Gas detectors: general principles

- 24/1:
  - reminder how they work,
  - history,
  - ionisation,
  - electric field,
  - electron transport,
  - mean gas gain,

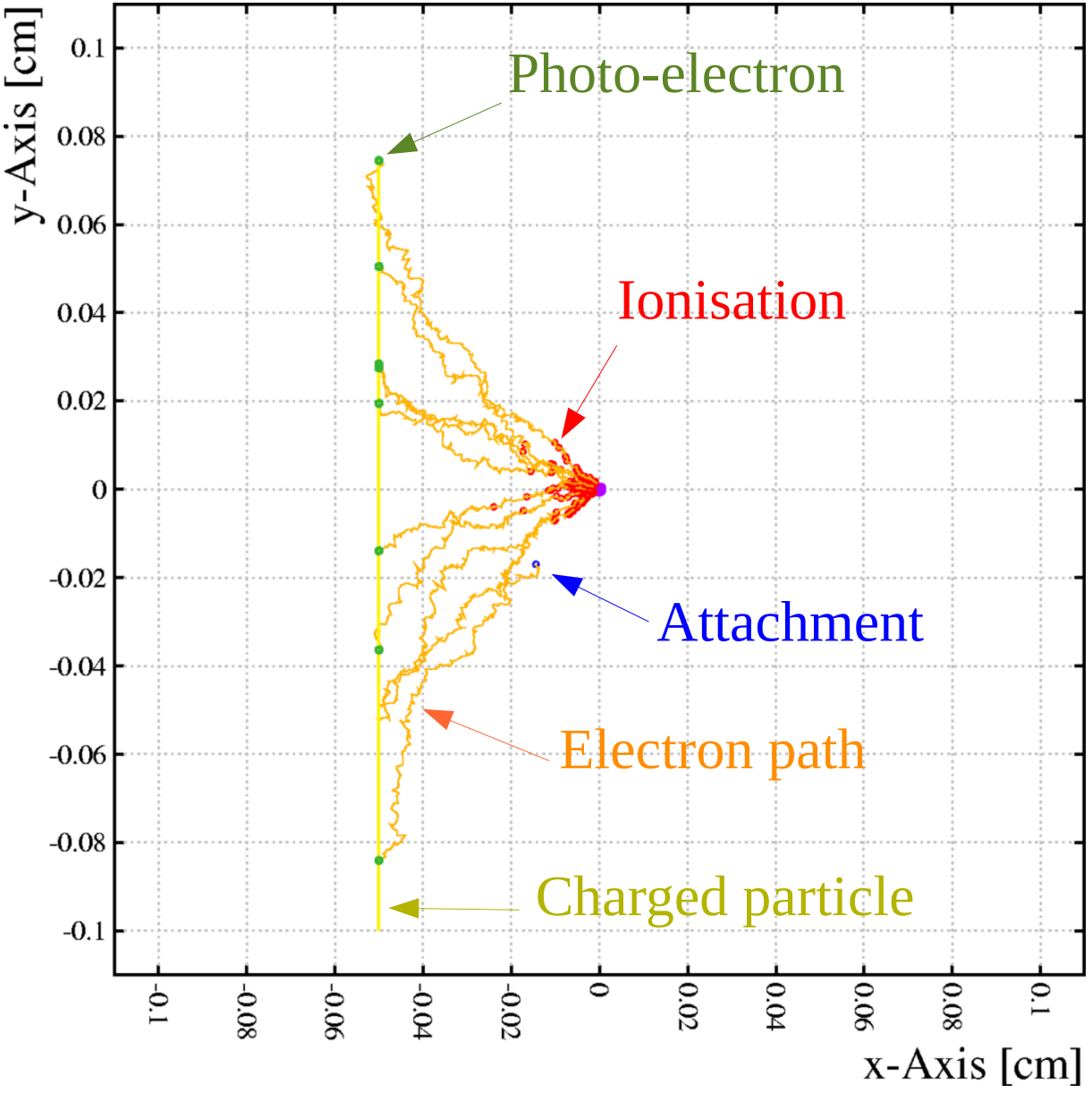
- 25/1:
  - gas gain fluctuations,
  - ion transport,
  - signals.

How they work

- Gas-based detectors all work according to much the same principles:
  - a charged particle passing through the gas ionises a few gas molecules;
  - the electric field in the gas volume transports the ionisation electrons and provokes multiplication;
  - the movement of electrons and ions leads to induced currents in electrodes;
  - the signals are processed and recorded.

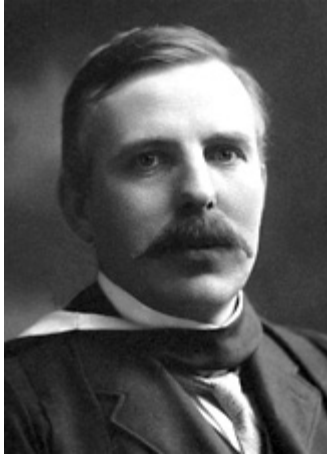
At the 100 µm – 1 mm scale

- Example:
  - CSC-like structure,
  - Ar 80 % CO_2 20 %,
  - 10 GeV µ.
- Electron are shown every 100 collisions, but have been tracked rigorously.
- Ions are not shown.



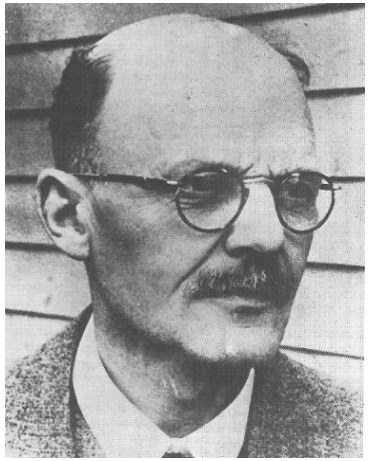
A brief history

E(a)rnest Rutherford
(1871-1937)



Geiger counter

- Detects radiation by discharge;
- can count α, β and γ particles (at low rates ...);
- no tracking capability.
- 1908: Ernest Rutherford and Hans Geiger
- 1928: Hans Geiger and Walther Müller



Hans Geiger
(1882-1945)

Walt(h)er Müller
(1905-1979)

A Geiger-Muller counter built in 1939 and used in the 1947-1950 for cosmic ray studies in balloons and on board B29 aircraft by Robert Millikan et al.

Made of copper, 30 cm long

Motivation for the Geiger counter

In considering a possible method of counting the number of α-particles, their well-known property of producing scintillations in a preparation of phosphorescent zinc sulphide at once suggests itself.

The doubt, however, at once arises whether every α-particle produces a scintillation, for it is difficult to be certain that the zinc sulphide is homogeneous throughout. No confidence can be placed in such a method of counting the total number of α-particles (except as a minimum estimate),

α detection by eye using ZnS scintillation suffers from efficiency losses + is laborious.

It has been recognised for several years that it should be possible by refined methods to detect a single α-particle by measuring the ionisation it produces in its path.

Ionisation signal is usable but small (z^2 !)

We then had recourse to a method of automatically magnifying the electrical effect due to a single α-particle. For this purpose we employed the principle of production of fresh ions by collision. In a series of papers, Townsend* has worked out the conditions under which ions can be produced by collisions with the neutral gas molecules in a strong electric field. The effect is best shown in gases at a pressure of several millimetres of mercury.

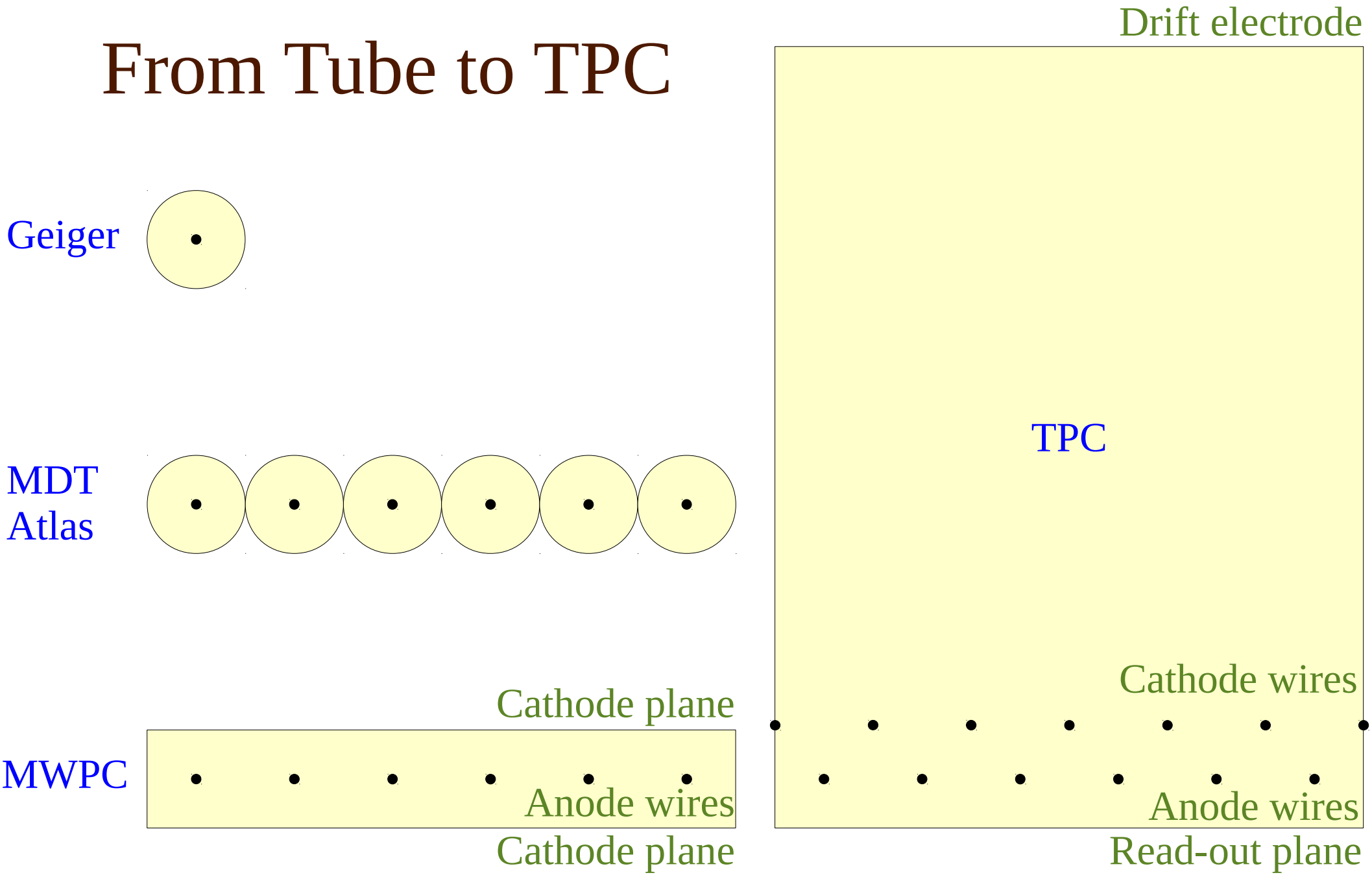
Use multiplication at low pressure as discovered in 1901 by JS Townsend.

"ion" = electron here.

* 'Phil. Mag.,' February, 1901 ; June, 1902 ; April, 1903 ; September and November, 1903.

[E. Rutherford and H. Geiger, *An Electrical Method of Counting the Number of α-Particles from Radio-Active Substances*, Proc. R. Soc. Lond. A **81** (1908) 141-161]

From Tube to TPC



MWPC

- First gaseous tracking device
- 1968: Georges Charpak

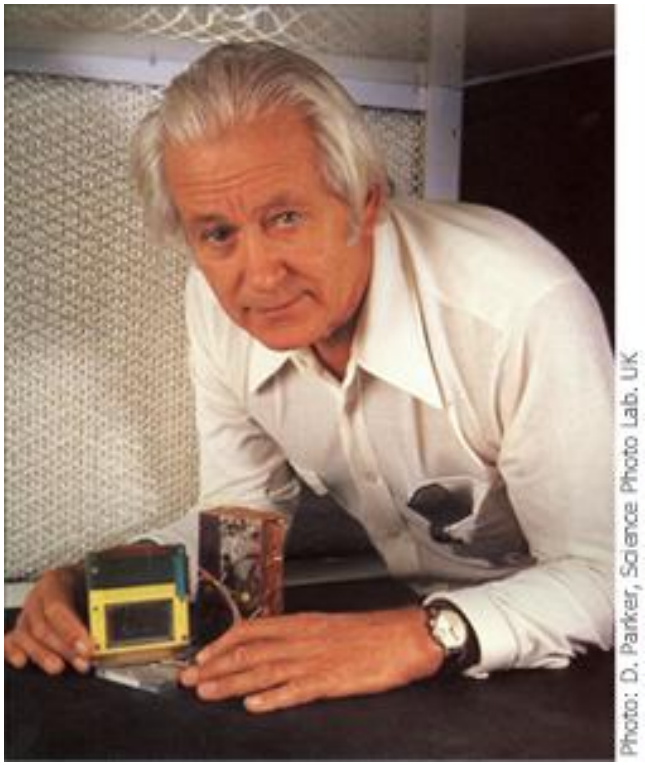
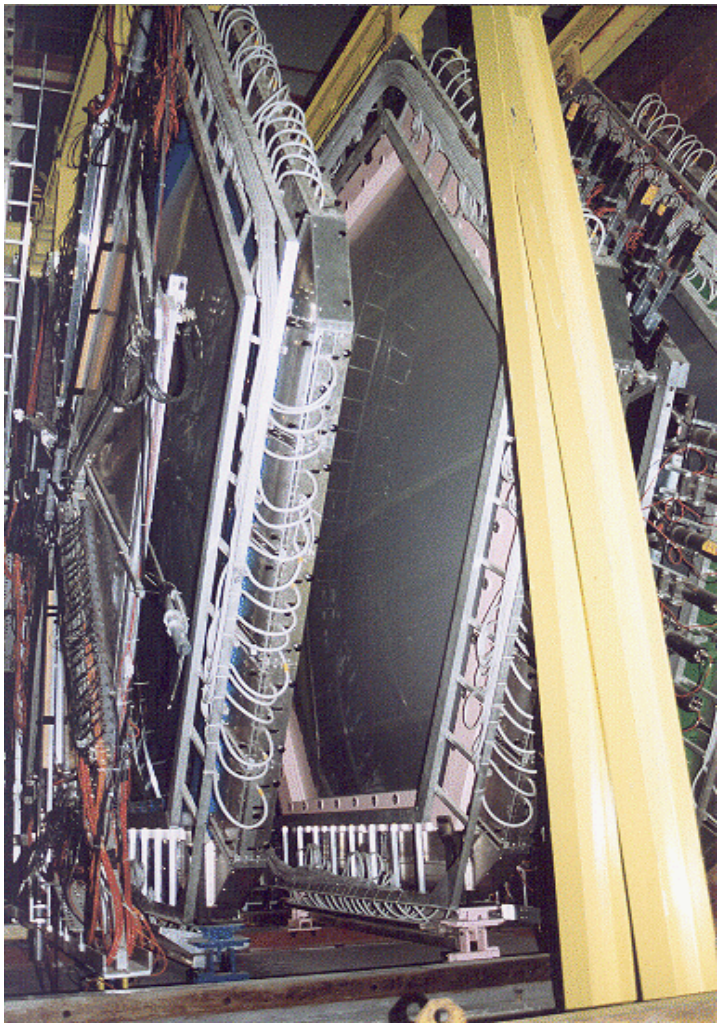


Photo: D. Parker, Science Photo Lab. UK

Georges Charpak
(1924-1992-2010)



One of the NA60 muon chambers

TPC

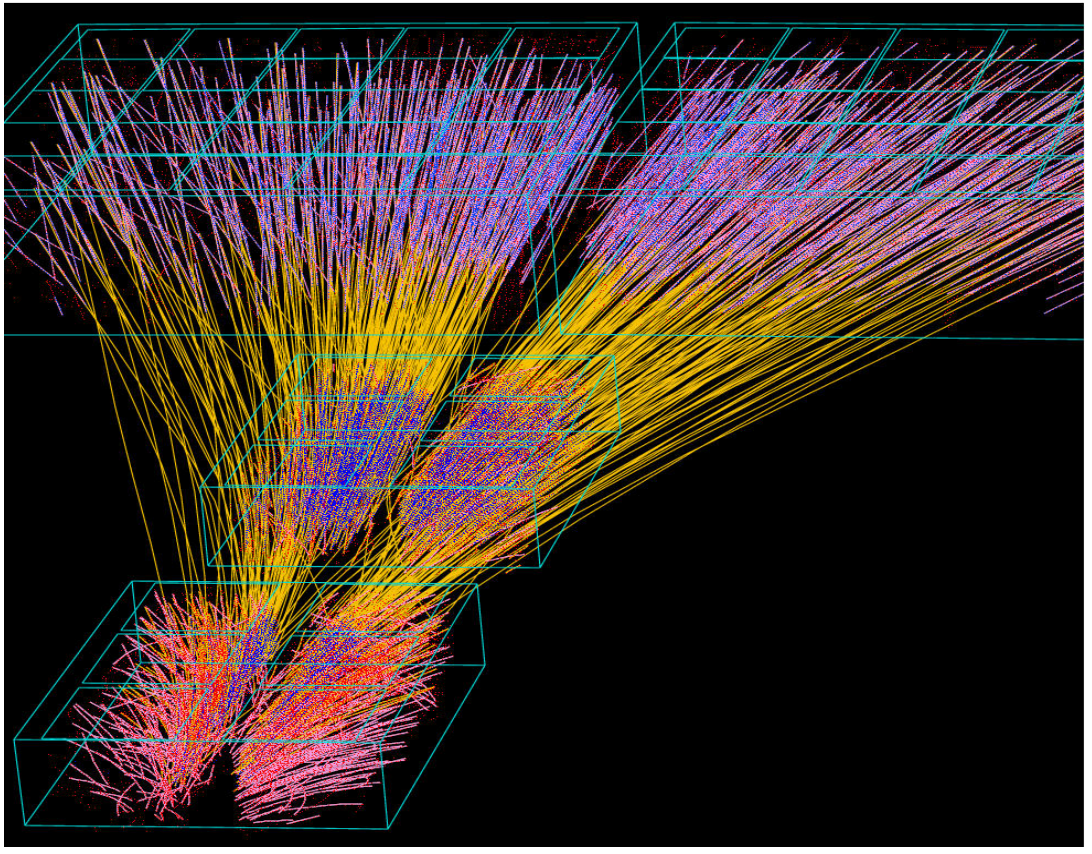
- Typically very large
- Almost empty inside
- Excellent for dealing with large numbers of tracks

- 1976: David Nygren (for PEP4)

David Nygren

Alice

Star

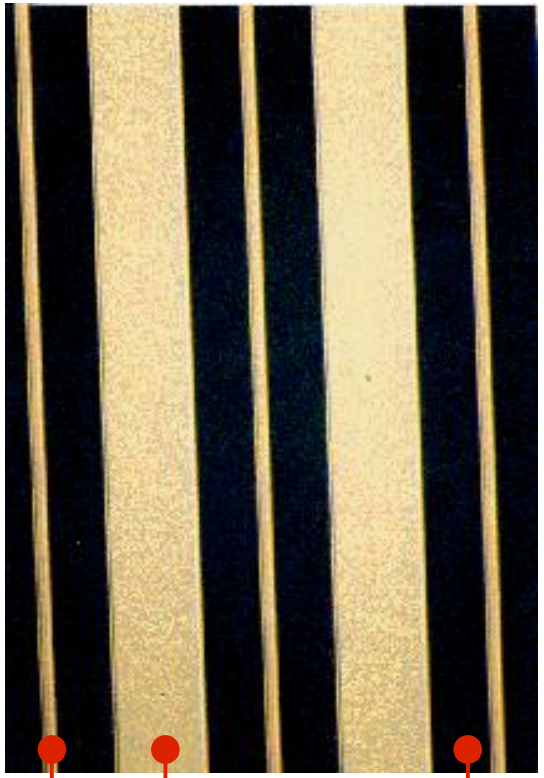


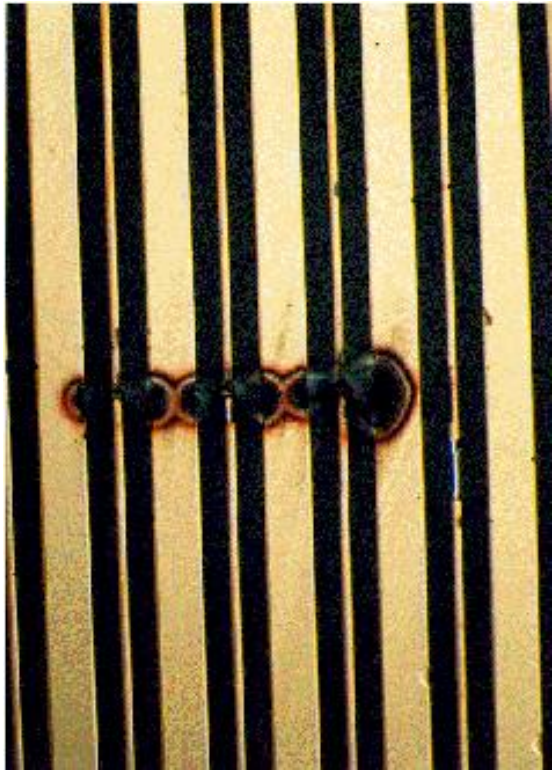
NA49

MSGC: an early MPGD

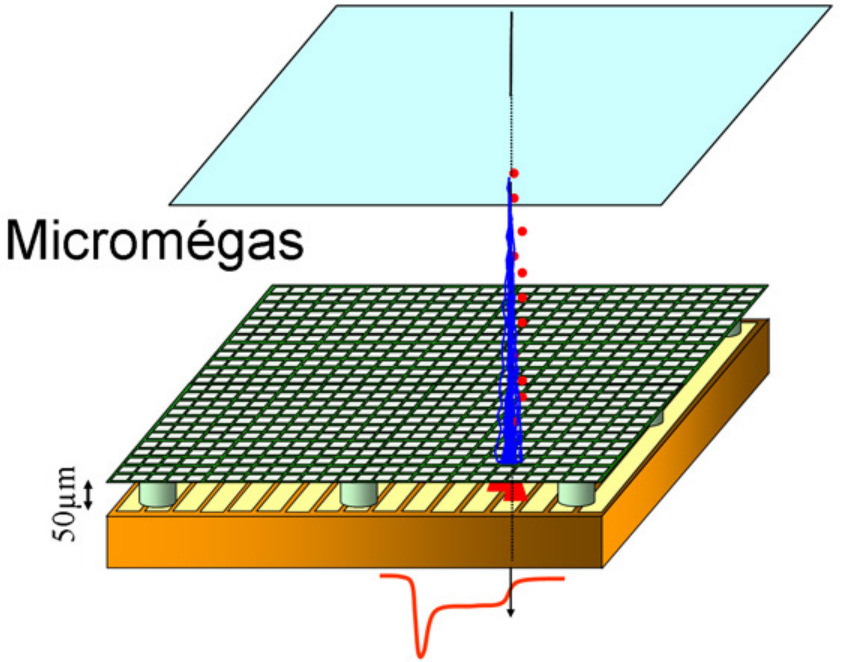
- Built using solid-state techniques;
- good resolution;
- poor resistance to high rates.

- 1988: Anton Oed

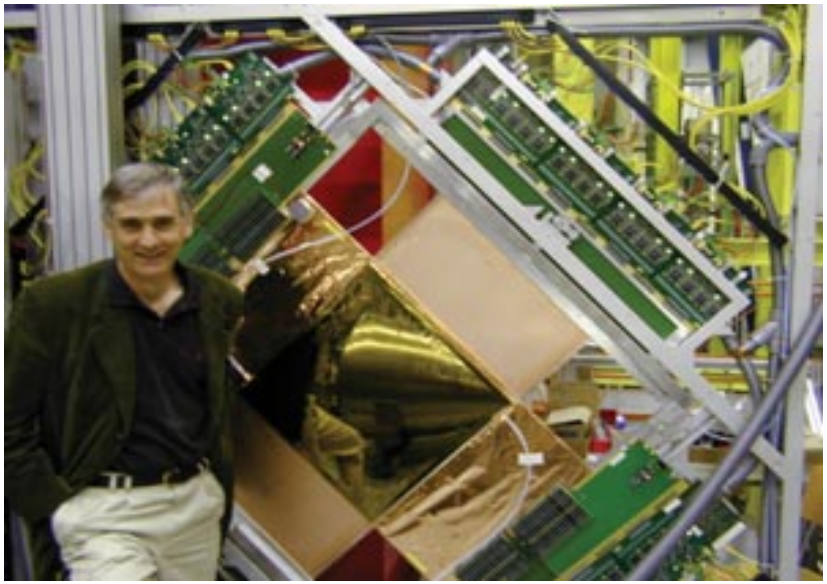




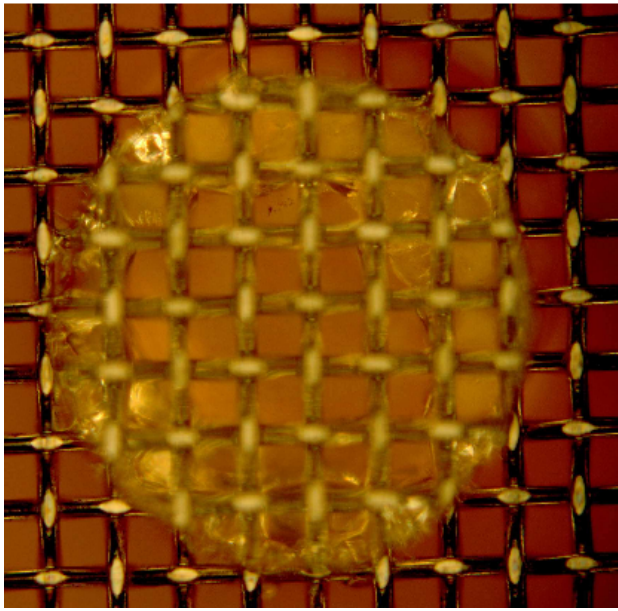
Micromégas



- Fast, rate tolerant tracking device
- 1994: Yannis Giomataris and Georges Charpak



Yannis Giomataris

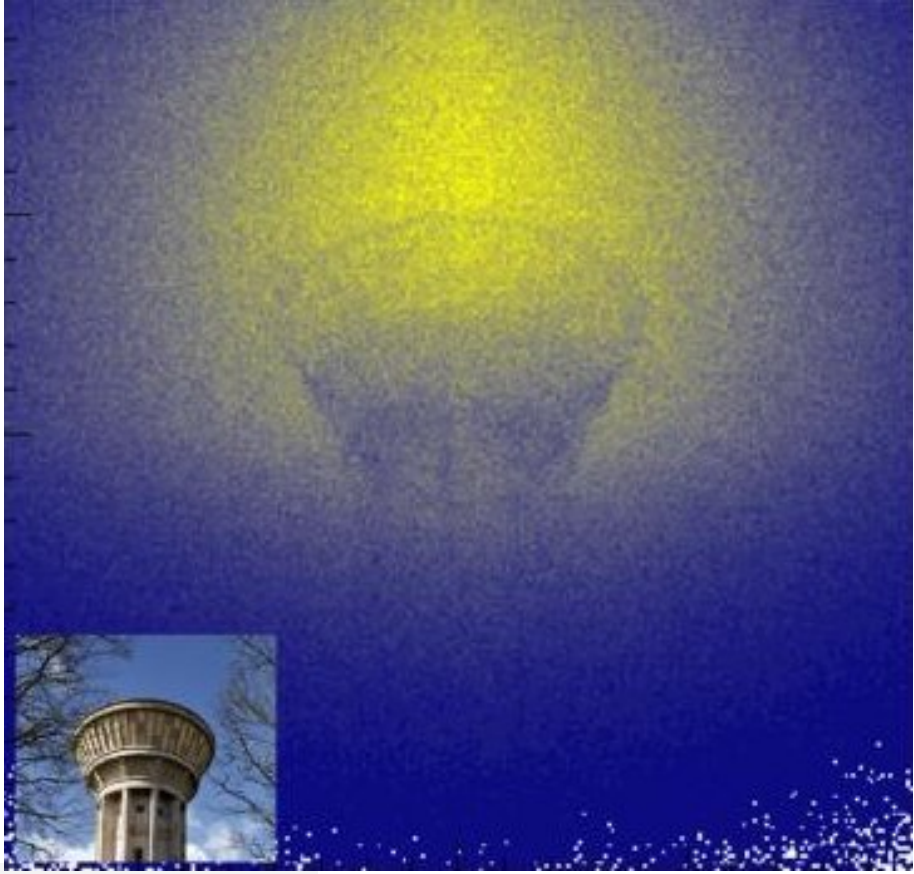


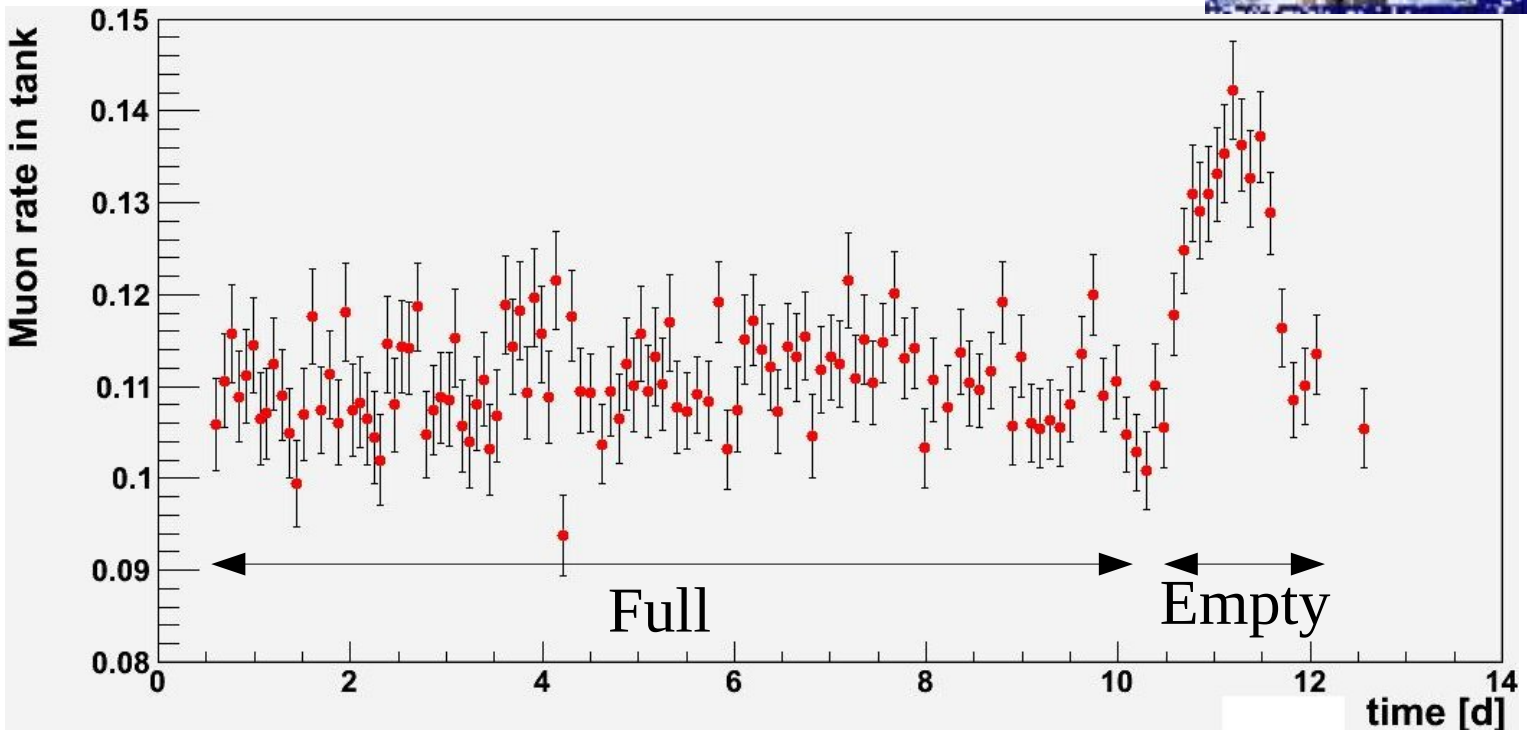
Wire diameter: 18 µm,
Pitch: 63 µm, Gap: 192 µm

[Purba Bhattacharya et al., 10.1016/j.nima.2013.07.086; ILC NewsLine]

Muon tomography

- Tower structure and water level are visible.
- Portable system (30 W).

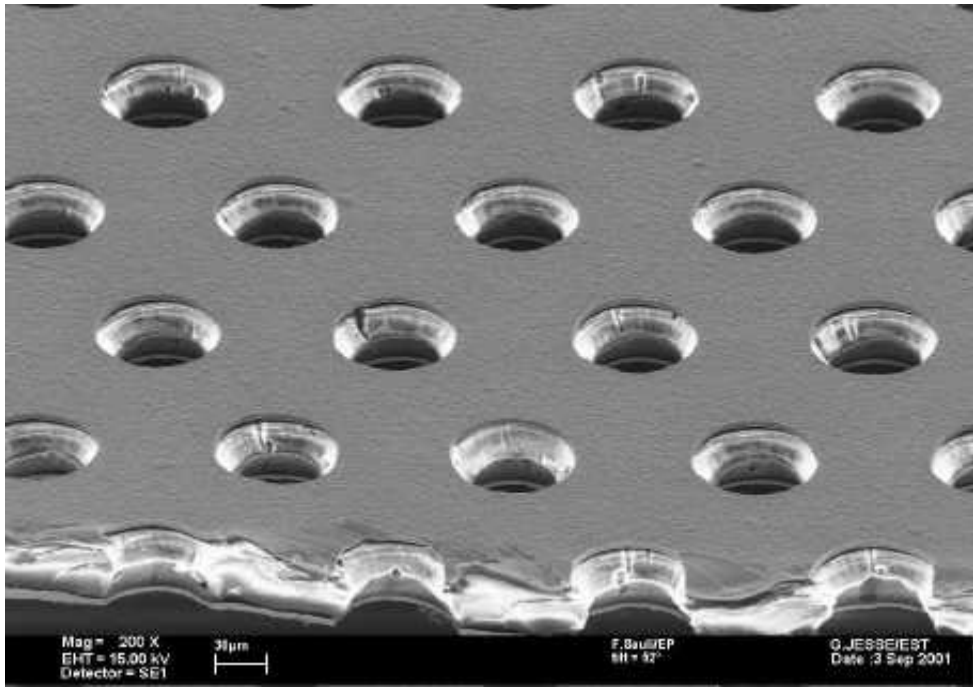




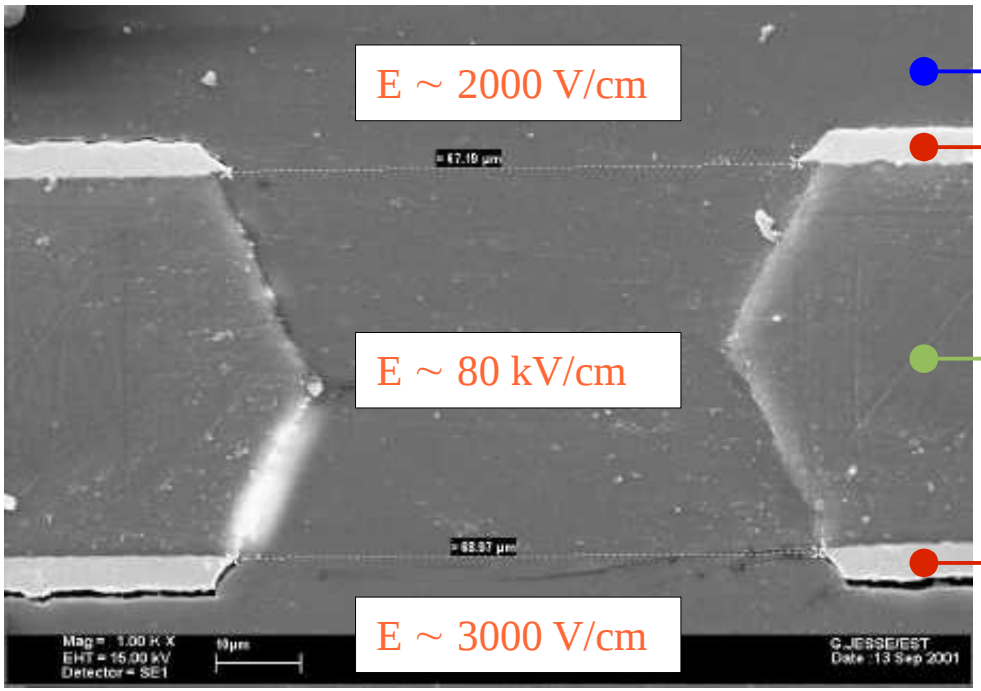
[Sébastien Procureur, Simon Bouteille, David Attié]

GEMs

- Acts as a “pre-amplifier”
- 1996: Fabio Sauli



A few electrons enter here



Gas

Metal

Dielectric

Metal

Fabio Sauli

Many electrons exit here

Ionisation

[Four Curies: Pierre, Marie, Irène and Pierre's father, around 1904 at the BIPM]

1896: Ionisation by radiation

- Early in the study of radioactivity, ionisation by radiation was recognised:

” Becquerel discovered in 1896 the special radiating properties of uranium and its compounds. Uranium emits very weak rays which leave an impression on photographic plates. These rays pass through black paper and metals; they make air electrically conductive. “

[Pierre Curie, Nobel Lecture, June 6th 1905]

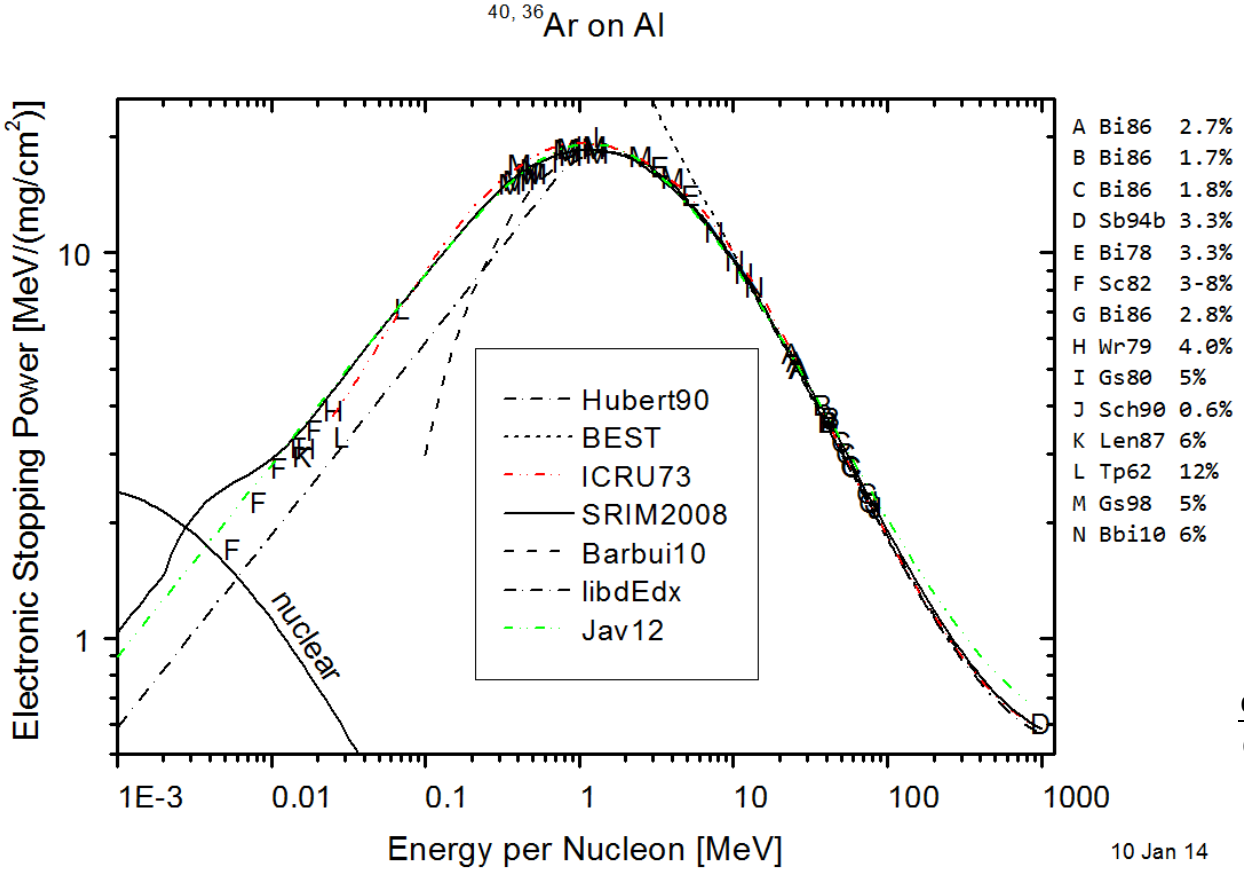
“A sphere of charged uranium, which discharges spontaneously in the air under the influence of its own radiation, retains its charge in an absolute vacuum. The exchanges of electrical charges that take place between charged bodies under the influence of the new rays, are the result of a special conductivity imparted to the surrounding gases, a conductivity that persists for several moments after the radiation has ceased to act.”

[Antoine Henri Becquerel, Nobel Lecture, December 11th 1903]

Helmut Paul
(1929-2015)

Electronic losses at low energy

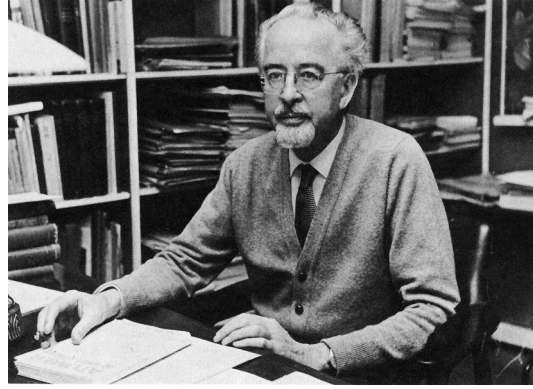
- Nuclear effects abound at very low energy.
- Numerous models: SRIM, MSTAR, CasP, PASS ...



$$\frac{\mathrm{d}E}{\mathrm{d}x} = 20\,\frac{\mathrm{MeV\,cm^2}}{\mathrm{mg}}\,2.7\,\frac{\mathrm{g}}{\mathrm{cm^3}} = 5.4\,\frac{\mathrm{MeV}}{\mu m}$$

[Ref: Helmut Paul, https://www-nds.iaea.org/stopping/]

Christian Møller
(1904-1980)



1930-1933: EM energy loss

- 1930 - Hans Bethe, non-relativistic quantum calculation:

The loss in kinetic energy per centimeter path is

$$-\frac{dT}{dx} = NE = \frac{4\pi e^4 z^2 N}{m v^2} \ln \frac{(2)\, m v^2}{c R h} .$$

Formula for hydrogen (2): only for heavy particles, not electrons

[H. Bethe, Zur Theorie des Durchgangs schneller Korpuskularstrahlen durch Materie, Ann. Physik **5** (1930) 325-400.]

- 1931 - Christian Møller solves relativistic e^- scattering.
- 1932 - Hans Bethe, relativistic quantum calculation:

Ein Teilchen der Ladung ez möge sich mit der Geschwindigkeit v durch eine Substanz hindurchbewegen, welche in der Volumeneinheit N Atome der Ordnungszahl Z enthält. Dann verliert das Teilchen pro Zentimeter Weg die Energie

$$-\frac{dT}{dx} = \frac{2\pi e^4 N Z z^2}{m v^2}\left(\lg \frac{2 m v^2 W}{\bar{E}^2\left(1-\frac{v^2}{c^2}\right)} - \frac{v^2}{c^2}\right),$$

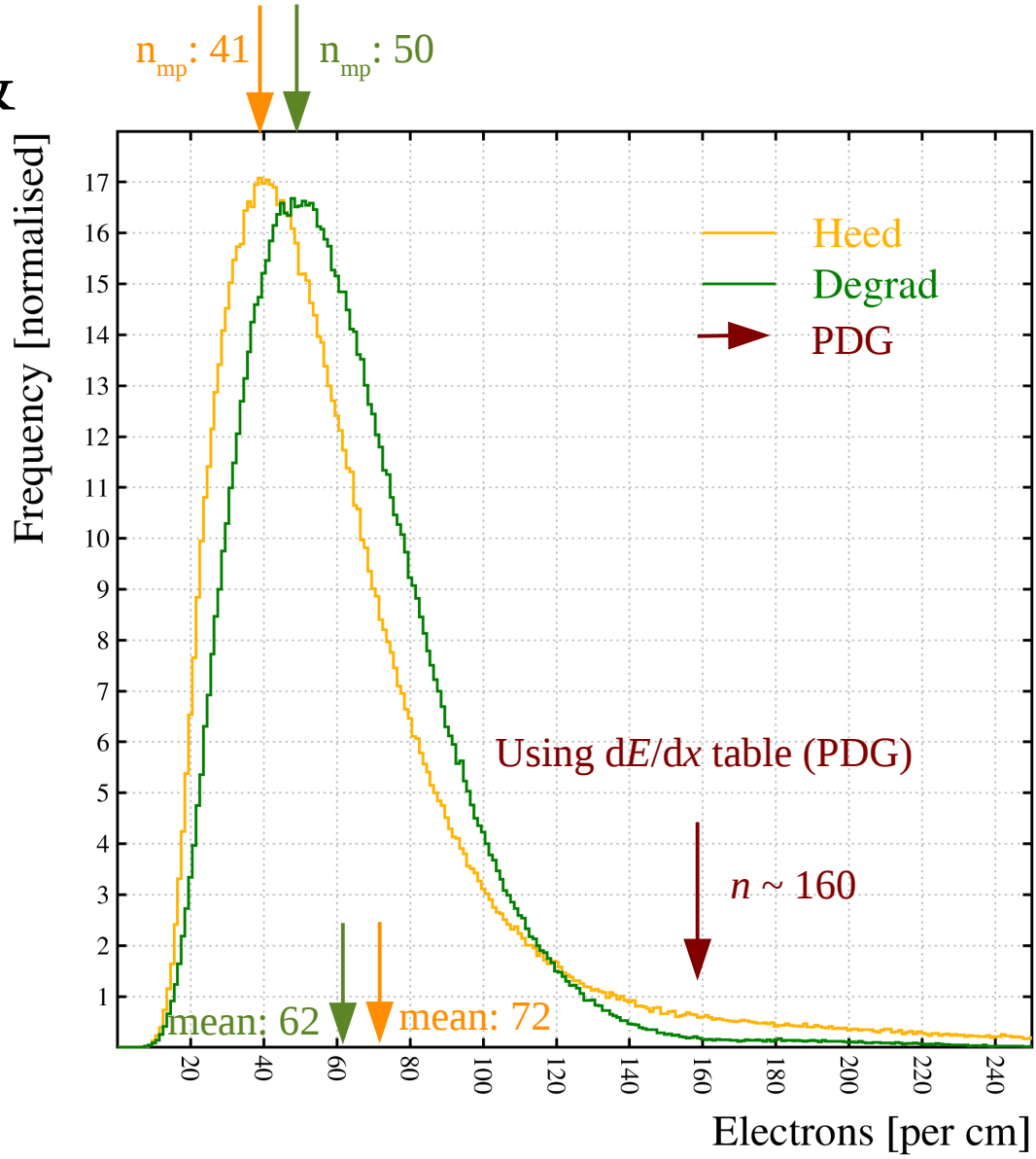
falls wir nur den Energieverlust durch solche Stöße ins Auge fassen, bei denen im einzelnen höchstens die Energie W auf das Atom übertragen wird[3]).

$\bar{E}$: average atomic ionisation energy

W: largest energy transfer per collision

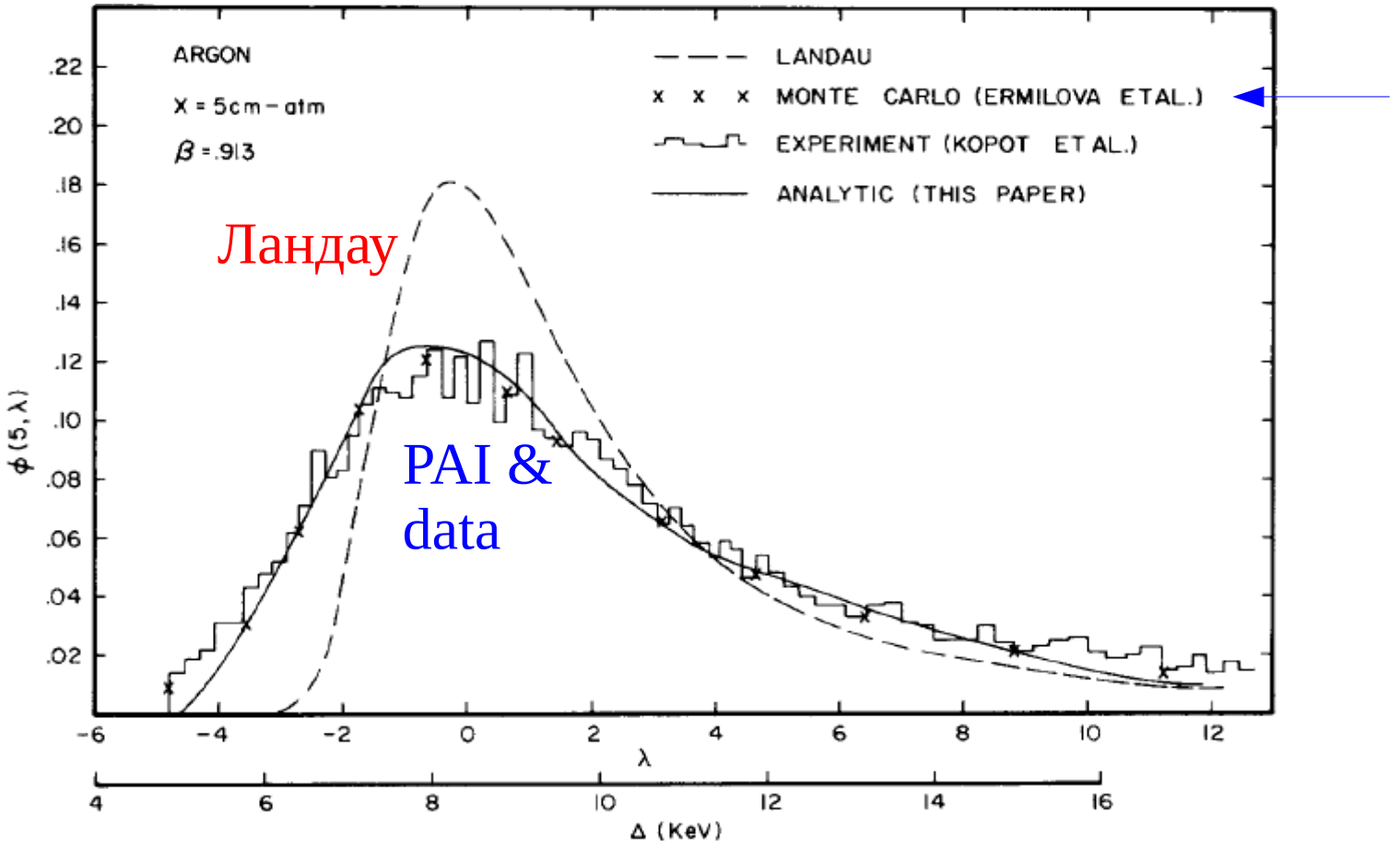
Compare PDG with ionisation models

- Heed, a photo-absorption & ionisation model, finds for a minimum ionising $\mu^{\pm}$:
  - Peak: $n_e = 41/cm$
  - "Mean": $n_e = 72/cm$
- Degrad, an e^- transport program, finds for an e^- at the same $\beta\gamma$:
  - Peak: $n_e = 50/cm$
  - "Mean": $n_e = 62/cm$
- Mean is ill-defined due to rare but large deposits.



Energy loss fluctuations

- 2 GeV protons on an (only !) 5 cm thick Ar gas layer:



[Diagram: Richard Talman, NIM A **159** (1979) 189-211]

Clustering – primary interactions

- Electrons are not evenly spaced, not even exponentially:
  -

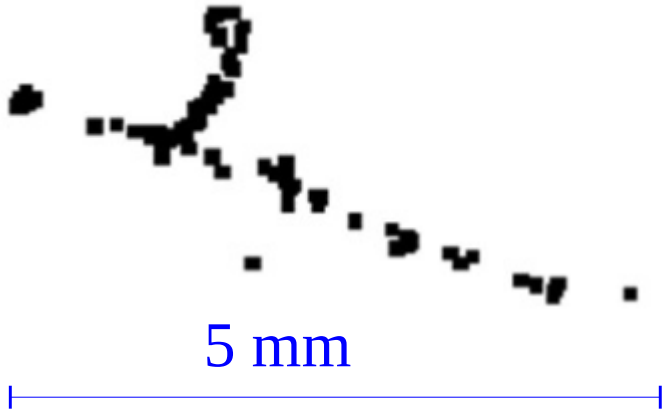
  (reported to have 25-30 clusters/cm, hard to see)

- From ILD TPC test beam studies:
  - 4 × 2 InGrid Octopuce,
  - pixels: 55 × 55 µm^2,
  - T2K gas: Ar 95 %, CF_4 3 %, iC_4H_{10} 2 %;
  - DESY II, 5 GeV e^-.

[Michael Lupberger, AIDA-PUB-2014-010,
Robert Menzen, AIDA-THESIS-2013-001]

δ-electrons

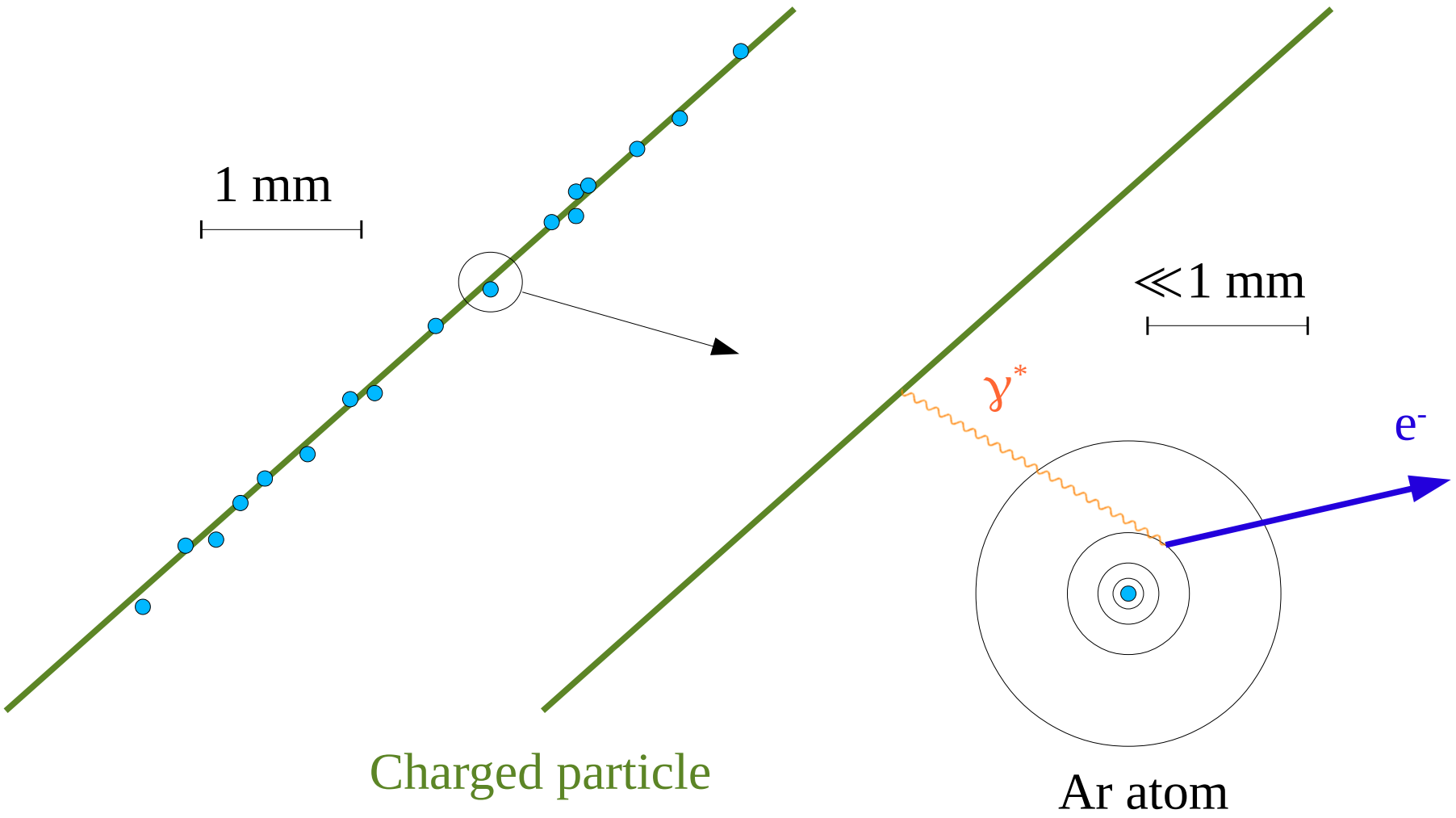
- Deposits are not always “lumps”:



- Laboratory tests:
  - modified MediPix;
  - pixels: 55 × 55 μm^2;
  - He 80 %, iC_4H_{10} 20 %.

[Harry van der Graaf and co-workers (2004)]

Virtual photon exchange



Core formulae PAI model

Wade Allison

John Cobb

- Key: photo-absorption cross section $\sigma_\gamma(E)$

$$\frac{\beta^2\pi}{\alpha}\frac{d\sigma}{dE}=\frac{\sigma_\gamma(E)}{E}\log\left(\frac{1}{\sqrt{(1-\beta^2\epsilon_1)^2+\beta^4\epsilon_2^2}}\right)+$$ Relativistic rise

Cross section to transfer energy E

$$\frac{1}{N\hbar c}\left(\beta^2-\frac{\epsilon_1}{|\epsilon|^2}\right)\theta+$$ Черенков radiation

$$\frac{\sigma_\gamma(E)}{E}\log\left(\frac{2m_e c^2\beta^2}{E}\right)+$$ Resonance region

$$\frac{1}{E^2}\int_0^E \sigma_\gamma(E_1)\,dE_1$$ Rutherford scattering

With: $$\epsilon_2(E)=\frac{N_e\hbar c}{E\,Z}\sigma_\gamma(E)$$

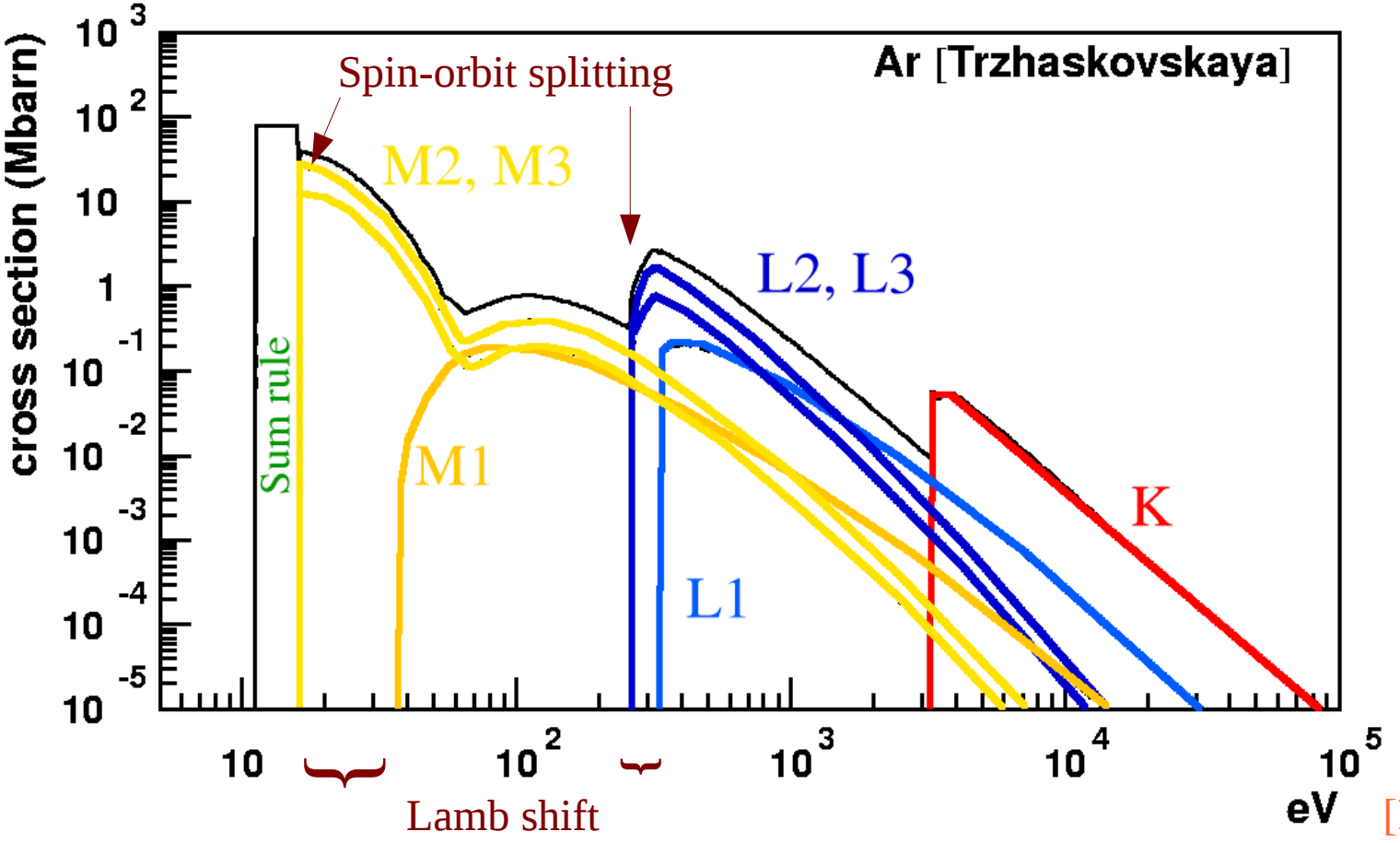
$$\epsilon_1(E)=1+\frac{2}{\pi}\mathrm{P}\int_0^\infty\frac{x\,\epsilon_2(x)}{x^2-E^2}dx$$

$$\theta=\arg(1-\epsilon_1\beta^2+i\,\epsilon_2\beta^2)=\frac{\pi}{2}-\arctan\frac{1-\epsilon_1\beta^2}{\epsilon_2\beta^2}$$

Photo-absorption in Ar (Heed)

Igor Smirnov

- Argon has 3 shells, hence 3 groups of lines:



K = 1s

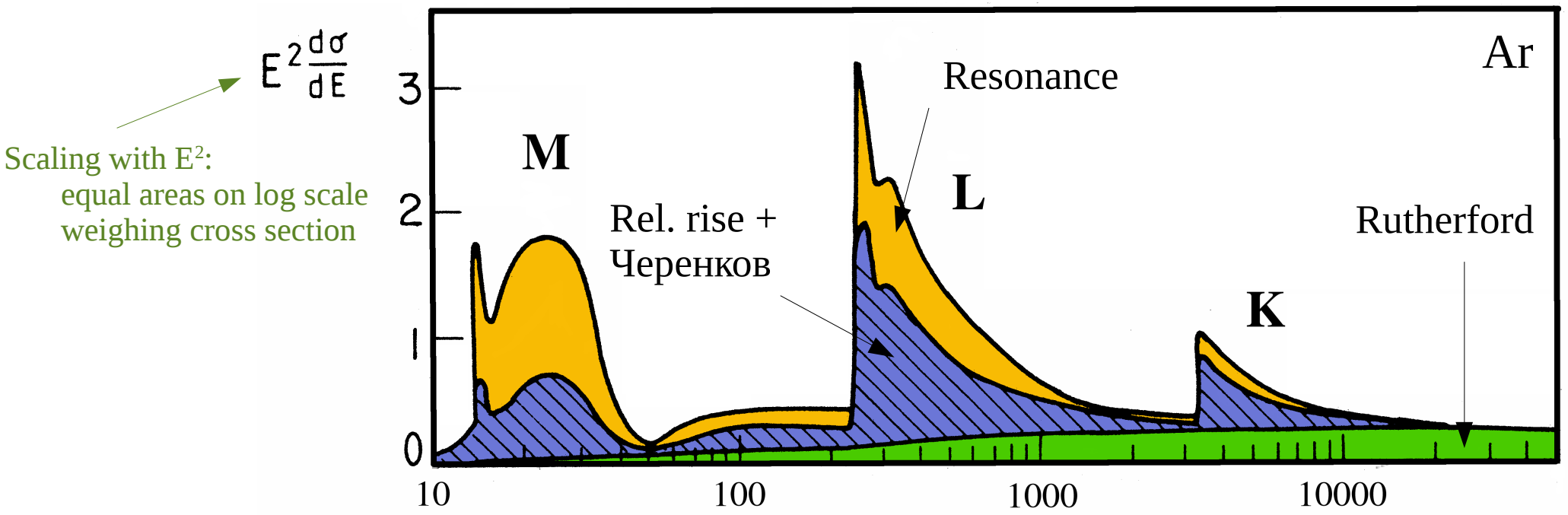
L1 = 2s
L2 = 2p 1/2
L3 = 2p 3/2

M1 = 3s
M2 = 3p 1/2
M3 = 3p 3/2

[Plot from Igor Smirnov]

Importance of the PAI model terms

- All electron orbitals (shells) participate:
  - outer shells: frequent interactions, few electrons;
  - inner shells: few interactions, many electrons.
- All terms in the formula are important.



[Adapted from Allison & Cobb, Ann. Rev. Nucl. Part. Sci. **30** (1980) 253-298]

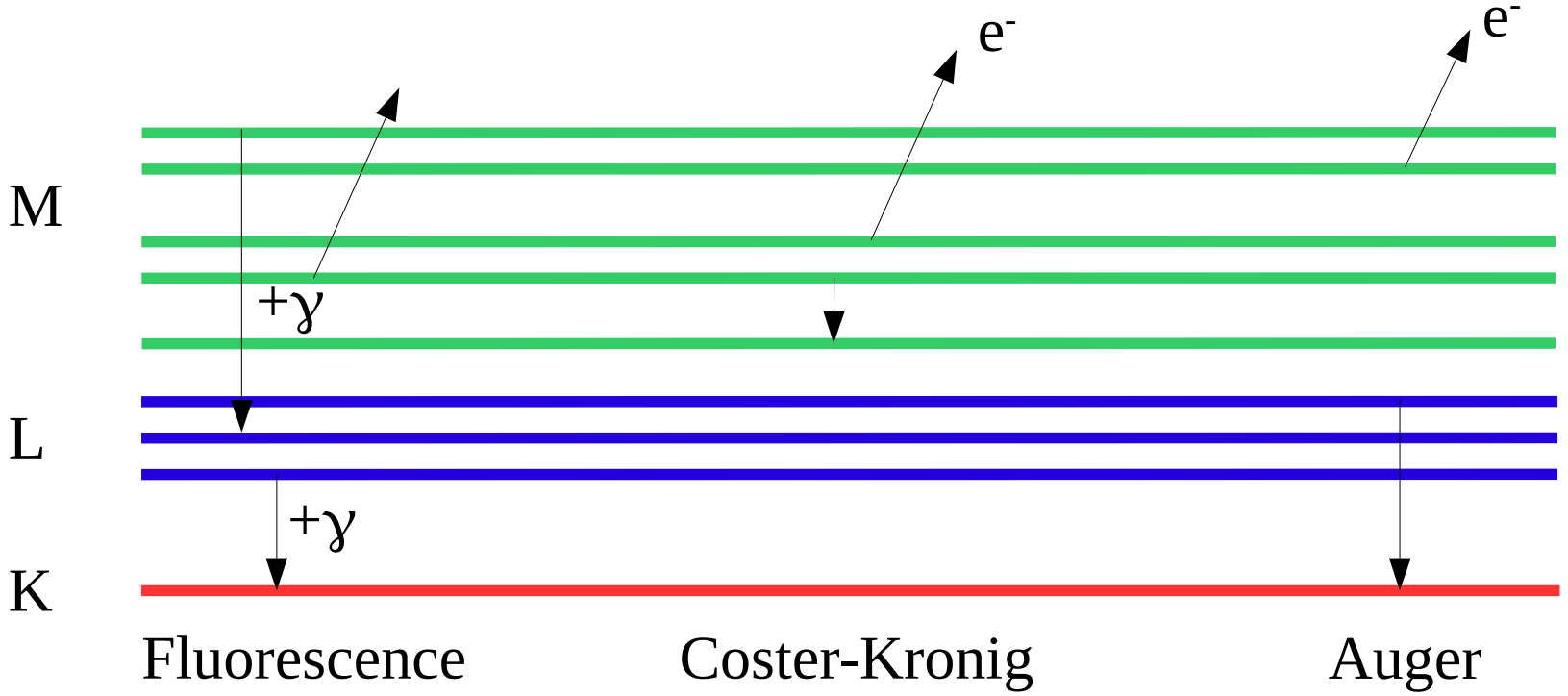
De-excitation

Ralph de Laer Kronig
(1904-1995)

Dirk Coster
(1889-1950)

Lise Meitner
(1878-1968)

Pierre Victor Auger
(1899-1993)



References:

D. Coster and R. de L. Kronig, Physica **2** (1935) 13-24.

Lise Meitner, *Über die β-Strahl-Spektra und ihren Zusammenhang mit der γ-Strahlung*, Z. Phys. **11** (1922) 35-54.

L. Meitner, *Das β-Strahlenspektrum von UX_1 und seine Deutung*, Z. Phys. **17** (1923) 54-66.

P. Auger, Comptes rendus hebdomadaires des séances de l'Académie des sciences, 1923/07 (T177)-1923/12, 169-171.

P. Auger, J. Phys. Radium **6** (1925) 205.

Electric fields

William Gilbert
(1544-1603)

1600: “Electric force”

- 1544: William Gilbert born in Colchester
- 1600: De magnete, magneticisque corporibus, et de magno magnete tellure.
- Concluded that the Earth is a magnet and credited with the first use of the term “electric force”:

> vim illam electricam nobis placet appella-
> re quæ ab humore prouenit

- 1601: Physician to Elizabeth I and James I.

[Guilielmi Gilberti, *De magnete* ..., excudebat Petrus Short anno MDC, Londini, courtesy Universidad Complutense de Madrid and Google books]

Field calculation techniques

- Closed expressions, “analytic method”:
  - almost all 2d structures of wires, planes + periodicities;
  - dielectrics and space/surface charge are laborious;
  - fast and precise, if applicable.

- Finite element method:
  - 2d and 3d structures, with or without dielectrics;
  - several major intrinsic shortcomings.

- Integral equations or Boundary element methods:
  - equally comprehensive without the intrinsic flaws;
  - technically challenging and emerging;
  - consumes more CPU time than FEM, but catching up.

- Finite differences:
  - used for iterative, time-dependent calculations.

1814: Cauchy-Riemann equations

Augustin Louis Cauchy
(Aug 21st 1789 – May 23rd 1857)

- Express the existence of a derivative of a complex analytic function $f = u + \mathrm{i}\, v$:

$$f'(z) = \frac{\partial f}{\partial x} = \frac{\partial u}{\partial x} + \mathrm{i}\frac{\partial v}{\partial x}$$
$$= \frac{\partial f}{\partial \mathrm{i}\, y} = -\mathrm{i}\frac{\partial u}{\partial y} + \frac{\partial v}{\partial y}$$

Georg Friedrich Bernhard Riemann
(Sep 17st 1826 – Jul 20th 1866)

- implies that the real part u is harmonic:

$$\frac{\partial^2 u}{\partial x^2} = \frac{\partial^2 v}{\partial x \partial y} = \frac{\partial^2 v}{\partial y \partial x} = -\frac{\partial^2 u}{\partial y^2} \quad \rightarrow \quad \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = \nabla^2 u = 0$$

Reference: A.L. Cauchy, *Sur les intégrales définies* (1814). This *mémoire* was read in 1814, but only submitted to the printer in 1825.

Jean le Rond d'Alembert
(Nov 16th 1717 –Oct 29th 1783)

1749: 2d flow of liquids

- Jean le Rond d'Alembert takes part in a hydrodynamics contest in Berlin. Euler gives the price to Jaques Adami.
- d'Alembert and Euler don't speak for 10 years, but:

59. On peut encore trouver M & N par la méthode ſuivante qui eſt un peu plus ſimple. Puiſque $\frac{dp}{dz} = -\frac{dq}{dx}$ & $\frac{dp}{dx} = \frac{dq}{dz}$, donc $q\,dx + p\,dz$ & $p\,dx - q\,dz$ ſeront des différentielles complettes.

J. le Rond d'Alembert, "*Theoria resistentiae quam patitur corpus in fluido motum, ex principiis omnino novis et simplissimus deducta, habita ratione tum velocitatis, figurae, et massae corporis moti, tum densitatis compressionis partium fluidi*" (1749). Manuscript at the Berlin-Brandenburgische Akademie der Wissenschaften as document I-M478.

J. le Rond d'Alembert, "*Essai d'une nouvelle théorie de la résistance des fluides*" (1752) Paris.
Available from Gallica BnF.

Stigler's law

“no scientific discovery is named after its original discoverer”

Why not 3d ?

Caspar Wessel (1745-1818)
Jean-Robert Argand (1768-1822)
Johann Carl Friedrich Gauss (1777-1855)
Sir William Rowan Hamilton (1805-1865)
Charles Sanders Peirce (1839-1914)
Georg Frobenius (1849-1917)

- The complex numbers $(\mathbb{R}^2,+,\times)$ form a field, like the real numbers $(\mathbb{R},+,\times)$, but $(\mathbb{R}^3,+,\times)$ does not. As a result, 2d arithmetic can be done with complex numbers, but there is no 3d equivalent for this.

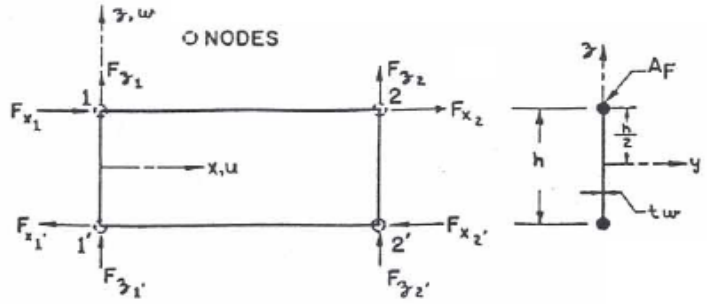
- It can be proven that only $\mathbb{R}$ and $\mathbb{C}$ can form a commutative, associative division algebra.

- $(\mathbb{R}^4,+,\times)$ can be made into a non-commutative division algebra known as quaternions, but this does not help since $\nabla \cdot E$ links all dimensions.

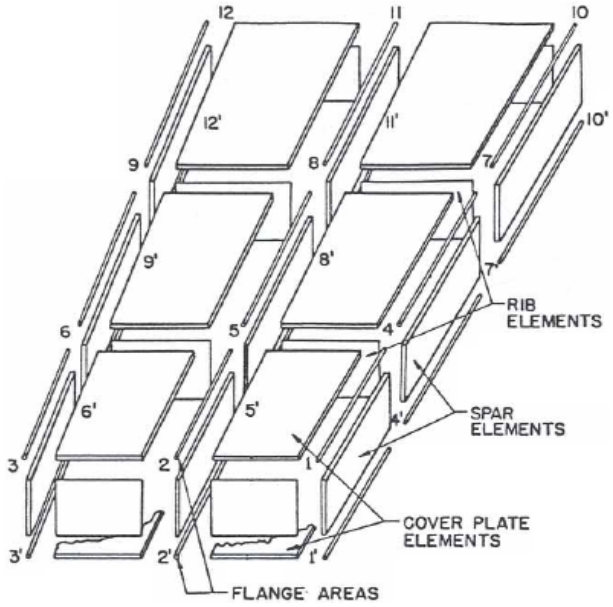
Ιωάννης Αργύρης
(1913-2004)

Aircraft wings – finite elements

- "*Stiffness and Deflection Analysis of Complex Structures*", a study in the use of the finite element technique (then called "direct stiffness method") for aircraft wing design.



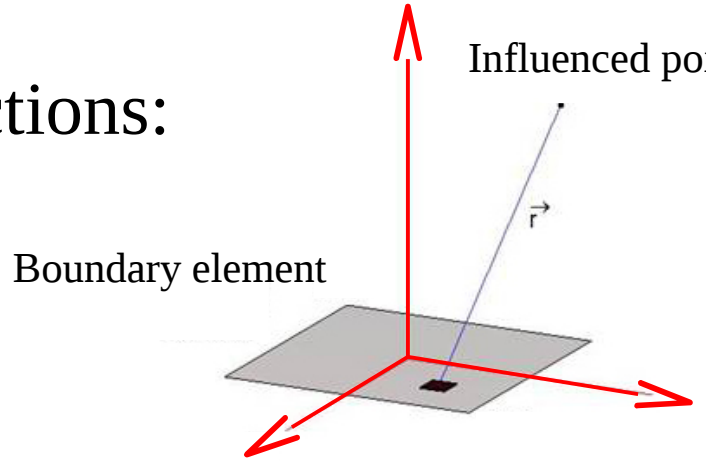
$$[K] = \frac{6EI}{Lh^2(1+4n)} \begin{bmatrix} u_1 & v_1 & w_1 & u_2 & v_2 & w_2 \\ (4/3)(1+n) & & & & & \\ 0 & 0 & & & & \\ -(h/L) & 0 & h^2/L^2 & & & \\ (2/3)(1-2n) & 0 & -(h/L) & (4/3)(1+n) & & \\ 0 & 0 & 0 & 0 & 0 & \\ h/L & 0 & -(h^2/L^2) & h/L & 0 & h^2/L^2 \end{bmatrix}$$



[M.J. Turner, R.W. Clough, H.C. Martin and L.J. Topp, *Stiffness and Deflection Analysis of Complex Structures*, J. Aero. Sc. **23** (1956), 805-824. MJT & LJT with Boeing.]

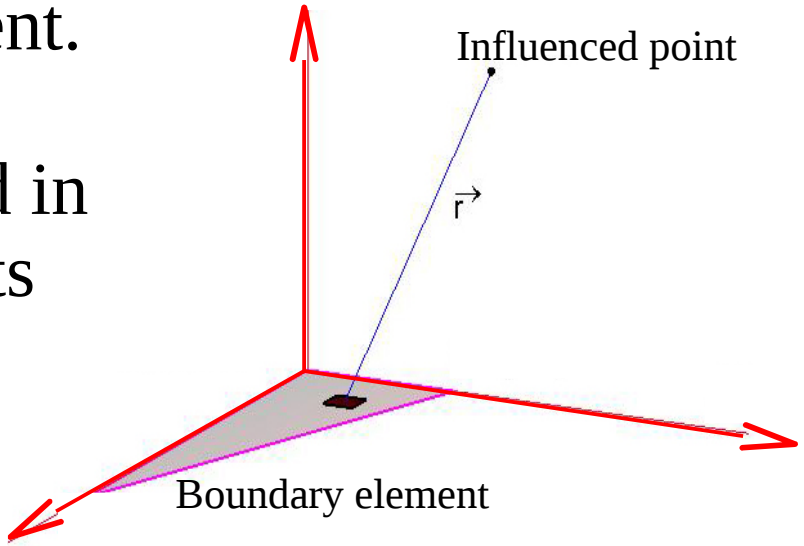
neBEM's Green's functions

- neBEM has only 3 Green's functions:
  - rectangle;
  - right-angled triangle;
  - line segment.



- The Green's functions have been computed by integrating a uniform charge distribution across the element.

- This avoids the nodal charges found in several BEM methods. But the joints between elements still have a jump.



Electron transport

Mean free path in argon

- Literature will tell you — cf webelements.com
  - e^- cross section Ar atom: $\sigma \approx 1.5\ 10^{-16}$ cm^2
  - atoms per unit volume: $n_0 \approx 2.7\ 10^{19}$ $atoms/cm^3$

- Mean free path for an electron ?
  - An electron hits all atoms of which the centre is less than a cross section σ radius from its path;
  - over a distance L, the electron hits $n_0\ \sigma\ L$ atoms;
  - mean free path = distance over which it hits 1 atom;

$$\lambda_e = 1/(\sigma\ n_0) \approx 2.5\ \mu m$$

  - much larger than
    - 4 nm — distance between atoms, and
    - 140-600 pm — typical gas molecule diameters.

MPGDs and the mean free path

- Recall:
  - Mean free path of electrons in Ar: 2.5 µm,

- Compare with:
  - Micromegas mesh pitch: 63.5 µm
  - GEM polyimide thickness: 50 µm
  - Micromegas wire diameter: 18 µm
  - GEM conductor thickness: 5 µm

- Hence:
  - mean free path approaches small structural elements;
  - such devices should be treated at a molecular level.

Velocity in electric fields

- Imagine that an electron stops every time it collides with a gas molecule and then continues along E.

- To cover a distance λ_e it will need a time t:

$$\frac{1}{2}\frac{qE}{m_e}t^2 = \lambda_e, \qquad t = \sqrt{\frac{2\lambda_e m_e}{qE}}, \qquad \bar{v} = \frac{\lambda_e}{t} = \sqrt{\frac{\lambda_e qE}{2m_e}}$$

- which gives:

$$\bar{v} \approx 13\,\mathrm{cm}/\mu\mathrm{s} \quad \text{for} \quad E = 1\,\mathrm{kV}/\mathrm{cm}$$

Drift velocity in argon

- Compare with a Magboltz calculation for pure argon:
  - $\sqrt{E}$ dependence is not too far off, although linearly proportional is more common at low field),

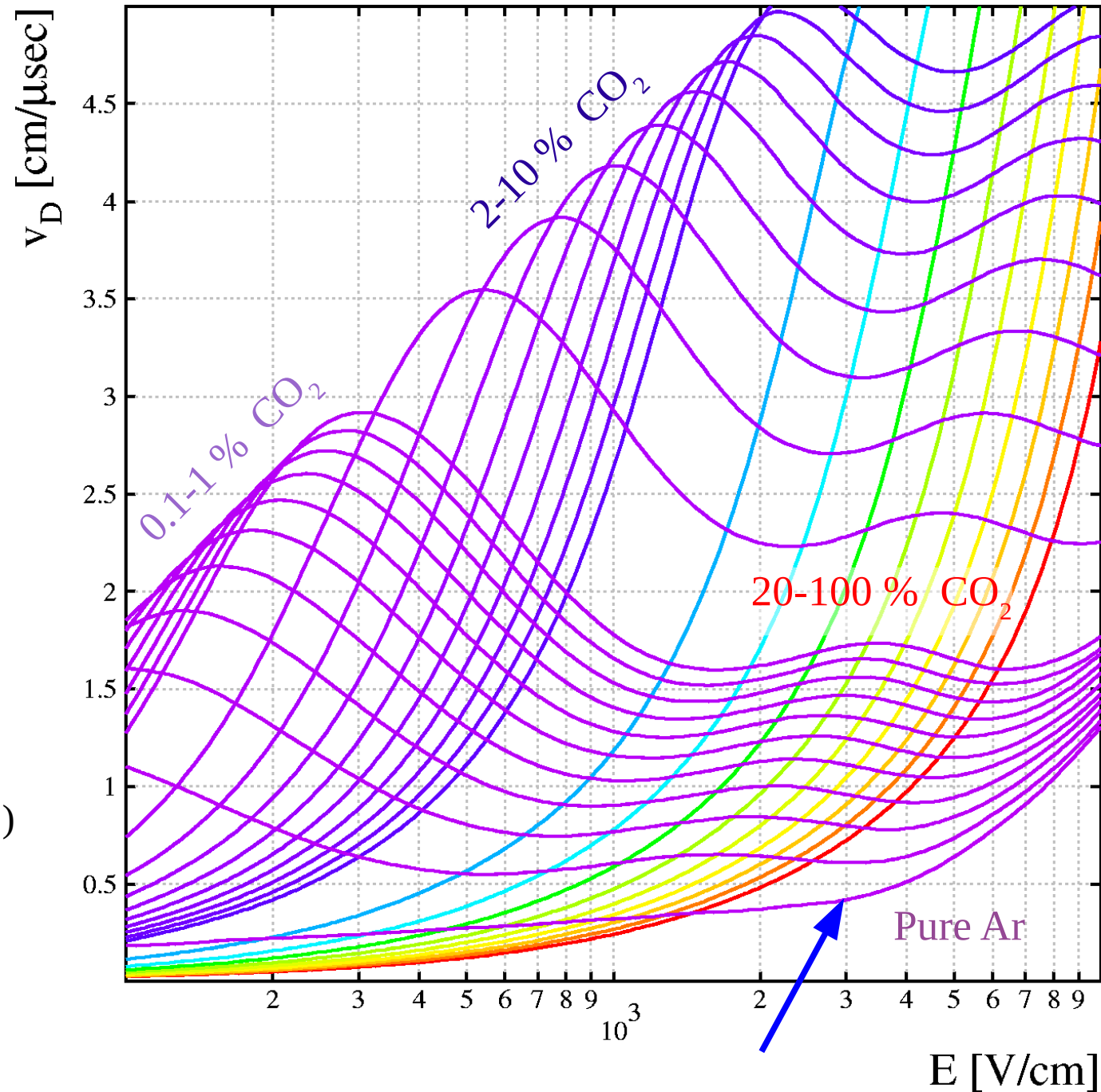
    BUT
  - the velocity is *vastly* overestimated ! Magboltz finds a velocity that is *30 times* smaller ...

    WHY ?

Adding CO_2

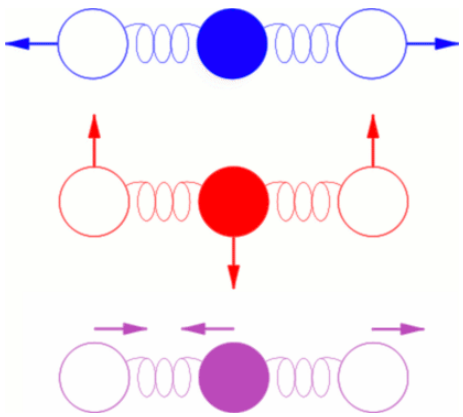
- CO_2 makes the gas faster, dramatically.
- Drift velocities calculated by Magboltz for Ar/CO_2 at 3 bar.

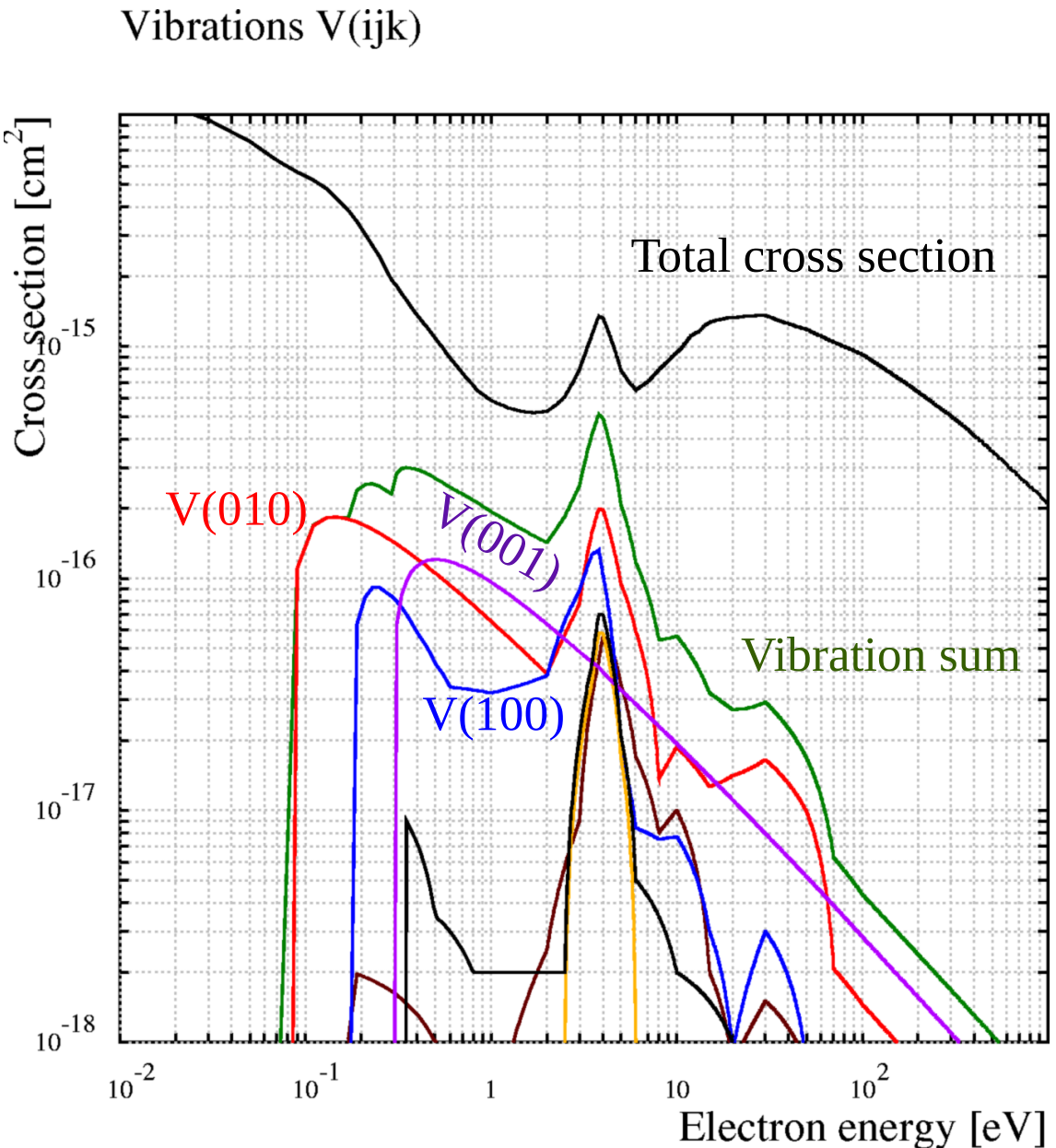
(Note where the arrow is !)



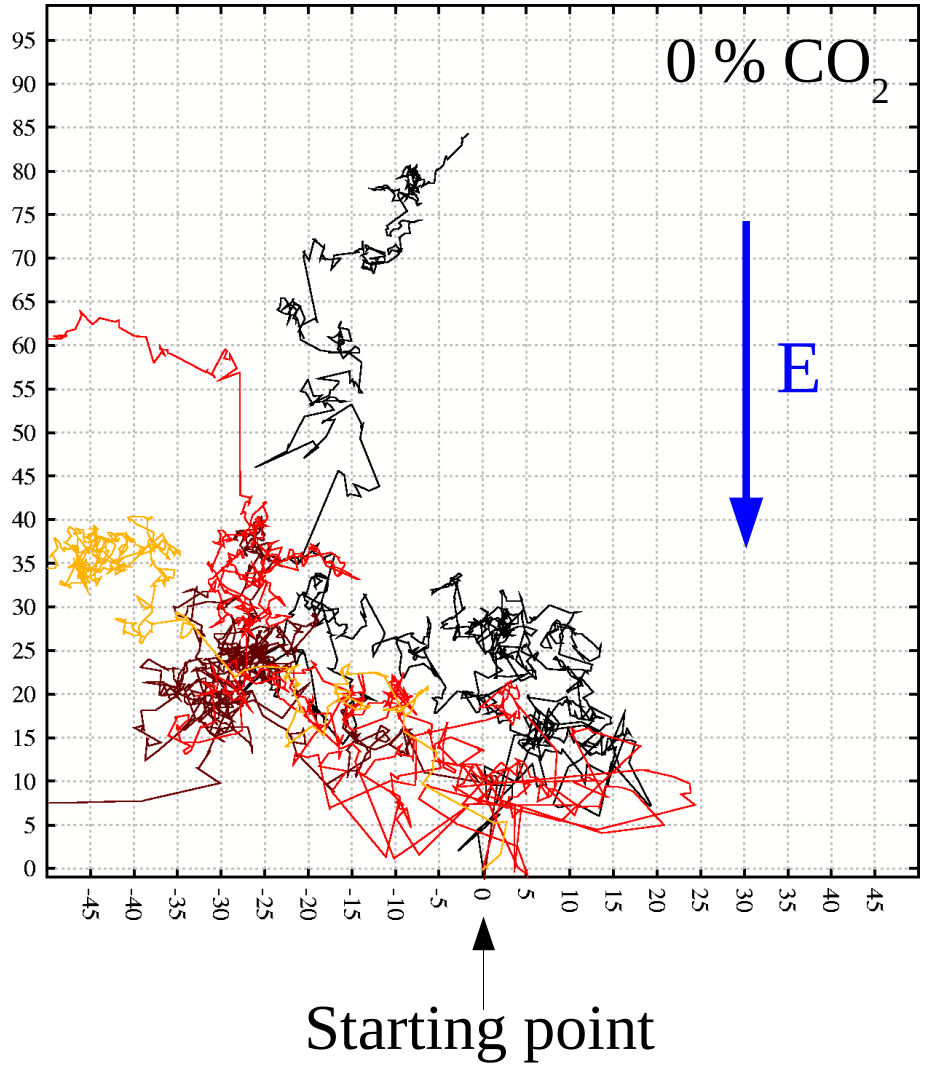
CO_2 – vibration modes

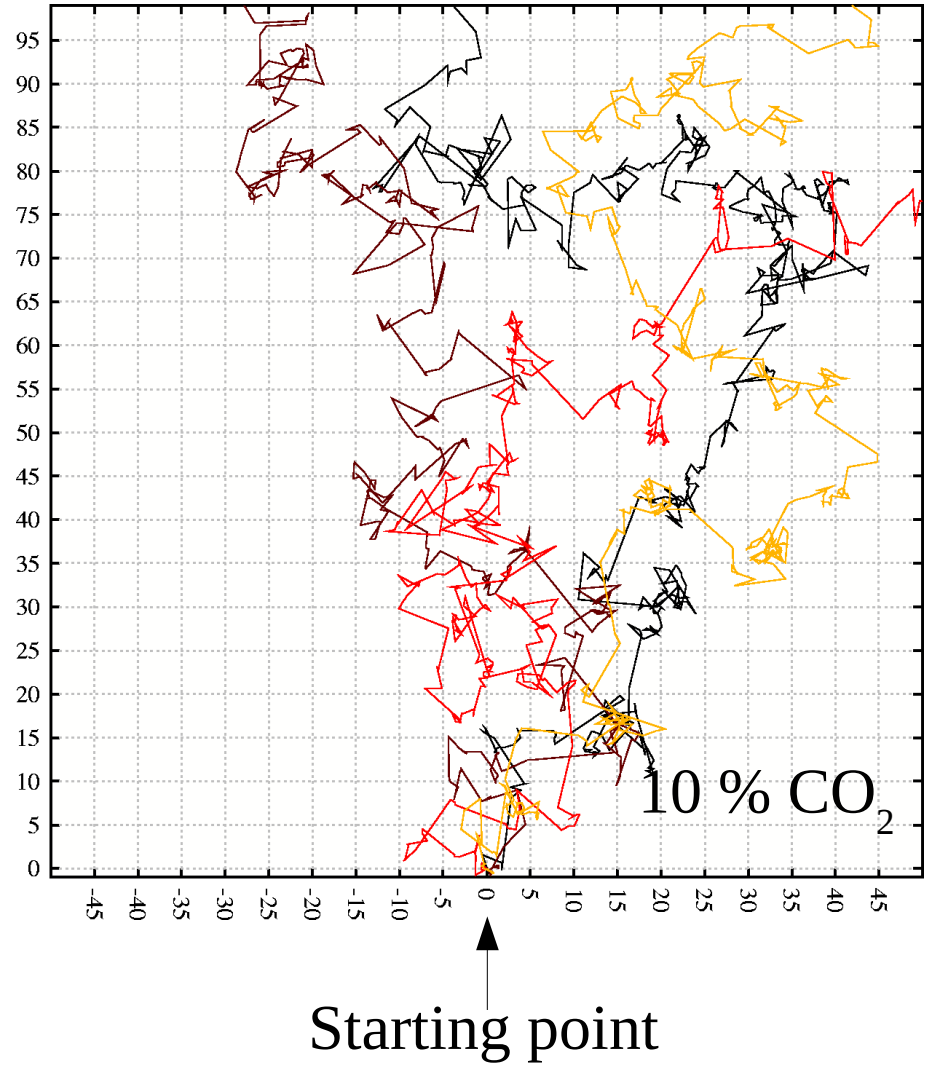
- CO_2 is linear:
  - O – C – O
- Vibration modes are numbered V(*ijk*)
  - *i*: symmetric,
  - *j*: bending,
  - *k*: anti-symmetric.



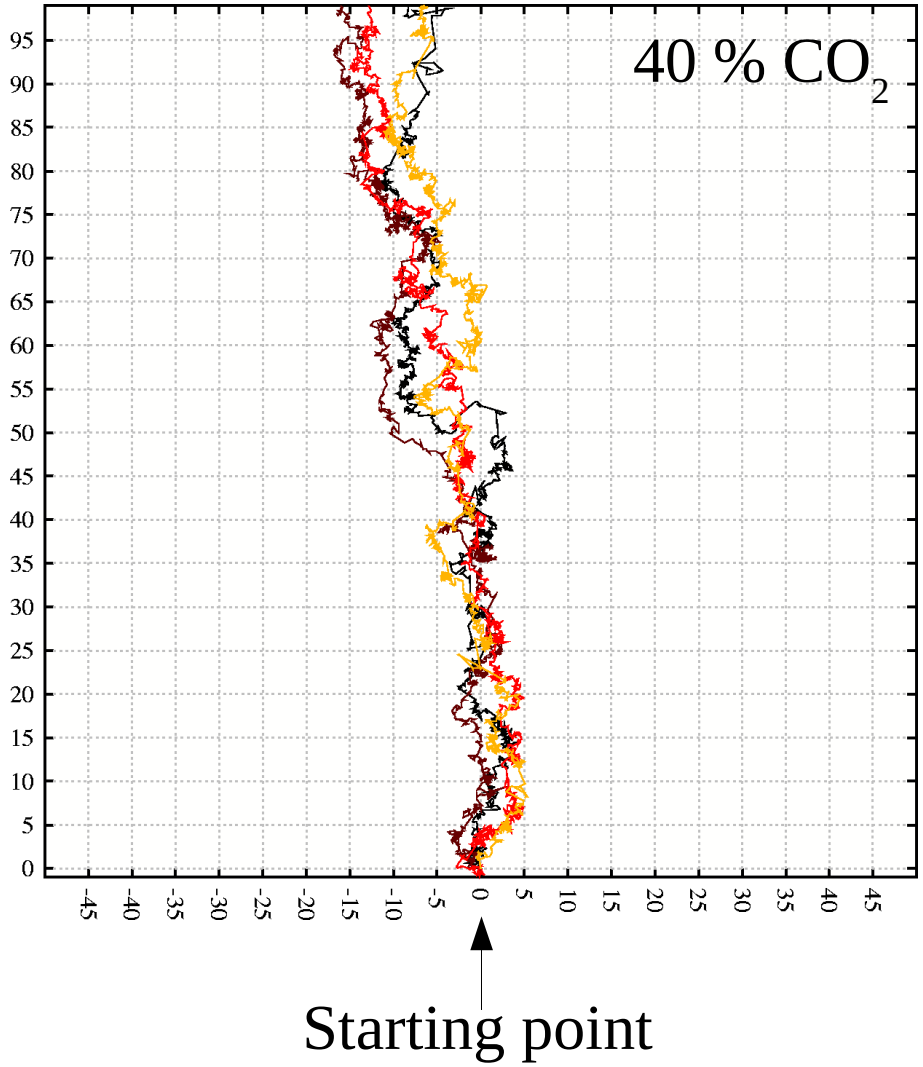


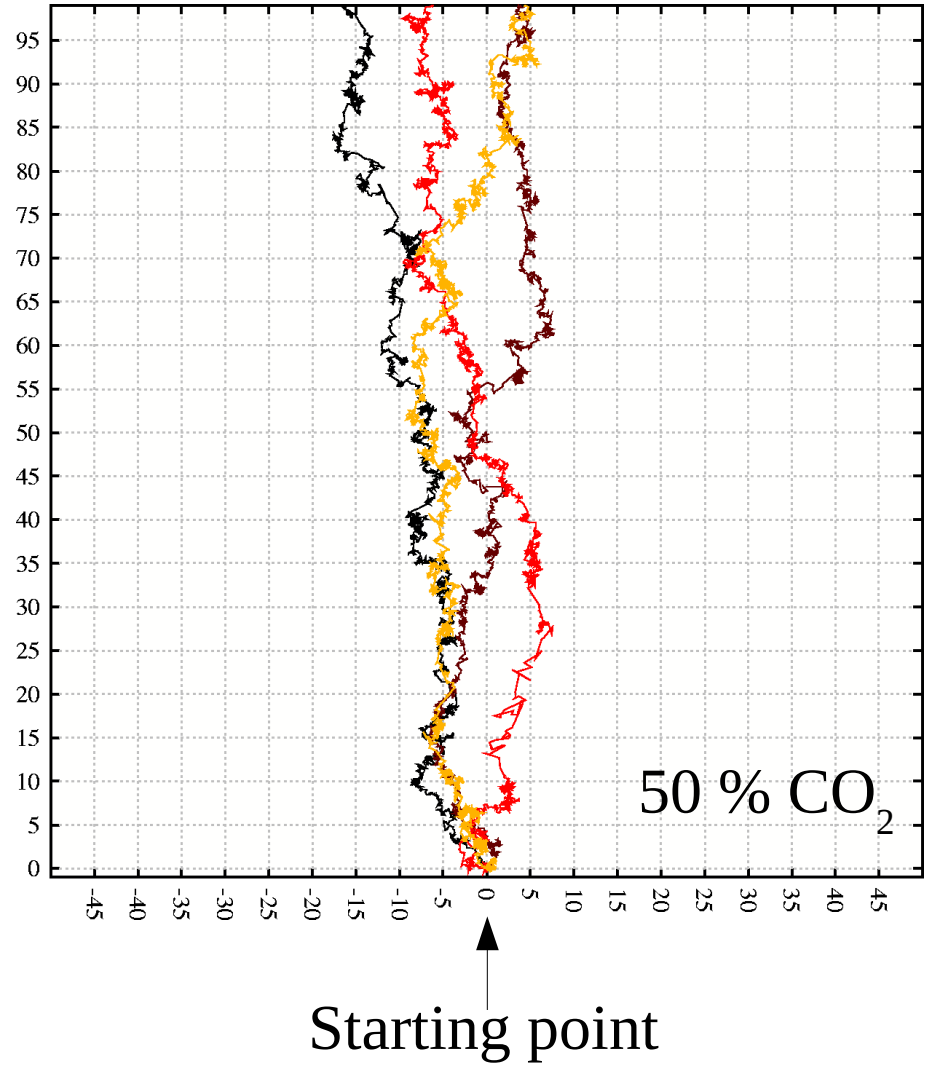
Electrons in Ar/CO_2 at E=1 kV/cm





Electrons in Ar/CO_2 at E=1 kV/cm





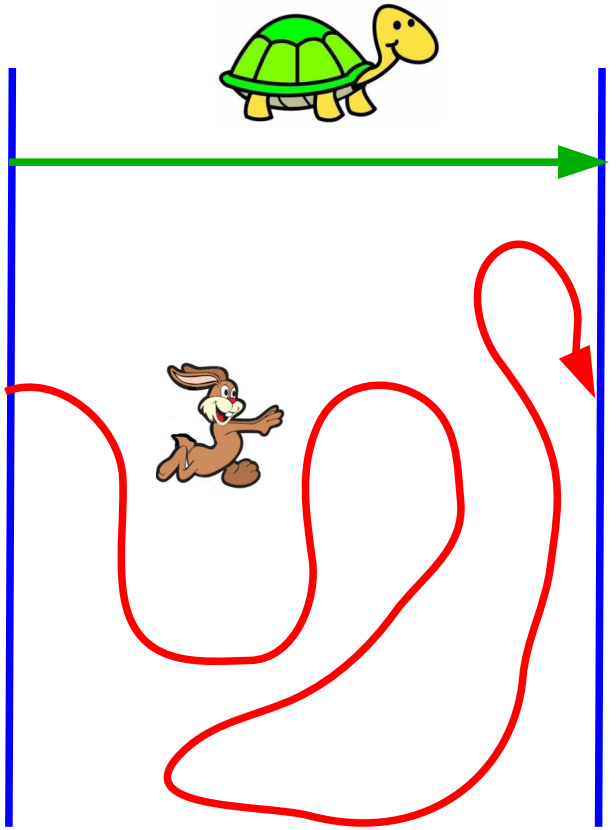
Drift velocity vs Mean velocity

- Drift velocity v_D:
  distance effectively travelled ÷ time needed.

- Compare rabbit and turtle:

$$v_D = \bar{v}$$

$$v_D \ll \bar{v}$$



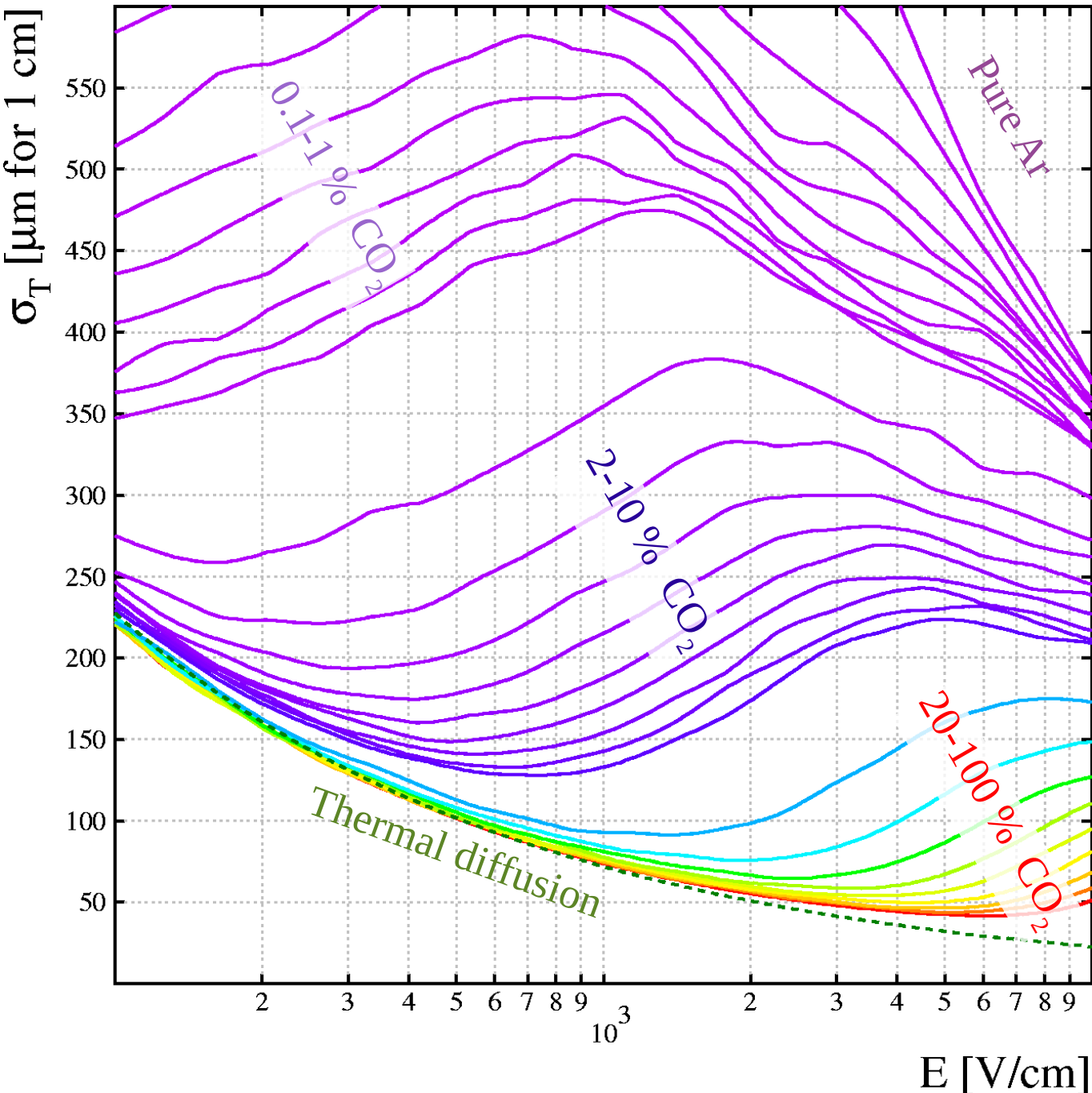
Diffusion

- The combination of a high velocity and low drift velocity implies that the electrons scatter a lot.
- Diffusion = RMS of the difference between the actual and the average movement

In a homogeneous field, if the diffusion over 1 cm of drift is 100 µm, how large is the diffusion over 1 m ?

Adding CO_2

- Transverse diffusion is much reduced by CO_2.
- Calculated by Magboltz for Ar/CO_2 at 3 bar.



Attachment

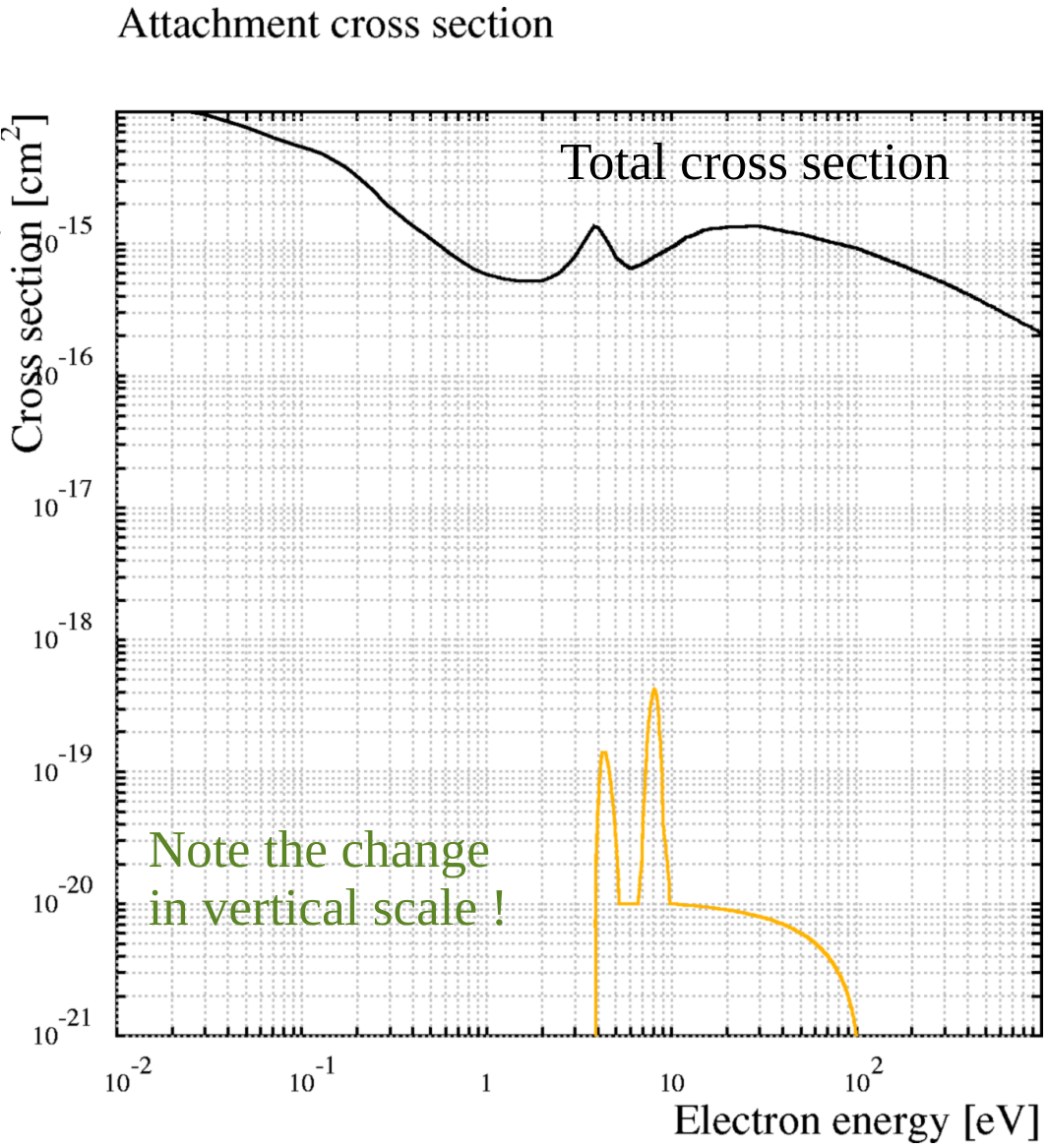
- Some quencher gases can attach electrons.
- Energy-momentum conservation: 3-body or dissociation.
- Examples:
  - O_2: mostly 3-body O_2^- and at higher ϵ 2-body dissociative;
  - H_2O: $[H_2O]_n$ has positive electron affinity, H_2O probably not;
  - CF_4: mostly dissociative F^- + CF_3, F + CF_3^- (below 10 eV);
  - SF_6: SF_6^{-*} < 0.1 eV, $\sigma=10^{-18}$ cm^2, then F^- + SF_n^- (n=3, 4, 5)
  - CS_2: negative ion TPC;
  - CO_2: O^-, $[CO_2]_n^-$ but no CO_2^- (4 eV and 8.2 eV).

CO_2 – dissociative attachment

- CO_2 has a tiny attachment cross section at low energy.
- The 4 eV peak is linked to a short-lived $^2\Pi_u$ shape resonance which decays $e^- CO_2 \rightarrow CO + O^-$;

[A. Moradmand et al. (2013) 10.1103/PhysRevA.88.032703]

- The 8.2 eV peak is thought to be a Feshbach resonance.



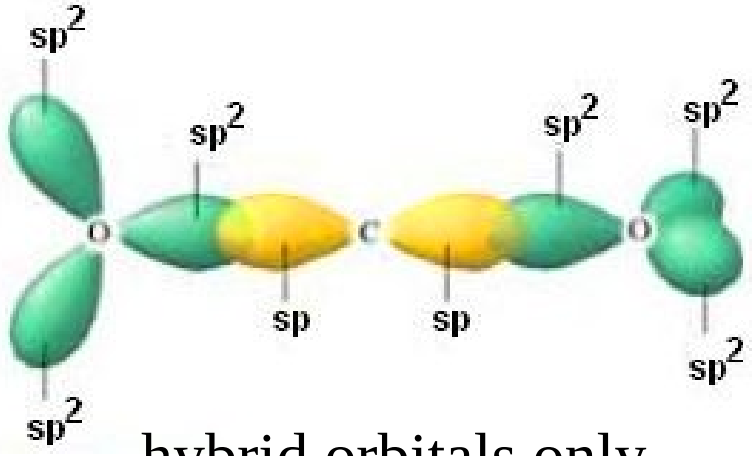
Feshbach and Shape resonances

- Feshbach: e^- attached to electronically excited CO_2^* states of the neutral CO_2 molecule.
- Shape: e^- trapped within barrier.

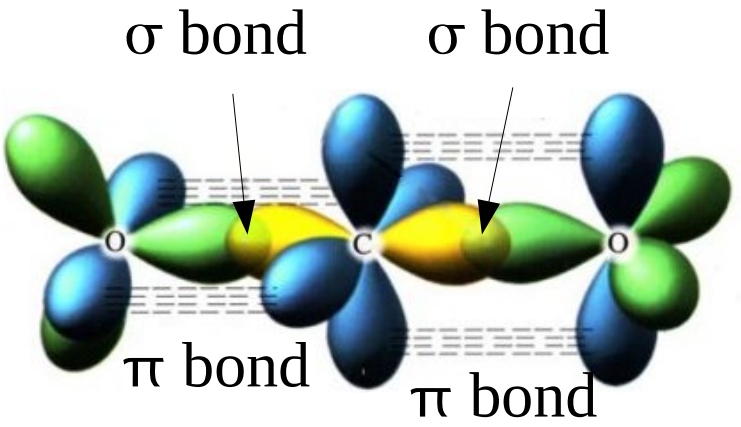
[E. Leber et al., Eur. Phys. J. D **12** (2000) 125-131]

Attachment in CO_2

- CO_2 is a linear molecule:



hybrid orbitals only,
p-orbitals not shown



[Source: presumably SS Zumdahl, Chemistry (1983) DC Heath and Company.]

Calculating transport properties

- One can of course measure every mixture one needs …
- … but it would be far more efficient if one could compute the transport properties of arbitrary mixtures.

1935: Electron energy distribution

- Calculation of the electron energy distribution
  - allowing for energy loss in elastic collisions;
  - detailed balancing of energy and momentum gain (E-field, diffusion) and loss (elastic collision);
  - velocity dependent cross section;
  - use of Legendre expansion (crediting H.A. Lorentz, 1916):

$$f(x, v, \omega) = f_0(x, v) + P_1(\cos\omega) f_1(x, v) + P_2(\cos\omega) f_2(x, v) + \cdots$$
$$= f_0(x, v) + (\xi/v) f_1(x, v) + \cdots .$$

(P_1, P_2: Legendre polynomials)

The function f_0 determines the random distribution in velocity, and f_1 determines the electron drift. The higher terms in the series are nearly always very small and do not correspond to any simple physical property of the distribution, but serve simply to improve the form of the distribution function.

[Philip M. Morse, W.P. Allis and E.S. Lamar, *Velocity Distributions for Elastically Colliding Electrons*, Phys. Rev. **48** (1935) 412–419]

Arthur V. Phelps
(1923 - 2012)

1962: Numerical e^- transport

- Iterative approach, allowing for inelastic cross section terms:
  - educated guess of cross sections (elastic & inelastic);
  - numerically solve the Boltzmann equation (no moments);
  - compare calculated and measured mobility and diffusion;
  - adjust cross sections.

"... more than 50,000 transistors plus extremely fast magnetic core storage. The new system can simultaneously read and write electronically at the rate of 3,000,000 bits of information a second, when eight data channels are in use. In 2.18 millionths of a second, it can locate and make ready for use any of 32,768 data or instruction numbers (each of 10 digits) in the magnetic core storage. The 7090 can perform any of the following operations in one second: 229,000 additions or subtractions, 39,500 multiplications, or 32,700 divisions. " (IBM 7090 documentation)

[L.S. Frost and A.V. Phelps, *Rotational Excitation and Momentum Transfer Cross Sections for Electrons in* H_2 *and* N_2 *from Transport Coefficients*, Phys. Rev. **127** (1962) 1621–1633.]

Magboltz: microscopic e^- transport

- A large number of cross sections for 60 molecules...
  - Numerous organic gases, additives, *e.g.* CO_2:
    - elastic scattering,
    - 44 inelastic cross sections (5 vibrations and 30 rotations + super-elastic and 9 polyads),
    - attachment,
    - 6 excited states and
    - 3 ionisations.
  - noble gases (He, Ne, Ar, Kr, Xe):
    - elastic scattering,
    - 44 excited states and
    - 7 ionisations.

LXcat

- LXcat (pronounced *elecscat*) is an open-access website for collecting, displaying, and downloading ELECtron SCATtering cross sections and swarm parameters (mobility, diffusion coefficient, reaction rates, etc.) required for modeling low temperature plasmas. [...]”

[http://www.lxcat.laplace.univ-tlse.fr/]

LXcat people

- Art Phelps,
- Leanne Pitchford – Toulouse,
- Klaus Bartschat – Iowa,
- Oleg Zatsarinny – Iowa,
- Michael Allan – Fribourg,
- Steve Biagi
- ...

Art Phelps

Leanne Pitchford

Michael Allan

Klaus Bartschat

Gas gain

Sir John Sealy Edward Townsend
(1868-1957)

1901: Gas multiplication

- John Townsend:

Let a force X be applied to N_0 negative ions in a gas at pressure p and temperature t. Let N be the total number of negative ions after the N_0 ions have travelled a distance x. The new negative ions travel with the same velocity as the original N_0 ions, so that all the negative ions will be found together during the motion. The number of negative ions produced by N ions travelling through a distance dx will be $\alpha N dx$; where α is a constant depending on X, p, and t.

Then

$$dN = \alpha N dx.$$

Hence

$$N = N_0 \epsilon^{\alpha x}$$

[J.S. Townsend, "*The conductivity produced in gases by the motion of negatively charged ions*", Phil. Mag. **6-1** (1901) 198-227. If access to the Philosophical Magazine is restricted, then consult a German-language abstract at http://jfm.sub.uni-goettingen.de/.]

Mean size of the avalanche

- Townsend coefficient α: probability per unit length that an electron creates an additional electron.

- Avalanches grow proportionally to their size:

$$\mathrm{d}\,n(x) = n(x)\alpha(x)\ \mathrm{d}\,x$$

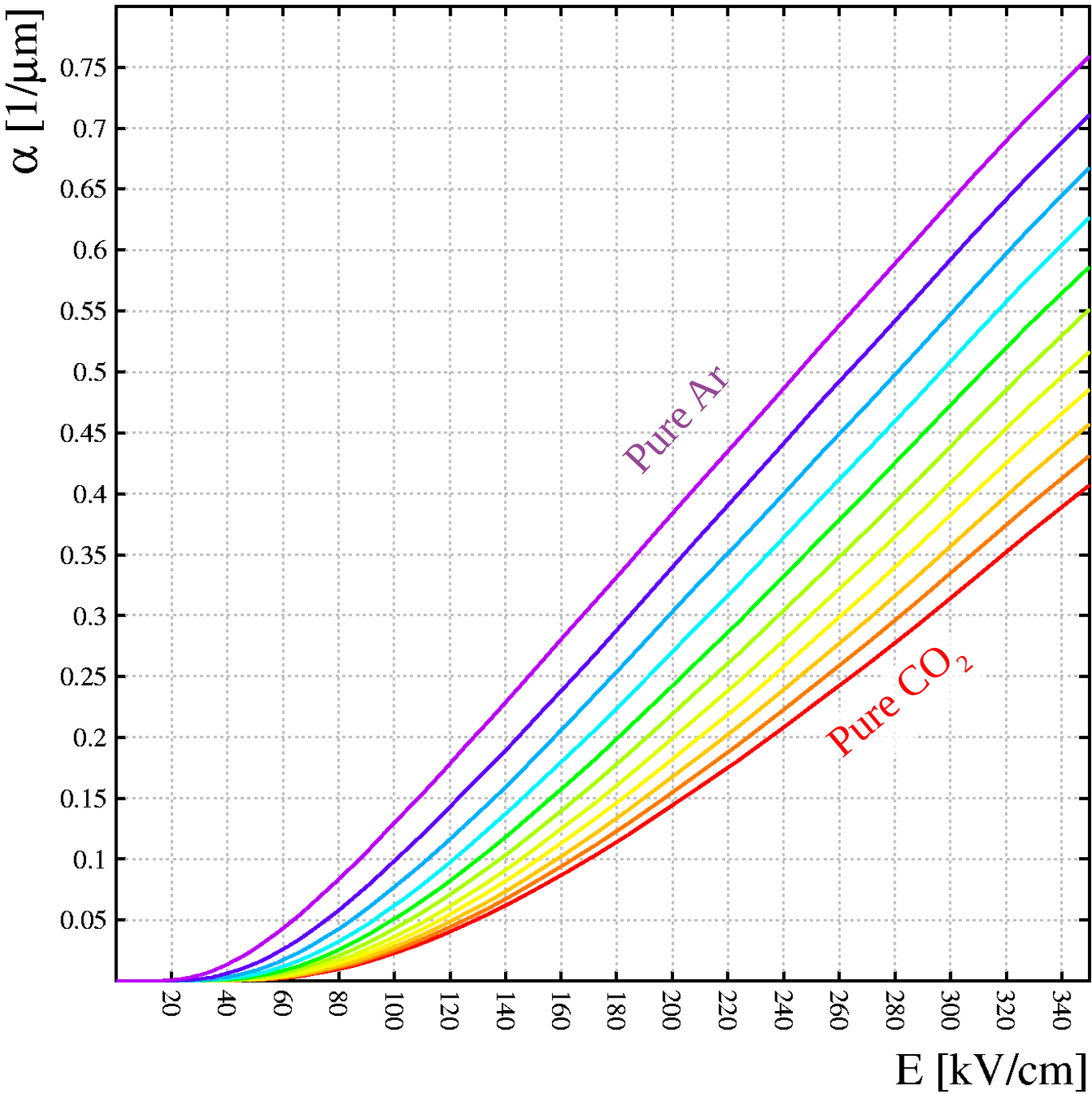
$$n(x) = n(0)e^{\int_0^x \alpha(y)\,\mathrm{d}\,y}$$

- α Depends on the electric field which in turn varies across the detector, symbolically written here as x, and also on pressure and temperature.

- Intuitively, gain is merely a matter of ionisation.

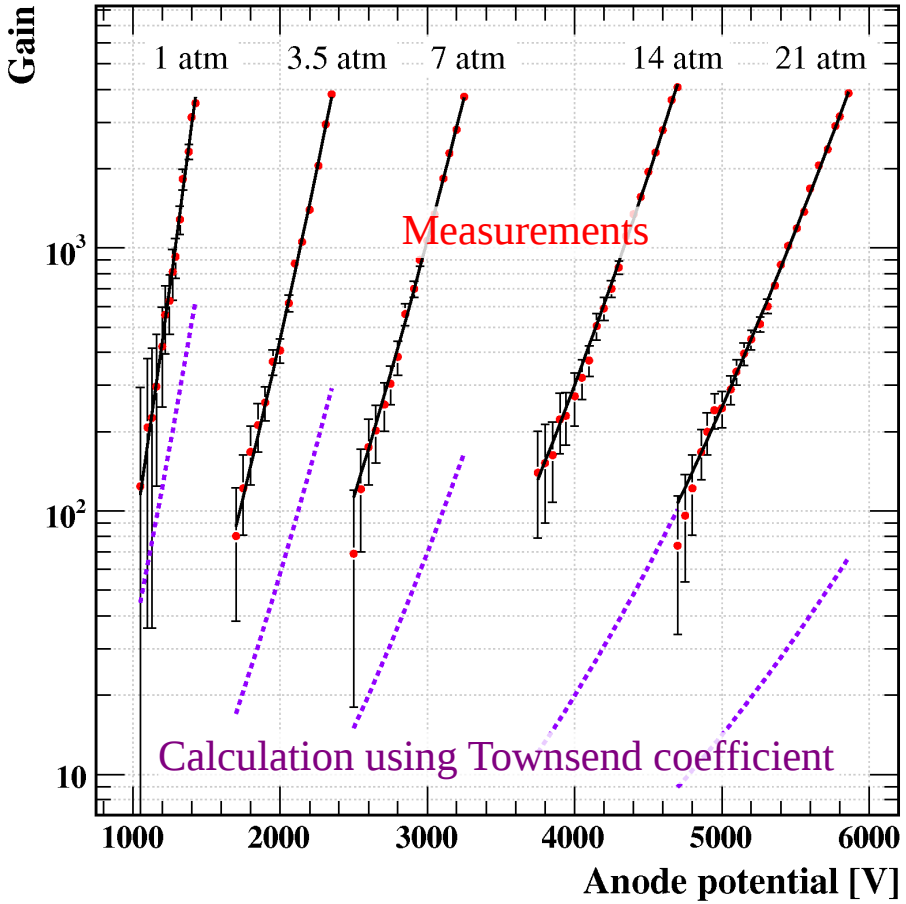
$\alpha(Ar\text{-}CO_2)$

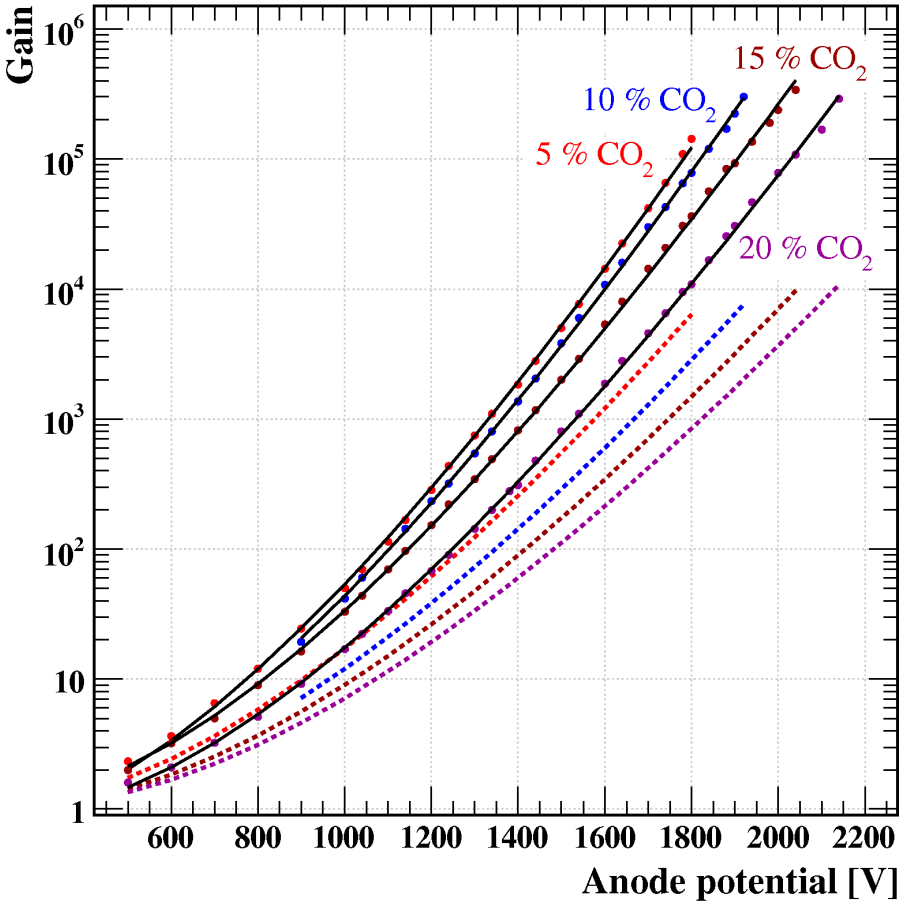
- α = number of e^- an avalanche e^- creates per cm.
- Adding CO_2 reduces the gain.
- Calculated by Magboltz for Ar/CO_2 at 3 bar.

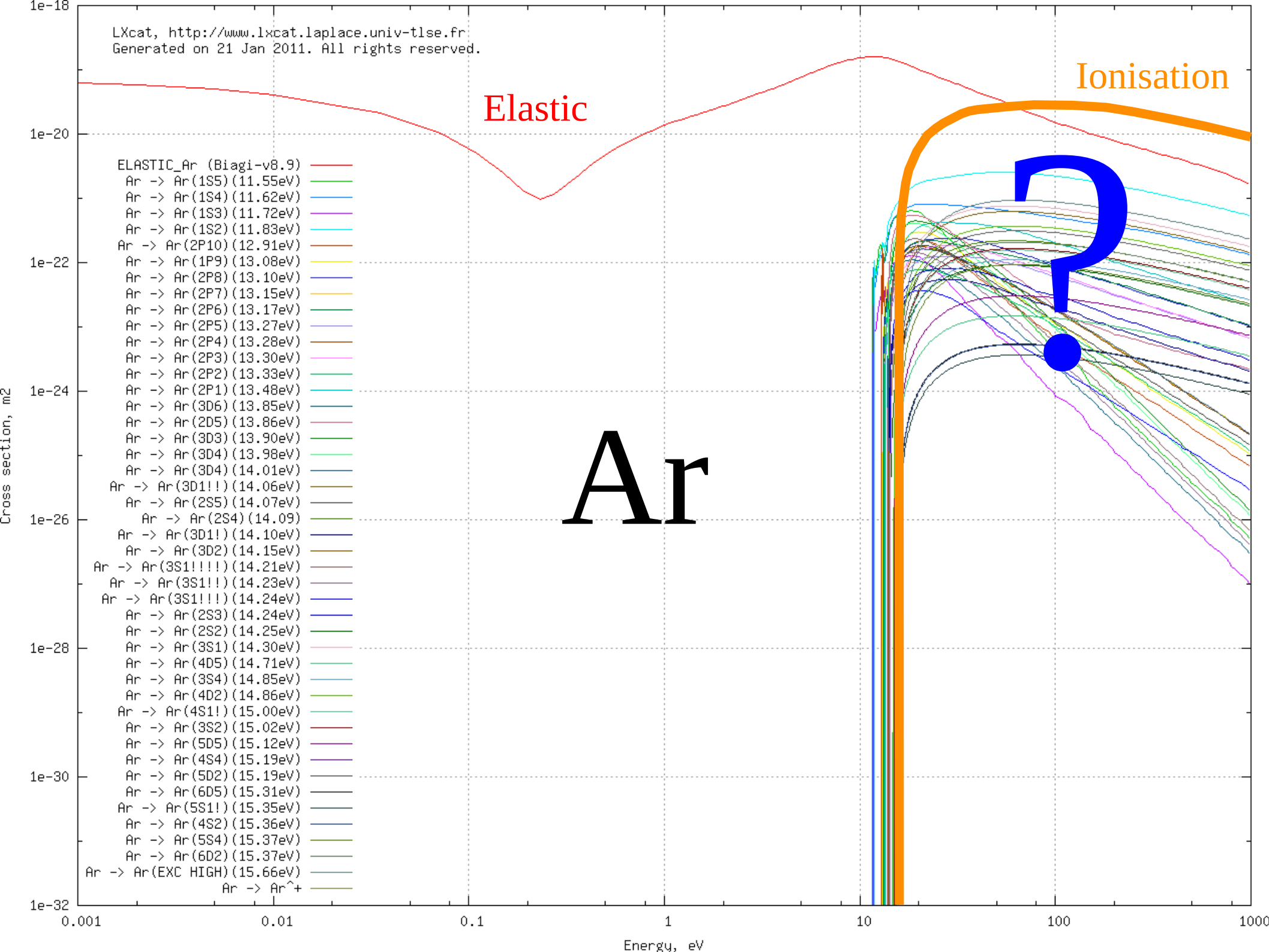


Does this reproduce the measurements ?

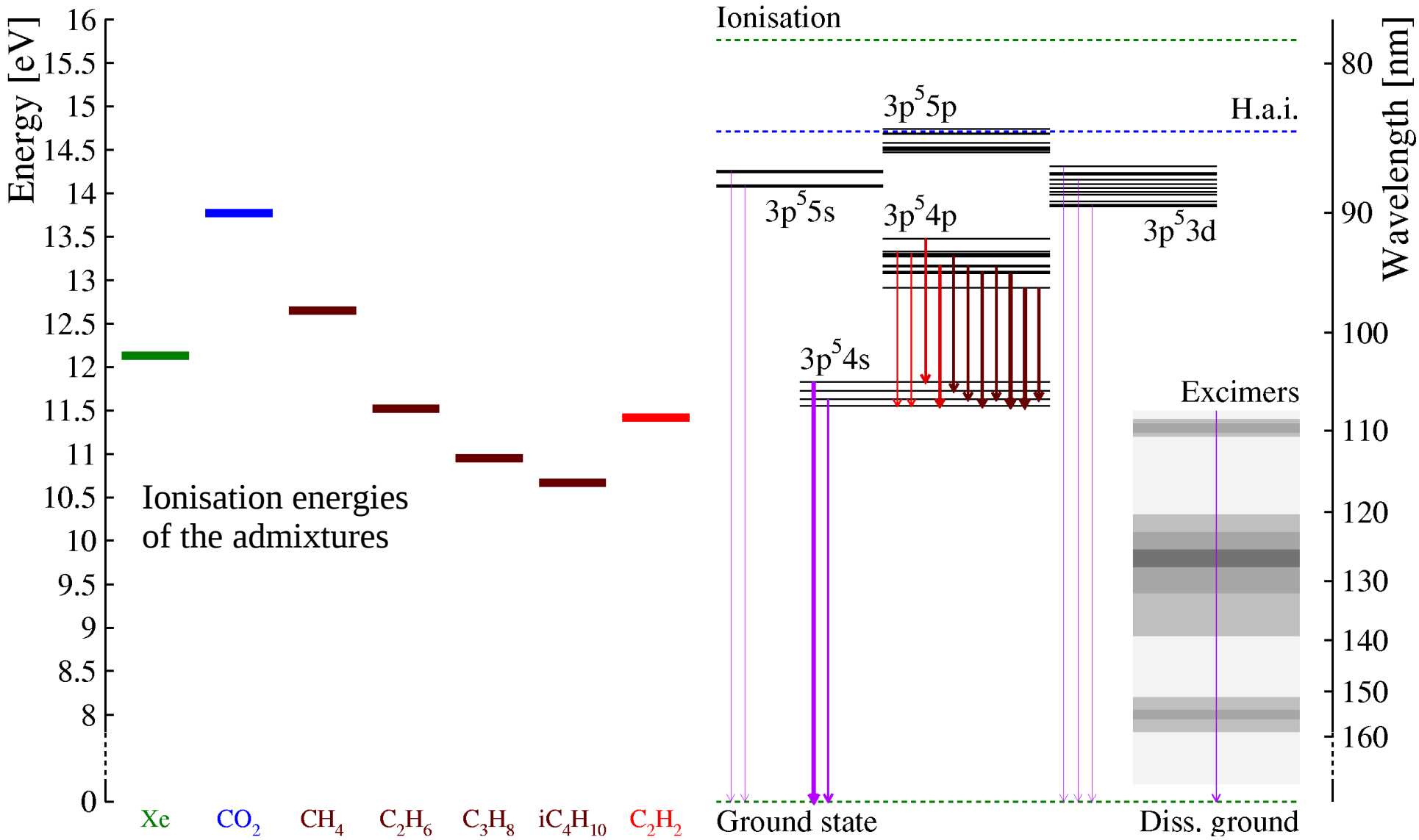
- Ar - CH_4
- Ar - CO_2






LXcat, http://www.lxcat.laplace.univ-tlse.fr
Generated on 21 Jan 2011. All rights reserved.
Elastic
Ionisation
Ar
?
ELASTIC_Ar (Biagi-v8.9)
Ar -> Ar(1S5)(11.55eV)
Ar -> Ar(1S4)(11.62eV)
Ar -> Ar(1S3)(11.72eV)
Ar -> Ar(1S2)(11.83eV)
Ar -> Ar(2P10)(12.91eV)
Ar -> Ar(1P9)(13.08eV)
Ar -> Ar(2P8)(13.10eV)
Ar -> Ar(2P7)(13.15eV)
Ar -> Ar(2P6)(13.17eV)
Ar -> Ar(2P5)(13.27eV)
Ar -> Ar(2P4)(13.28eV)
Ar -> Ar(2P3)(13.30eV)
Ar -> Ar(2P2)(13.33eV)
Ar -> Ar(2P1)(13.48eV)
Ar -> Ar(3D6)(13.85eV)
Ar -> Ar(2D5)(13.86eV)
Ar -> Ar(3D3)(13.90eV)
Ar -> Ar(3D4)(13.98eV)
Ar -> Ar(3D4)(14.01eV)
Ar -> Ar(3D1!!)(14.06eV)
Ar -> Ar(2S5)(14.07eV)
Ar -> Ar(2S4)(14.09)
Ar -> Ar(3D1!)(14.10eV)
Ar -> Ar(3D2)(14.15eV)
Ar -> Ar(3S1!!!!)(14.21eV)
Ar -> Ar(3S1!!!)(14.23eV)
Ar -> Ar(3S1!!!)(14.24eV)
Ar -> Ar(2S3)(14.24eV)
Ar -> Ar(2S2)(14.25eV)
Ar -> Ar(3S1)(14.30eV)
Ar -> Ar(4D5)(14.71eV)
Ar -> Ar(3S4)(14.85eV)
Ar -> Ar(4D2)(14.86eV)
Ar -> Ar(4S1!)(15.00eV)
Ar -> Ar(3S2)(15.02eV)
Ar -> Ar(5D5)(15.12eV)
Ar -> Ar(4S4)(15.19eV)
Ar -> Ar(5D2)(15.19eV)
Ar -> Ar(6D5)(15.31eV)
Ar -> Ar(5S1!)(15.35eV)
Ar -> Ar(4S2)(15.36eV)
Ar -> Ar(5S4)(15.37eV)
Ar -> Ar(6D2)(15.37eV)
Ar -> Ar(EXC HIGH)(15.66eV)
Ar -> Ar^+
Cross section, m2
1e-18
1e-20
1e-22
1e-24
1e-26
1e-28
1e-30
1e-32
0.001
0.01
0.1
1
10
100
1000
Energy, eV

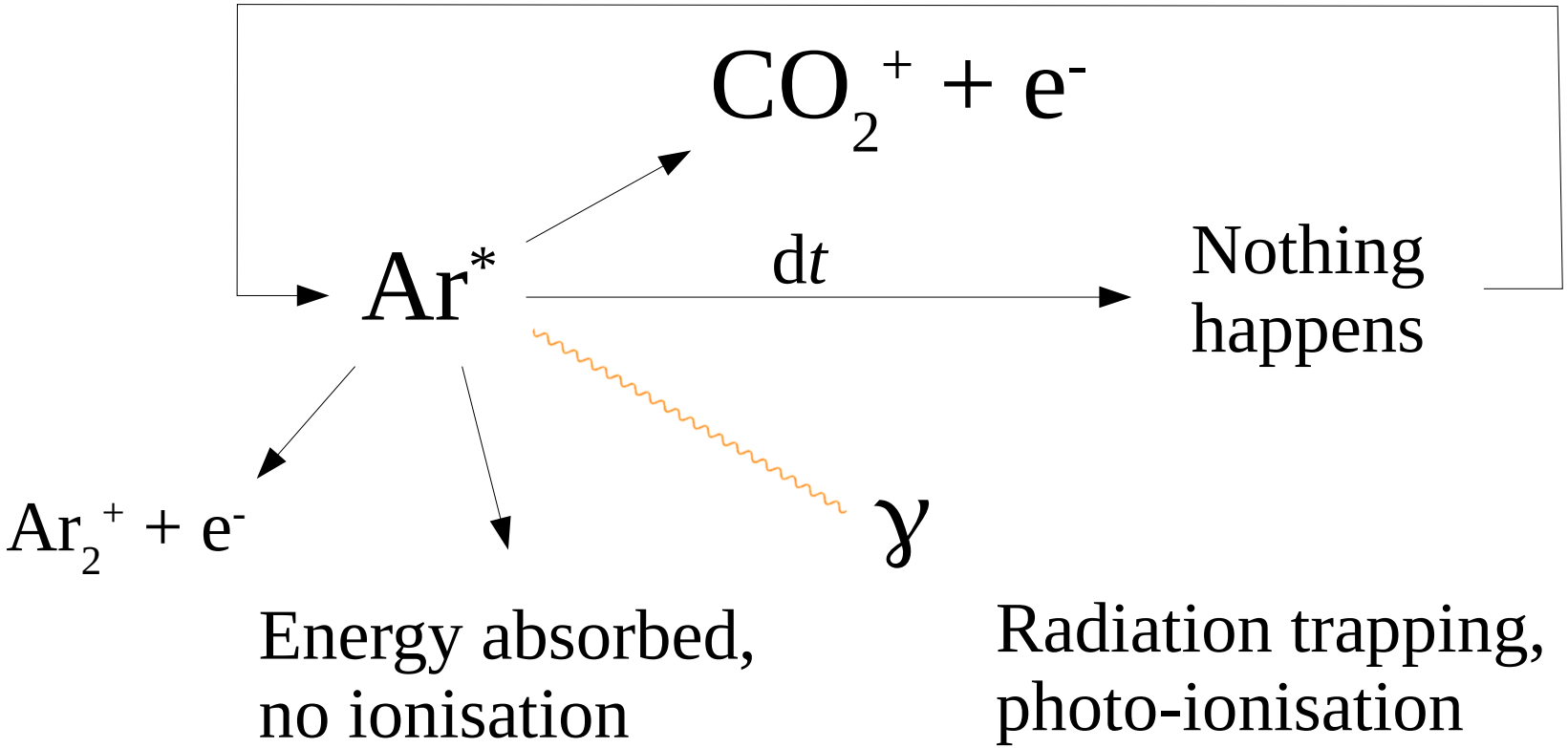
Level diagram argon and admixtures



Frans Michel Penning
(1894-1953)

Simplified Penning model

- Take small steps until the energy has been used up



Radiation trapping

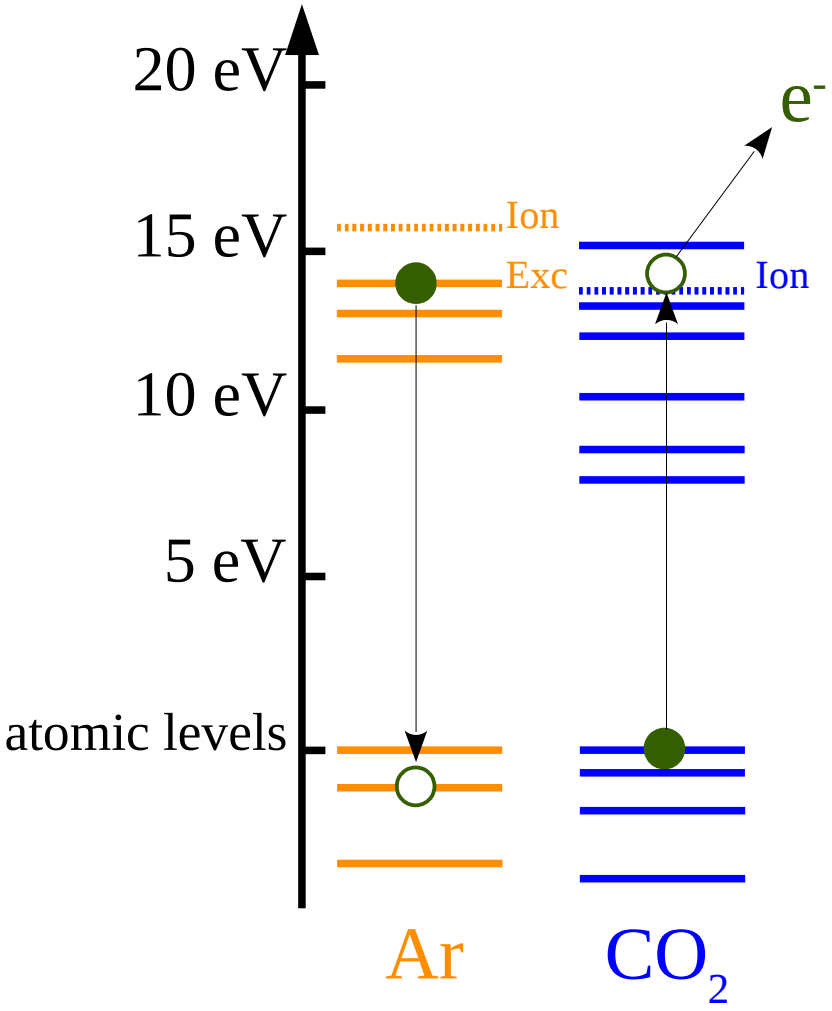
- Photons emitted by radiative decay to ground of excited noble gas atoms have a high probability of being re-absorbed and subsequently re-emitted by the noble gas: radiation trapping.

- Eventually, after many absorption/emission cycles, the photons are absorbed by a quencher gas molecule.

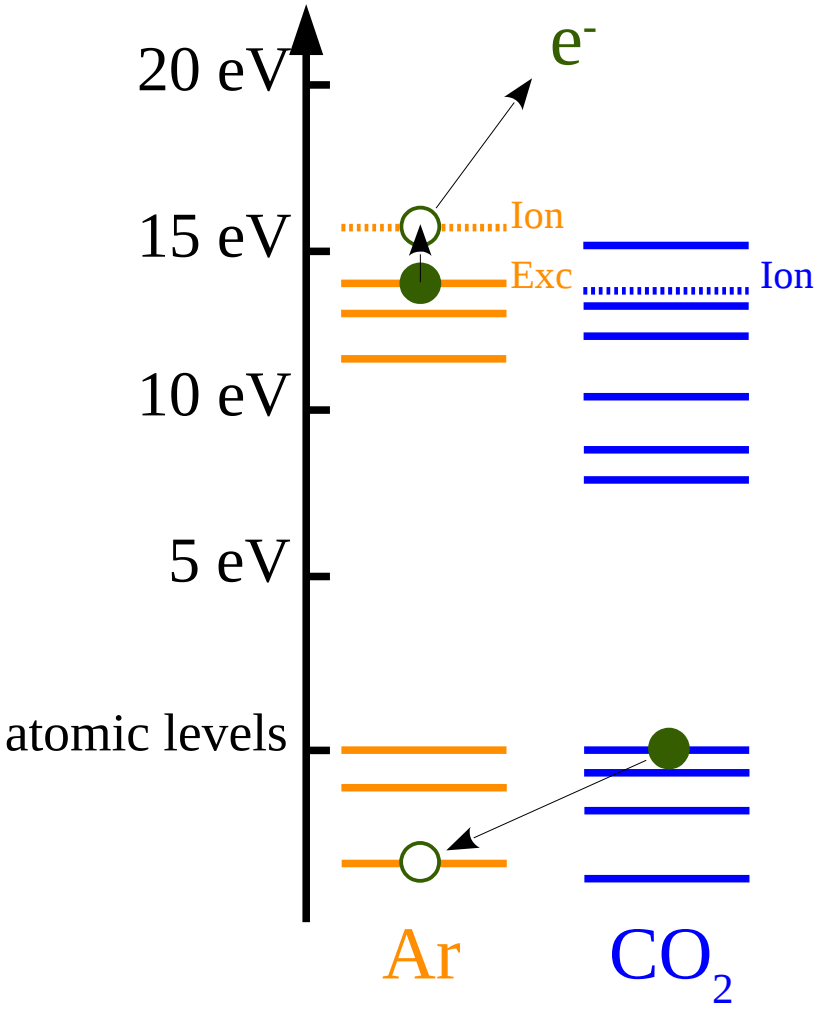
- Excited states can effectively have a long lifetime.

Direct vs Exchange ionisation

Direct (“radiative”)



Exchange (“Auger”)



Simplified Penning model (cont'd)

- Let A be a noble gas and B a quencher, A^* is excited with excitation energy > ionisation energy of B^+.

- In a time-step dt, A^* produces $n\,\mathrm{d}t$ electrons:
  - A^* collides with B and transfers its excess energy, or
  - A^* decays and radiatively ionises B

$$n = p\,c\,\frac{f_{B^+}}{\tau_{A^*B}} + \frac{f_{\mathrm{rad}}}{\tau_{A^*}}$$

- or ... A* survives with probability:

$$1 - \frac{\mathrm{d}t}{\tau_{\mathrm{P}}}, \qquad \frac{1}{\tau_{\mathrm{P}}} = p\,c\,\frac{f_{B^+} + f_{\bar{B}}}{\tau_{A^*B}} + \frac{1}{\tau_{A^*}}$$

p = pressure
c = quencher fraction
f_{B^+} = collision transfer
$f_{\bar{B}}$ = collision loss
f_{rad} = radiative decay
τ_{A^*B} = collision time
τ_{A^*} = decay time

Simplified Penning model (cont'd)

- Summing to get the number of electrons from A^*:

$$r(p,c) = n\,\mathrm{d}t + n\,\mathrm{d}t\left(1-\frac{\mathrm{d}t}{\tau_P}\right) + n\,\mathrm{d}t\left(1-\frac{\mathrm{d}t}{\tau_P}\right)^2 + \ldots$$

$$= n\,\tau_P$$

Nothing happened in the first step

- $r(p,c)$ is the fraction of the excitation frequency to be added to the ionisation frequency in order to correct the Townsend coefficient for the Penning effect.

- There are only two a priori unknown parameters:
  - f_{rad}: radiative ionisation probability,
  - f_{B^+}: collision ionisation probability.

Determining the Penning parameters

- The Penning transfer rate $r(p,c)$ is measured by finding, in experimental data, the fraction of excitations to be added to α:

$$G = \exp \int \alpha \left(1 + r(p,c) \frac{\nu_{\text{exc}}}{\nu_{\text{ion}}} \right)$$

- The model parameters may be found by fitting:

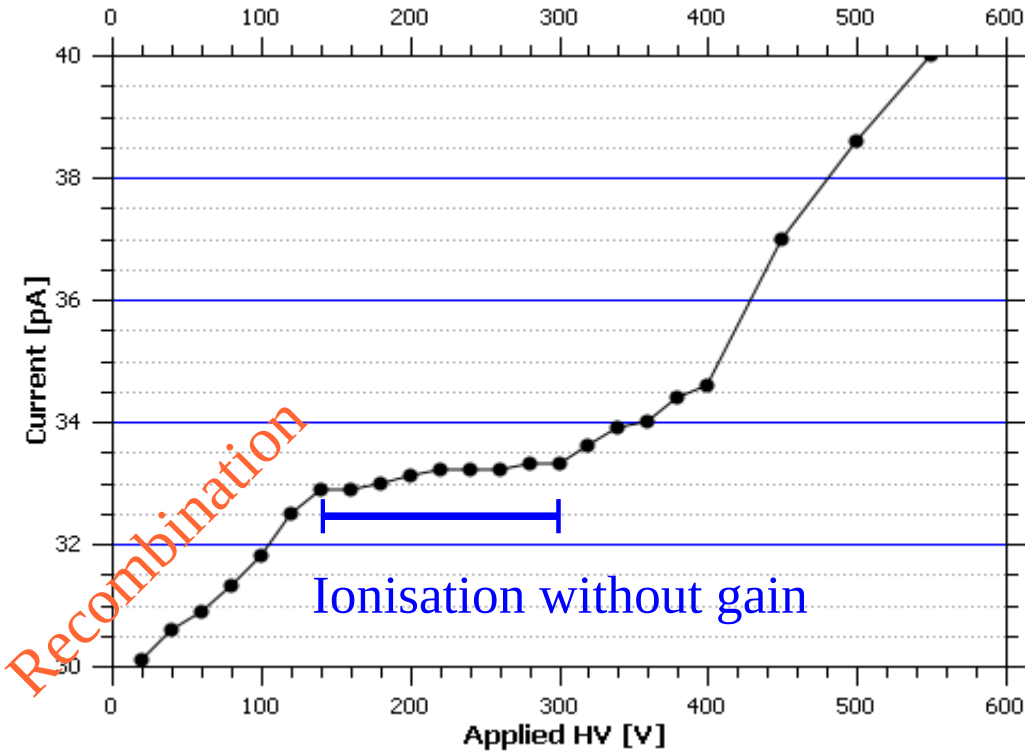
$$r(p,c) = \frac{p\,c\,f_{B^+}/\tau_{AB} + p(1-c)\,f_{A^+}/\tau_{AA} + f_{\text{rad}}/\tau_{A^*}}{p\,c\,(f_{B^+} + f_{\bar{B}})/\tau_{AB} + p(1-c)(f_{A^+} + f_{\bar{A}})/\tau_{AA} + 1/\tau_{A^*}}$$

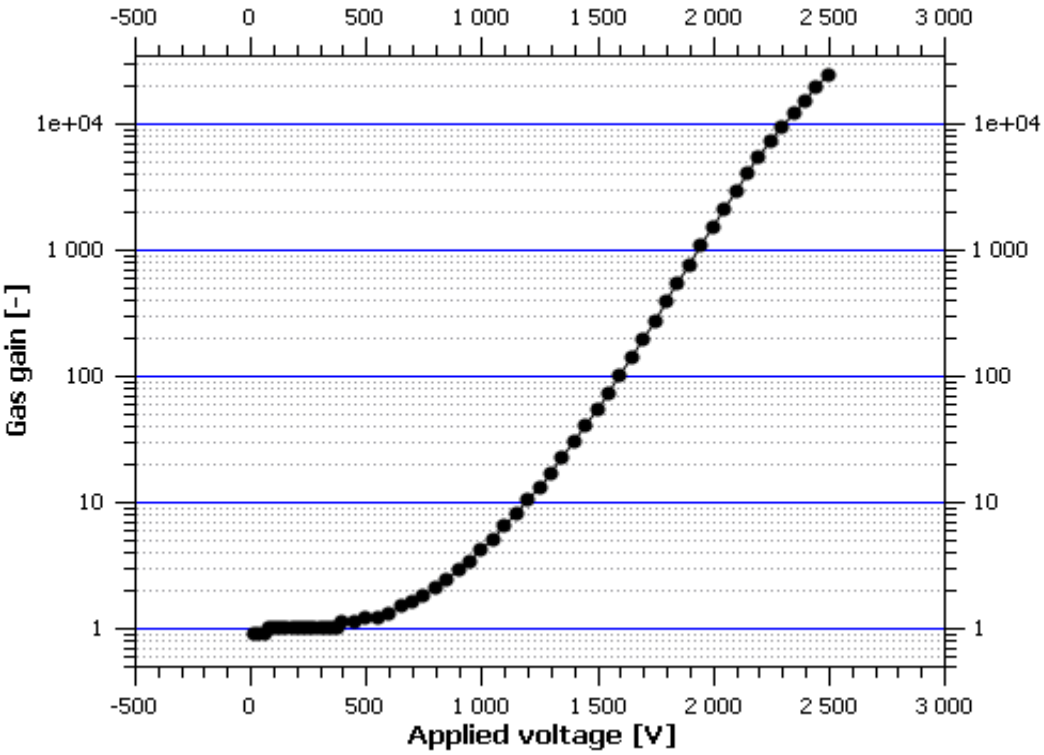
$A^* \rightarrow B^+$ $\qquad$ $A^* \rightarrow A^+$ $\qquad$ $A^* \rightarrow A\,\gamma$

AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY

Data covers 5 orders of magnitude !

- Current reference is taken at the ionisation level.
- Main source of error: ~5 %.

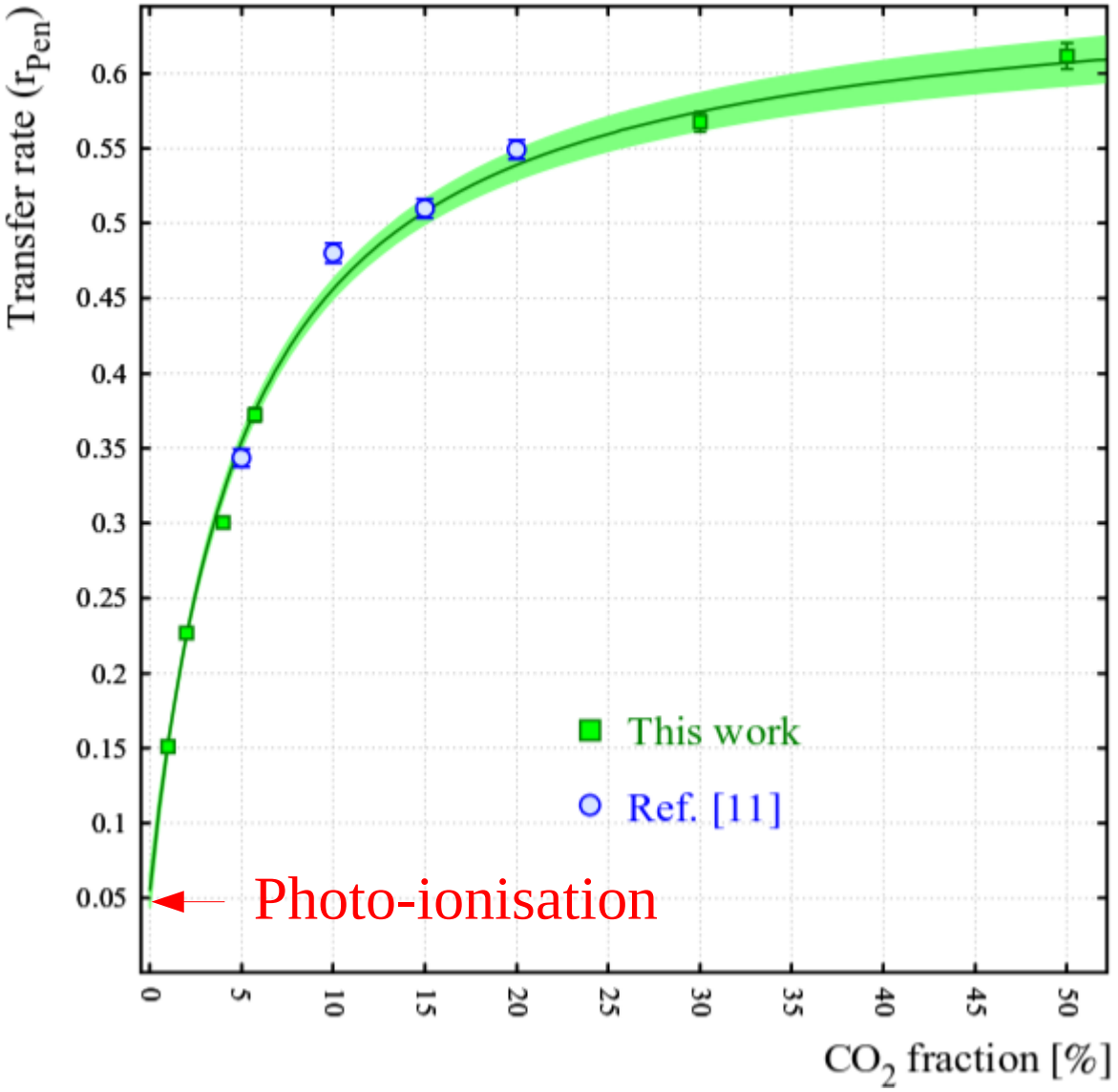




Ar-CO_2 transfer rates

- Penning parameter fits with data from Tadeusz Kowalski et al. 1992 and 2013.
- At p = 1070 hPa.

[10.1016/0168-9002(92)90305-N, 10.1016/j.nima.2014.09.061]



Gas gain fluctuations

G.U. Yule (1923), W.H. Furry (1937), R.A. Wijsman (1949) & others

- If the distance between ionisations fluctuates exponentially with a mean of 1/α (reciprocal of the Townsend coefficient),

- then, the avalanche size fluctuates (nearly) exponentially:

$$p(n) = \frac{1}{\bar{n}}\left(1-\frac{1}{\bar{n}}\right)^{n-1}$$

George Udny Yule (1871-1951)

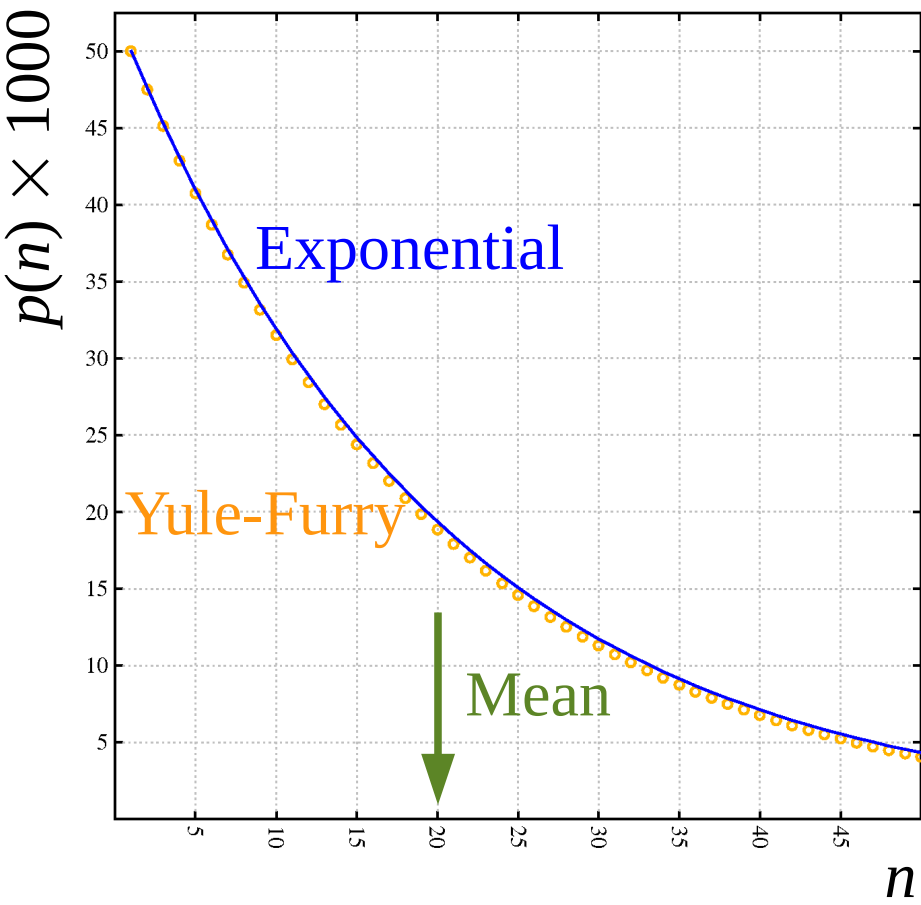
[G. Udny Yule, *A Mathematical Theory of Evolution, based on the Conclusions of Dr. J.C. Willis, F.R.S.*, Phil. Trans. Roy. Soc. London B **213** (1925) 21-87.
W.H. Furry, *On Fluctuation Phenomena in the Passage of High Energy Electrons through Lead*, Phys. Rev. **52** (1937) 569-581.
Robert A. Wijsman, *Breakdown Probability of a Low Pressure Gas Discharge*, Phys. Rev. **75** (1949) 833-838.]

$$f \equiv \sigma^2/\bar{n}^2 \approx 1$$

Statistics Yule-Furry

- Yule-Furry is exponential for large mean avalanche sizes:

$$p(n) = \frac{1}{\bar{n}}\left(1-\frac{1}{\bar{n}}\right)^{n-1} \approx \frac{e^{-n/\bar{n}}}{\bar{n}-1}$$

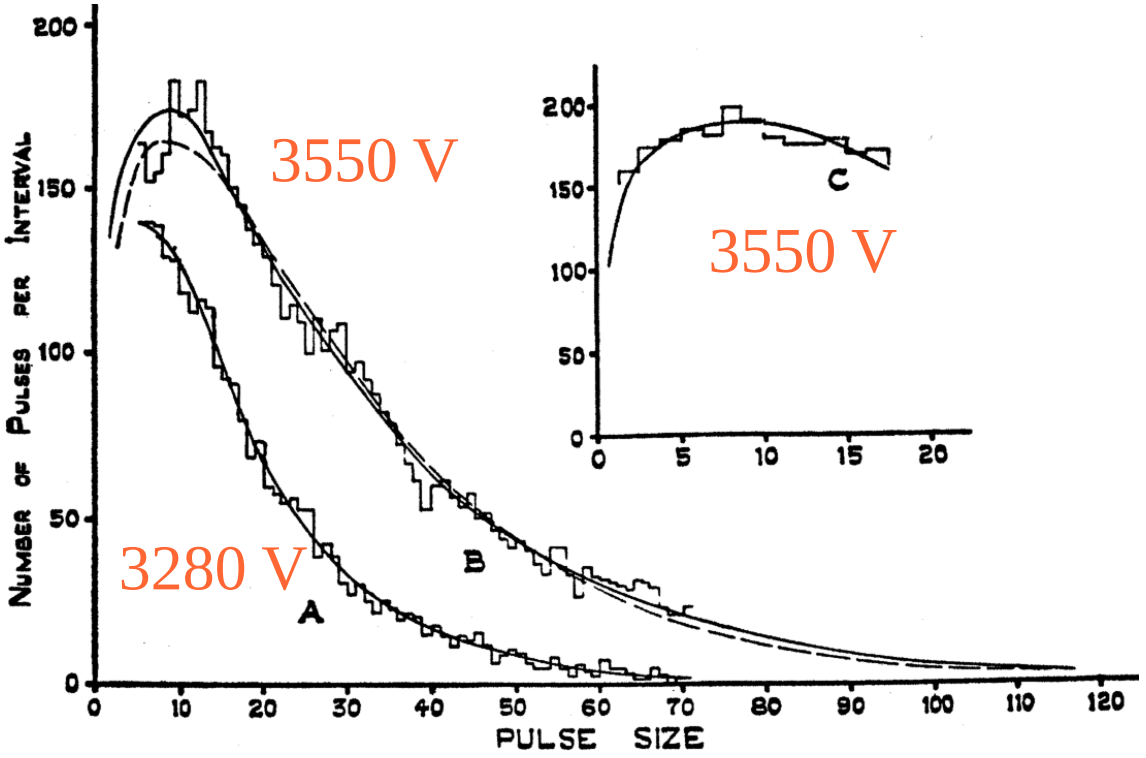


- Mean: $\bar{n}$

  RMS: $\bar{n}\sqrt{1-1/\bar{n}} \approx \bar{n}$

S.C. Curran (1949)

- S.C. Curran *et al*. measured the pulse height distribution in a cylindrical counter (d = 150 μm wire, Ar 50 % CH_4 50 %, p = 670 mbar) at G ~10^4-10^5:



$$p(n) = \sqrt{n}\,e^{-n}$$

$$f \equiv \left(\frac{\sigma}{\bar{n}}\right)^2 \approx \frac{2}{3}$$

Pólya distribution

- When mathematicians speak of a Pólya distribution, they refer to a negative binomial distribution.

- Avalanche papers may mean a Γ-distribution:

$$P(g) \propto g^{\theta} e^{-(1+\theta)g}$$

Note: we sometimes shift θ by one unit !

- and sometimes make reference to a 1923 paper which deals with railway accidents, diseases and flowers.

Der Tod einer Person infolge Eisenbahnunfalls muß als eine außerordentliche Verschlechterung der Chancen aller Mitreisenden angesehen werden.

- [F. Eggenberger and G. Pólya, Über die Statistik verketteter Vorgänge, Zeitschrift für Angewandte Mathematik und Mechanik **3** (1923) 279-289.]

$$f \equiv \sigma^2 / \bar{n}^2$$

Hump – good or bad ?

- Smaller gain fluctuations:
  - better energy resolution.
- Smaller probability of small gain:
  - higher detection efficiency.
- Smaller probability of high gain:
  - fewer discharges.

Assumptions

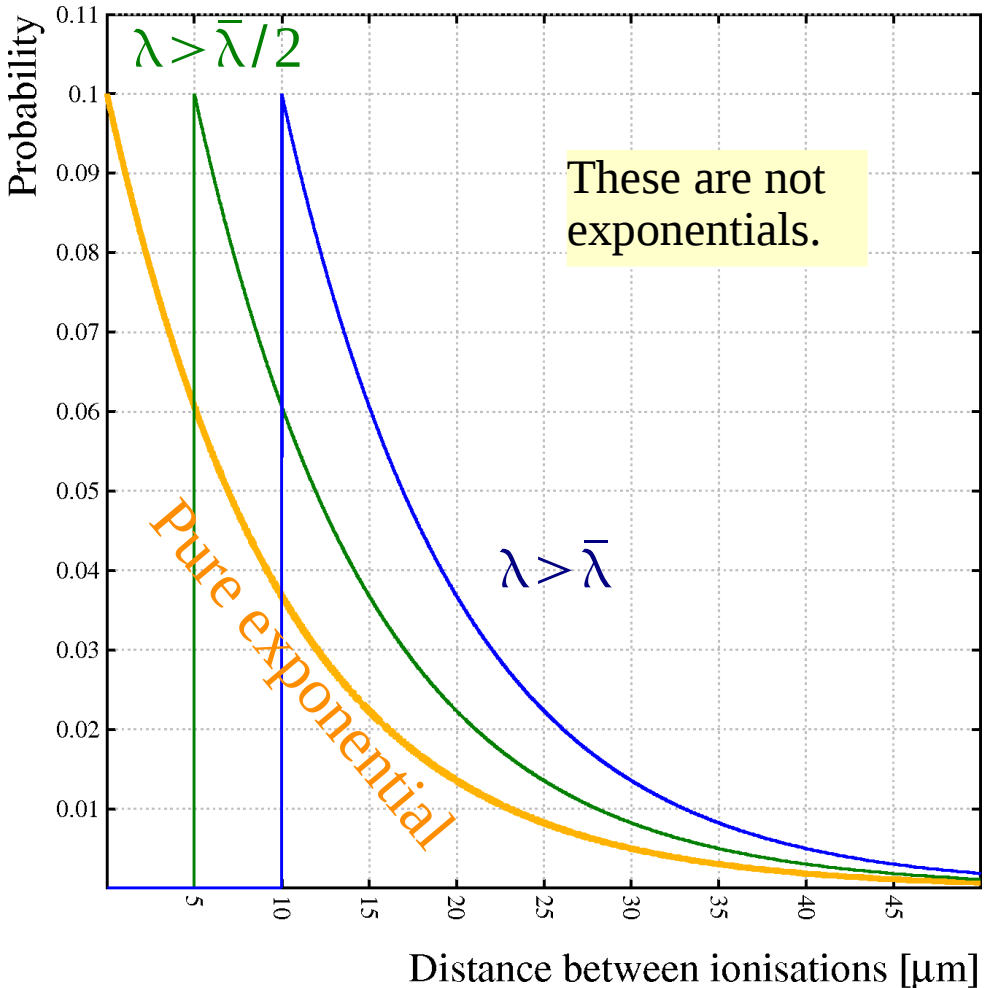
- Yule-Furry follows if one assumes:
  - probability to ionise over a distance dx is α dx
    =
    distance between ionisations fluctuates exponentially with mean $1/\alpha$.
  - no history: Townsend coefficient α is constant,
  - no attachment losses.

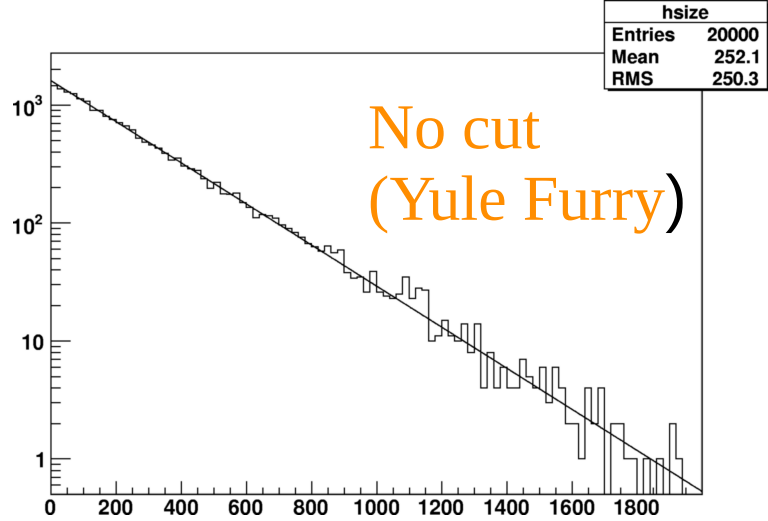
Two schools of thought ...

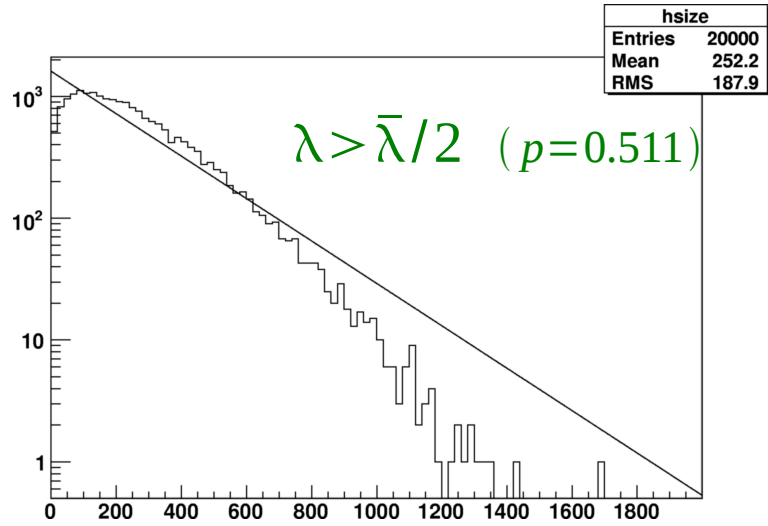
- The distance between ionisations does not simply vary exponentially (e.g. the Raether group).
- The Townsend coefficient is not constant (e.g. Byrne, Lansiart & Morucci).

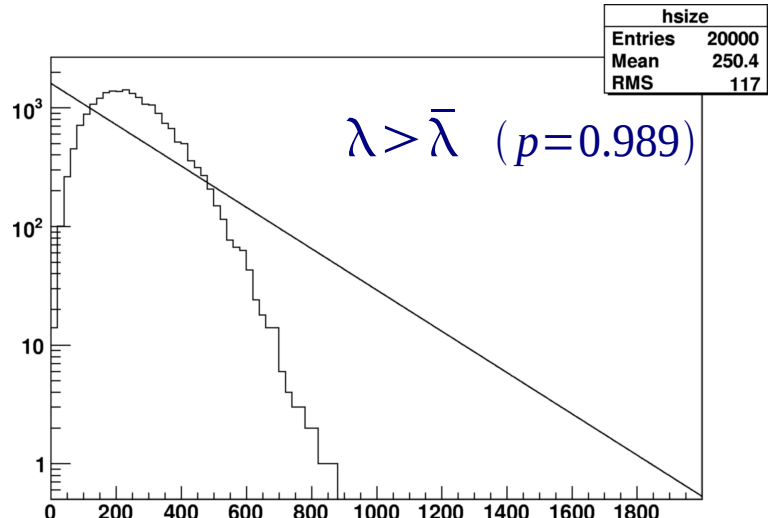
Minimum step length

- Imposing a minimum distance between ionisations adds a hump.









Mean and Minimum step size

- Mean distance between successive ionisations:

$$\bar{\lambda} = \frac{1}{\alpha}$$

- Minimum distance between successive ionisations:

$$\lambda_{\min} > \frac{IP}{E}$$

- Define

$$\frac{\bar{\lambda}}{\lambda_{\min}} = \frac{E}{\alpha\, IP} = \kappa$$

large κ minimum distance has no effect → exponential

$\kappa \simeq 1$ little room for fluctuations → hump

Heinz Raether's group (Hamburg)

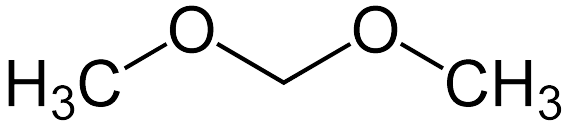
- After ionisation, electrons have to travel a minimum distance before their energy again suffices to ionise.

- $\kappa = E / \alpha.IP$ is an indicator of the avalanche shape

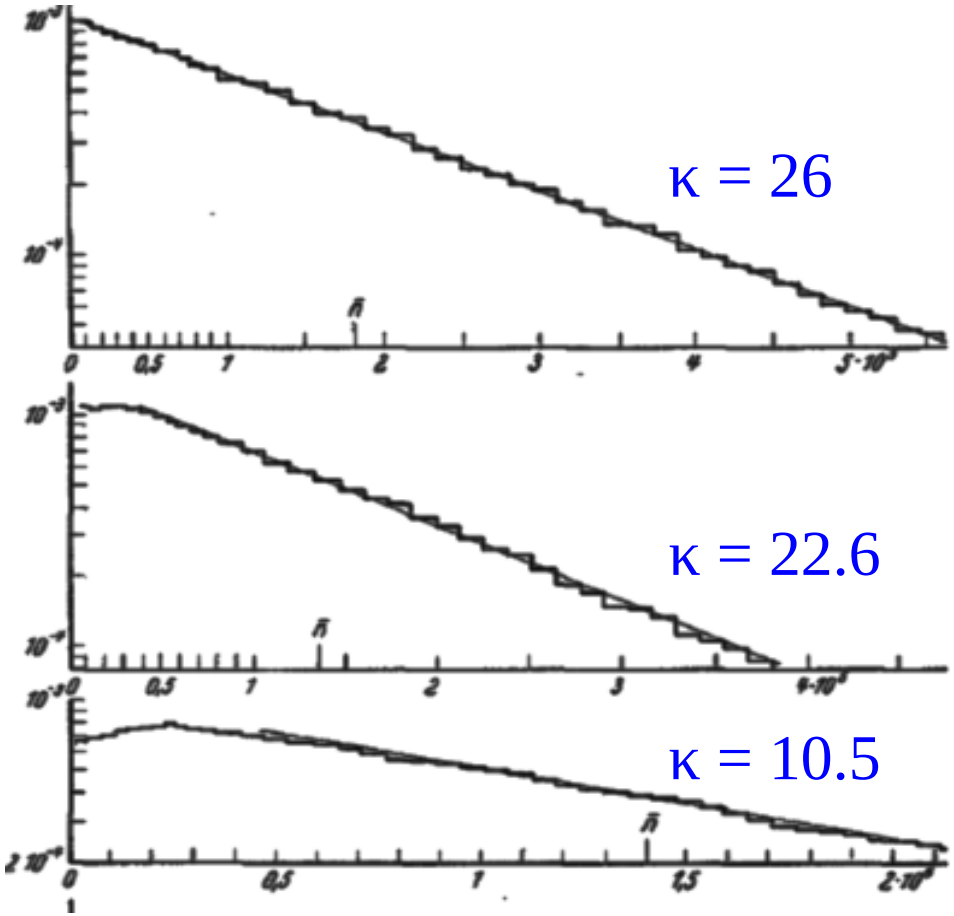
- Lothar Frommhold (1956)
  - κ = 12-110: exponential
- Hans Schlumbohm (1958)
  - $\kappa > 23$: exponential
  - $23 > \kappa > 10$: levels off towards small sizes
  - $10 > \kappa$: a maximum appears
- Werner Legler (1961)
  - any κ model calculation.

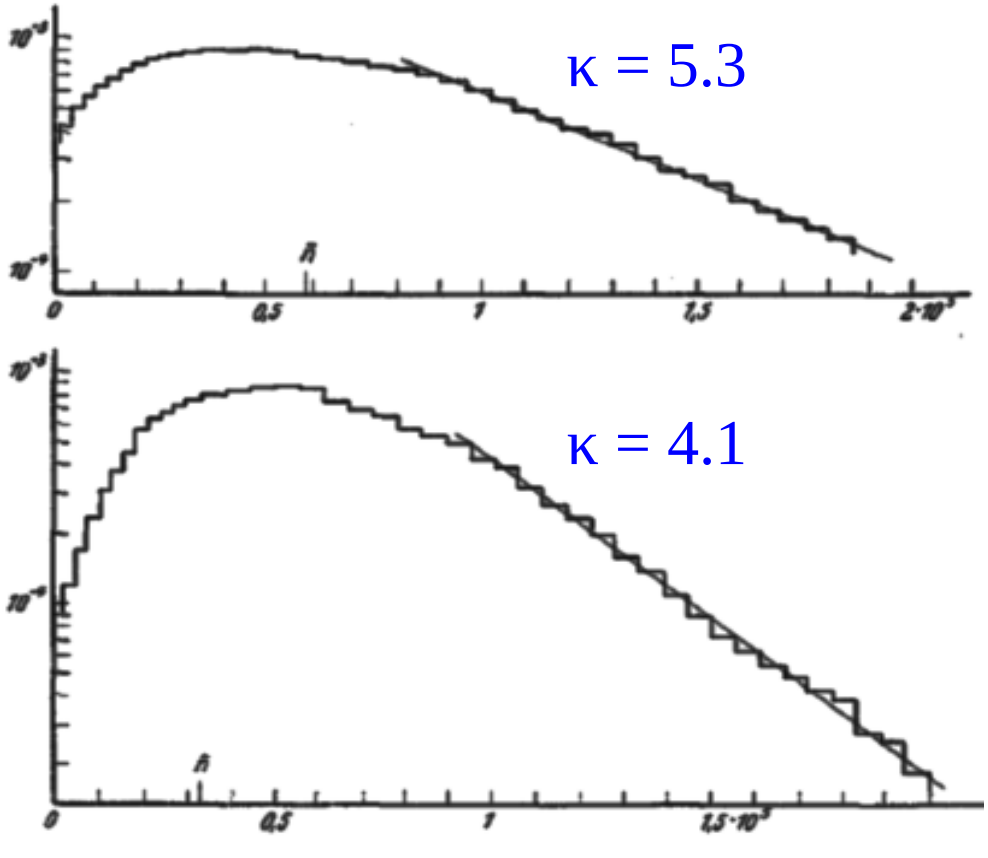
Heinz Artur Raether (1909-1986)

Hans Schlumbohm (1958)



- Dimethoxymethane spectra: increasing *E*, decreasing *p d* and ~constant mean gain.





- Hans Schlumbohm, *Zur Statistik der Elektronenlawinen im ebenen Feld III*, Z. Phys. **151** (1958) 563-576.

The *Magnettrommelrechner* (1961)

- Excellent agreement ... but no closed form

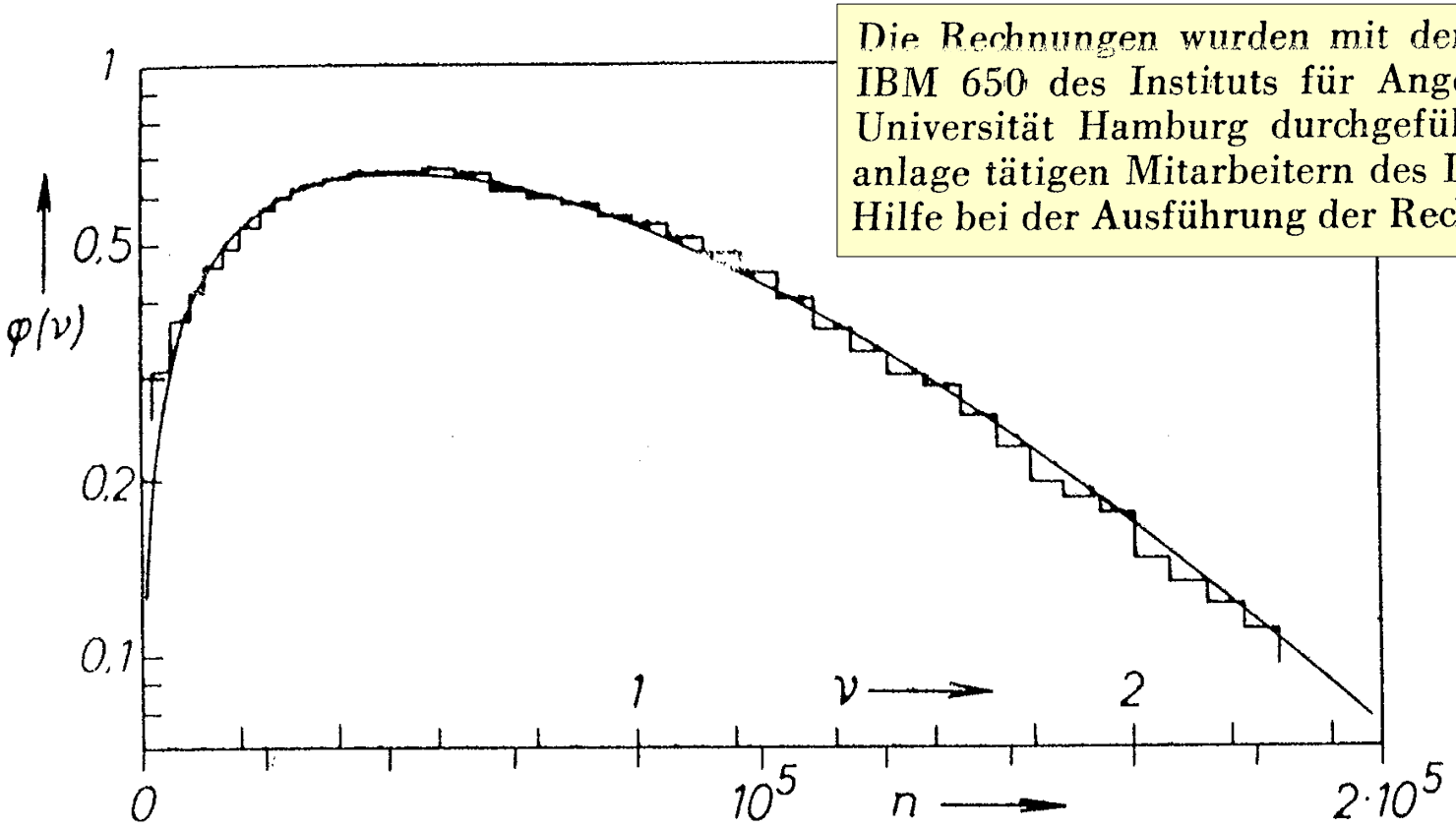


Abb. 5. Lawinenverteilung in Methylal nach SCHLUMBOHM [8]. $E/p = 186{,}5$ Volt/cm·Torr, $\alpha \cdot U_i/E = 0{,}19$. Ausgezogene Kurve: Theoretische Verteilung im Modellgas für $\alpha\, x_0 = 0{,}18$.

$\kappa = 5.3$

The alternative school

- Townsend coefficient not constant ...

A. Lansiart & J.P. Morucci (1962)

- Small avalanches are composed of electrons that
  - have ionised less, hence
  - have more energy, hence
  - will ionise more easily.

- They modeled this with an avalanche size-dependent α:

$$\alpha(n) = \alpha(0)\left(1 + \frac{k}{n}\right)$$

- Implies that $f = (\sigma/\mu)^2 = 1/(1+k) < 1$, in agreement with Curran's measurements.

- Electron energy distribution continues to decrease, without reaching an equilibrium.

Werner Legler's response (1967)

" To do this in general one has to use an ionization coefficient $\alpha(n, x)$ which depends not only on n but also on the distance x the avalanche has covered from the starting point (cathode) of the primary electron.

Besides the experimental doubts, the introduction instead of $\alpha(n, x)$ of an ionization coefficient which depends on n only leads to serious theoretical difficulties.

The suppression of the dependence on x means that the electron swarm has constant ionization probability between successive ionizations and relaxation effects are neglected, completely contrary to the intention of Cookson and Lewis.

Furthermore, a dependence of the ionization coefficient on n alone is understandable only if there are space-charge effects, and these are quite negligible at the beginning of the avalanche development."

[W. Legler, *The influence of the relaxation of the electron energy distribution on the statistics of electron avalanches*, Brit. J. Appl. Phys. **18** (1967) 1275-1280,]

Г.Д. Алхазов (1970)

- "Statistics of electron avalanches and ultimate resolution of proportional counters", NIM **89** (1970) 155-165.

- Classic paper – examines various geometries, and the ionisation probability as function of distance travelled.

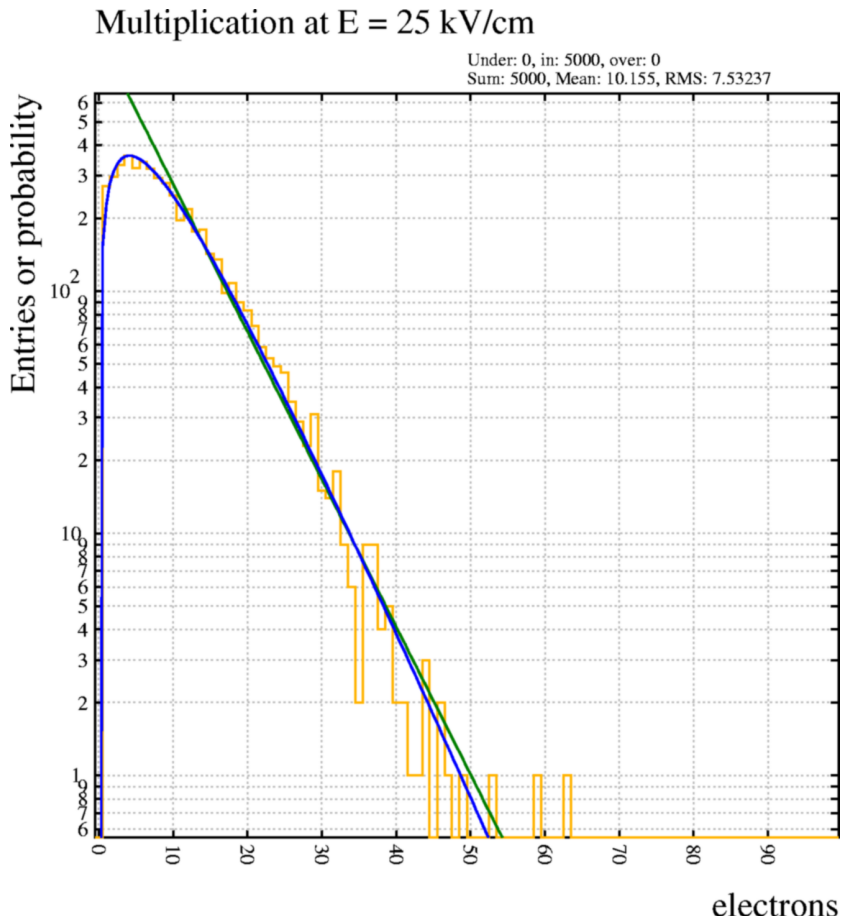
- [...] indeed there exists some correlation between α, and *K* [number of electrons already in the avalanche] but it has a much more complicated form as compared to that in eq. (3) [$\alpha \propto 1 + \mu/K$] so that the assumption that the ionization probability depends only on *K* is in principle unsuitable for the description of the electron avalanche statistics. [...] the distribution of the number of electrons in the single avalanche in uniform fields deviates from a Polya distribution. [...] In proportional cylindrical counters the distribution is in close agreement with a Polya one

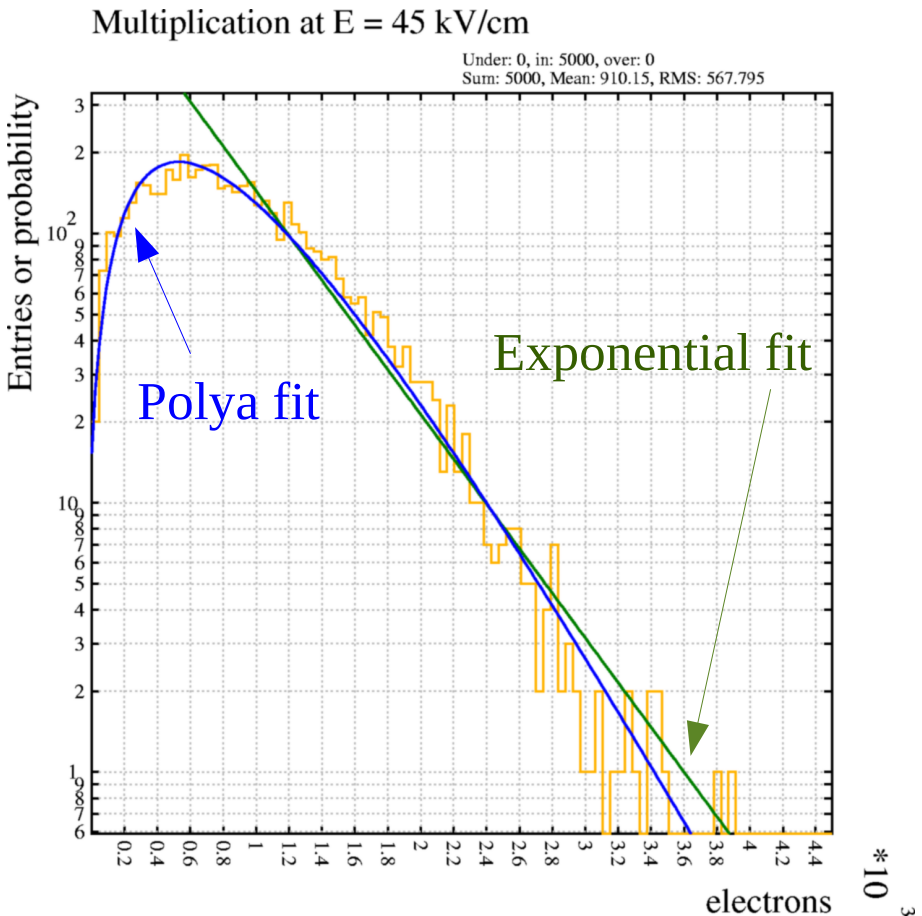
Monte Carlo approach – a way out ?

- Analytic models are precious for the insight they afford.
- But the complexity of real gases and detectors make realistic models unwieldy:
  - inelastic collisions (vibrations, rotations, polyads);
  - excitations and Penning transfers;
  - ionisation;
  - attachment;
  - intricate, position-dependent *E* and *B* fields.
- Predictions for experiments are more practical using a Monte Carlo approach, here based on Magboltz.

Pure argon: Magboltz distribution

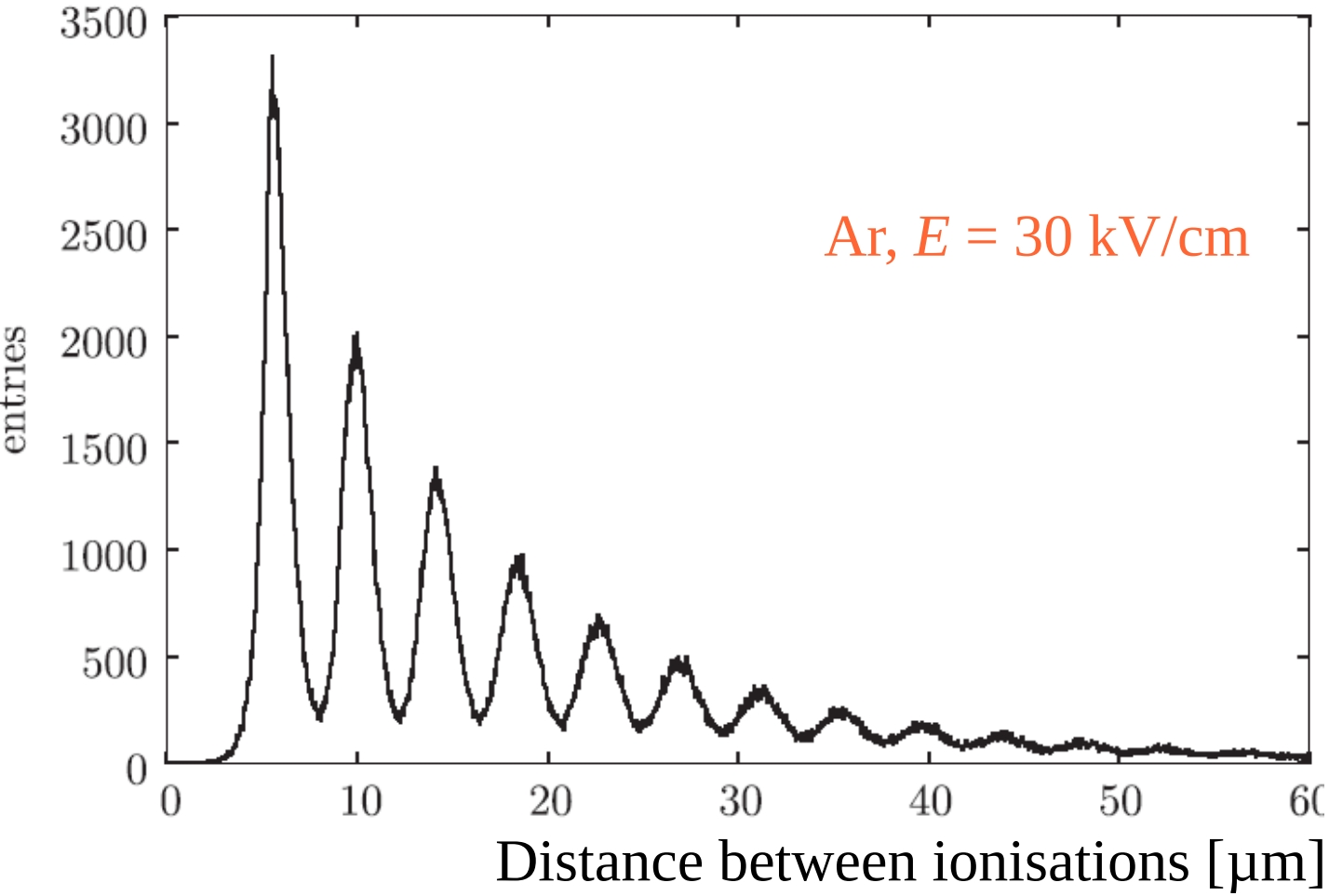
- With increasing E, $\kappa = E/\alpha.IP$ *decreases*: the size distribution becomes more rounded:



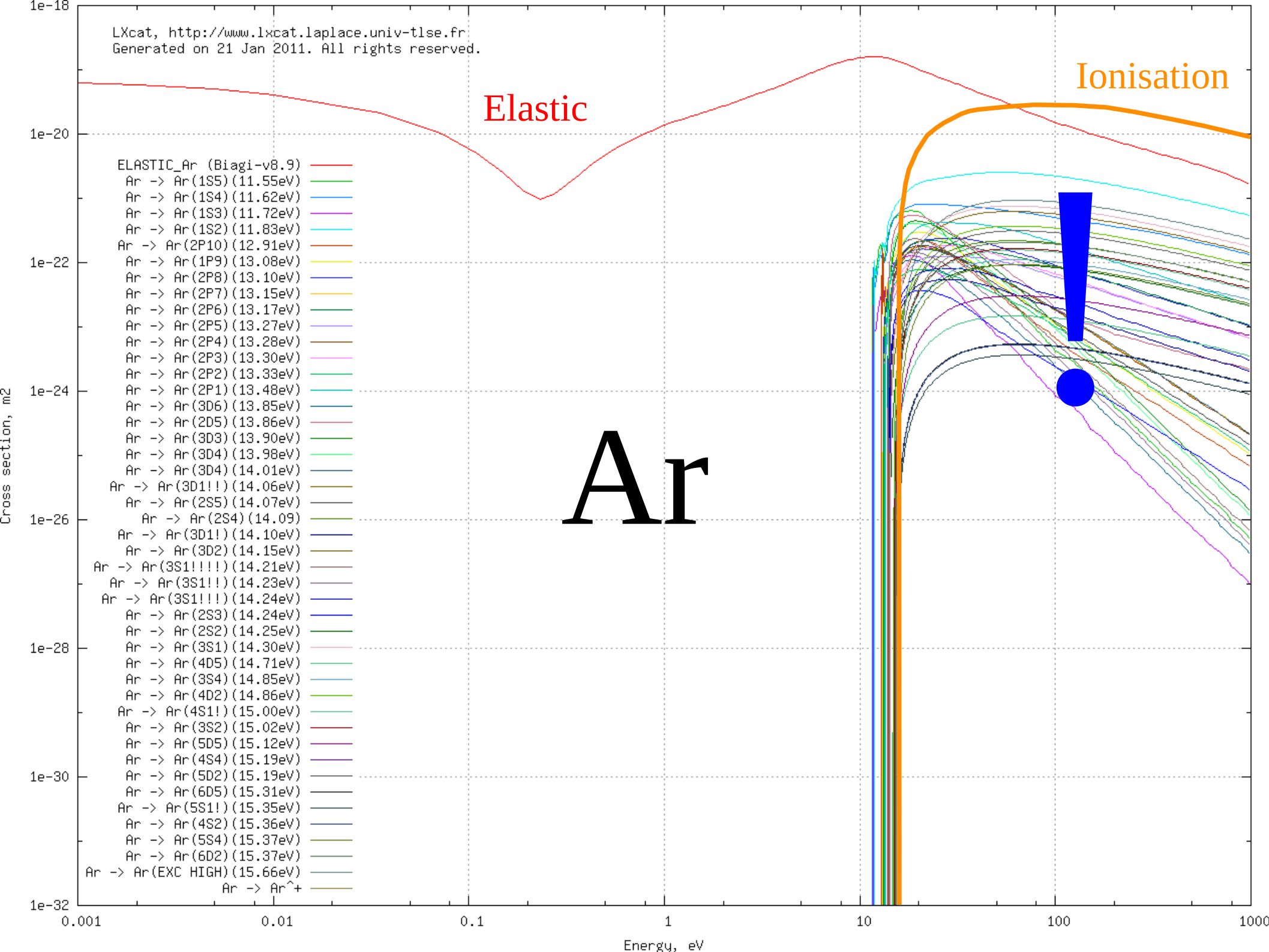


Distance between ionisations

- The distance between successive ionisations oscillates, shown here for Ar (also happens in CH_4 for instance).
- Why ?



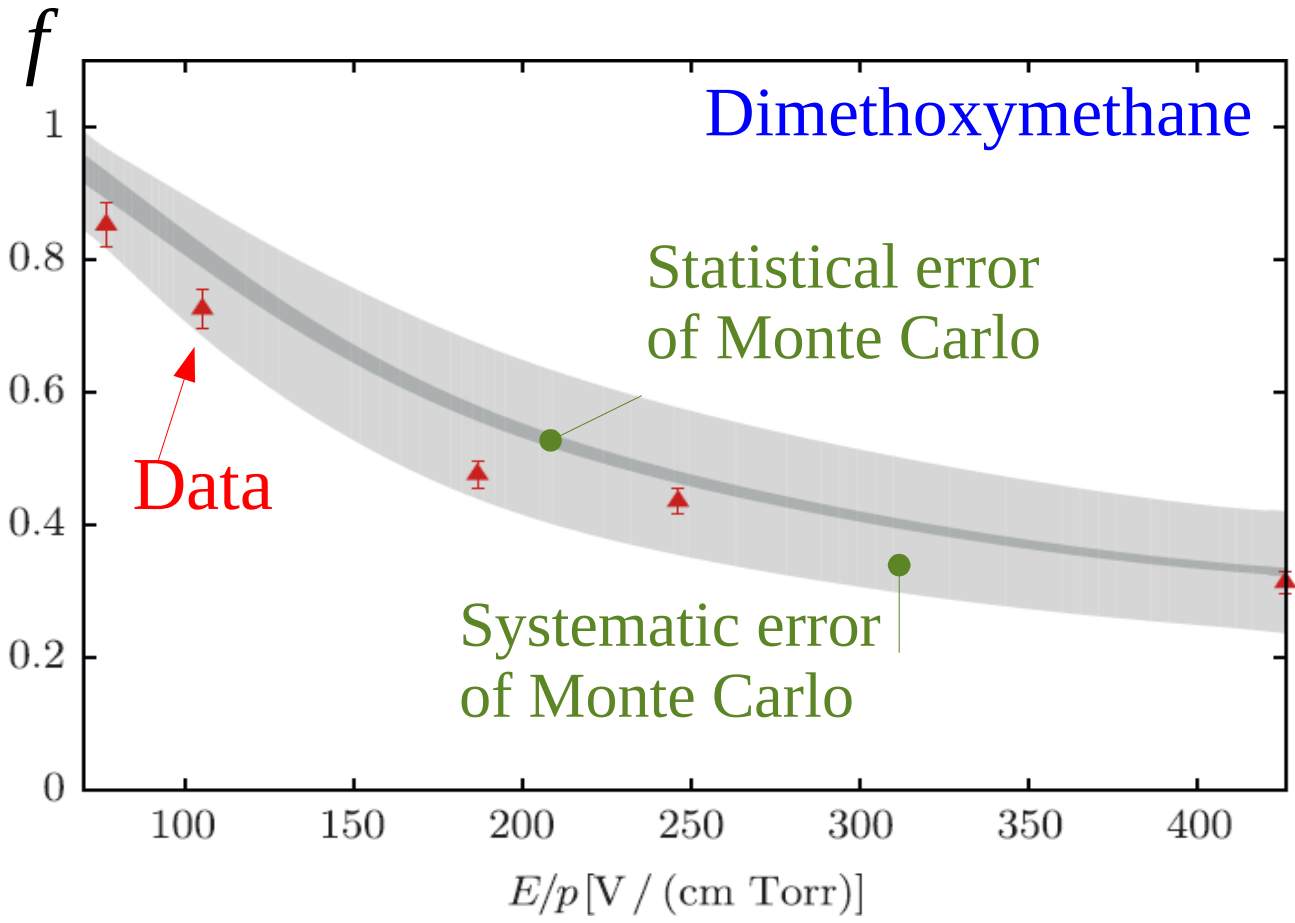
[Magboltz calculations by Heinrich Schindler]


LXcat, http://www.lxcat.laplace.univ-tlse.fr
Generated on 21 Jan 2011. All rights reserved.
Elastic
Ionisation
Ar
ELASTIC_Ar (Biagi-v8.9)
Ar -> Ar(1S5)(11.55eV)
Ar -> Ar(1S4)(11.62eV)
Ar -> Ar(1S3)(11.72eV)
Ar -> Ar(1S2)(11.83eV)
Ar -> Ar(2P10)(12.91eV)
Ar -> Ar(1P9)(13.08eV)
Ar -> Ar(2P8)(13.10eV)
Ar -> Ar(2P7)(13.15eV)
Ar -> Ar(2P6)(13.17eV)
Ar -> Ar(2P5)(13.27eV)
Ar -> Ar(2P4)(13.28eV)
Ar -> Ar(2P3)(13.30eV)
Ar -> Ar(2P2)(13.33eV)
Ar -> Ar(2P1)(13.48eV)
Ar -> Ar(3D6)(13.85eV)
Ar -> Ar(2D5)(13.86eV)
Ar -> Ar(3D3)(13.90eV)
Ar -> Ar(3D4)(13.98eV)
Ar -> Ar(3D4)(14.01eV)
Ar -> Ar(3D1!!)(14.06eV)
Ar -> Ar(2S5)(14.07eV)
Ar -> Ar(2S4)(14.09)
Ar -> Ar(3D1!)(14.10eV)
Ar -> Ar(3D2)(14.15eV)
Ar -> Ar(3S1!!!!)(14.21eV)
Ar -> Ar(3S1!!!)(14.23eV)
Ar -> Ar(3S1!!!)(14.24eV)
Ar -> Ar(2S3)(14.24eV)
Ar -> Ar(2S2)(14.25eV)
Ar -> Ar(3S1)(14.30eV)
Ar -> Ar(4D5)(14.71eV)
Ar -> Ar(3S4)(14.85eV)
Ar -> Ar(4D2)(14.86eV)
Ar -> Ar(4S1!)(15.00eV)
Ar -> Ar(3S2)(15.02eV)
Ar -> Ar(5D5)(15.12eV)
Ar -> Ar(4S4)(15.19eV)
Ar -> Ar(5D2)(15.19eV)
Ar -> Ar(6D5)(15.31eV)
Ar -> Ar(5S1!)(15.35eV)
Ar -> Ar(4S2)(15.36eV)
Ar -> Ar(5S4)(15.37eV)
Ar -> Ar(6D2)(15.37eV)
Ar -> Ar(EXC HIGH)(15.66eV)
Ar -> Ar^+
Cross section, m2
1e-18
1e-20
1e-22
1e-24
1e-26
1e-28
1e-30
1e-32
0.001
0.01
0.1
1
10
100
1000
Energy, eV

Relative variance $f \equiv \sigma^2/\bar{n}^2$

- f is the experimental measure of "roundness":

$f > 1$	attachment
$f = 1$	exponential
$f = 0$	no spread

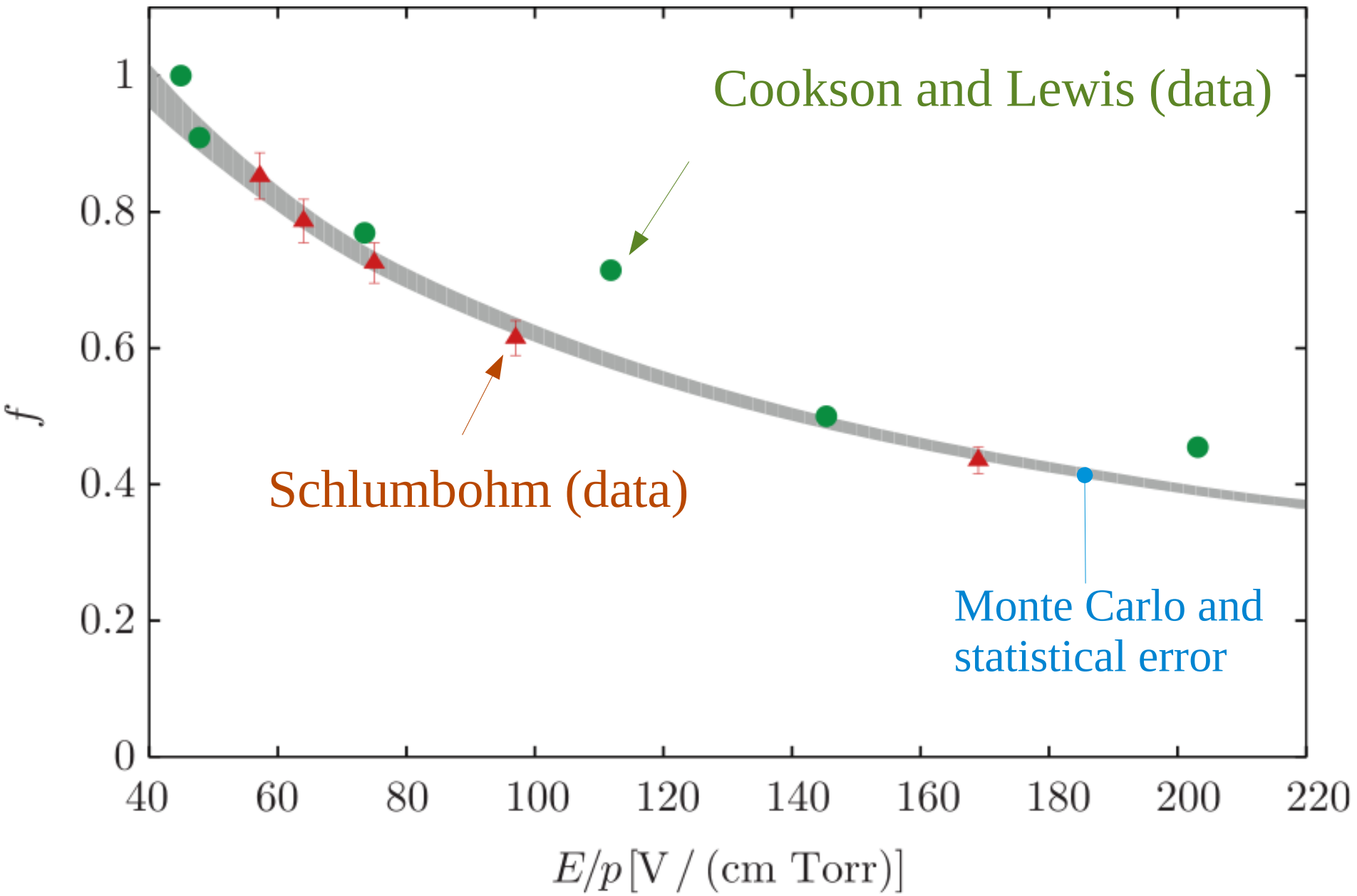


- $f \leftrightarrow \kappa$ translation:

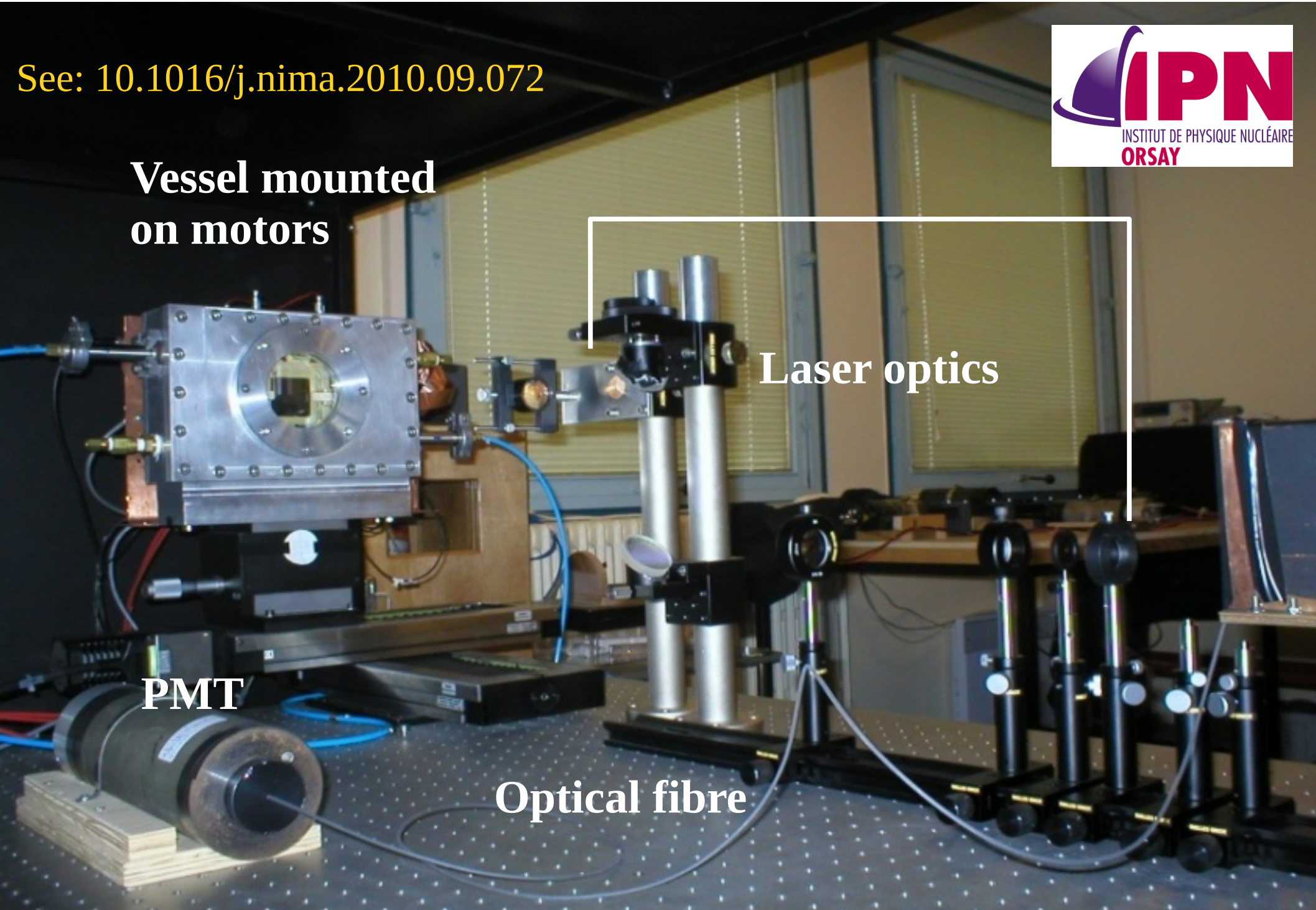
$\kappa \gg 20 \quad f \approx 1$

$\kappa < 10 \quad f \downarrow 0$

MC verification: methane



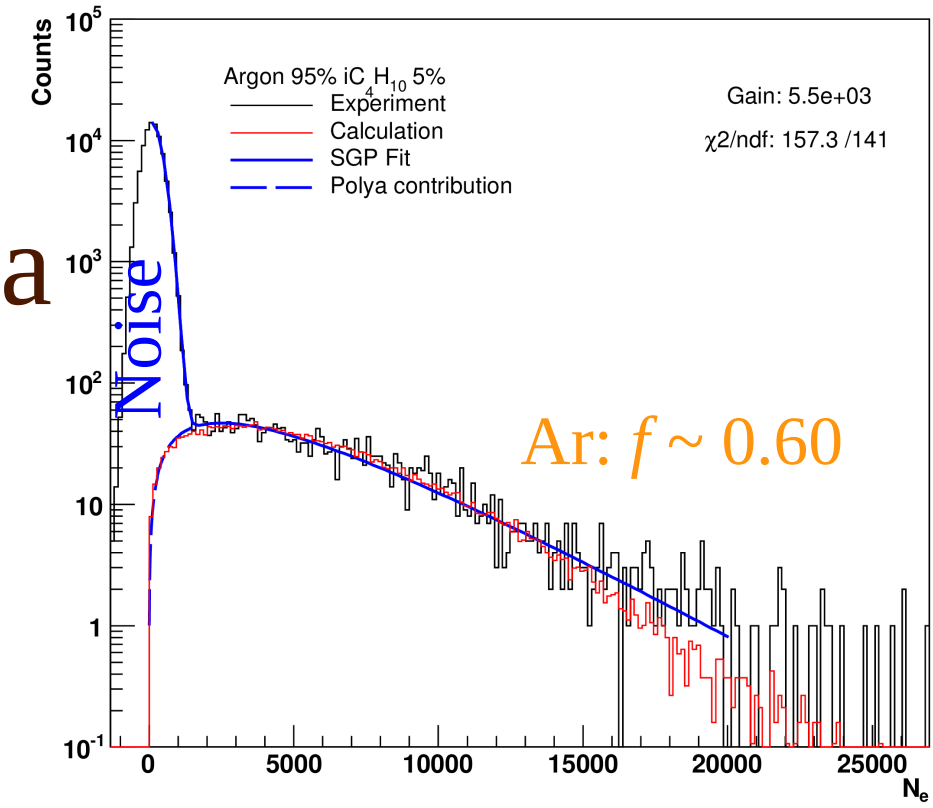
Experimental setup

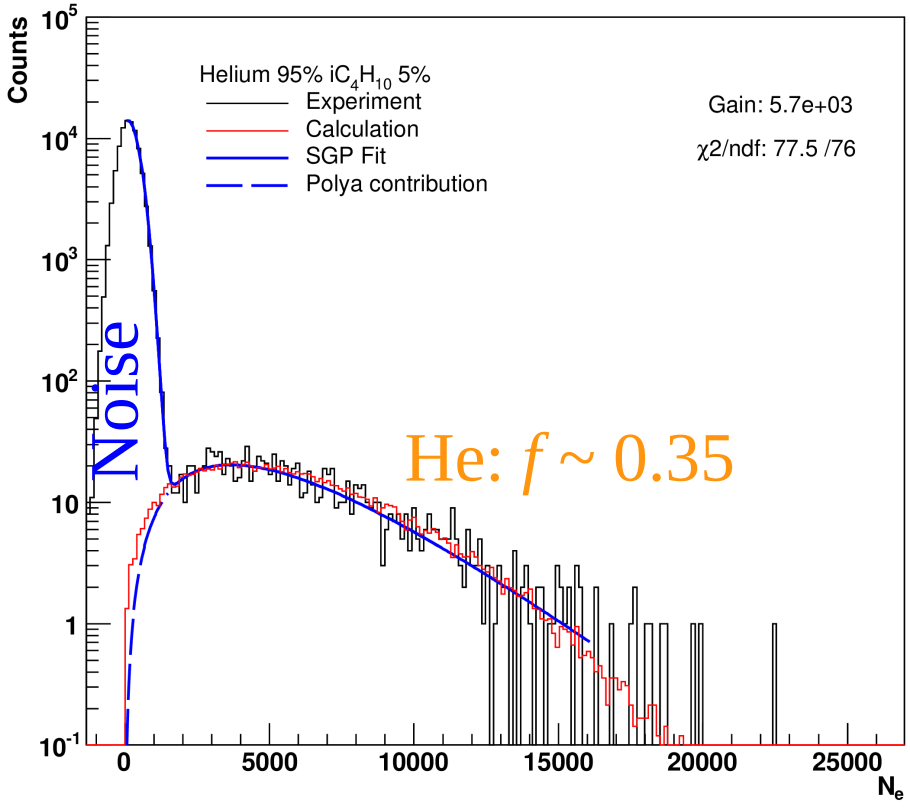


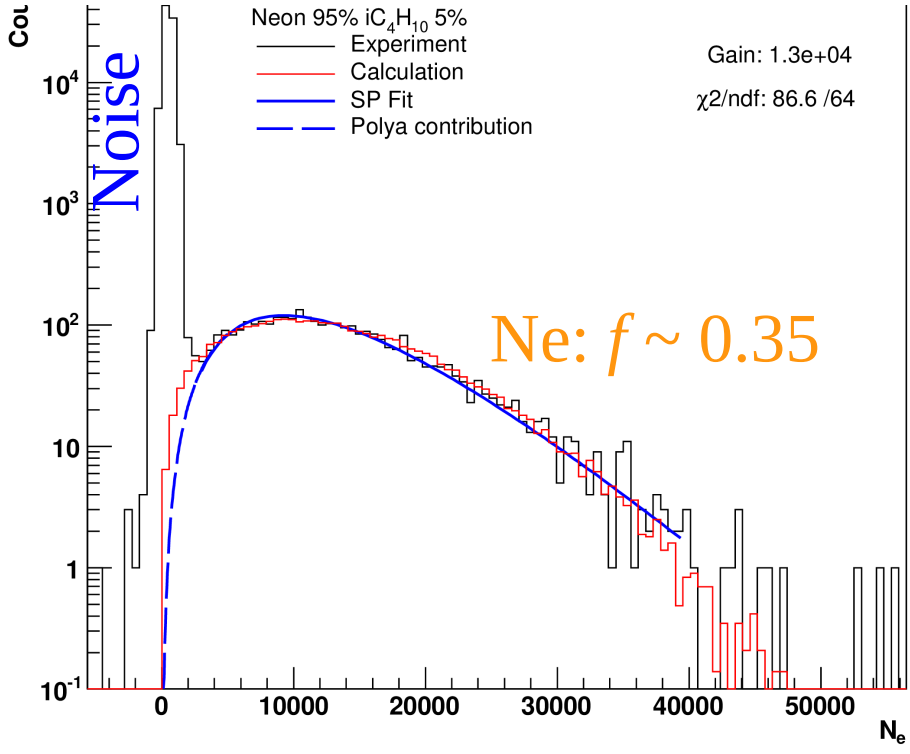
Single-electron spectra

blue: Pólya signal + Gaussian noise fit;
red: Monte Carlo (Magboltz), not fits !

Ar 95 % iC_4H_{10} 5 %, E=28.12 kV/cm,
Ne 95 % iC_4H_{10} 5 %, E=26.25 kV/cm,
He 95 % iC_4H_{10} 5 %, E=26.25 kV/cm,







Ion transport

Ions

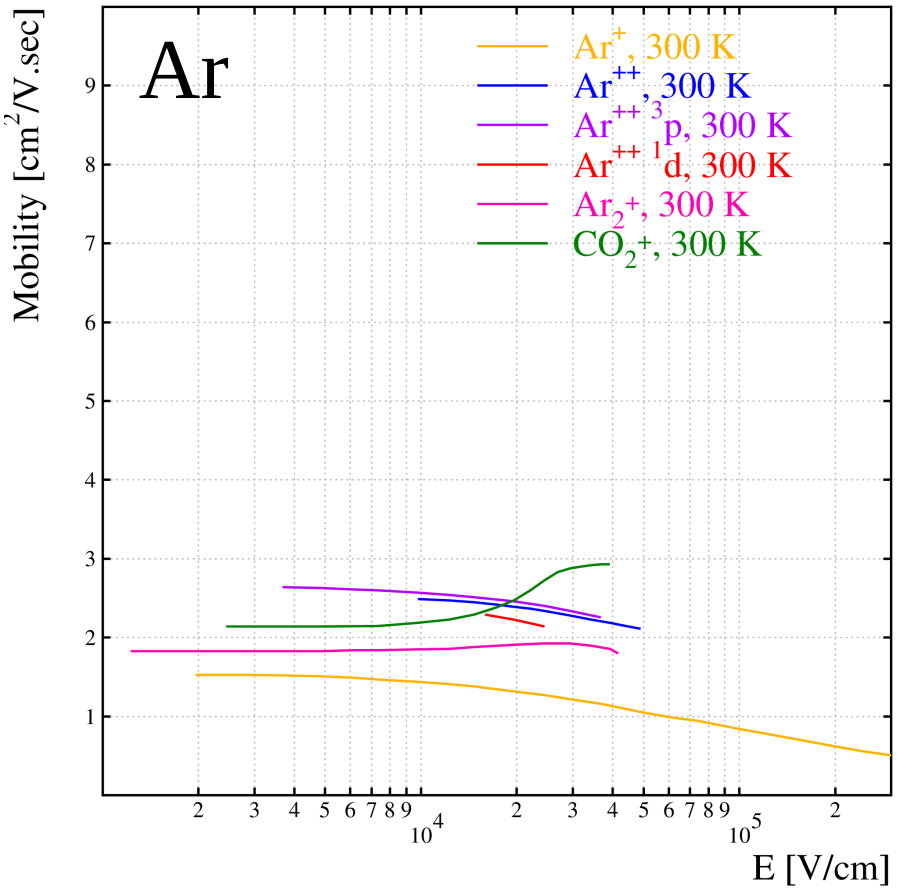
- Avalanches produce not only electrons, but also ions – at least as many.

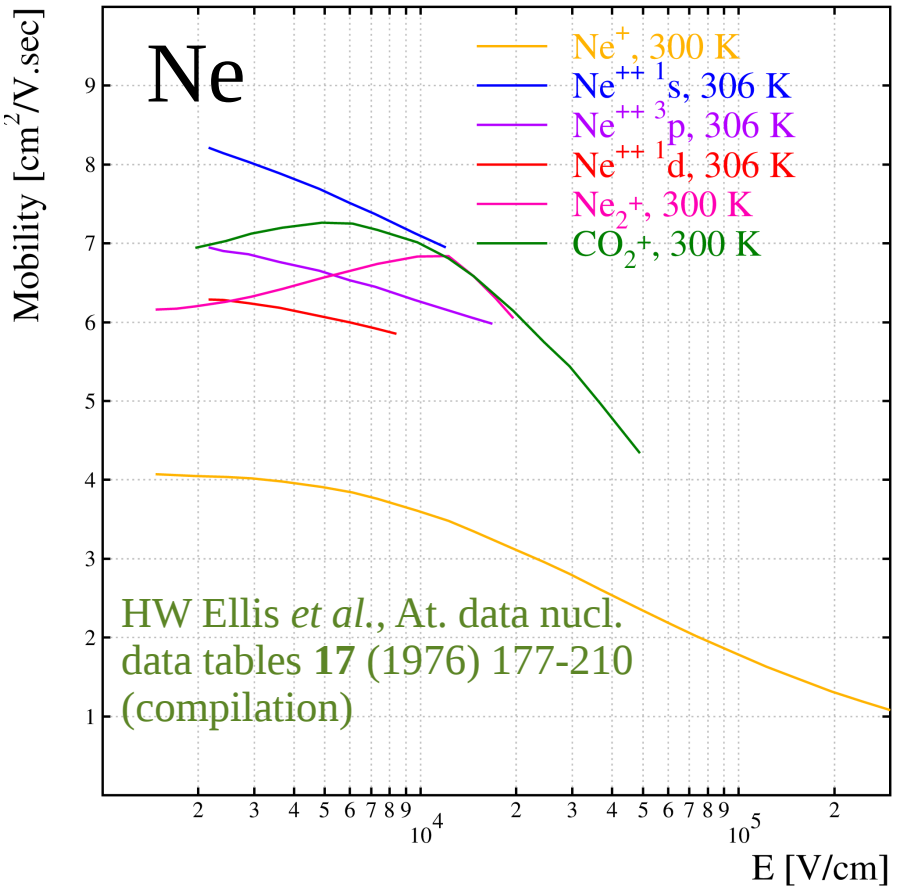
- Detectors like Micromegas and wire chambers get their signal mostly from ion motion (→ Signals).

- Hence we better know the basics of ions:
  - *how fast* do the ions move ?
  - are they subject to *diffusion* ?
  - *which ions* are moving ?

Ar^+ and Ne^+ mobility $\equiv$ $v_D(E) / E$

- The mobility of e.g. noble gas ions in their parent gas has been measured:

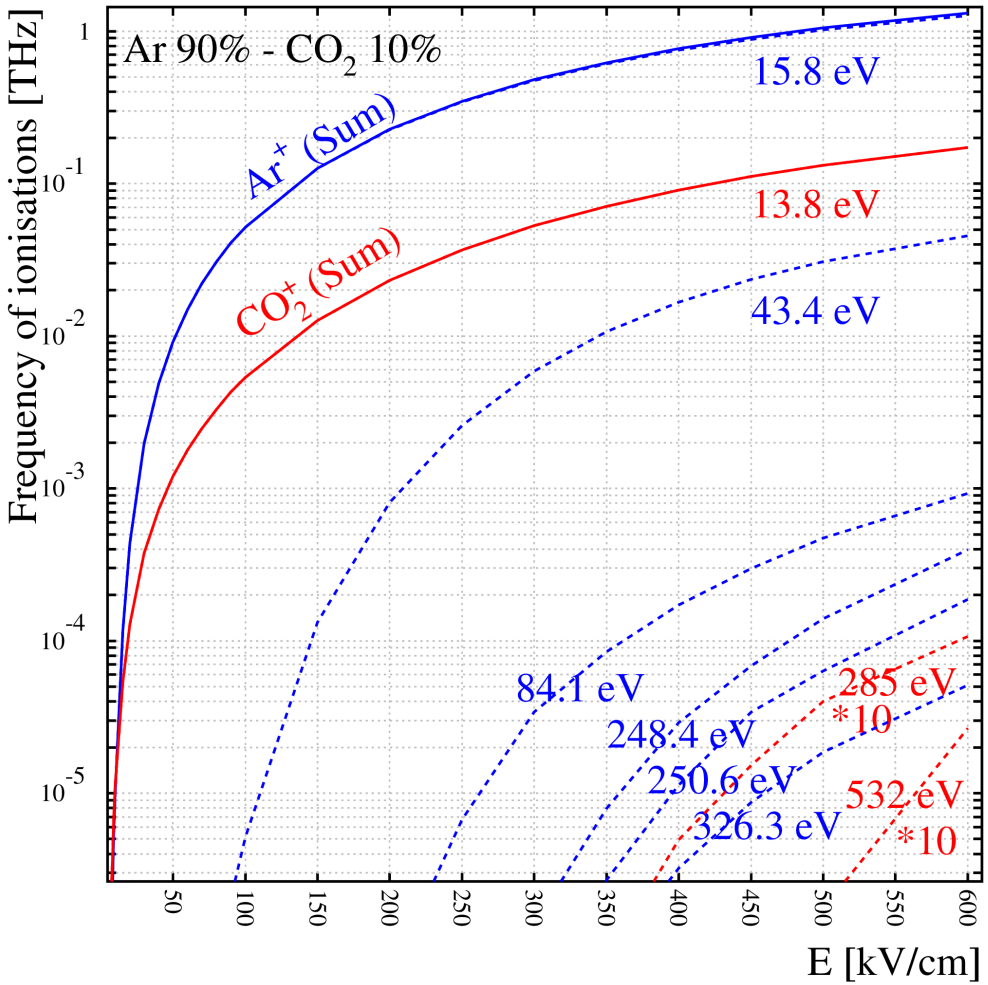


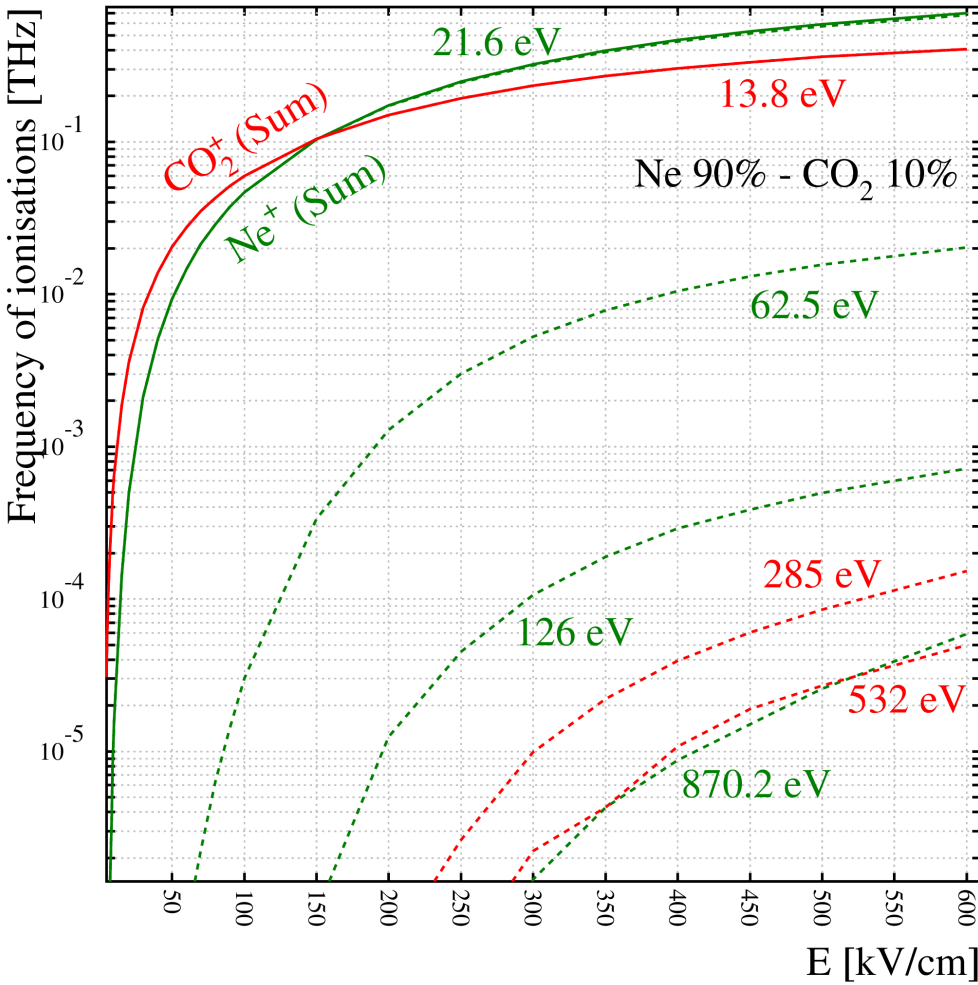


Avalanche products

- Ar^+ dominates in Ar-CO_2,

CO_2^+ dominates in Ne-CO_2 below 150 kV/cm:

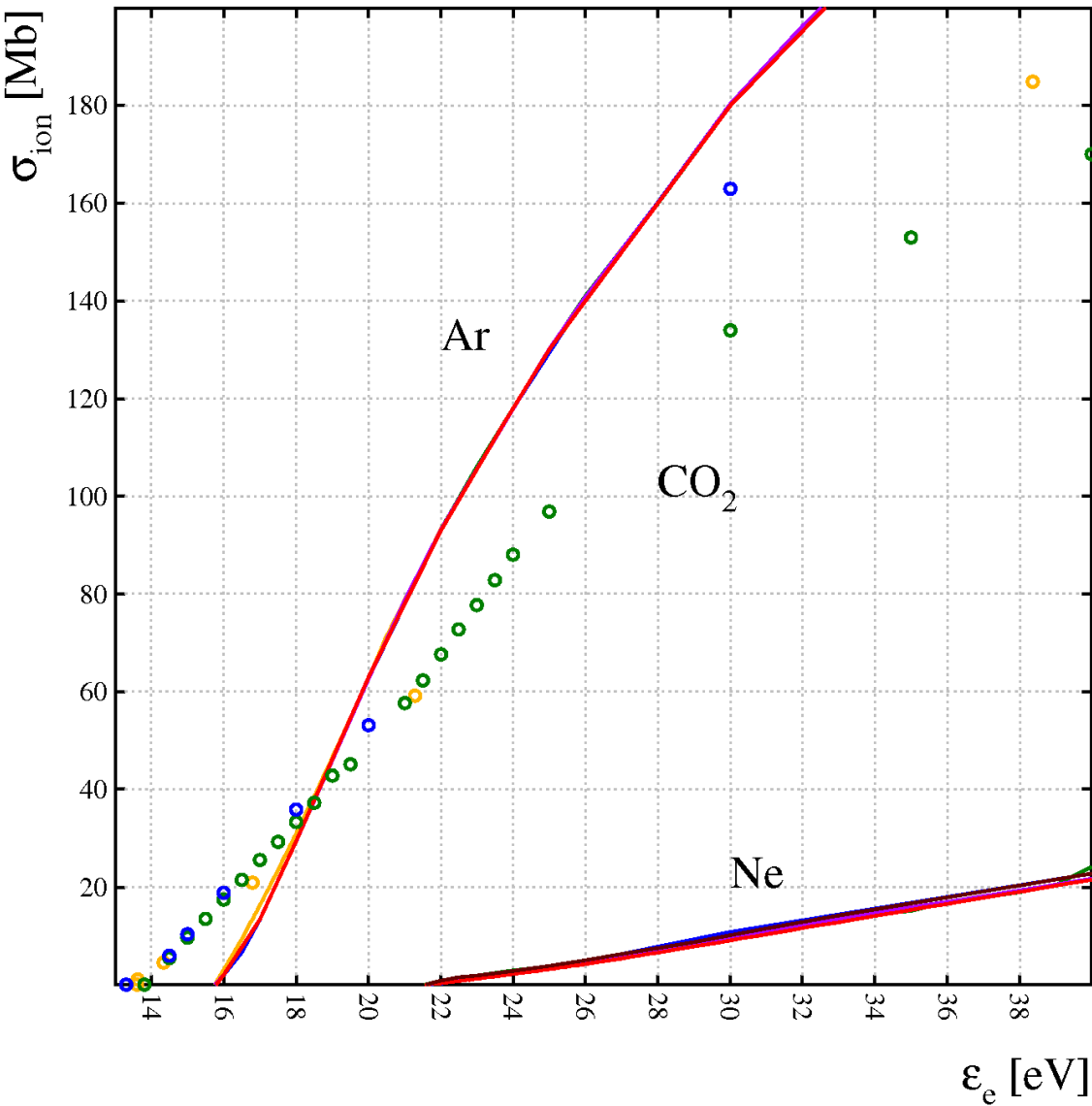




Electron-impact cross sections

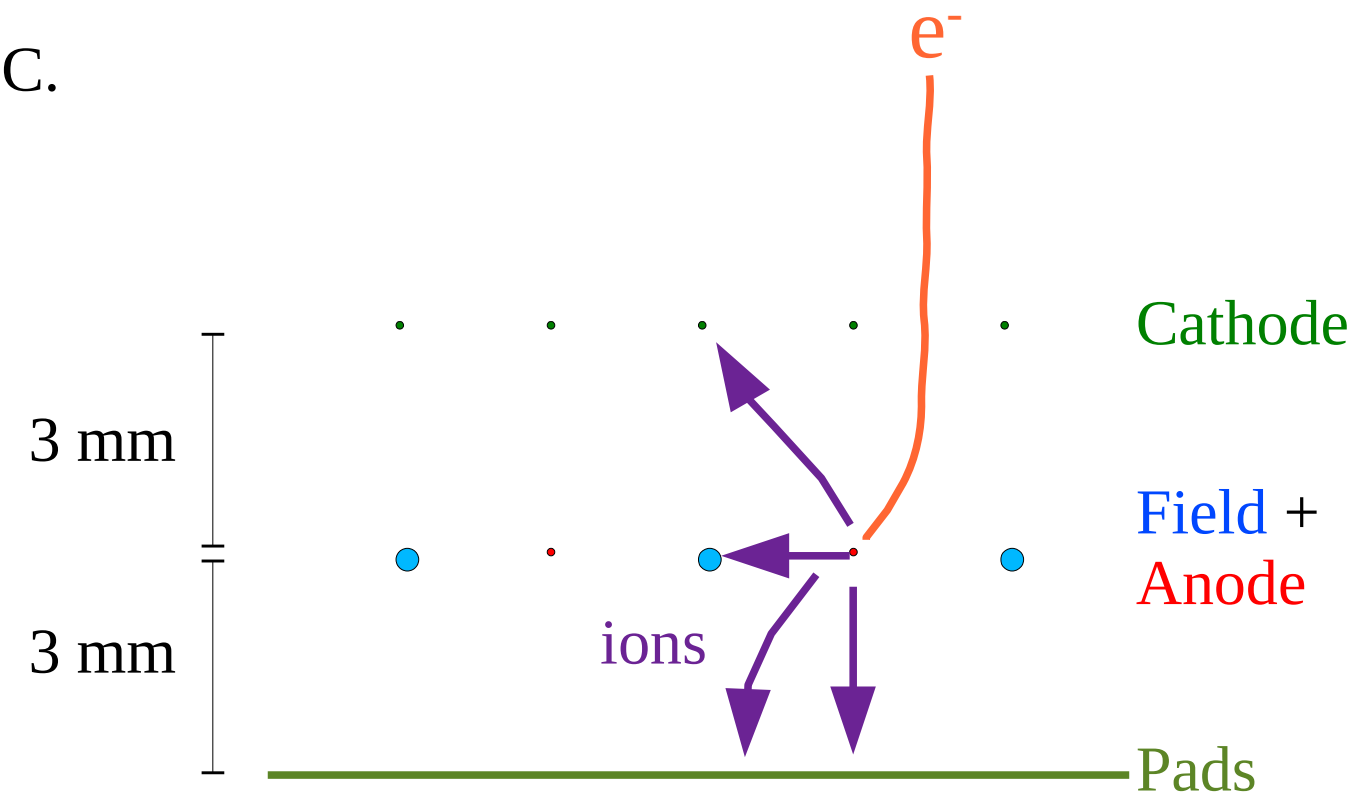
- CO_2^+ and Ar^+ compete.
- Ne^+ has higher threshold and is produced less.
- Mix: Ne 90 % CO_2 10 %

[Pure gases, data from LXcat]



Ion induced signals

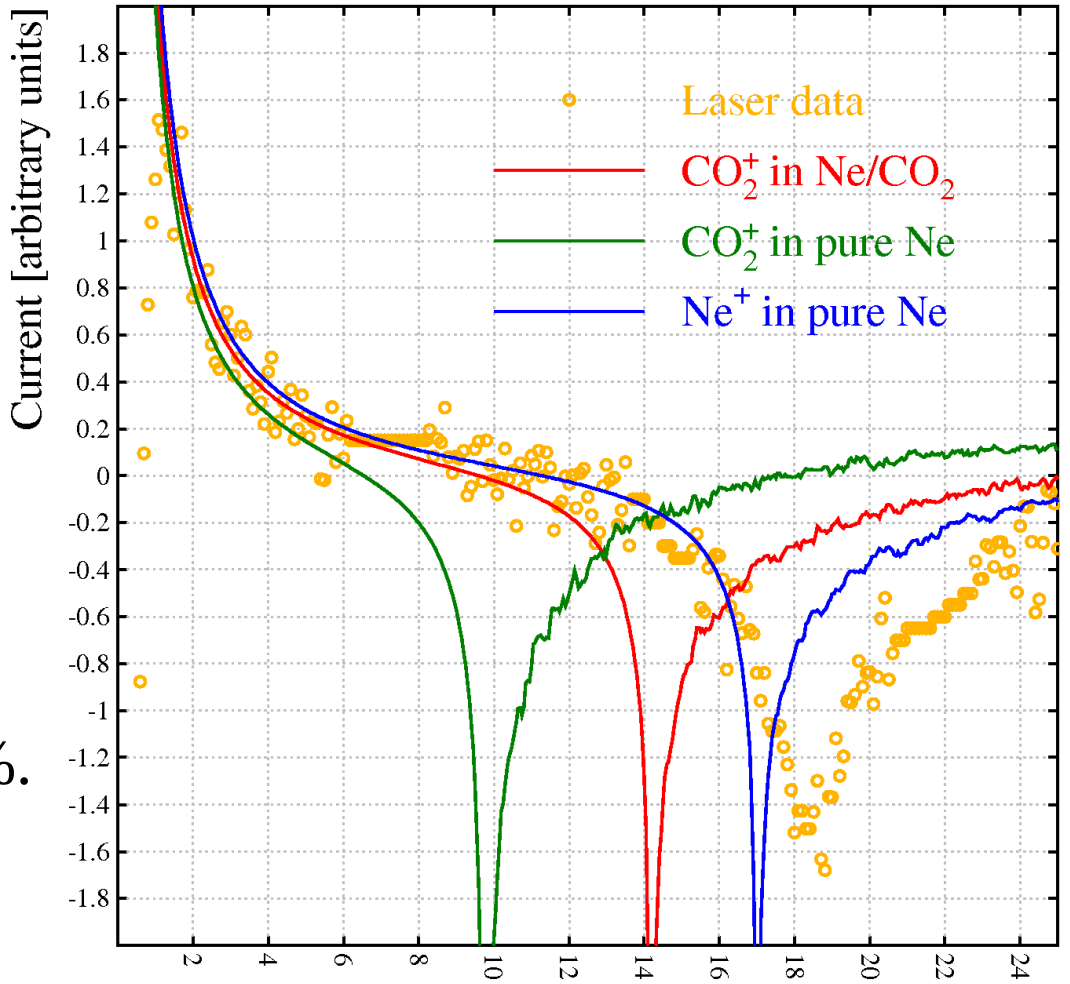
- One can calculate the current induced on the pads of a TPC by ions moving from the anode wires to the field wires where they give a signal.
- Example: NA49 TPC.



How about Ne^+ in Ne ?

- Ne^+ ions in Ne come reasonably close to the measurements ...
- we've used it for years ...
- but does it make sense ?
- NA49 TPC: Ne 90 % CO_2 10 %.

[Data: Rainer Renfordt]



Reaction time and Rate constant: 2-body

- Consider a charge transfer reaction $A^+ B \rightarrow A B^+$:
  - rate $\propto$ density of B molecules N_B [1/cm^3];
- The proportionality factor is called rate constant, k:
  - rate = k [cm^3/s] N_B [1/cm^3].
  - The reaction time τ is the reciprocal of the rate.
- Example: Ar^+ in Ar (resonant charge exchange)
  - $k = 4.6\ 10^{-10}$ cm^3/s, $N \approx 2.45\ 10^{19}$/cm^3,
  - rate = $1.1\ 10^{10}$/s, $\tau = 100$ ps,
  - Main effect: reduces mobility.

Thermal collision frequency

- Mean relative velocity:

$$\bar{v}_{\mathrm{rel}} = \sqrt{\frac{8 k_{\mathrm{B}} T}{\pi \mu}} \approx 570 \ \mathrm{m/s}$$

Values for Ar-Ar^+ at 300 K and 1 atm, μ: reduced mass for Ar,
σ: empiric momentum transfer cross section $\Omega^{(1,1)} = 157\ 10^{-16}\ \mathrm{cm}^2$.

- Multiplying with the cross section σ gives the rate constant:

$$k = \sigma \bar{v}_{\mathrm{rel}} \approx 9 \ 10^{-10} \ \mathrm{cm}^3/\mathrm{s}$$

- Combining with the number density gives the reaction time:

$$\tau = \frac{1}{N \sigma \bar{v}_{\mathrm{rel}}} = \frac{k_{\mathrm{B}} T}{p} \frac{1}{\sigma \bar{v}_{rel}} = \frac{1}{p \sigma} \sqrt{\frac{\pi \mu k_{\mathrm{B}} T}{8}} \approx 46 \ \mathrm{ps}$$

(cf Ar_2)

3-body reactions

- Bound state formation requires the evacuation of excess energy & momentum through internal degrees of freedom (rotation, vibration), or via a "helper".

- The rate constant in 3-body reactions has the unit of cm^6/s.

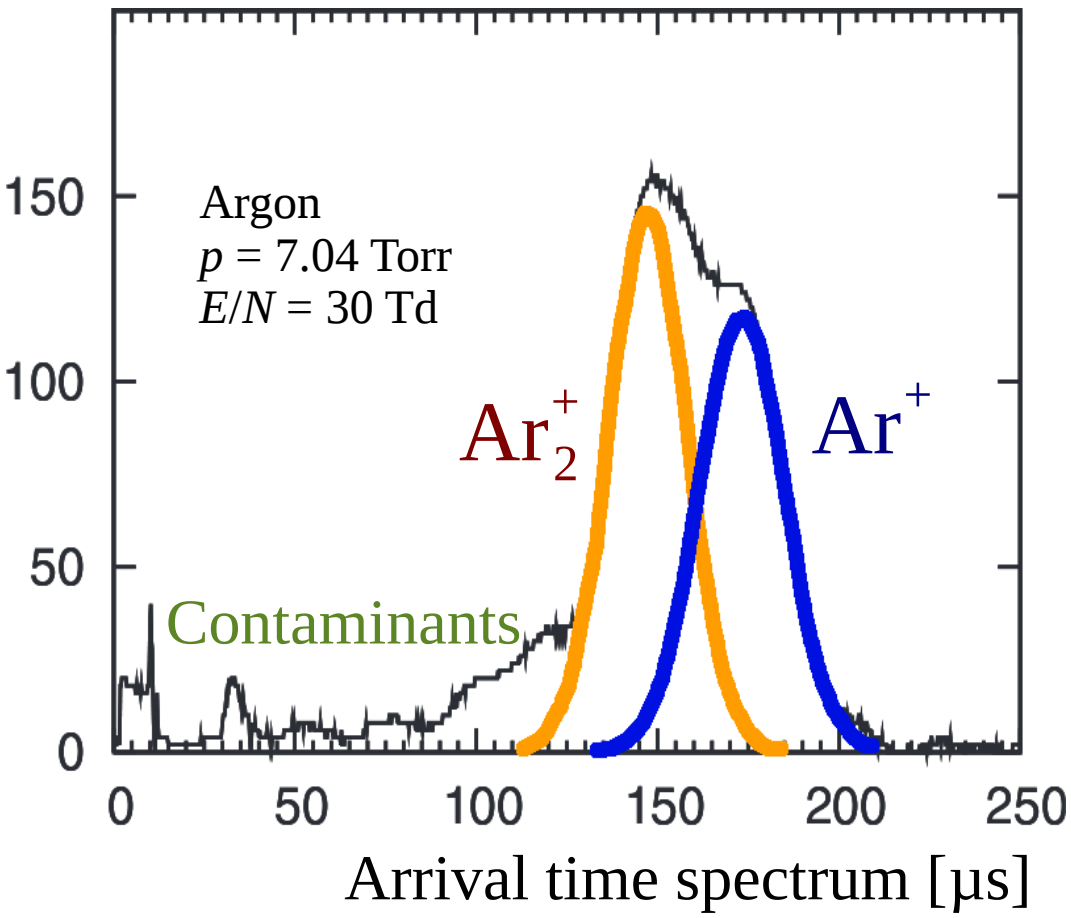
- Example 1: $Ar^+ + Ar + Ar \rightarrow Ar^+ \bullet Ar + Ar$
  - $k = 2.3\ 10^{-31}\ cm^6/s$, assuming $N \approx 2.45\ 10^{19}/cm^3$
  - rate = $k\ N^2 = 1.3\ 10^8/s$, $\tau = 7$ ns

- Example 2: $CO_2^+ + CO_2 + CO_2 \rightarrow CO_2^+ \bullet CO_2 + CO_2$
  - $k = 2.4\ 10^{-28}\ cm^6/s$
  - rate = $k\ N^2 = 1.4\ 10^{11}/s$, $\tau = 7$ ps

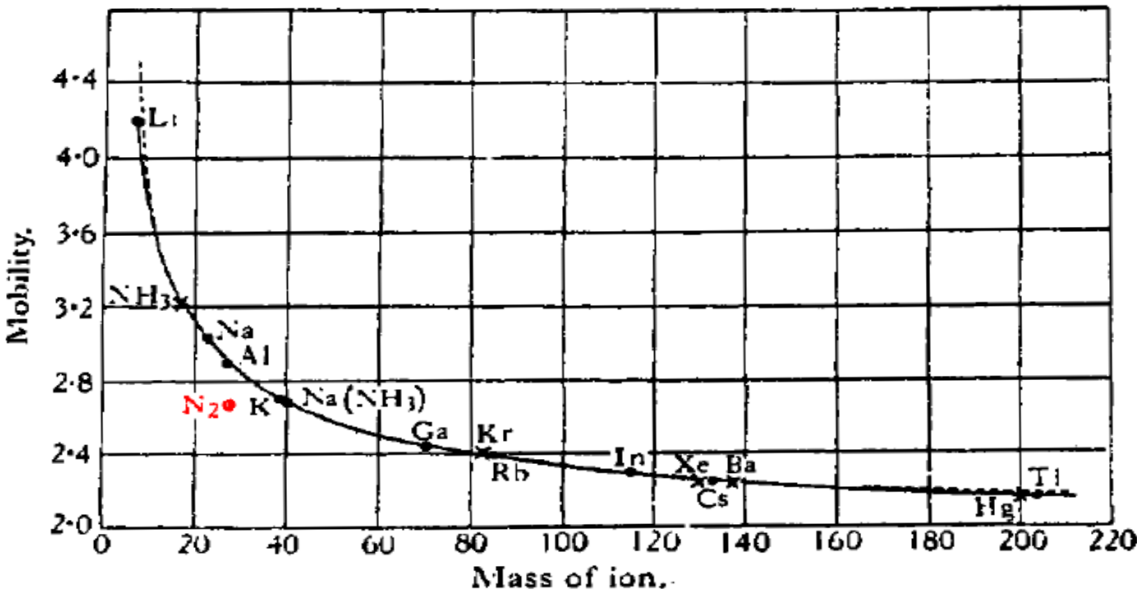
Ions drifting in pure Ar

- In pure argon, dimers are formed:
  - $Ar^+(^2P^o_{3/2}) + 2Ar \rightarrow Ar^+ \bullet Ar + Ar$ ($k = 2.3 \pm 0.1\ 10^{-31}$ cm^6/s, 7 ns)
  - Note: dimers move *faster* than ions due to $Ar \leftrightarrow Ar^+$ resonant charge exchange

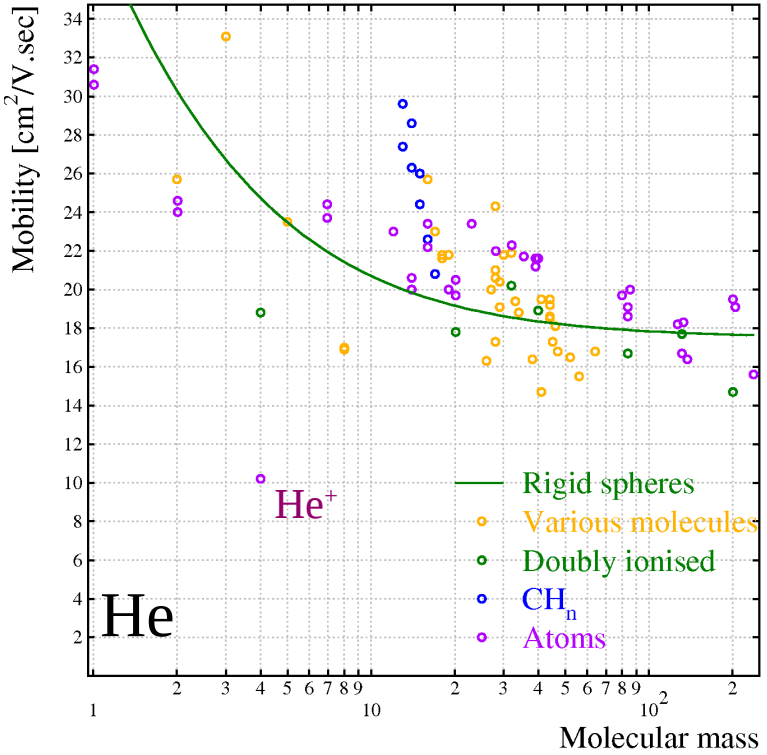
[P.N.B. Neves et al. 10.1063/1.3497651]

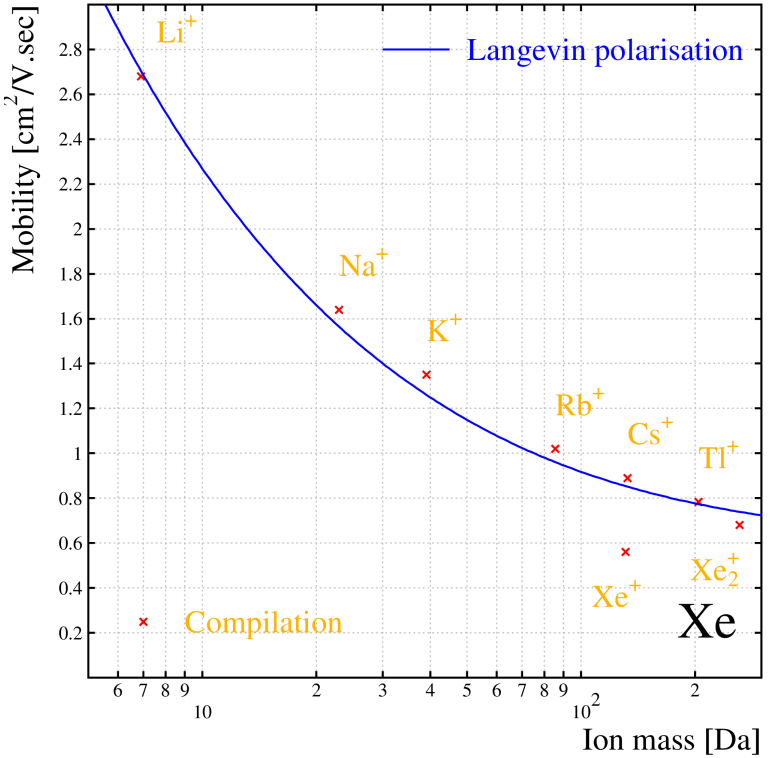


He, Xe, N_2



[J. A. Hornbeck, J. Phys. Chem. **56** (1952) 829–831 10.1021/j150499a003, copied from J.H. Mitchell and K.E.W. Ridler, Proc. Roy. Soc (London) A **146** (1934) 911.]





Principal reactions involving CO_2

- Ar^+: charge exchange, $\tau \approx 0.85$ ns
  - $Ar^+ + CO_2 \rightarrow Ar + CO_2^+$
- Ne^+: charge transfer in 2-steps, $\tau \approx 8$ ns
  - $Ne^+ + CO_2 \rightarrow Ne + CO^+ + O$
  - $CO^+ + CO_2 \rightarrow CO + CO_2^+$
- CO_2: 3-body association, 7-20 ps
  - $CO_2^+ + 2CO_2 \rightarrow CO_2^+ \bullet CO_2 + CO_2$
- [For 10 % CO_2, atmospheric pressure, room temperature]

Mathematica

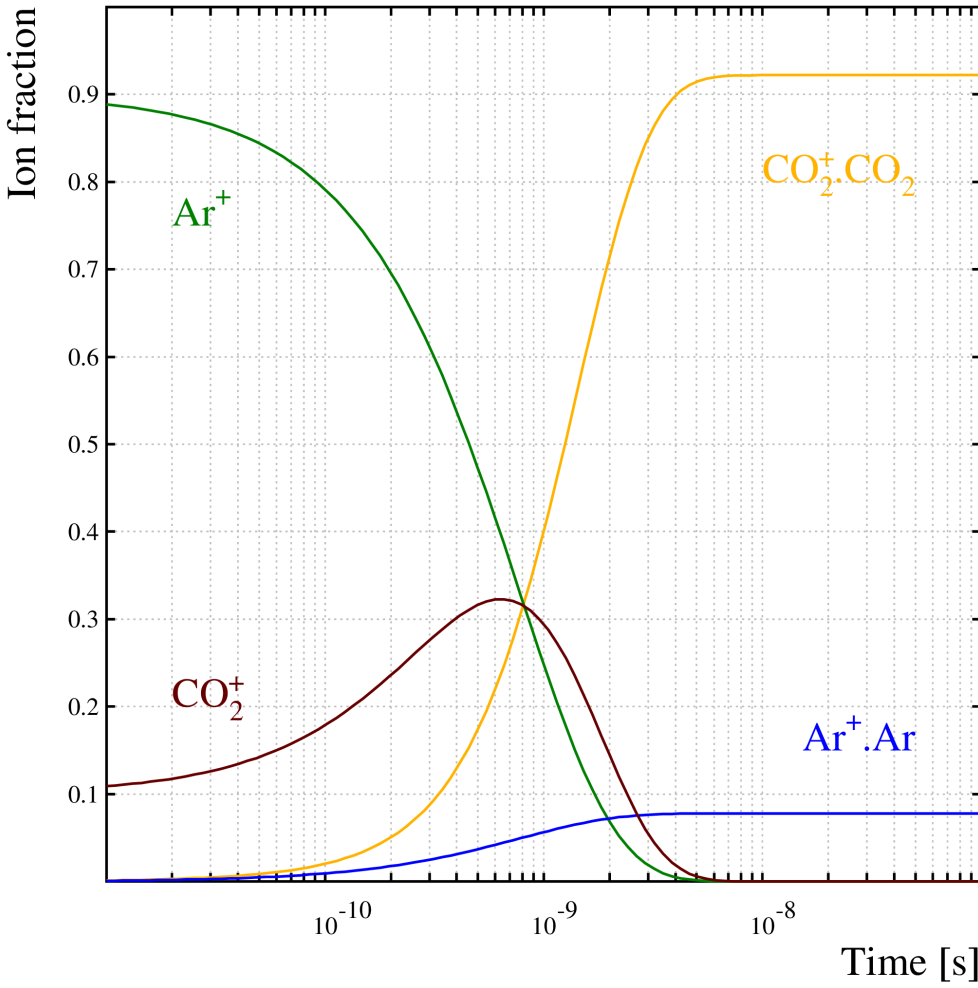
```
Clear[nXe, nXe2, nXeC2H6, nC2H4, nC2H5, nC2H6]
evol = Assuming[{rXeXe2 > 0, rXe2XeC2H6 > 0,  rXeC2H4 > 0, rXeC2H5 > 0,
    rXeC2H6 > 0, n0Xe > 0, n0C2H4 > 0, x > 0},
  Simplify[DSolve[
    {nXe'[x] == -(rXeXe2 + rXeC2H4 + rXeC2H5 + rXeC2H6) nXe[x],
     nXe[0] == n0Xe,
     nXe2'[x] == rXeXe2 nXe[x] - rXe2XeC2H6 nXe2[x],
     nXe2[0] == 0,
     nXeC2H6'[x] == rXe2XeC2H6 nXe2[x],
     nXeC2H6[0] == 0,
     nC2H4'[x] == rXeC2H4 nXe[x],
     nC2H4[0] == n0C2H4,
     nC2H5'[x] == rXeC2H5 nXe[x],
     nC2H5[0] == 0,
     nC2H6'[x] == rXeC2H6 nXe[x],
     nC2H6[0] == 0},
    {nXe[x], nXe2[x], nXeC2H6[x], nC2H4[x], nC2H5[x], nC2H6[x]},
    x]]]
CForm[%]
```

$$\left\{\left\{nC2H4[x] \to \left(\left(1 - e^{-(rXeC2H4+rXeC2H5+rXeC2H6+rXeXe2)\,x}\right) n0Xe\, rXeC2H4 + n0C2H4\,(rXeC2H4 + rXeC2H5 + rXeC2H6 + rXeXe2)\right) \Big/ (rXeC2H4 + rXeC2H5 + rXeC2H6 + rXeXe2),\right.\right.$$

$$\left.\left. nC2H5[x] \to -\frac{\left(-1 + e^{-(rXeC2H4+rXeC2H5+rXeC2H6+rXeXe2)\,x}\right) n0Xe\, rXeC2H5}{rXeC2H4 + rXeC2H5 + rXeC2H6 + rXeXe2},\right.\right.$$

Reaction dynamics in Ar CO_2

- Reactions:
  - $Ar^+ + CO_2 \rightarrow Ar + CO_2^+$
  - $CO_2^+ + 2CO_2 \rightarrow CO_2^+ \bullet CO_2 + CO_2$
  - $Ar^+ + 2Ar \rightarrow Ar^+ \bullet Ar + Ar$
- Parameters:
  - p = 1 bar
  - mix: 90 % Ar + 10 % CO_2



Situating cluster ions

- Chemically bound molecules: 0.75 - 11.1 eV
  - covalent or ionic bond.
- Cluster ions: 0.09 - 1.7 eV
  - bound by charge-induced dipole forces,
  - constituents retain their identity.
- van der Waals molecules: 0.0009 - 0.1 eV
  - bound by van der Waals forces
  - observed at low temperatures.

[B.M. Smirnov, “Cluster Ions and Van Der Waals Molecules,” CRC press]

Binding energy of CO_2 cluster ions

- Binding energy when successively adding more CO_2
  - $CO_2^+ \bullet CO_2$: 0.60 eV (16.2 kcal/mol)
  - $CO_2^+ \bullet 2CO_2$: 0.26 eV (6.0 kcal/mol)

[M. Meot-Ner and F.H. Field, J. Chem. Phys., **66** (1977) 4527]

  - $CO_2^+ \bullet CO_2$ 0.51 eV (11.8 ± 1.0 kcal/mol)
  - $(CO_2)_2^+ \bullet CO_2$ 0.14 eV (3.3 ± 1.4 kcal/mol)
  - $(CO_2)_3^+ \bullet CO_2$ 0.12 eV (2.8 ± 1.4 kcal/mol)

[S.H. Linn and C.Y. Ng, J. Chem. Phys. **75** (1981) 4921]

(Conversion: 1 kcal/mole = 0.043 eV)

Life cycle of $CO_2^+ \bullet (CO_2)_n$

- $CO_2^+ \bullet CO_2$ has a dissociation energy of 0.6 eV
  - far above thermal energies at 1 bar (35 meV);
  - it is a long-lived cluster – calculated lifetime = 5 ns.

  [B.M. Smirnov, "Cluster Ions and Van Der Waals Molecules," CRC press]

- This is much longer than the formation time τ = 7-20 ps via 3-body association in 10 % CO_2 with Ar + CO_2 as "helpers".

- Hence, any isolated CO_2^+ rapidly binds again.

- $CO_2^+ \bullet (CO_2)_n$ probably lives shorter but will recombine. The cluster size *n* will therefore fluctuate at the ns time scale.

Ne^+ in Ne … did it make sense ?

- The avalanche produced little Ne^+ to begin with;
- $IP_{Ne^+} > IP_{CO_2^+}$: Ne^+ took 8 ns to generate a CO_2^+;
- which transformed to $CO_2^+ \bullet CO_2$.
- In nearly pure Ne, there could be some Ne_2^+.

Experimental check

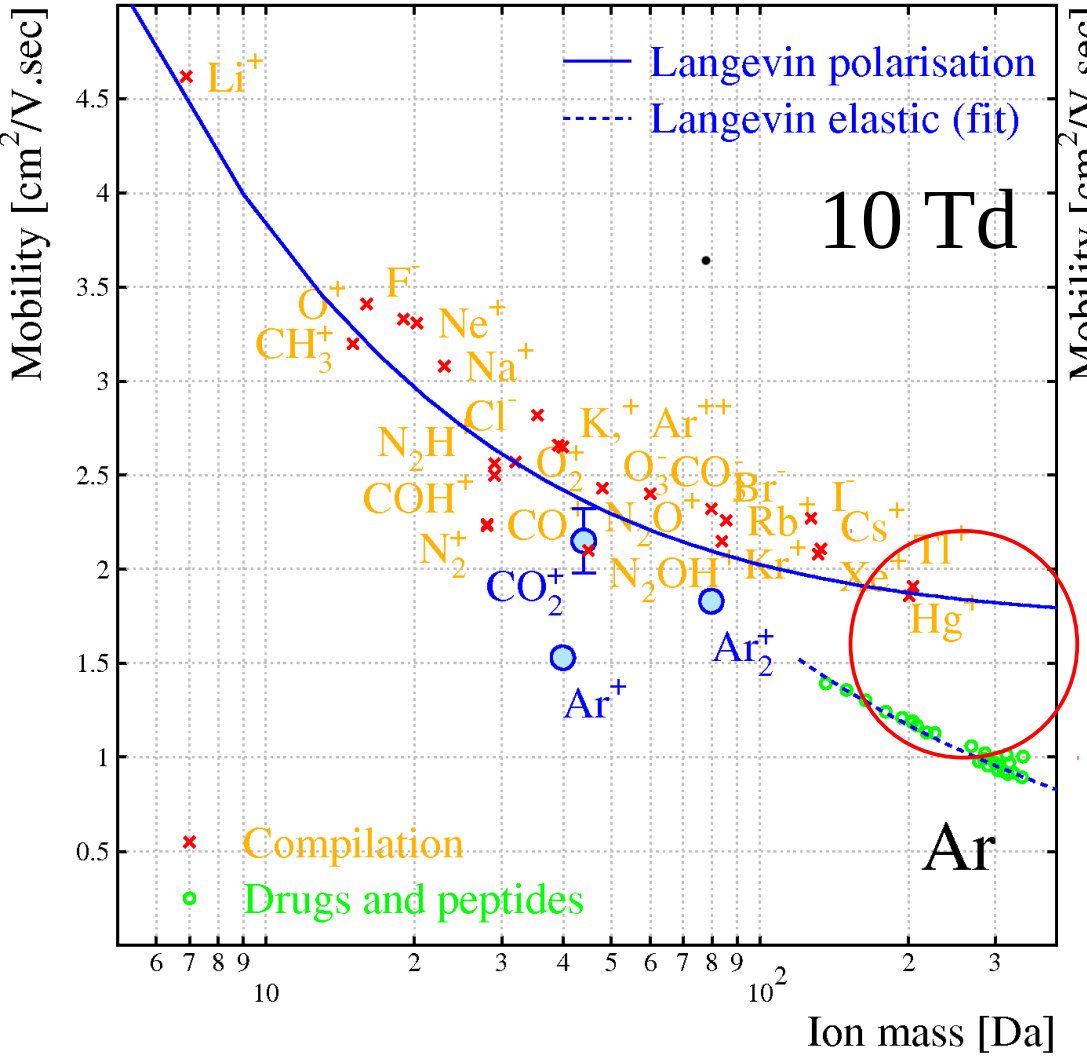
- Remains showing that experiments indeed observe $CO_2^+ \bullet (CO_2)_n$ and not e.g. Ar or CO_2^+ as assumed.

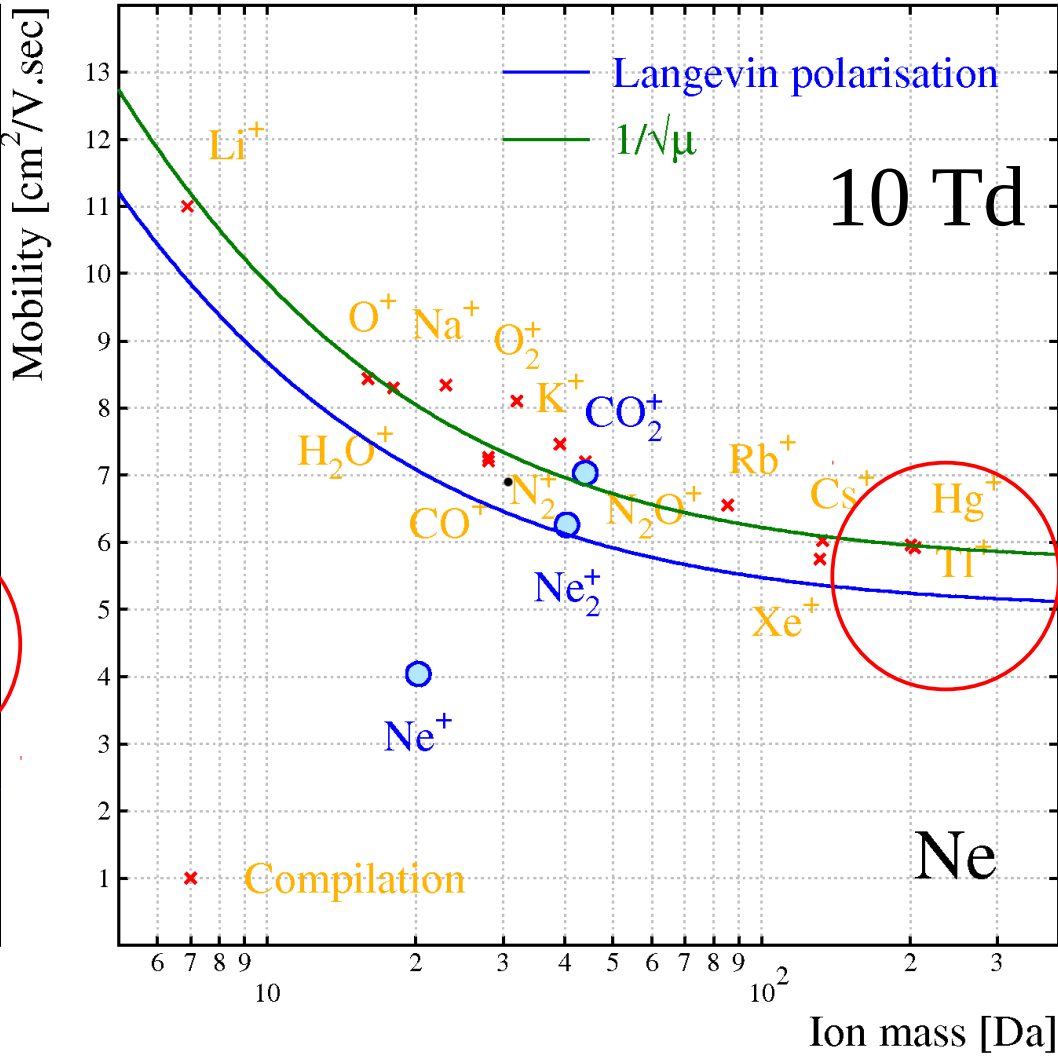
- This we do by comparing:
  - mobility for lots of mixing fractions (data);

    WITH
  - mobility of CO_2^+ in pure gases (literature);
  - mobility of $CO_2^+ \bullet (CO_2)_n$ in pure gases (mass-mobility);
  - mobility of $CO_2^+ \bullet (CO_2)_n$ in CO_2 (literature);
  - mobility of Ar^+ and Ne^+ (literature);

    USING
  - the Blanc interpolation formula.

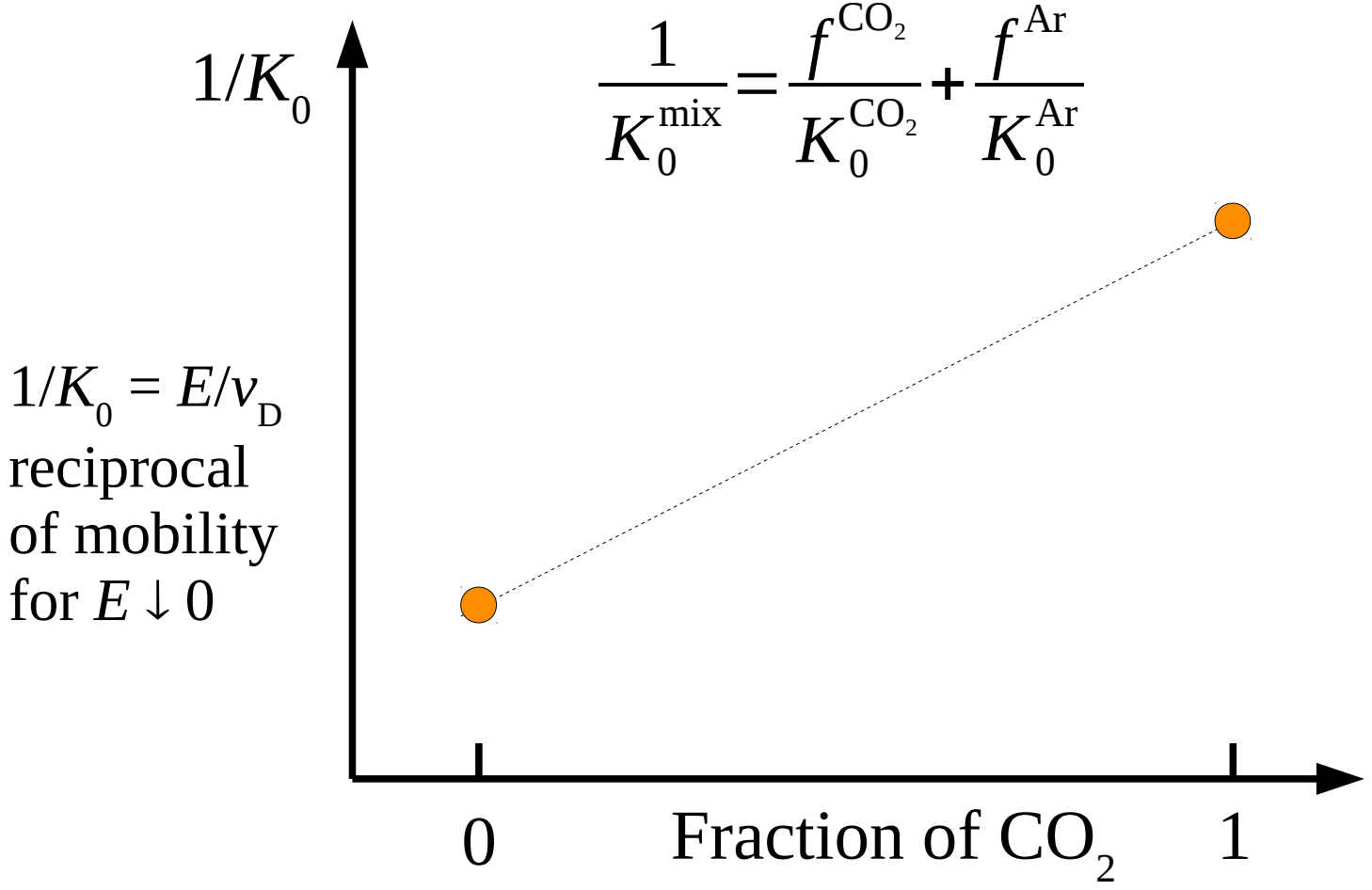
Mass-mobility in pure Ar and Ne





Blanc's mobility interpolation

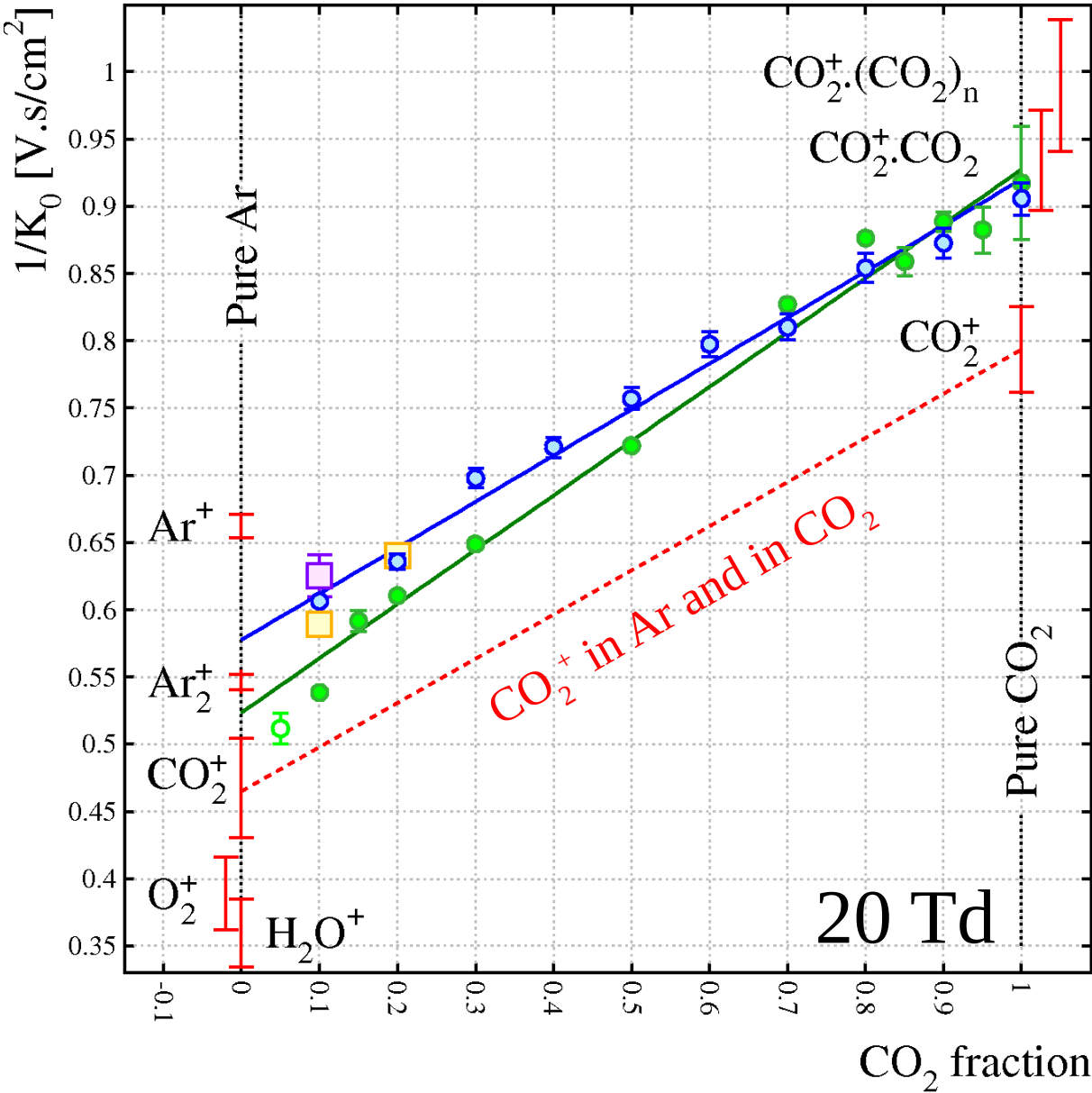
$$\frac{1}{K_0^{\text{mix}}} = \frac{f^{\text{CO}_2}}{K_0^{\text{CO}_2}} + \frac{f^{\text{Ar}}}{K_0^{\text{Ar}}}$$



[A. Blanc, *Recherches sur les mobilités des ions dans les gaz*,
J. Phys. Theor. Appl. **7** (1908) 825-839, 10.1051/jphystap:019080070082501]

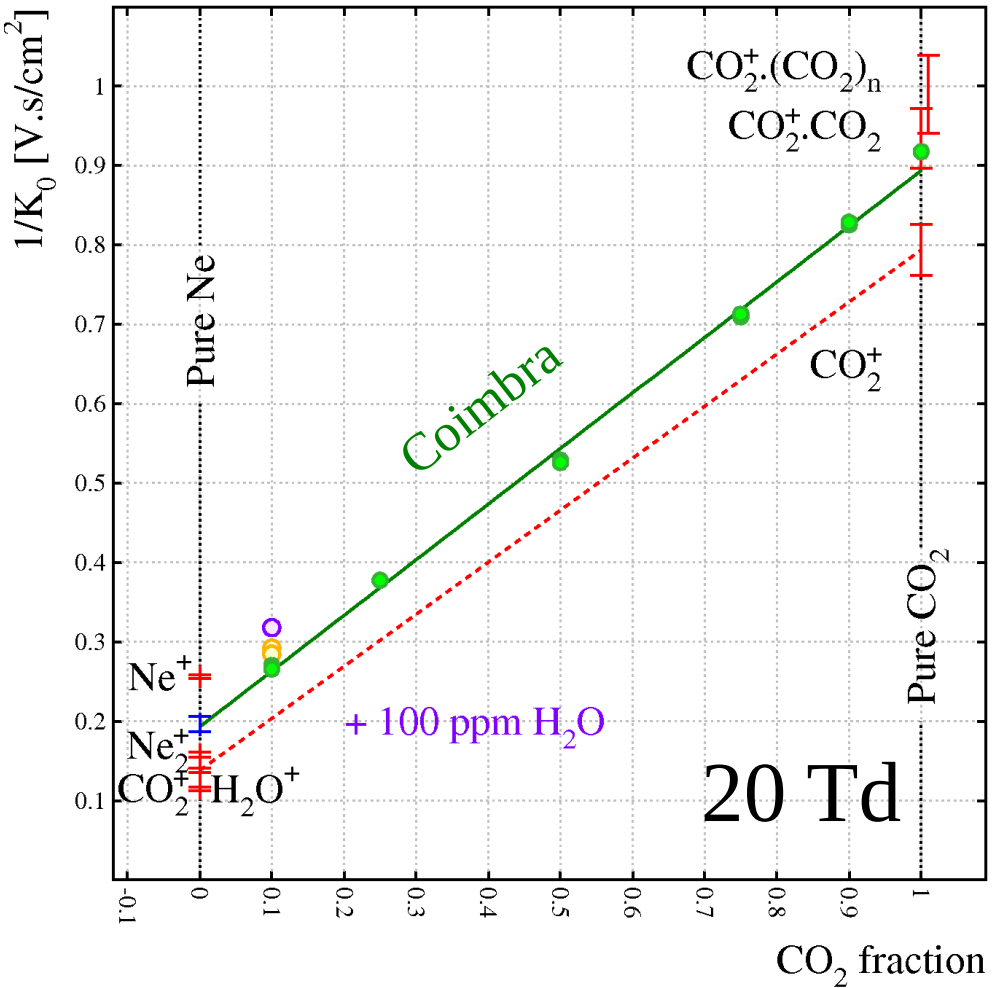
Blanc diagram for Ar-CO_2

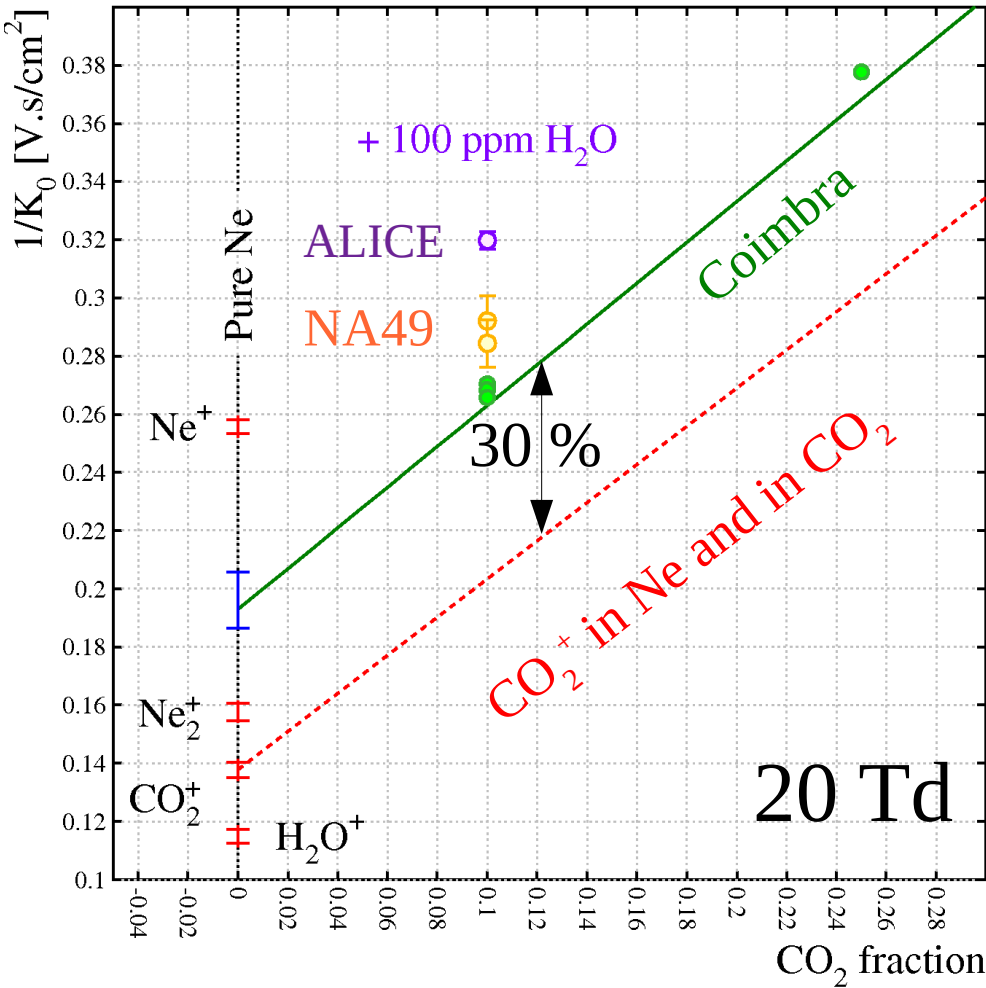
- Coxon: pure CO_2
- Schultz: 1 atm
- Coimbra: 0.01 atm, smaller clusters ?
- NA49: 1 atm
- ALICE: 1 atm, water clusters ?



Blanc diagram for Ne-CO_2

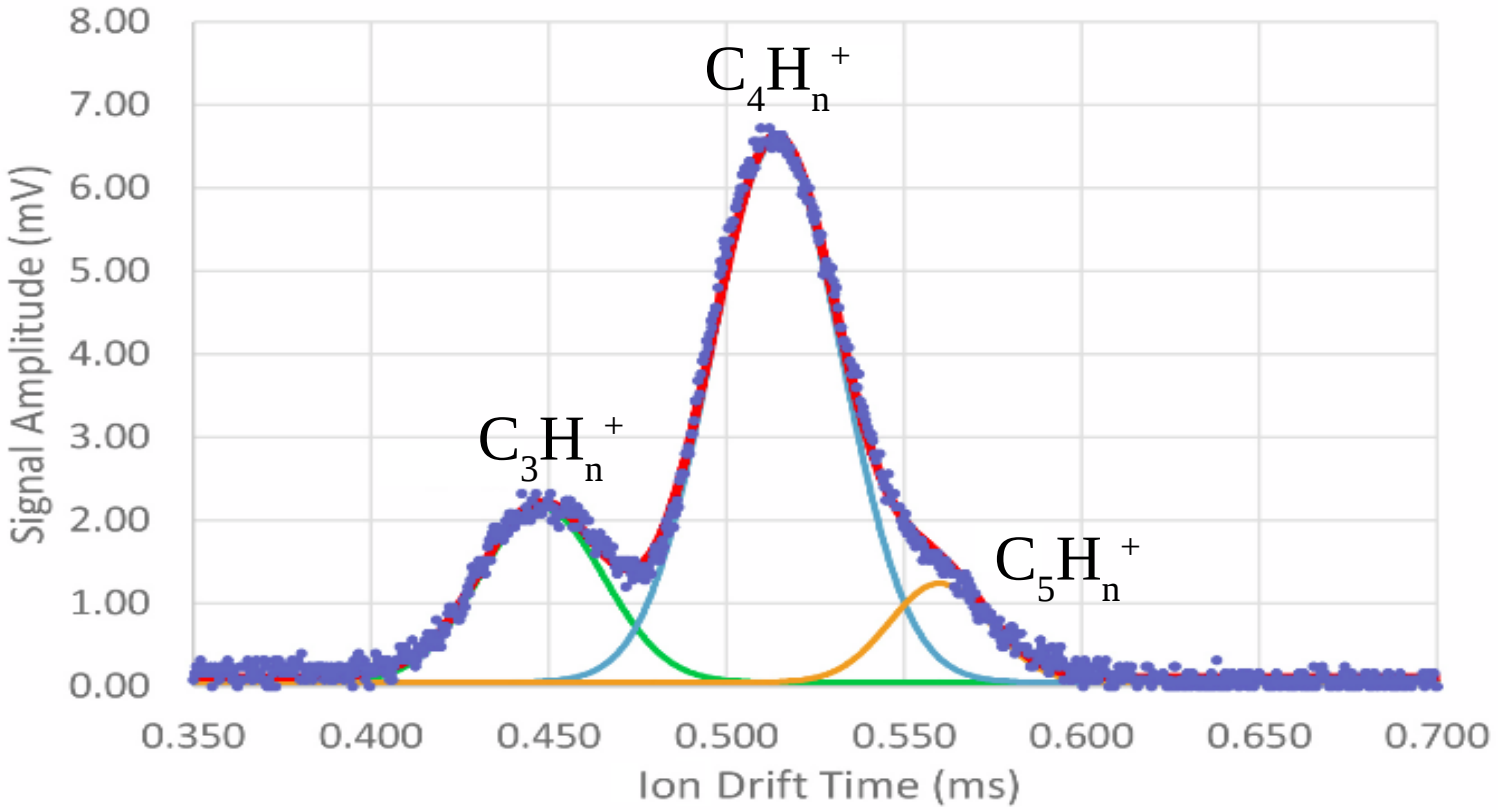
- Like in Ar-CO_2, CO_2^+ forms clusters in Ne-CO_2.



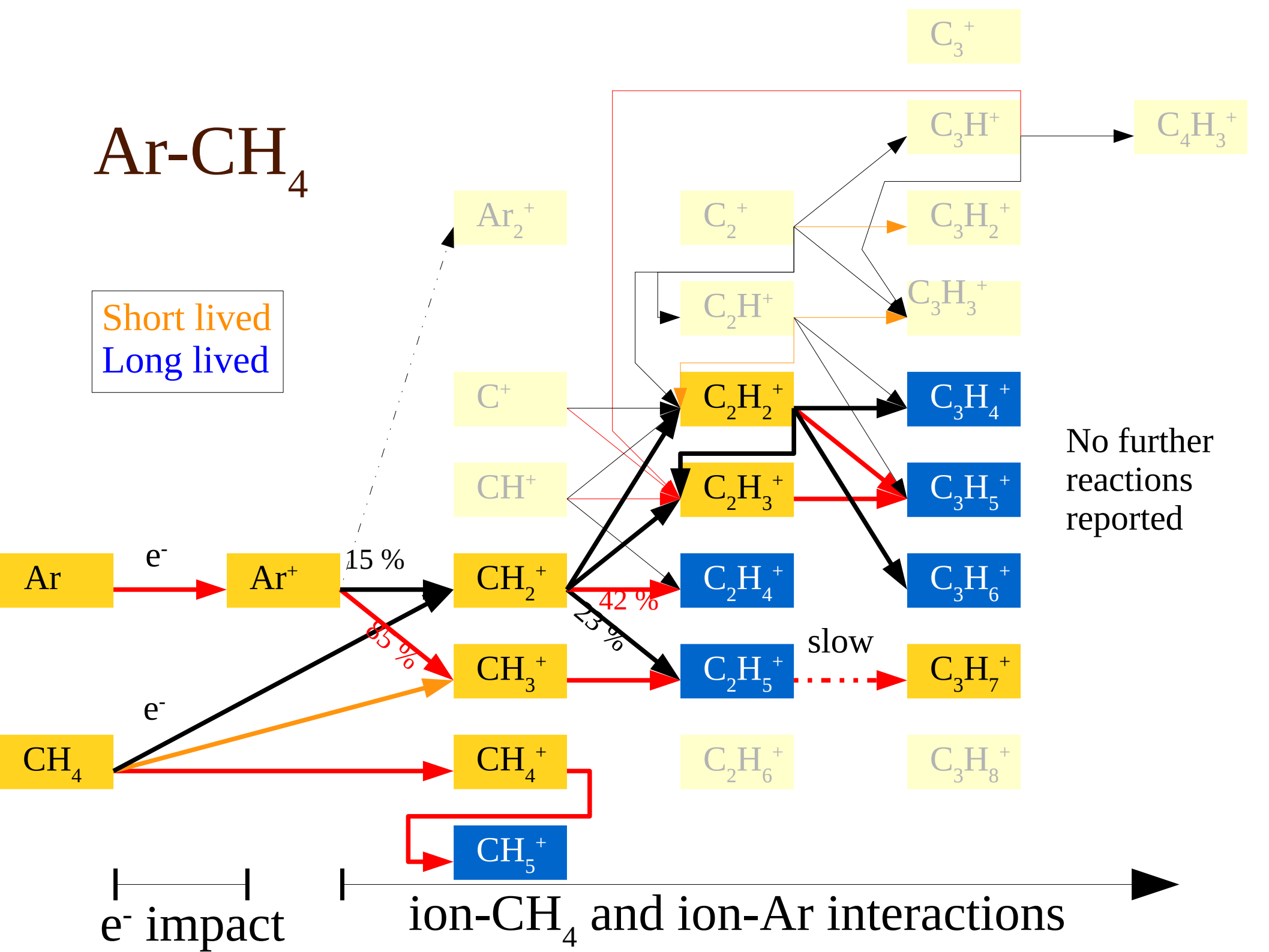


How about alkanes ?

- Ar 90 % - C_2H_6 10 %, at low pressure.
- Expect Ar^+ or C_2H_6 but ... none are seen – why ?



[André Cortez et al. 10.1088/1748-0221/8/12/P12012]


Ar-CH4
Short lived
Long lived
Ar
e-
Ar+
15 %
85 %
CH4
e-
Ar2+
C+
CH+
CH2+
CH3+
CH4+
CH5+
C2+
C2H+
C2H2+
C2H3+
C2H4+
C2H5+
C2H6+
C3+
C3H+
C3H2+
C3H3+
C3H4+
C3H5+
C3H6+
C3H7+
C3H8+
C4H3+
42 %
23 %
slow
No further reactions reported
e- impact
ion-CH4 and ion-Ar interactions

Summary electrons

- Quenchers play a major role in electron transport:
  - increase drift velocity;
  - decrease diffusion.

- Some quenchers increase the gain:
  - Penning effect;
  - gain fluctuations are influenced by quenchers.

Summary ions

- Avalanches ionise the constituent gases, and the initial ions undergo a staggering sequence of reactions.
  - In Ar-CO_2 and Ne-CO_2 mixtures, the signal ions are $CO_2^+ \bullet (CO_2)_n$ clusters, which are slower than CO_2^+;
  - water forms larger clusters, further reducing the mobility;
  - pure noble gases form dimers, Ar_2^+, Ne_2^+ which are faster than Ar^+ and Ne^+ due to resonant charge exchange;
  - Xe forms dimers, trimers and probably bigger objects;
  - alkanes combine to form heavier molecules.
- There is room for theses in this field.