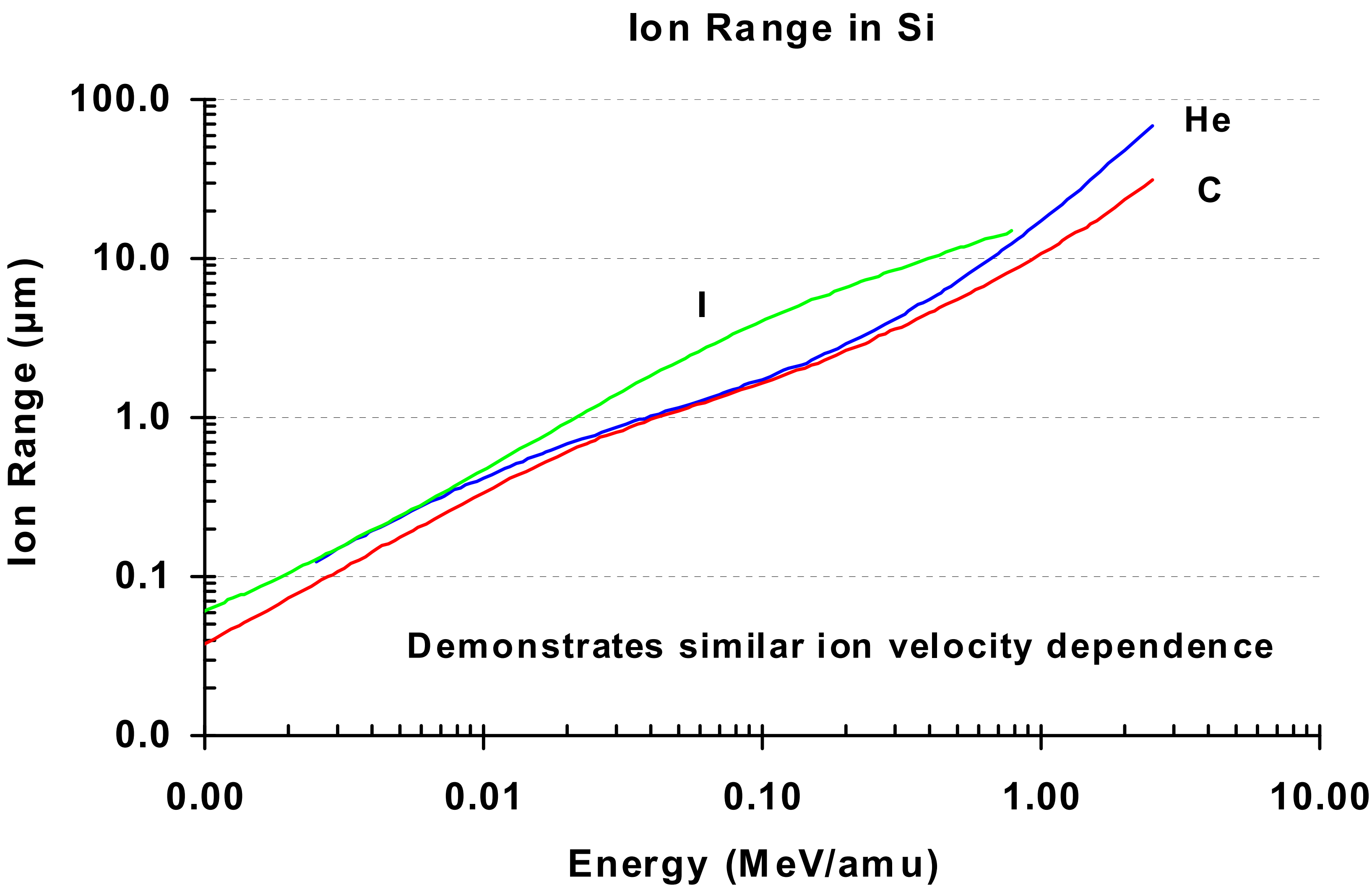
Energy MeV	R_{proj} µm	$Strag_{long}$ µm	$Strag_{lat}$ µm
1	12.3	0.53	0.44
3	73.5	2.8	2.2

For alphas in carbon,

Energy MeV	R_{proj} µm	$Strag_{long}$ µm	$Strag_{lat}$ µm
1	2.63	0.12	0.14
3	9.00	0.30	0.23

Ion Stopping in Si



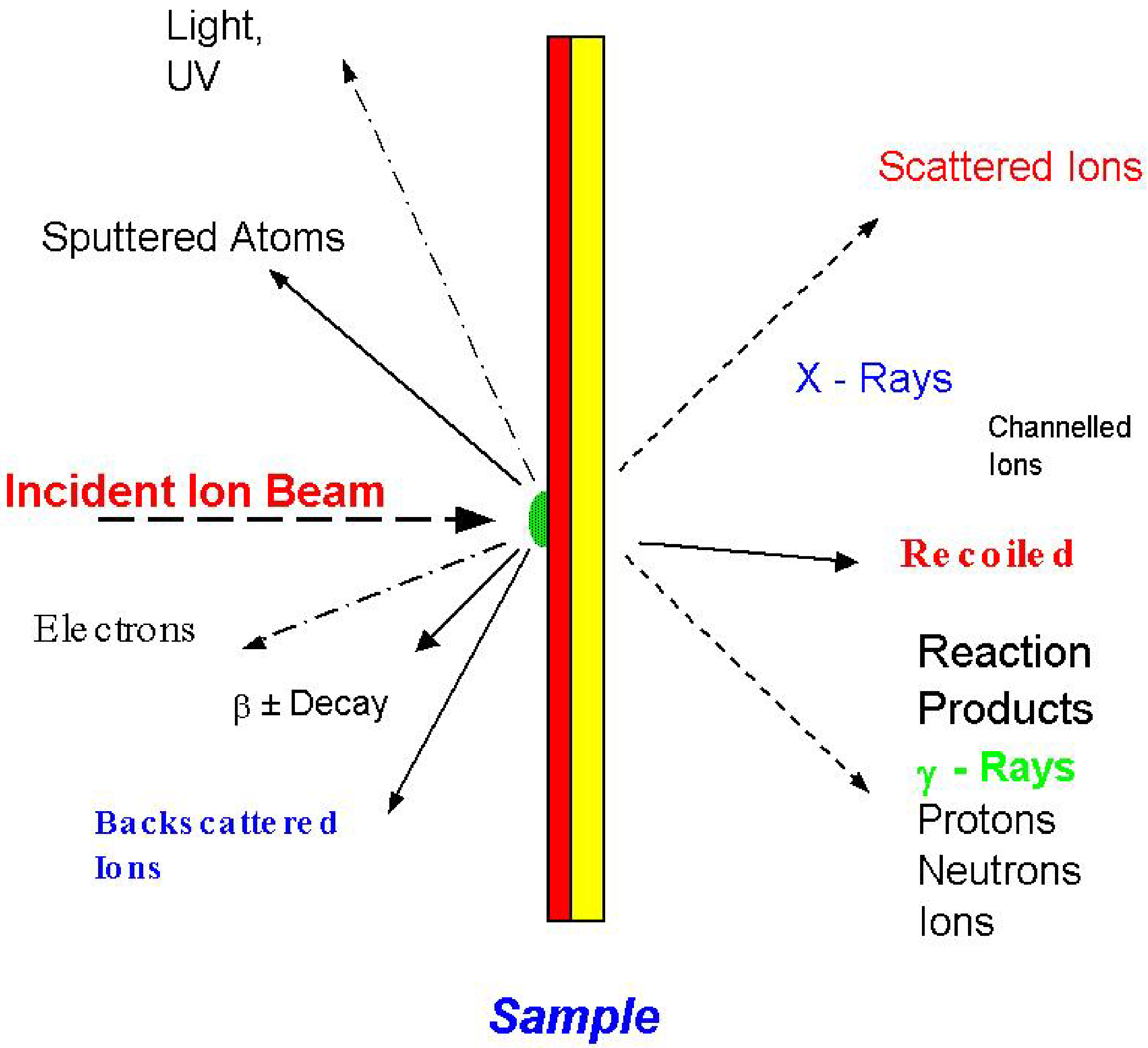


Typical ranges for PIXE are therefore from 1 to 100 µm only, depending on the ion and its energy.

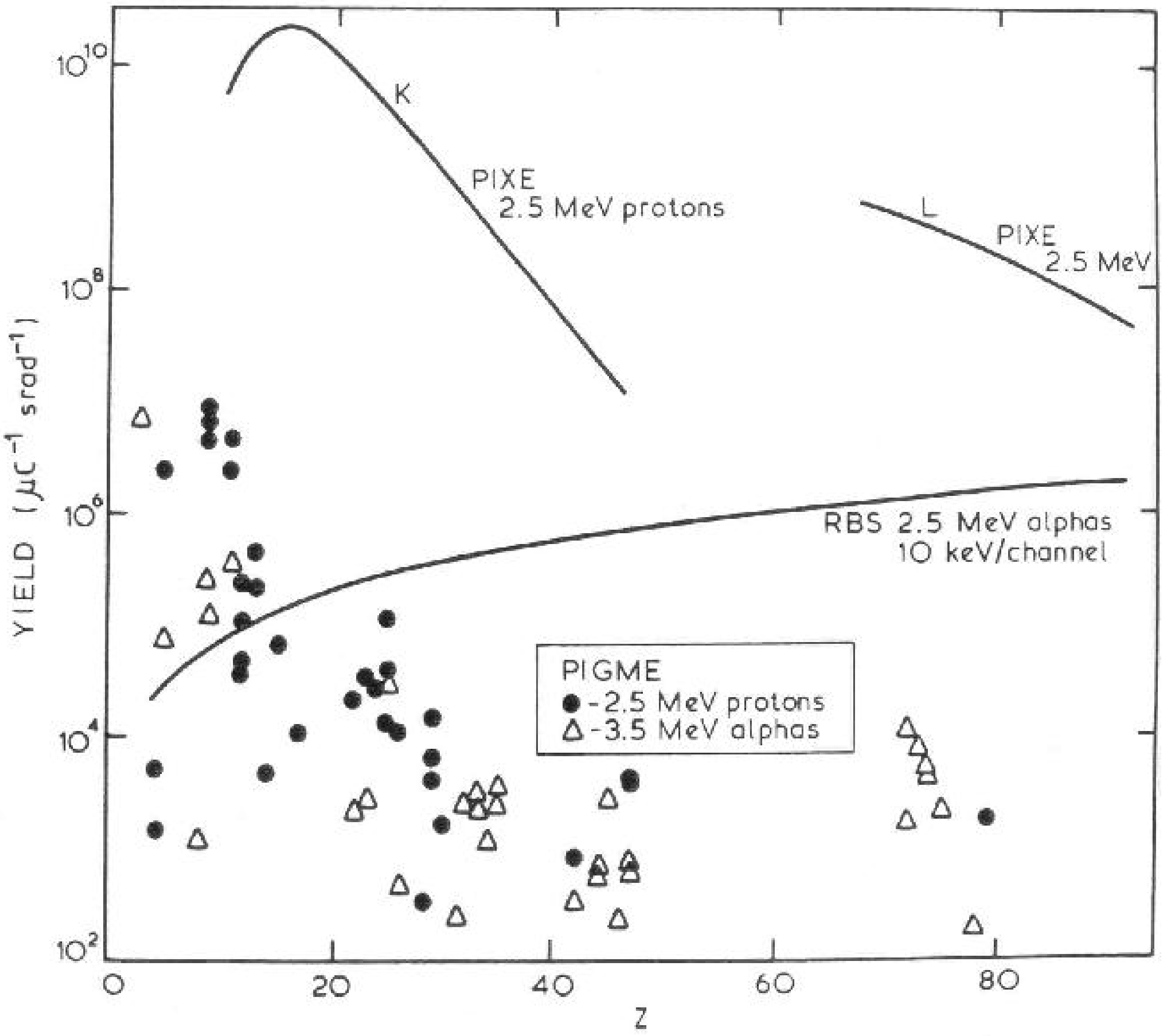
Now we know:-

(i)	What an ion is
(ii)	What an atom is
(iii)	Interaction times scales
(iv)	How far ions travel in matter

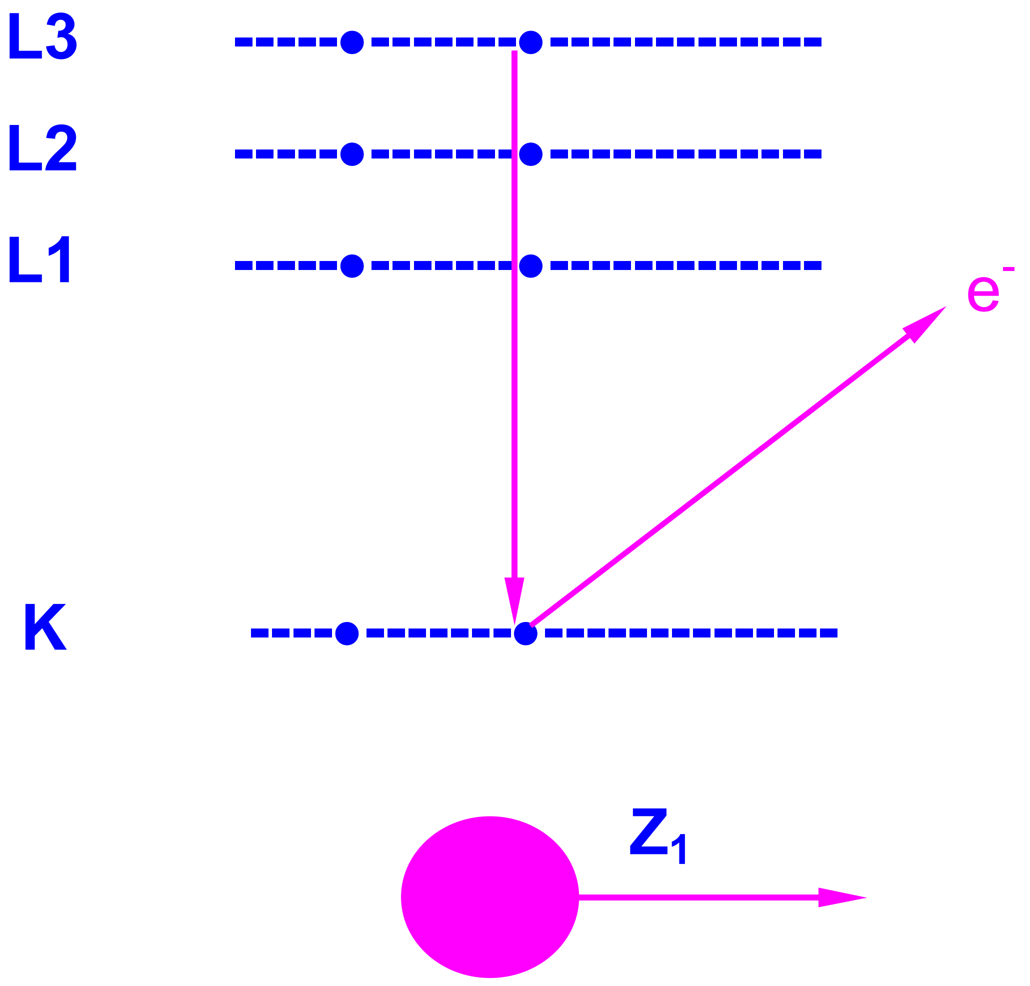
Ion Beam Interactions



Relative Yields for PIXE, PIGE, RBS

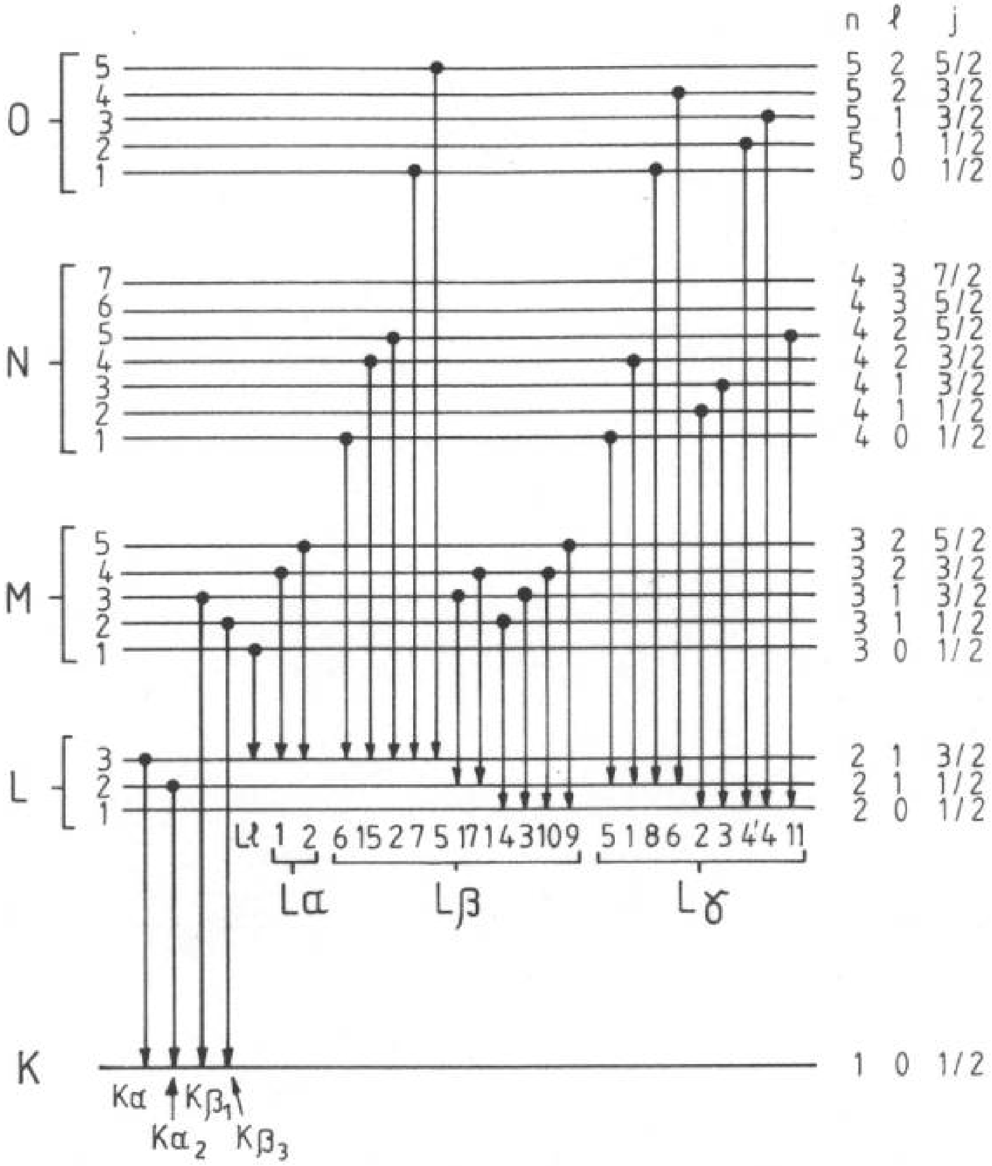


Direct Ionisation – what is it?



Holes, X-rays, Lifetimes

X-ray Transitions

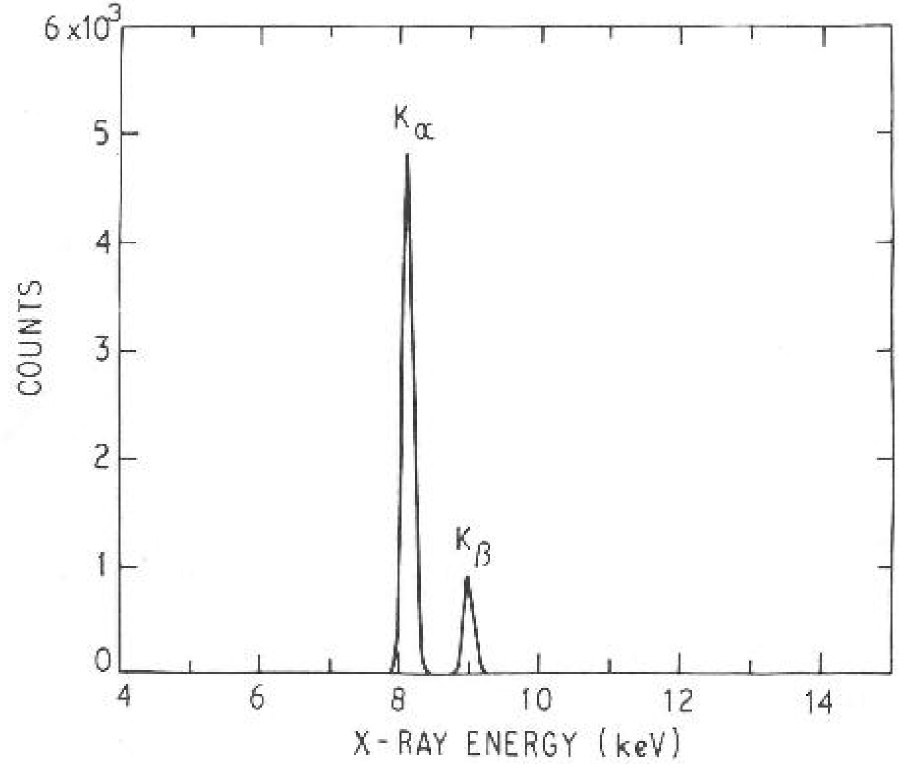


Allowed E_1 transitions
$\Delta l = \pm 1$, $\Delta j = 0, \pm 1$

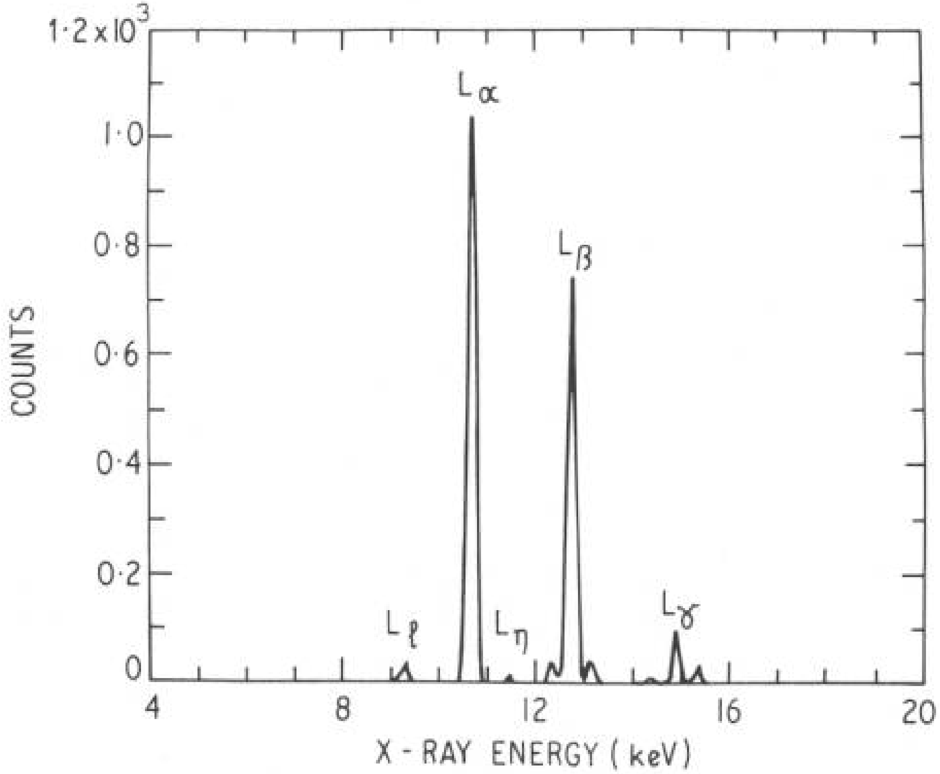
Number of electrons per sub-shell = $2(2l+1)$

Observable X-ray transitions for WDS system, K ~ 8, L ~ 25, M ~ 40.

CuK Shell X-ray Spectrum

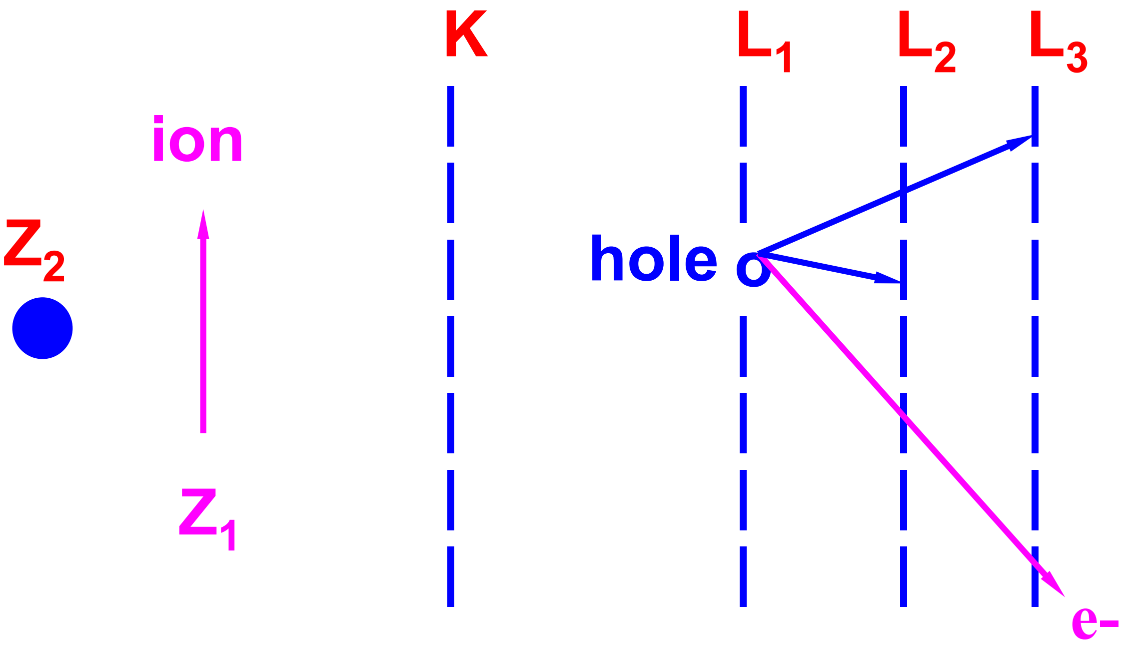


PbL Shell X-ray Spectrum



2.6 MeV protons.

Coster Kronig Transitions



PbL $f_{12} = 0.120$ for L_1 to L_2

$f_{23} = 0.116$ for L_2 to L_3

$f_{13} = 0.580$ for L_1 to L_3

- Ion Z_1 moving past atom creates an electron hole
- Wavefunctions overlap – holes move
- Lifetimes of states >> hole flipping time
- f_{ij} is the transition probability of hole jumping from subshell i to j in the same shell.

Ionisation Theories

(i) 1970's Binary Encounter Approximation (BEA).

Based on binary collision between two moving particles.

Energy/ momentum transferred to the electron.

Generally poor for low ion velocity near binding energy.

(ii) Semi-classical approximation (SCA), 1958-1970's

Coulomb interaction - electron excited to bound or continuum states.

Ion has hyperbolic path.

Cross section based on impact parameter giving close/ distant collisions.

Provides a good classical picture.

Good when $Z_1 << Z_2$ and $(v_1/v_2) << 1$

Ionisation Theories (cont.)

(iii) 1958 Merzbacher/ Lewis Plane Wave Born Approximation (PWBA).

Interaction is plane wave in/ out $(v_1/v_2) >> 1$,

1st order theory.

Works for $(v_1/v_2) \sim 1$

PWBA picked up by Brandt & Lapicki through 1970’s and 1980’s.

Developed ECPSSR corrections to PWBA so it works for $(v_1/v_2) < 1$.

E - Energy loss $\Delta E << E$

C - Coulomb correction, hyperbolic path not a straight line.

PSS - Perturbed stationary states

R - Relativistic inner electrons

The PWBA cross section is given by,

$$\sigma_s^{PWBA} = \sigma_{0s}\theta_s^{-1}F_s(\eta_s/\theta_s^2,\theta_s),$$

where,

$$\sigma_{0s} = 8\pi a_0^2(Z_1^2/Z_{2s}^4) \text{ and,}$$

$$F_s(\eta_s/\theta_s^2,\theta_s) = (\theta_s/\eta_s)f_s(\eta_s,\theta_s),$$

Where $f_s(\eta_s,\theta_s)$ is a double integral over the energy and momentum transferred to the ejected s electron. θ_s and η_s are the dimensionless electron binding energy and reduced ion energies respectively.

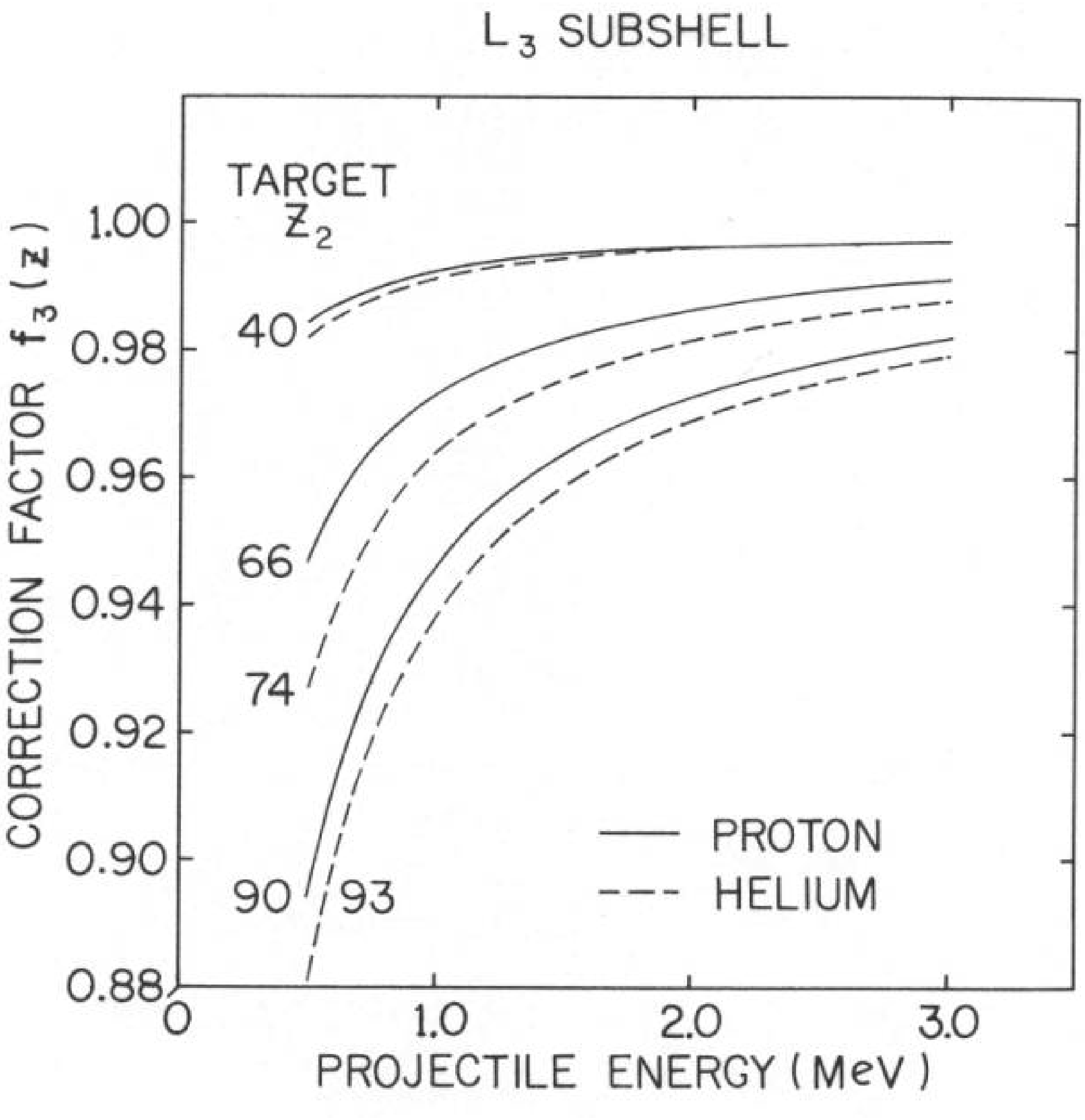
Tabulations for protons and helium ions from 100 keV to 10 MeV can be found in *D. Cohen and M. Harrigan, Atomic Data and Nuclear Data Tables 33 (1985) 255-343*

Energy Loss Effect (E)

- For slow moving ions ΔE is not $<< E_{in}$
- Need to change the limits in the form factor integrals of energy and momentum transfer from 0 to ∞ to ΔE to E_{in}
- Brandt and Lapicki account for this with a multiplicative correction factor $f(z_s)$.
- $f(z_s)$ is a function of the distance of closest approach and the minimum momentum transferred during the collision.
- $f(z_s) < 1$

This term is important for slow heavy ion collisions.

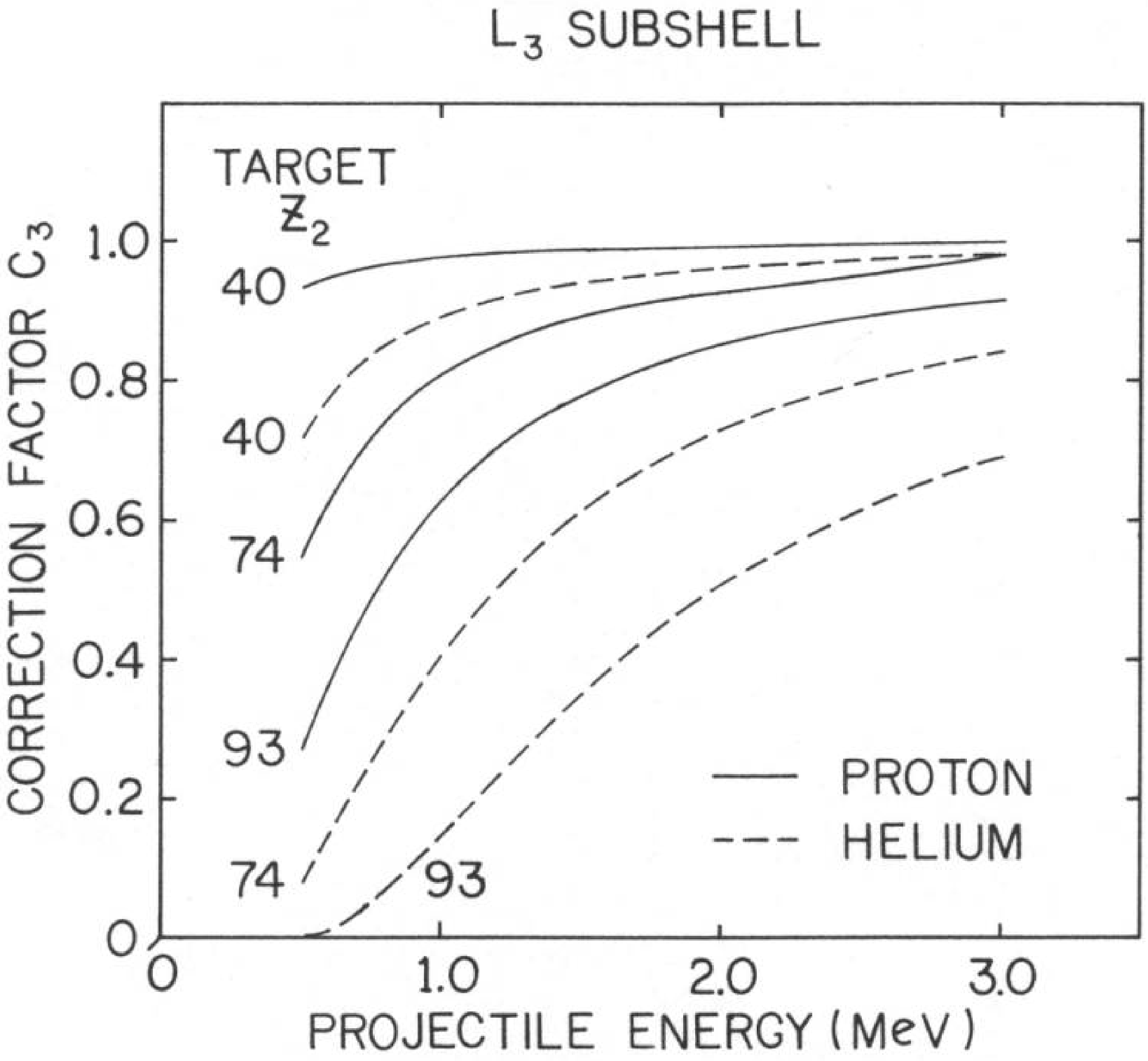
Energy Loss Corrections



Coulomb Correction (C)

- **Ion slows down as it approaches the target.**
- **Deviates from a straight line – hyperbolic.**
- **This reduces the ionisation cross section, especially for slow ions onto high Z targets.**
- **C is an exponential multiplicative factor, can reduce the PWBA cross sections by 10^{-4}.**

Coulomb Deflection Corrections



Perturbed Stationary States (PSS)

Presence of charged ion either inside or outside the atomic shells changes the binding energy (I_s) of shell s.

$$I_s \text{ (outside)} < I_s < I_s \text{ (inside)}$$

In the limit of very slow heavy ion collisions have a united atom with charge (Z_1+Z_2).

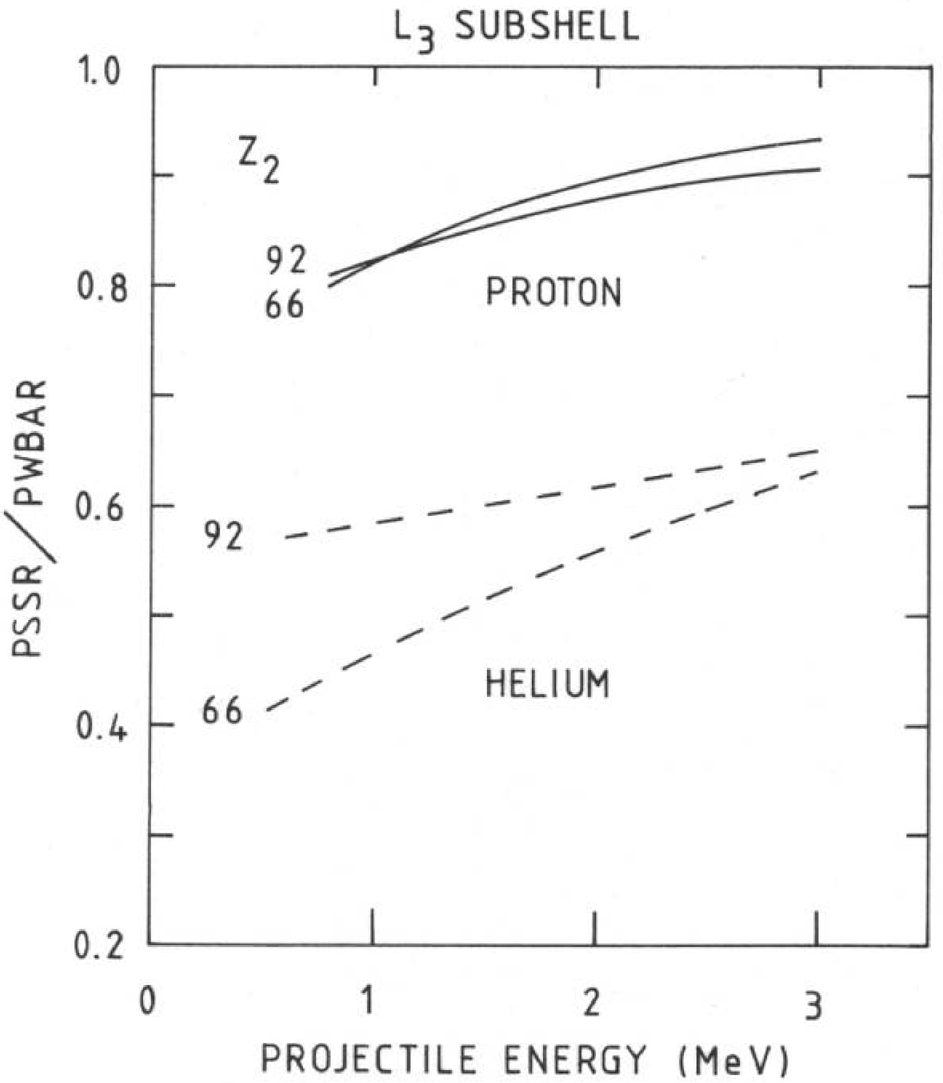
Most situations lie between these two extremes, so have to integrate over all impact parameters of the incoming ion.

This implies a binding transform from,

$$\theta_s \rightarrow \theta_s \xi_s$$

for each sub-shell s, where ξ_s is a function of (Z_1, Z_2, v_1, v_2) or order unity.

Binding Corrections



Relativistic Corrections (R)

Velocity of target inner shell electron s is,

$$v_{2s} = (Z_{2s}/137n)c$$

For PbK electrons $v_{2K} = 0.6c$ so need relativistic masses in equations. That is mass is a function of velocity.

Could also use relativistic wave functions.

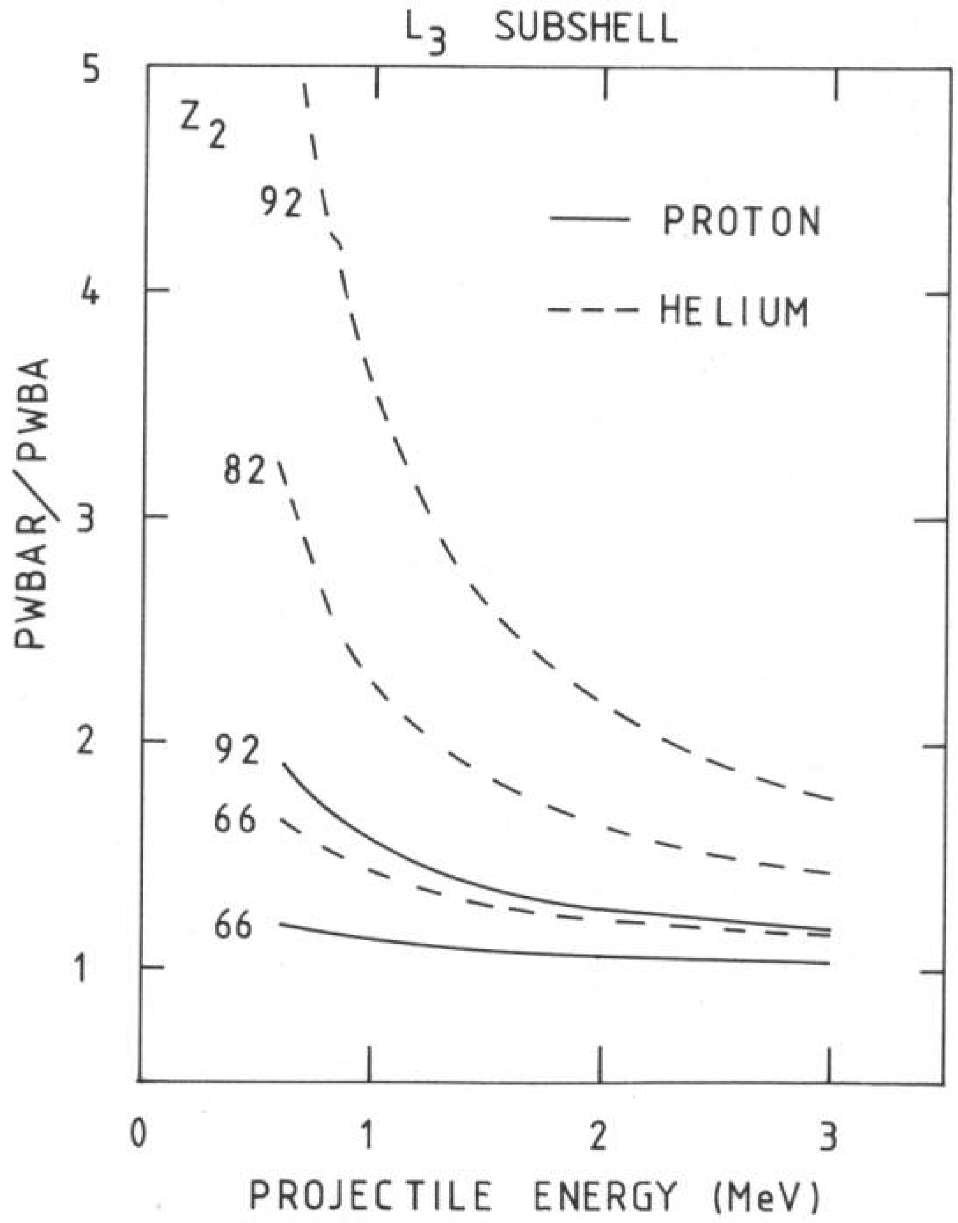
Relativistic corrections tend to increase the ionisation cross sections.

Obviously effects for K > L > M etc.

Note that relativistic and binding corrections have the opposite effect on the ionisation cross sections.

This accounts for some early success of the PWBA theory.

Relativistic Correction



Note that relativistic and binding corrections have the opposite effect on the ionisation cross sections.

This accounts for some early success of the PWBA theory.

ECPSSR K Shell Expt/ Theory

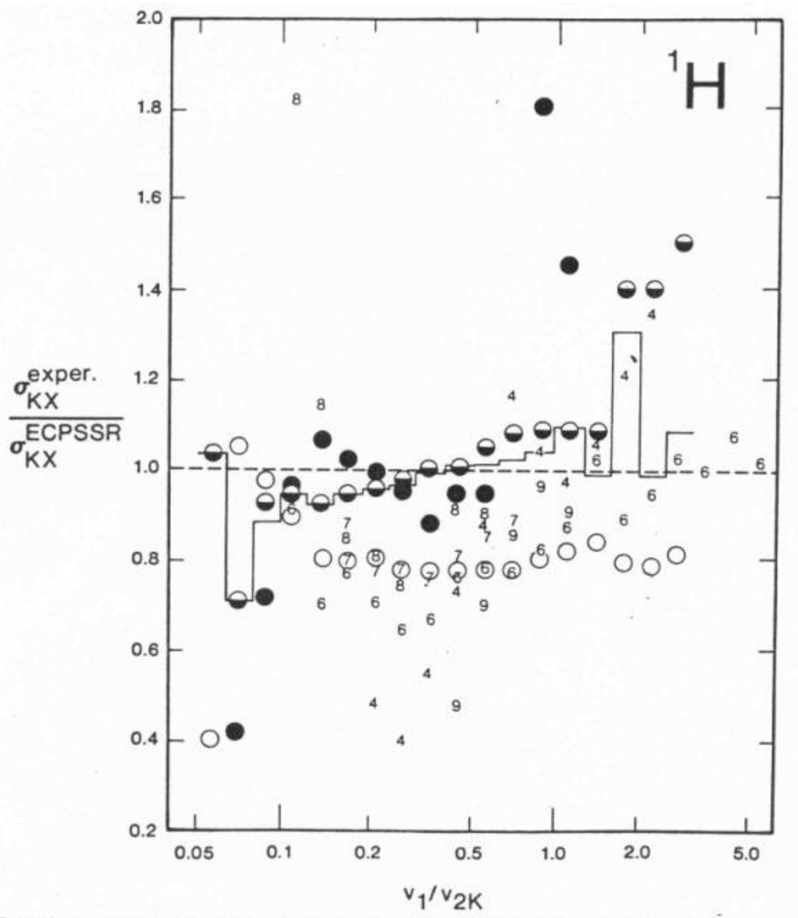


FIG. 6. Averaged [within the 0.1 intervals of log(v_1/v_{2K})] ratios of experimental cross sections to the ECPSSR predictions for relatively light (open circles), medium (half-open circles), and heavy (closed circles) target elements bombarded by protons. The solid curve is based on the averaged ratios for the $10 \leqslant Z_2 \leqslant 92$ targets; ratios for the $4 \leqslant Z_2 \leqslant 9$ elements are identified by the atomic numbers of these targets. The mean value of the solid curve is 0.96.

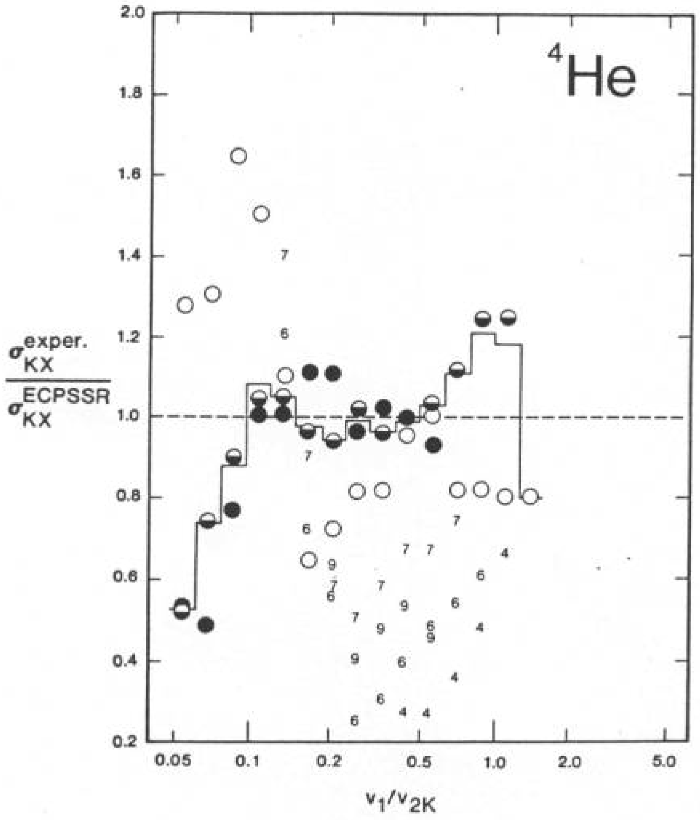
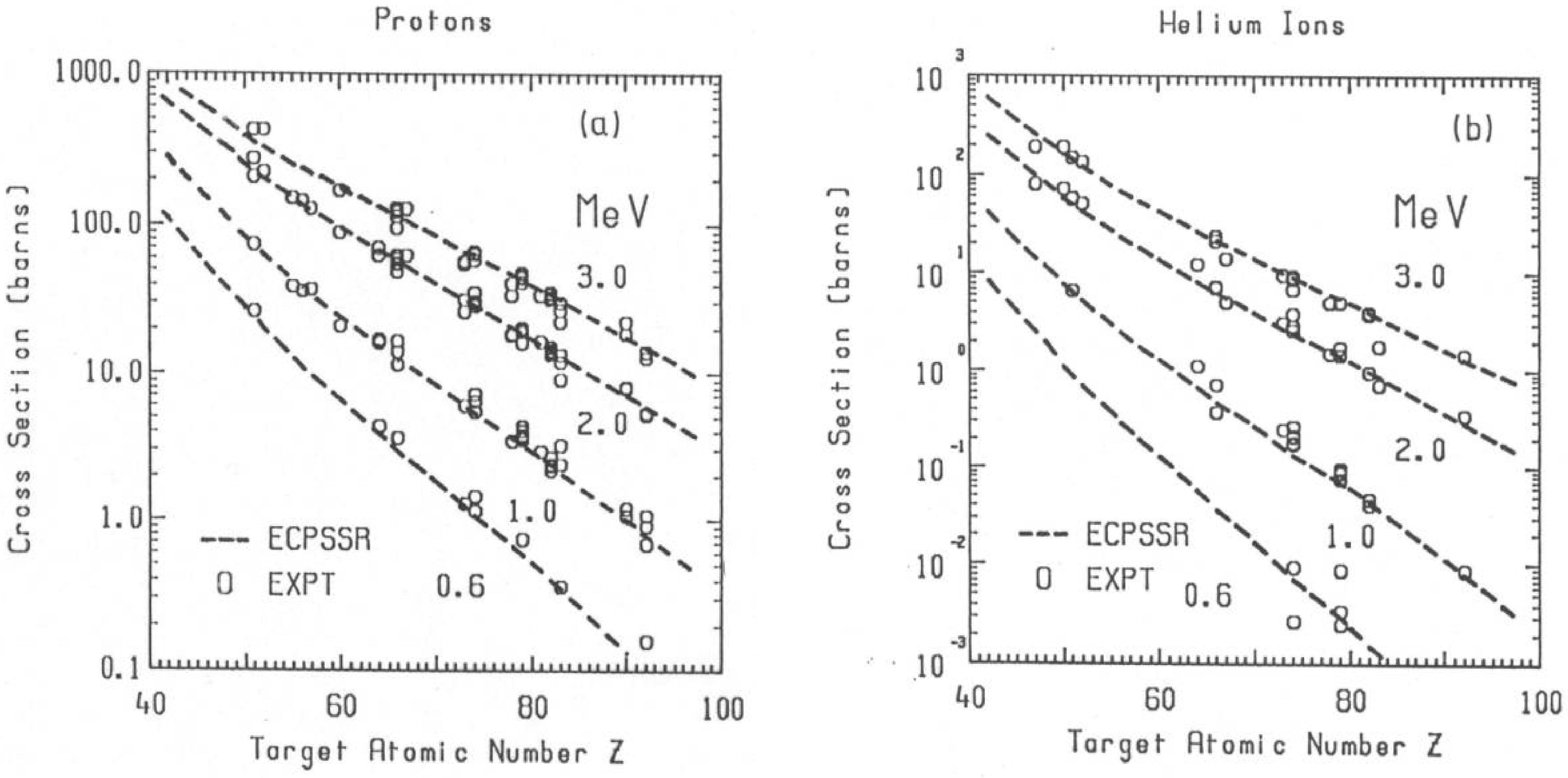


FIG. 9. Averaged [within the 0.1 intervals of log(v_1/v_{2K})] ratios of experimental cross sections to the ECPSSR predictions for light (open circles), medium (half-open circles), and heavy (closed circles) target elements bombarded by ^{4}He ions. The solid curve is based on the averaged ratios for the $10 \leqslant Z_2 \leqslant 92$ targets; ratios for the $4 \leqslant Z_2 \leqslant 9$ elements identified by the atomic numbers of these targets. The mean value of the solid curve is 1.00.

J. Phys. Chem. Ref. Data, Vol. 18, No. 1, 1989

Protons, He ions on L shell



X-ray Production

Previously we discussed vacancy production, known as Direct Ionisation (DI)

We do not measure σ(DI) directly.

The X-ray production cross section, σ(X), is related to σ(DI) through the fluorescence yield ω, where $0 \leq \omega \leq 1$.

For the K shell:

$$\sigma(X) = \omega_K \, \sigma(DI)$$

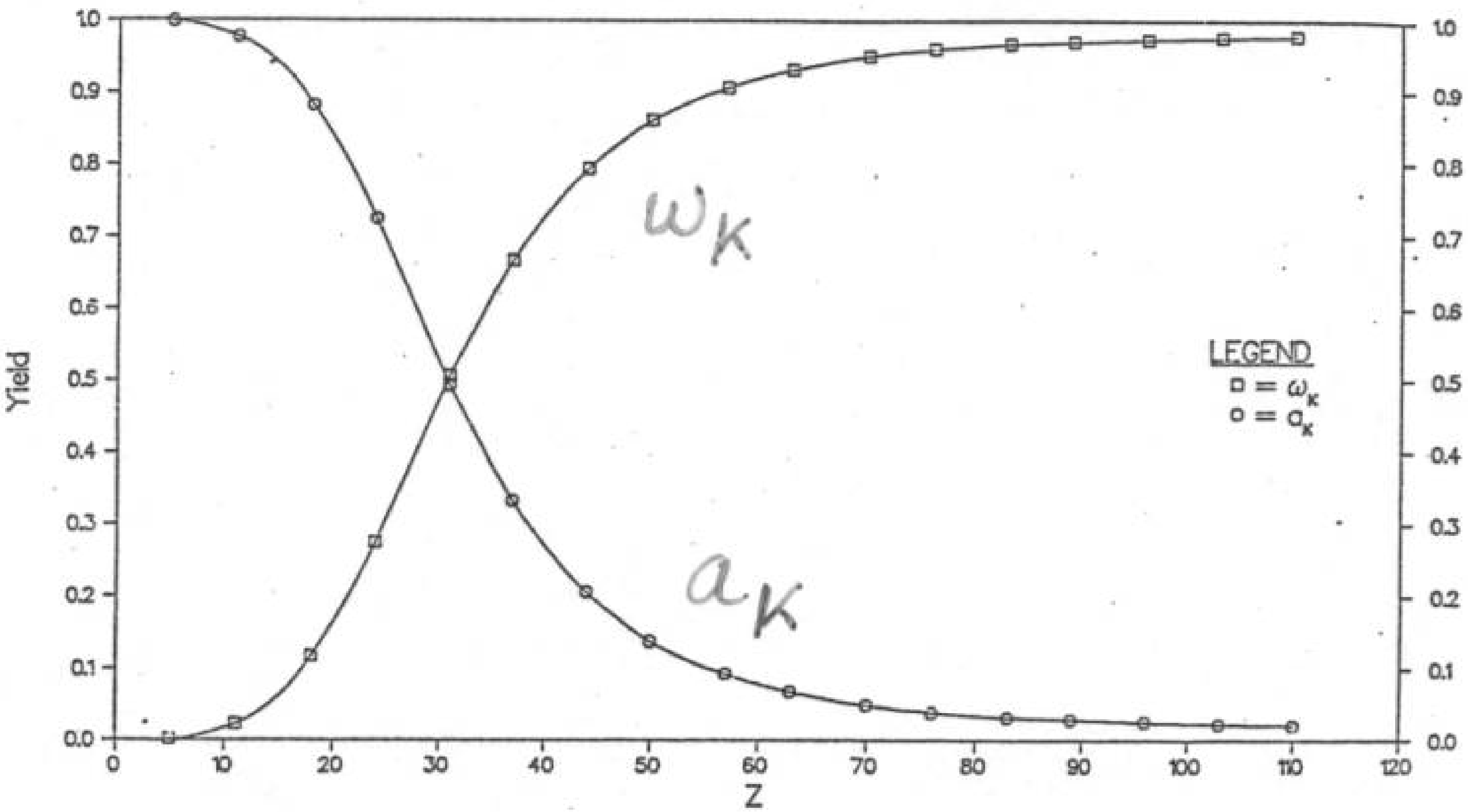
There is a complementary radiationless process also operating at the same time. This is known as the Auger electron process.

$$\sigma(\text{Auger}) = a_K \, \sigma(DI)$$

and

$$\omega_K + a_K = 1$$

K Shell Fluorescence Yields ω_K



For the L Shell:

As with the K Shell you can not measure σ(DI) directly.

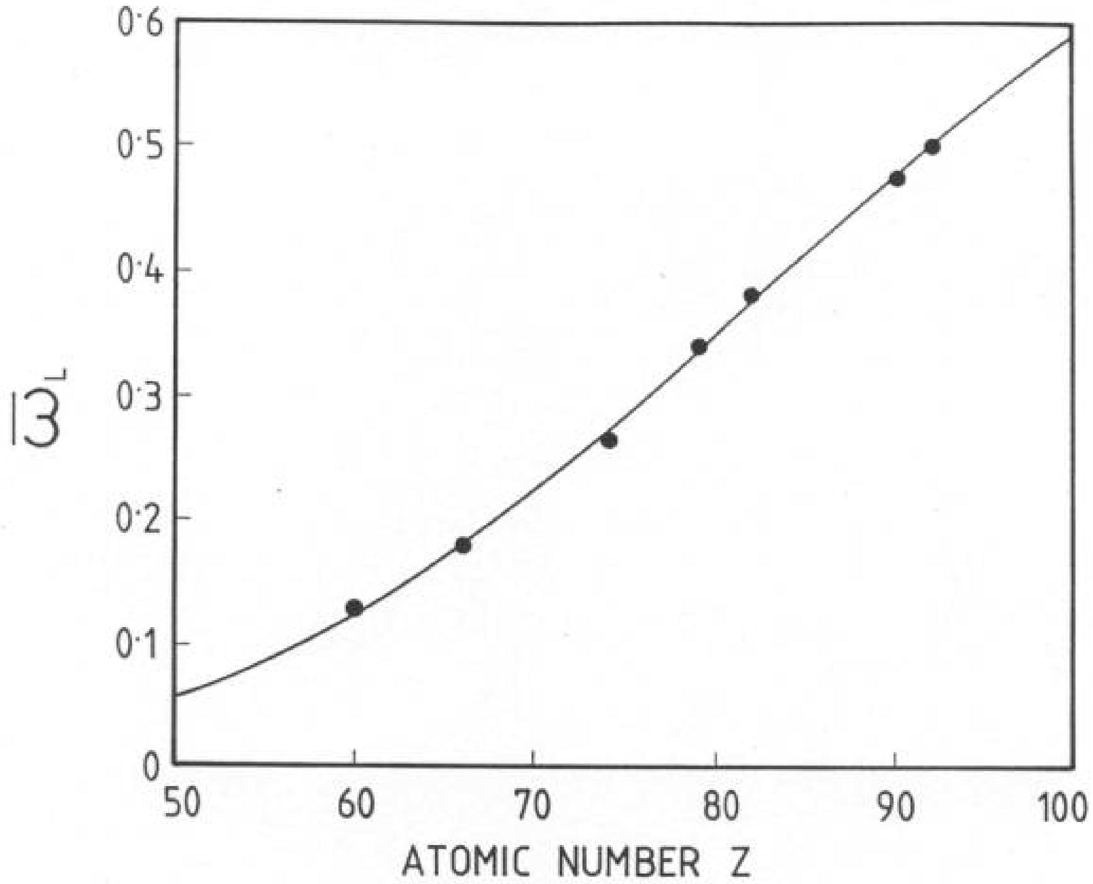
Also the L shell has 3 subshells L_1, L_2, and L_3, and Coster Kronig transitions must be considered.

In a similar way to the K shell, we can define an average total L shell fluorescence yield, ϖ_L,

$$\sigma_T(X) = \varpi_L \sigma_T(DI)$$

with $0 \leq \varpi_L \leq 1$.

L Shell Fluorescence Yields ω_L



Similar patterns hold for the M, N, … shells and their sub-shells.

For the L shell

For shells with sub-shell structure the sub-shell X-ray production cross sections are much more complicated as Coster Kronig transitions play a roll.

if,

$$\nu_1 = \omega_1 + f_{12}\omega_2 + (f_{13} + f_{12}f_{13})\omega_3$$

$$\nu_2 = \omega_2 + f_{23}\omega_3$$

$$\nu_3 = \omega_3$$

Then,

$$\sigma_1^x = [\sigma_1^1(f_{12}f_{23} + f_{13}) + \sigma_2^1 f_{23} + \sigma_3^1]\omega_3 S_{13}$$

$$\sigma_\alpha^x = [\sigma_1^1(f_{12}f_{23} + f_{13}) + \sigma_2^1 f_{23} + \sigma_3^1]\omega_3 S_{\alpha 3}$$

$$\sigma_\eta^x = (\sigma_1^1 f_{12} + \sigma_2^1)\omega_2 S_{\eta 2}$$

$$\sigma_\beta^x = \sigma_1^1[\omega_1 S_{\beta 1} + \omega_2 f_{12} S_{\beta 2} + \omega_3(f_{13} + f_{12}f_{23})S_{\beta 3}] + \sigma_2^1(\omega_2 S_{\beta 2} + \omega_3 f_{23} S_{\beta 3}) + \sigma_3^1 \omega_3 S_{\beta 3}$$

$$\sigma_\gamma^x = \sigma_1^1(\omega_1 S_{\gamma 1} + \omega_2 f_{12} S_{\gamma 2}) + \sigma_2^1 \omega_2 S_{\gamma 2}$$

$$\sigma_{\gamma 1}^x = \sigma_1^1 \omega_2 f_{12} S_{\gamma 1,2} + \sigma_2^1 \omega_2 S_{\gamma 1,2}$$

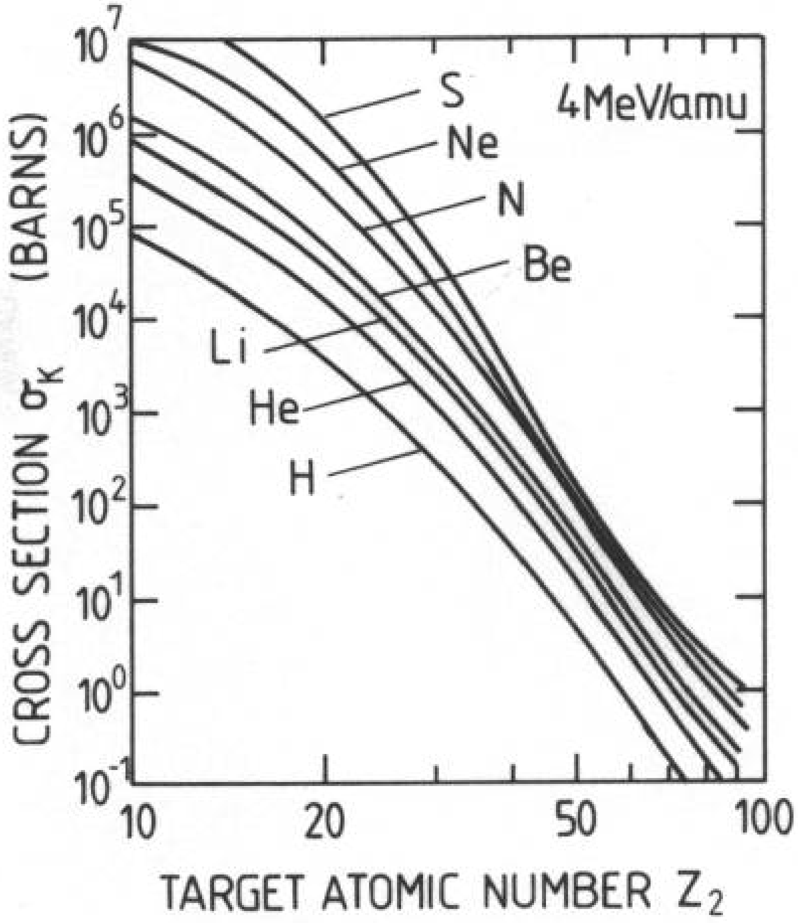
$$\sigma_{\gamma 5}^x = \sigma_1^1 \omega_2 f_{12} S_{\gamma 5,2} + \sigma_2^1 \omega_2 S_{\gamma 5,2}$$

$$\sigma_{\gamma 23}^x = \sigma_1^1 \omega_1 S_{\gamma 23,1}$$

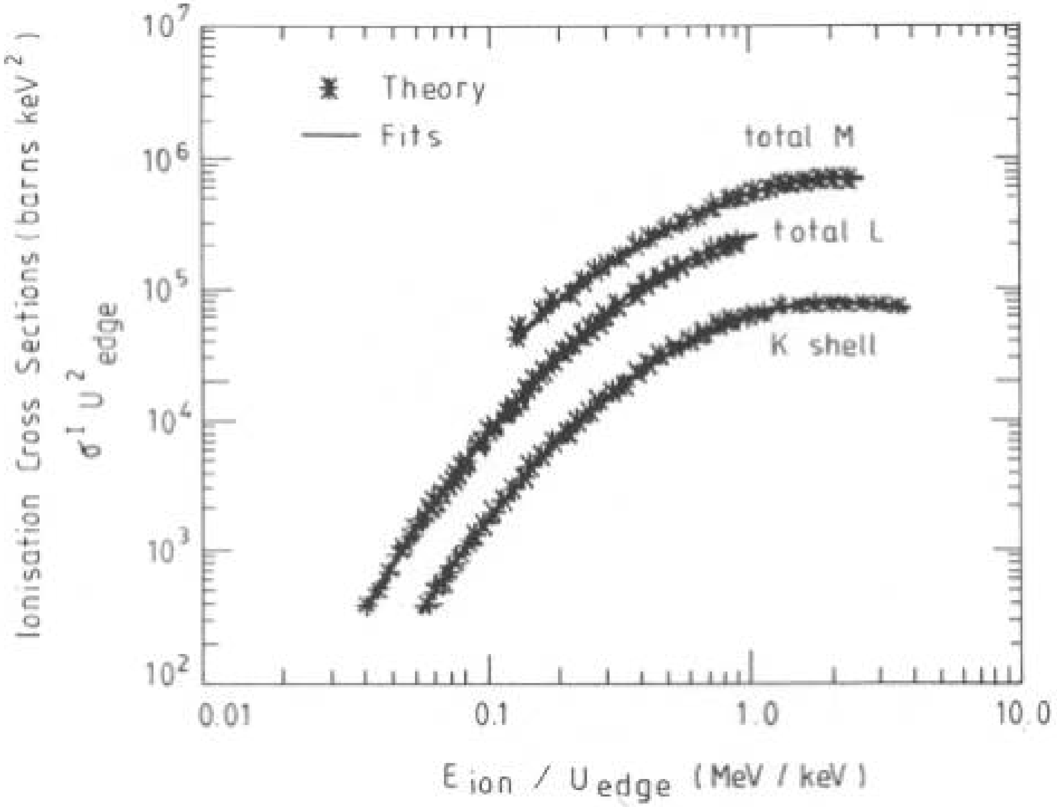
$$\sigma_{\gamma 44'}^x = \sigma_1^1 \omega_1 S_{\gamma 44',1}$$

$$\sigma_{TOT} = \bar{\omega}_1 \sigma_{TOT}^1 = \nu_1 \sigma_1^1 + \nu_2 \sigma_2^1 + \nu_3 \sigma_3^1$$

Direct Ionisation Cross Sections



ECPSSR K Shell for various ions



ECPSSR K, L and M ionisation cross sections

Transporting/ Bending Charged Particles

Range of MeV ions in materials is short – 10’s of microns

Need evacuated tubes, pressures < 1mPa

Bent by E, B fields

$$F = Q\,(E + v \times B)$$

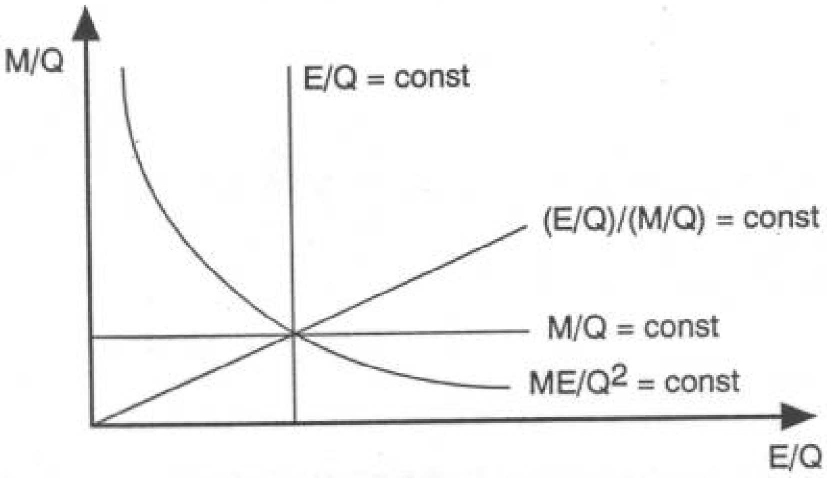
E fields ~ 10’skV/ cm for MeV ions

B fields ~ 5 kg for light MeV ions (H, He)

~ 15 kg for heavy MeV ions (Cl, I)

Require high voltages and large magnets

Ion Rigidity



Locii of values of M/Q versus E/Q determined by different analysers. Ions with equal E/Q ratios will be transmitted identically by an electrostatic analyzer, those with equal ME/Q^2 by a magnetic analyzer and those with equal (E/Q).(M/Q) by a velocity (or Wien) filter. Combinations of analyzers can be used to dramatically reduce background events. In order for an ion to pass all analyzers, it must have values of E, M and Q which are determined by the intersection point of all analyzer locii.

For magnets ions with the same (ME/Q^2) experience the same force.

For protons,

M=1, E=2MeV, Q=1 and

(ME/Q^2) = 2

For He^{2+}

M=4, E=2 MeV, Q=2 and

(ME/Q^2) = 2 also.

How to Accelerate Ions

If an ion of charge Q falls through a voltage V, then energy is given by,

$$E(\text{MeV}) = V(\text{MV})\,Q$$

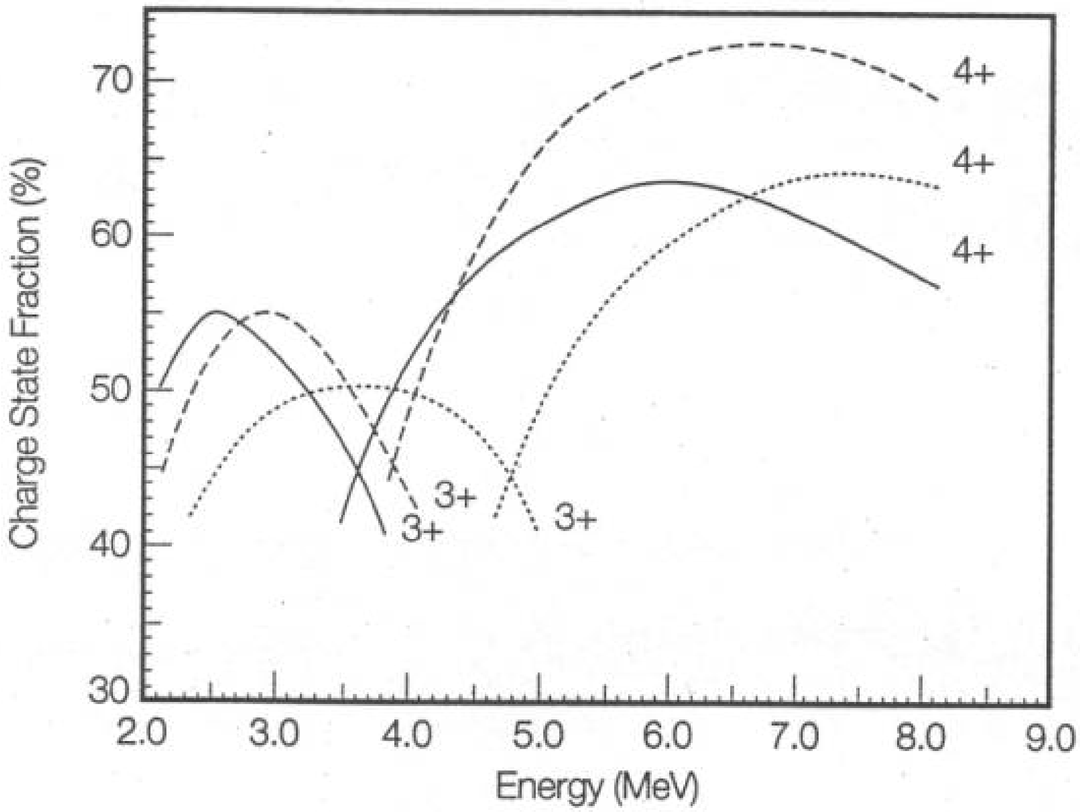
Need high Q large V to obtain large energies

Can strip the ion – gas or foil

Charge states Q = +1 to +10 are common depends on Z

= -1 (-2 unlikely)

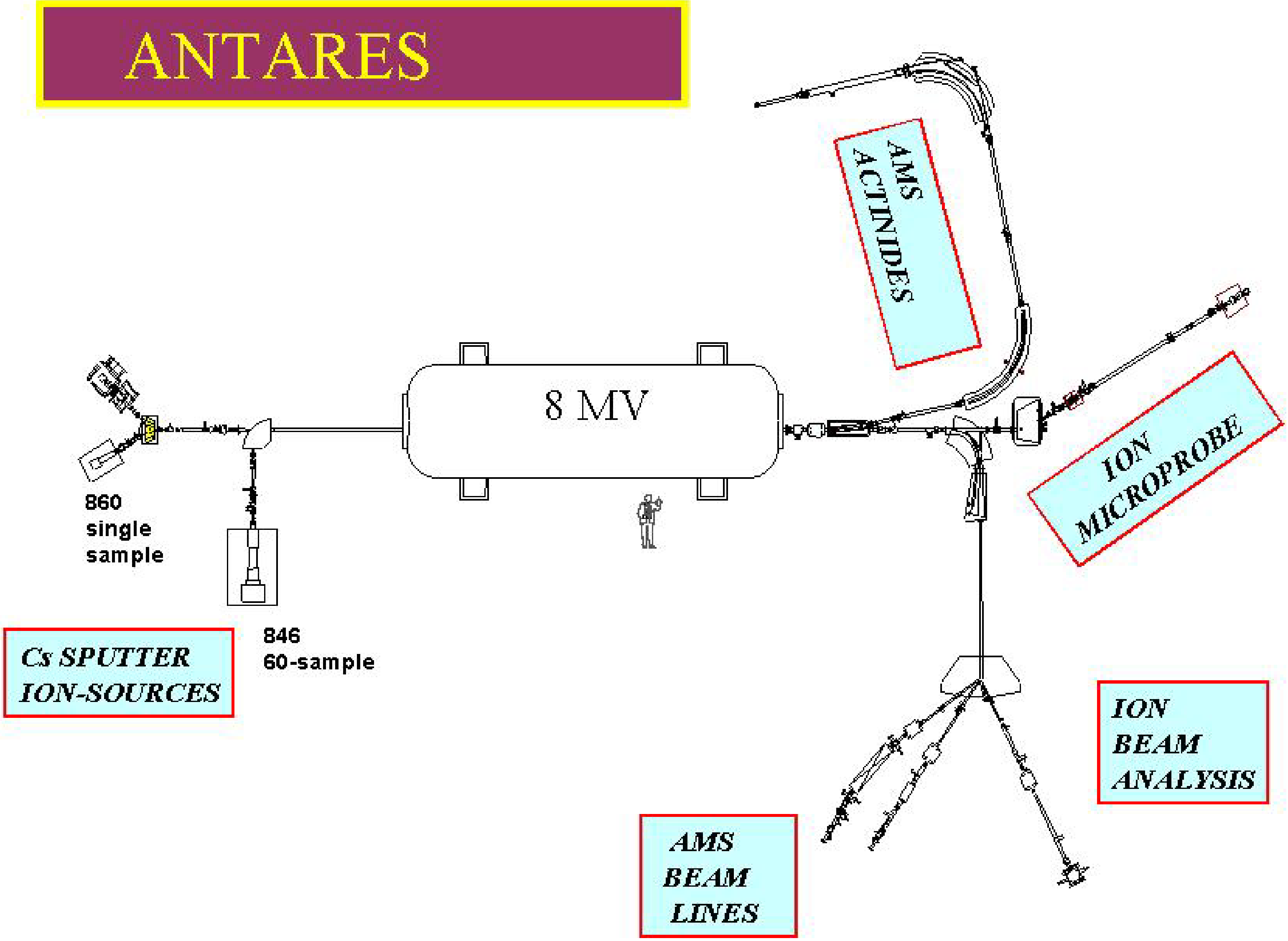
Typical Charge States in MeV Carbon Ions



Charge state fraction of 3+ and 4+ ions of ^{14}C from stripping in O_2 gas (dotted lines), Ar gas (dashed lines) and carbon foil (full lines) [Bonani, 1990].

10MV Tandem accelerator at ANSTO

ANTARES 10MV Accelerator at ANSTO



ANTARES

8 MV

AMS ACTINIDES

ION MICROPROBE

860 single sample

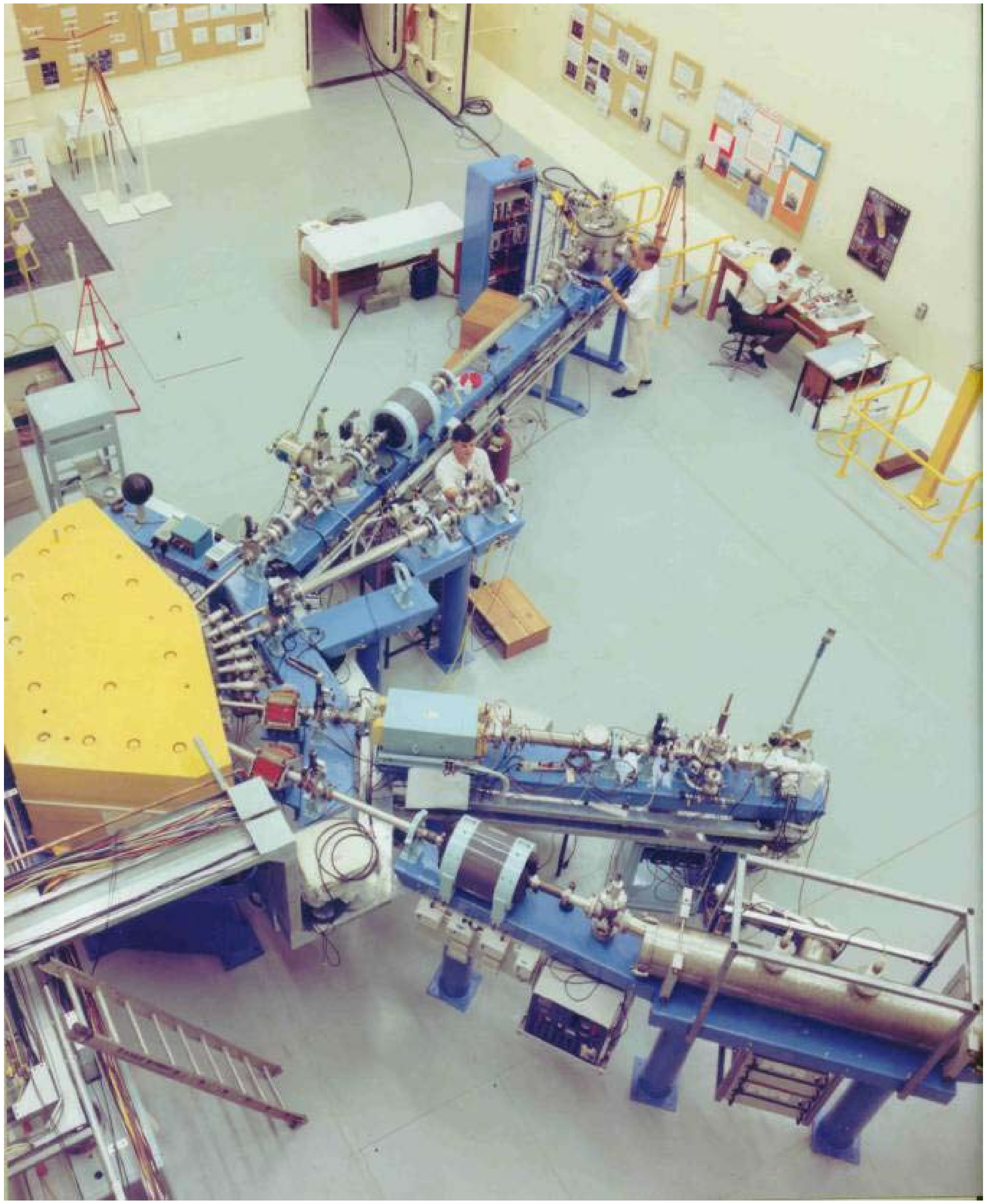
846 60-sample

Cs SPUTTER ION-SOURCES

ION BEAM ANALYSIS

AMS BEAM LINES

High Energy Beam Hall at ANSTO Tandem



Summary

We have discussed:-

What an ion is.

What an atom is.

How an ion interacts with an atom.

Vacancy production leading to X-ray production.

Ionisation theory, ECPSSR

Coster Kronig transitions

Charged particle transport

Next we will look at X-ray Systems specifically.