A PRACTICAL APPROACH TO ION MOBILITY

André Cortez
Gran Sasso Science Institute
Contact: andre.cortez@gssi.it

INFN Istituto Nazionale di Fisica Nucleare

GRAN SASSO SCIENCE INSTITUTE
SCHOOL OF ADVANCED STUDIES
Scuola Universitaria Superiore

OUTLINE

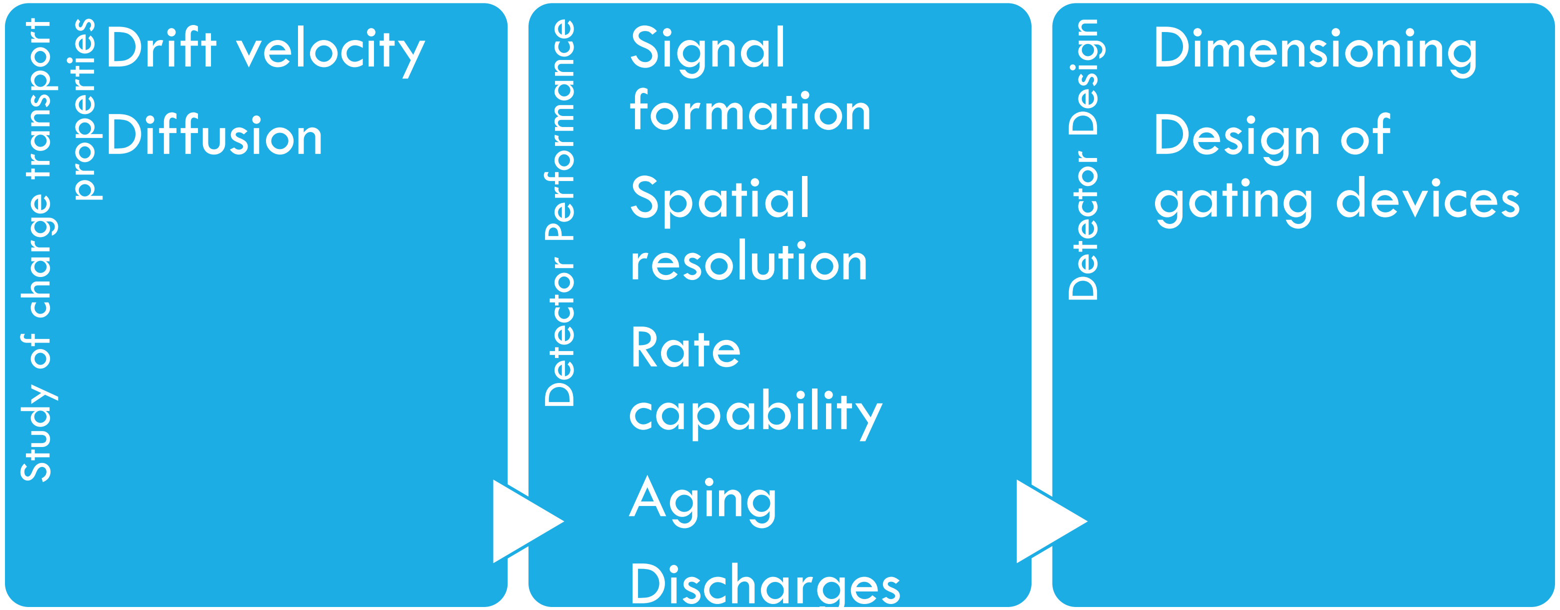
- Introduction
  - Relevance of Ion mobility*
  - Basic Concepts*
    - Diffusion of ions in gases*
    - Effect of electric field on ion motion*
    - Effect of gas density*
  - Models for Ion-neutral interactions*
  - Processes that affect ion mobility*
  - Techniques to identify ions (direct and indirect)*
- Experimental measurements
  - Experimental Setup and Working Principle*
  - Ion identification process*
  - Ion mobility in pure Xe and CO2*
  - Ion mobility in Xe-CO2 mixtures*
- Challenges and Future Prospects
  - Validity of Langevin Theory*
  - Mobility of negative ions*
  - High pressure*
- Summary

INTRODUCTION

GRAN SASSO SCIENCE INSTITUTE
SCHOOL OF ADVANCED STUDIES
Scuola Universitaria Superiore

INTRODUCTION

Relevance of gas choice and ion mobility in gaseous radiation detectors…



Study of charge transport properties
- Drift velocity
- Diffusion

Detector Performance
- Signal formation
- Spatial resolution
- Rate capability
- Aging
- Discharges

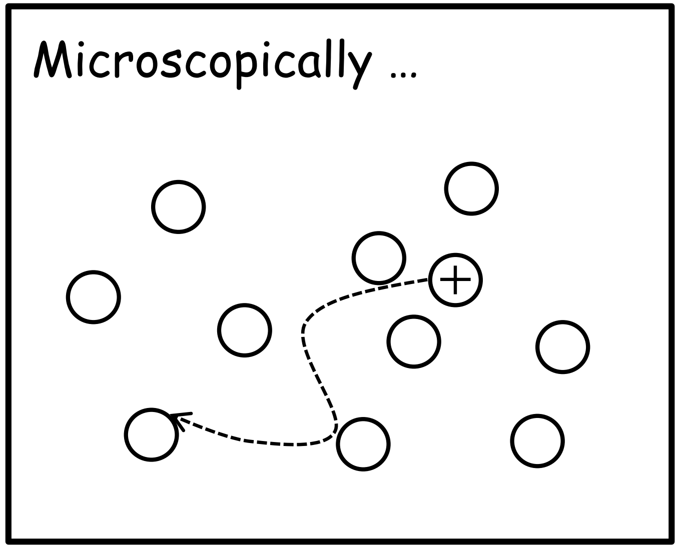
Detector Design
- Dimensioning
- Design of gating devices

INTRODUCTION

Basic concepts – Diffusion of ions in gases

Let us consider a group of ions moving in a gaseous medium. In the absence of a temperature gradient, electric or magnetic field and low charge density..

Microscopically …



- Ions will move from high concentration regions to low concentration regions;
- Rate is proportional to concentration gradient (∇n);

J – ion flux
D – ion diffusion

$$J = -D\nabla n$$

Continues until all ions are uniformly dispersed in neutral gas.

$J = vn$ (where *v* is the velocity of the diffusive flow)

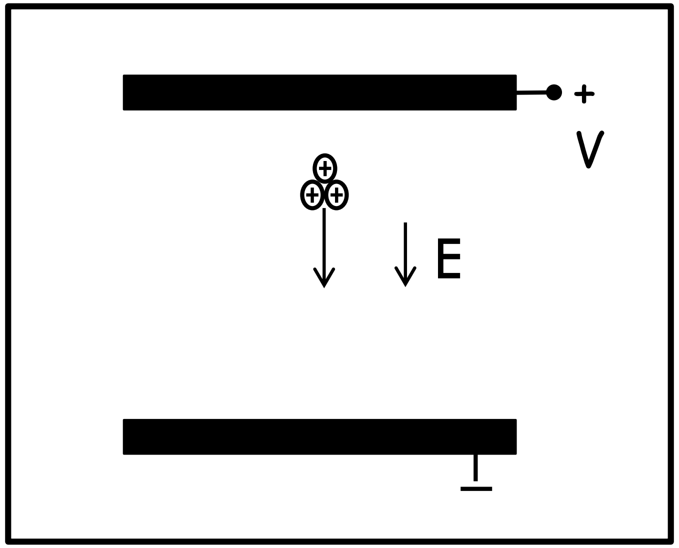
Under these circumstances the ions will display thermal velocity…

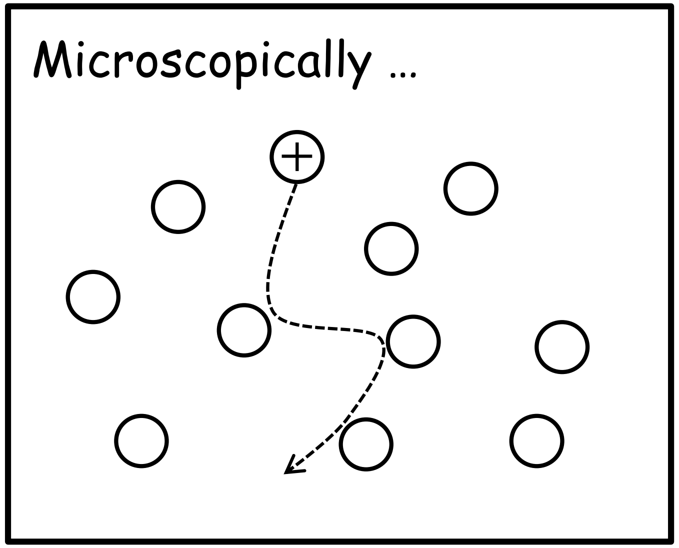
$$v = \sqrt{\frac{3}{2}k_B T}$$

INTRODUCTION

Basic concepts – Effect of electric field on ion motion

Let us consider a group of ions moving in a gaseous medium under the influence of a weak and uniform electric field…





- **Ions** will **flow along the field lines** so that the ion **motion** is **superimposed on the diffuse motion**.
- The **average speed** of the ions becomes **proportional** to the electric field and **diffusion** is **isotropic** (assuming that a steady state is reached).

Drift velocity

$$v_\mathrm{d} = KE$$

E- Electric Field
K-Ion Mobility

Diffusion

$$\varepsilon_\mathrm{m} = 3/2k_\mathrm{B}T$$
$$D_\mathrm{T} = D_\mathrm{L}$$

ε_m – Average energy
D_T (D_L) – Diffusion coefficients
T – Temperature

Nernst-Townsend relationship

$$K = \left({}^{eD}\!/_{k_B T}\right)$$

e – electric charge
k_B–Boltzmann constant

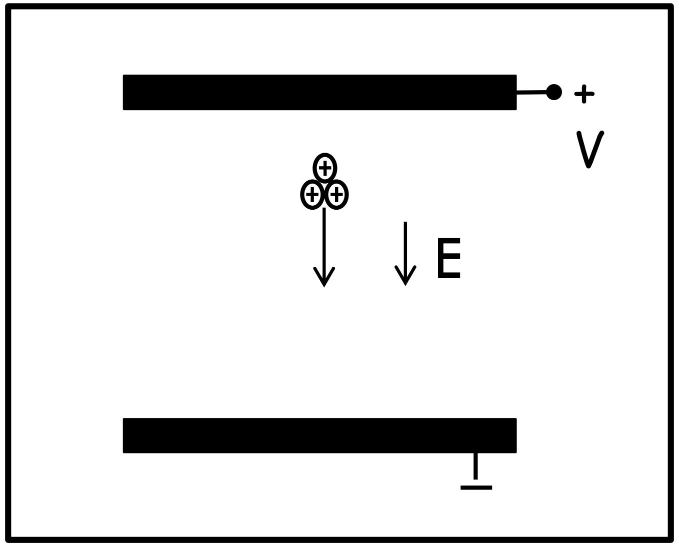
Mobility

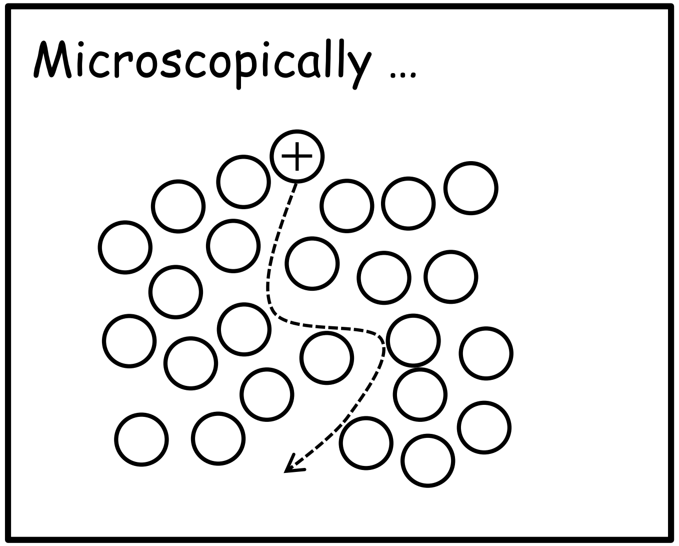
- Proportional to the diffusion coefficient
- Inversely proportional to gas temperature

INTRODUCTION

Basic concepts – Effect of gas density

Let us consider a group of ions moving in a gaseous medium under the influence of a weak and uniform electric field…





- Increase in the electric field strength will increase the drift velocity;
- Increase in the gas density will…

Mean free path between collisions

$$\lambda = \frac{1}{\sigma N}$$

Collision frequency

$$\nu = \bar{v}\sigma N$$

Energy loss per collision

$$\Delta\varepsilon = \frac{2mM}{(m+M)^2}\varepsilon_i$$

Energy gained between collisions

$$\varepsilon_i = qE\lambda$$

- Ion motion will therefore depend on E/N;
- Mobility will be independent of E/N only if energy acquired is neglegible if compared to the thermal energy;

Reduced Mobility

$$K_0 = KN/N_0$$

N – Gas number density
N_0–Loschmidt Number

INTRODUCTION

Models for Ion-neutral interaction

In addition to the diffusive forces and effects of external electric field…

Models for Ion-Neutral Interactions

Polarization Limit	Elastic Limit

If the **ion-neutral repulsive forces** are **negligible** when compared to the **polarization effect** the interaction between the ion and the neutral is a function of the polarizability of the neutral atom/molecule.

The collision between an ion and a gas molecule is treated as a rigid sphere collision in which the ion scattering is isotropic (in the center of mass coordinate system).

Langevin Polarization Limit

$$K_0 = 13.88\left(\frac{1}{\alpha\mu}\right)^{\frac{1}{2}}$$

Blanc's Law

$$\frac{1}{K_{0mix}} = \frac{f_1}{K_{0g1}} + \frac{f_2}{K_{0g2}}$$

f_1, f_2 – molar fraction of gas 1, 2
K_{0g1}, K_{0g2} – ion mobility in the gas 1 and gas 2

Langevin Elastic Limit

$$K_{elast} = (3e/16N)\left[2\pi/(\mu k T_{eff})\right]^{1/2}\left[1/(\pi d^2)\right]$$

μ – reduced mass
α – neutral polarizability
d – sum of radii of the ion and neutral molecule

$$\frac{1}{2}mv^2 = \frac{1}{2}m{v_T}^2 + \frac{1}{2}m{v_d}^2 + \frac{1}{2}M{v_d}^2$$

Ion mean energy	Thermal energy	Energy gained by the E field	Random motion of the neutral gas molecules gained from the field

INTRODUCTION

Processes that affect ion mobility

Since the amount of time needed for a certain ion to travel a known distance depends on its mass, it is only natural that ion mobility is dependent on the ion formed. Sometimes it leads to over simplifications that result in incomplete/inaccurate evaluation of the true mobility.

Chemical reactions

$$R_g^+ + R_g \xrightarrow{k} R_{g2}^+$$

k – reaction constant

→

Reaction time

$$\tau = \frac{1}{k[R_g]}$$

$$[R_g] = N\frac{P}{P_{Atm}}$$

$$N = 2.45 \times 10^{19}\ cm^{-3}$$

→

Ion concentration

$$\frac{[\mathrm{Rg}^+]}{[\mathrm{Rg}^+]_0} = e^{-\frac{t}{\tau}}$$

→

Reaction is complete or not and can be used estimate how much each ion species affects the overall ion mobility.

Rate constant tells us how fast a reaction occurs.

Depends on:

- Temperature
- Drift velocity of ions

Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

Ea – activation energy
A – frequency factor

Main contributions come from:

Resonant charge transfer

- Slows down ions
- Increasing impact with pressure

Cluster formation

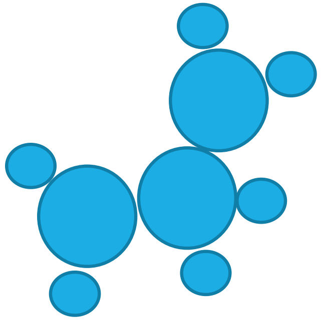
- Cluster size affects the drift of the ions
- Depend on the pressure

Impurities

- Water is a polar molecule
- Tends to form heavy clusters

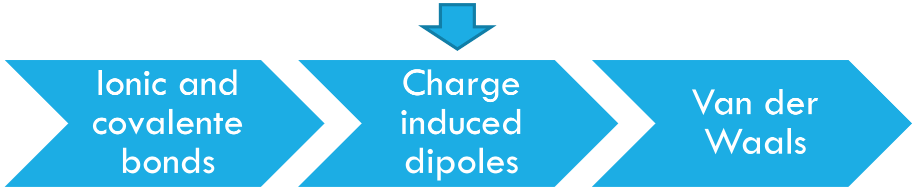
INTRODUCTION

Processes that affect ion mobility – Cluster Formation



- Clusters are composed by a central ion with one or more neutral atoms or molecules,
- bound together by charge induced dipoles.

Binding energy of Clusters



Ionic and covalente bonds

Charge induced dipoles

Van der Waals

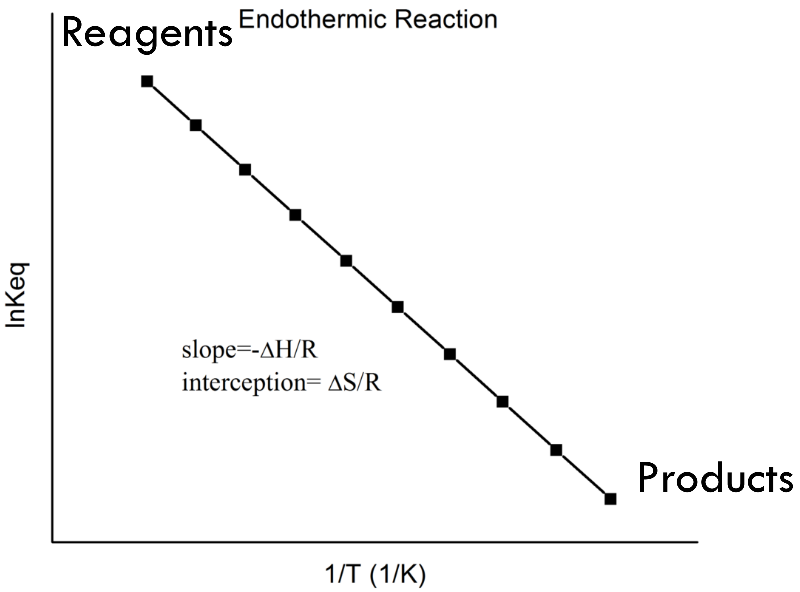
The trend to form clusters can be inferred from van't Hoff diagrams:

van't Hoff equation:

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Note:

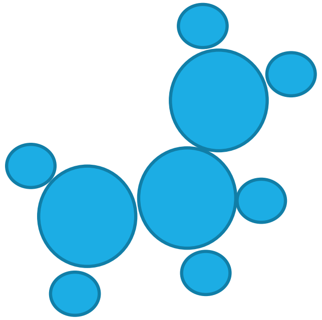
- Endothermic reactions display negative slope
- Exothermic reactions display positive slope



Taken from Wikipedia

INTRODUCTION

Processes that affect ion mobility – Cluster Formation



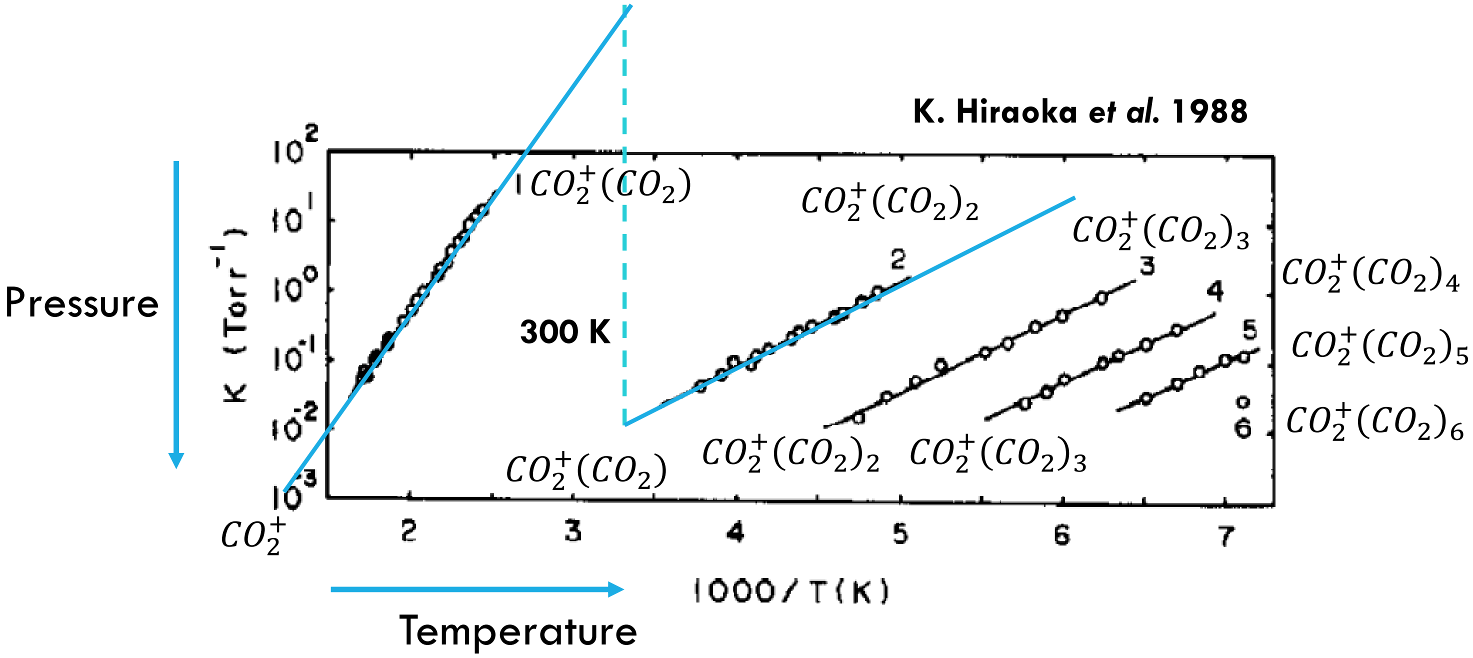
- Clusters are composed by a central ion with one or more neutral atoms or molecules,
- bound together by charge induced dipoles.

Binding energy of Clusters

Ionic and covalente bonds → Charge induced dipoles → Van der Waals

Example - CO_2^*

$$CO_2^+(CO_2)_{n-1} + 2CO_2 \leftrightarrow CO_2^+(CO_2)_n + CO_2$$



K. Hiraoka *et al.* 1988

- Cluster formation in CO_2 is an exothermic reaction (likely to take place)
- van't Hoff show that clusters of CO_2 can be formed even at low pressure
- Larger clusters can be formed at low temperature and high pressure

*Measurements taken at low pressure up to 3 Torr

INTRODUCTION

Processes that affect ion mobility – Water Content

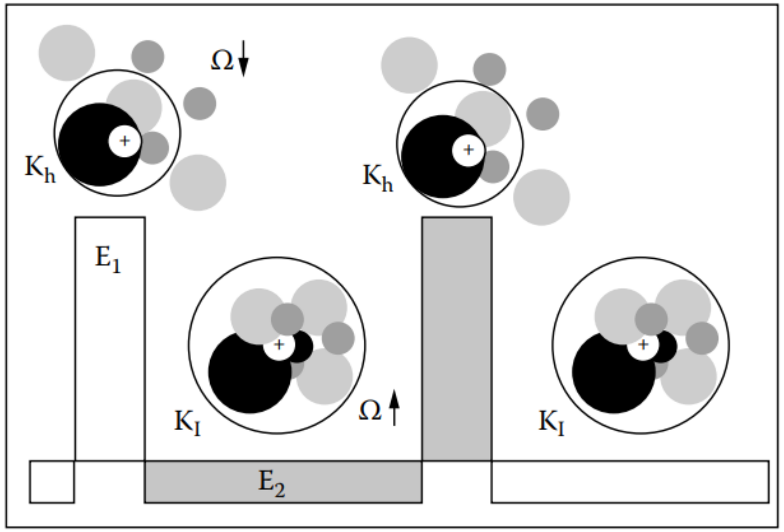
As seen before, cluster formation is highly probable even at low pressure, water molecules, being polar tend to form clusters.

- Low E/N favour the formation of water clusters.
- High E/N favour declustering*

Ion heating

Dissociation of hydrates

Declustering



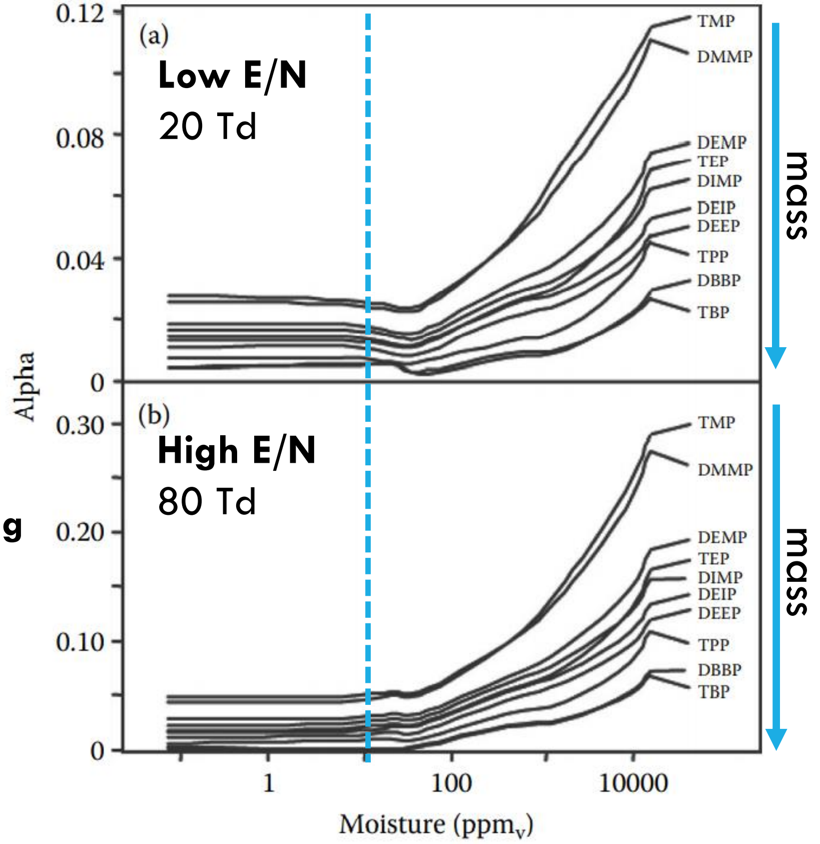
Clustering

G. Eiceman *et al.* 2013

Effect of water content

K constant **K decreases**

← **50 ppm** →



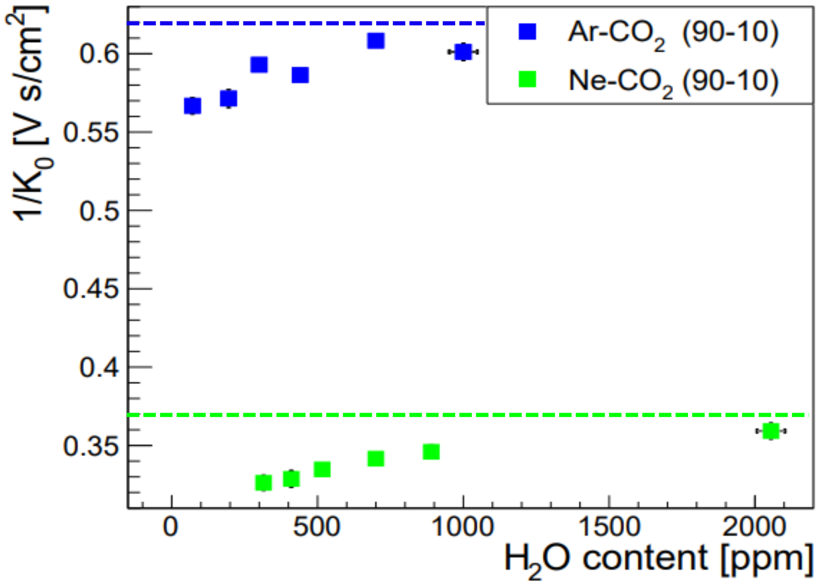
This work hints: The effect of water content on ion mobility should be less pronounced with increasing molecular weight of the gas.

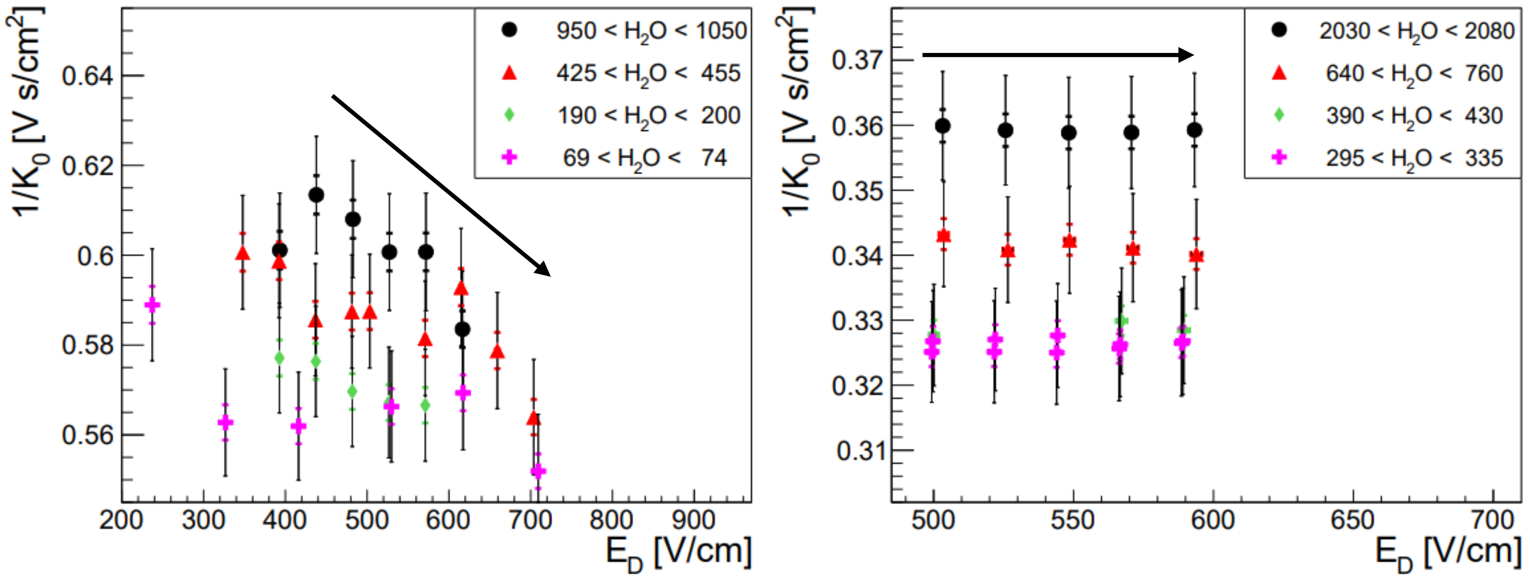
*Declustering reduction on the mass and size of a cluster ion.

INTRODUCTION

Processes that affect ion mobility – Water Content

A. Deisting *et al.* 2018





(a) Ar-CO_2 (90-10)

(b) Ne-CO_2 (90-10)

Decrease of ion mobility

Apparent limit for water content influence on K

Declustering effect with E/N

Significant impact on ion mobility.

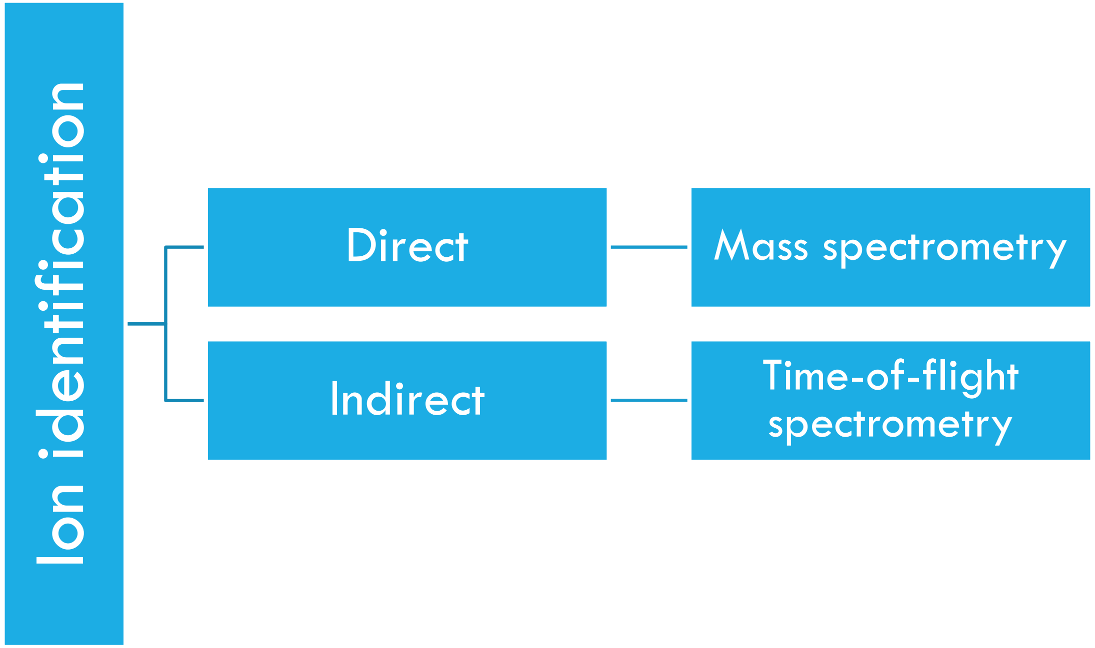
INTRODUCTION

Techniques to Identify Ions

Transport properties of ions in gases have been studied experimentally since shortly after the discovery of X-rays in 1895 and theoretically since 1903. Still in most data ions are being incorrectly identified.

Drifting ions can undergo chemical reactions changing their identities.

The identification of the nature of ions can be made using two different approaches:



INTRODUCTION

Techniques to Identify Ions – Mass Spectrometry

- Combines the ion drift chamber with a mass spectrometer

How does it work?

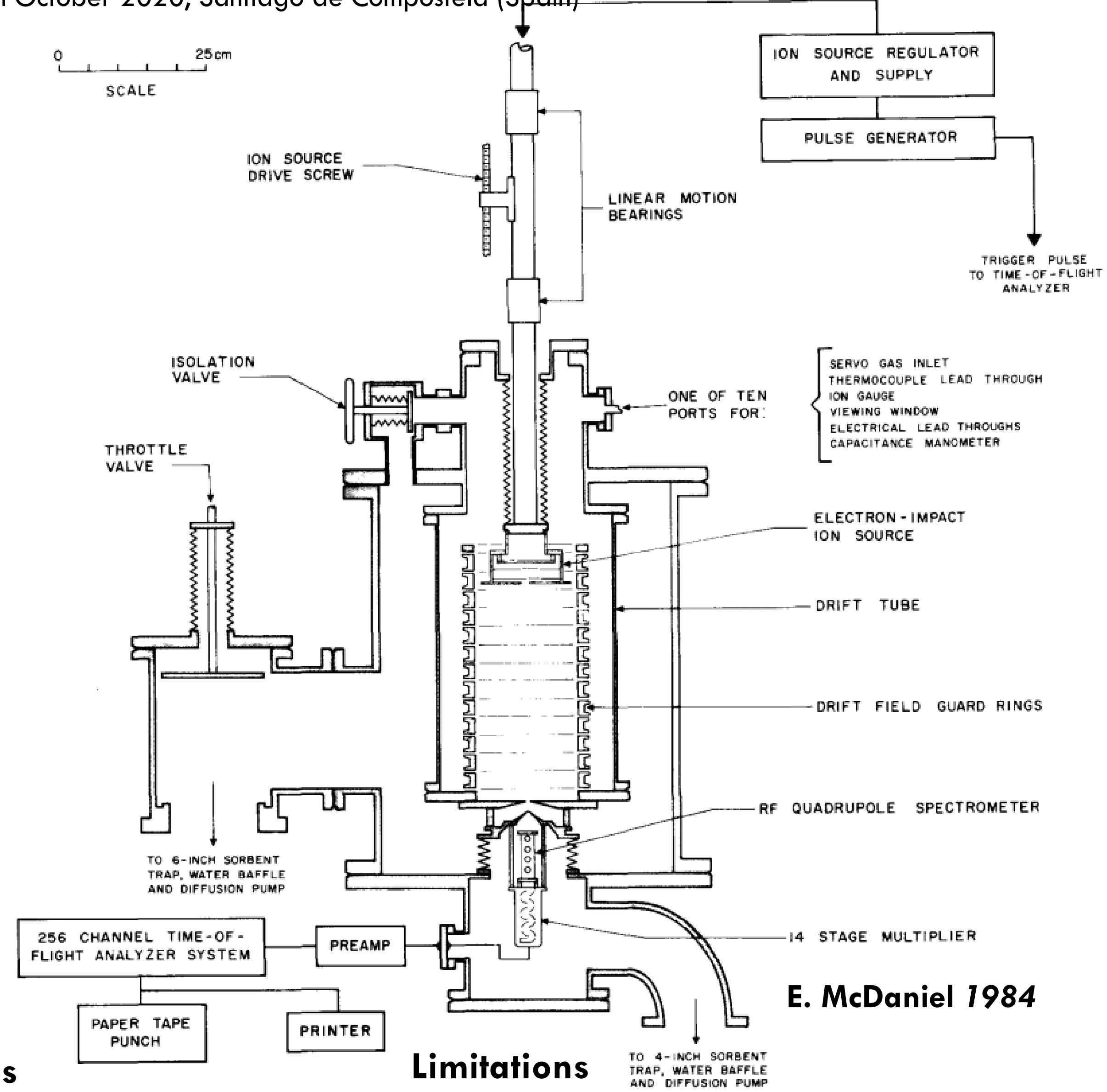
Ions are formed by electron impact

Cloud of ions drift along the

Ions enter a differentially pumped region where they are selected by mass;

Mass identified using a mass spectrometer;

A differencing technique is used to determine the ion drift velocity.



E. McDaniel *1984*

Advantages

- Clear identification
- Wide E/N range possible to study (0.3 Td to 5000 Td)

Limitations

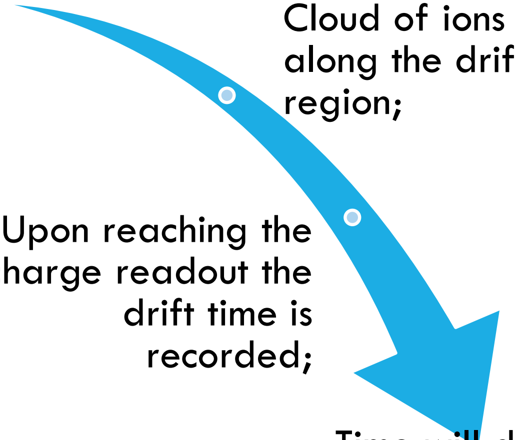
- Traditional operating pressures (7.5x10-2 to 10 Torr),

INTRODUCTION

Techniques to Identify Ions – Time-of-Flight (Mass) Spectrometry

- Makes use of a ion drift chamber

How does it work?



Ions are formed by electron impact;

Cloud of ions drift along the drift region;

Upon reaching the charge readout the drift time is recorded;

Time will depend on the mass-to-charge ratio, therefore enabling the indirect ion identification.

Time-of-flight mass spectrometry (TOFMS) is a method of mass spectrometry in which an ion's mass-to-charge ratio is determined via a time of flight measurement.

Advantages

- Operating pressure
- Possibility to study reactions

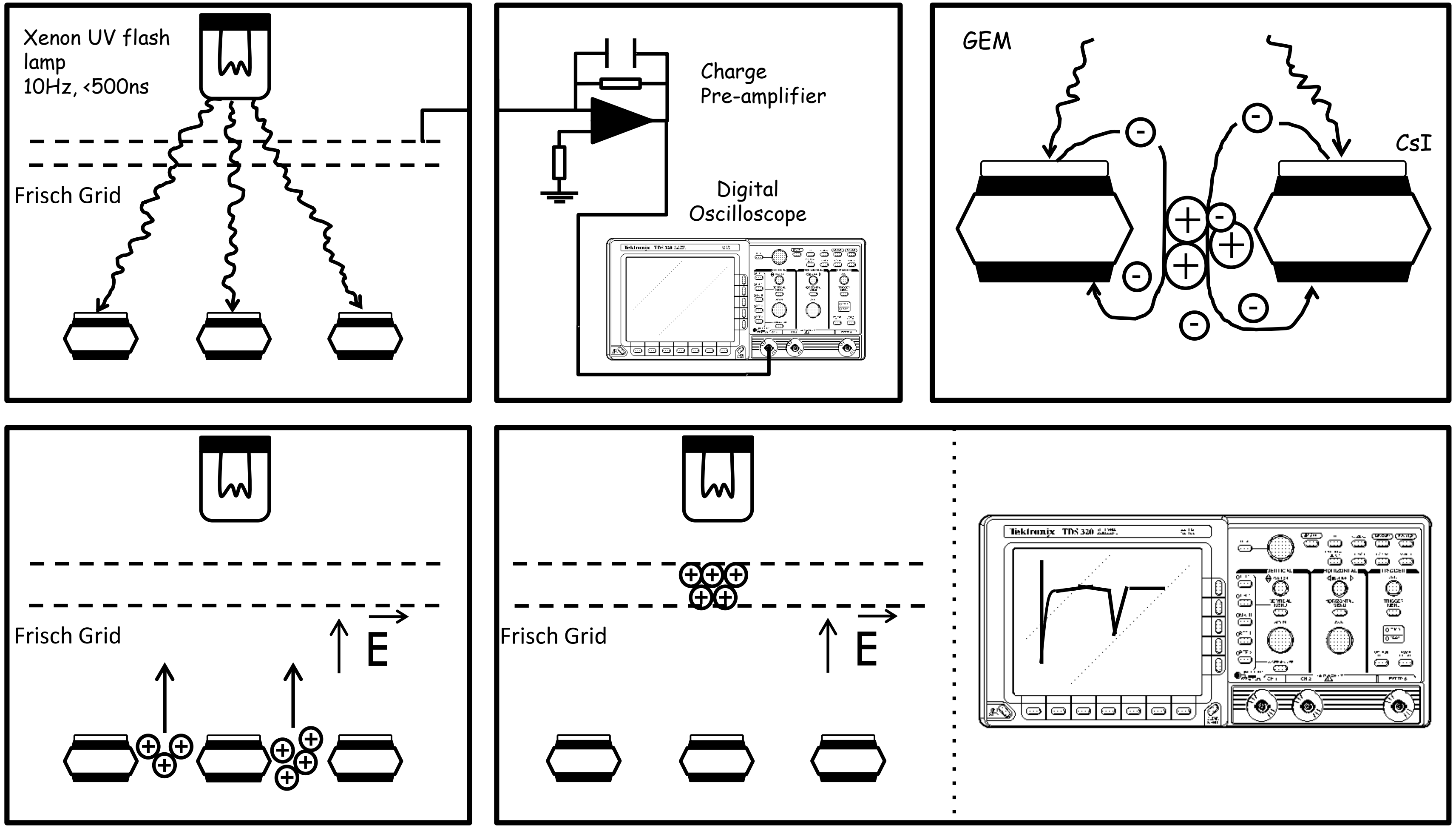
Limitations

- No direct identification is possible;
- E/N range is limited

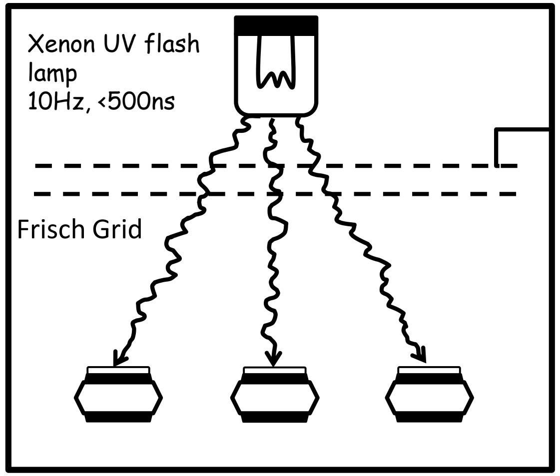
EXPERIMENTAL MEASUREMENTS

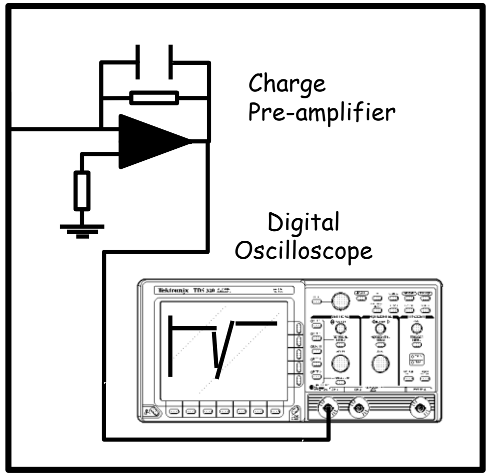
EXPERIMENTAL SETUP AND WORKING PRINCIPLE

P.N.B. Neves *et al.* 2007



EXPERIMENTAL SETUP AND WORKING PRINCIPLE





After the signal and the background were recorded…

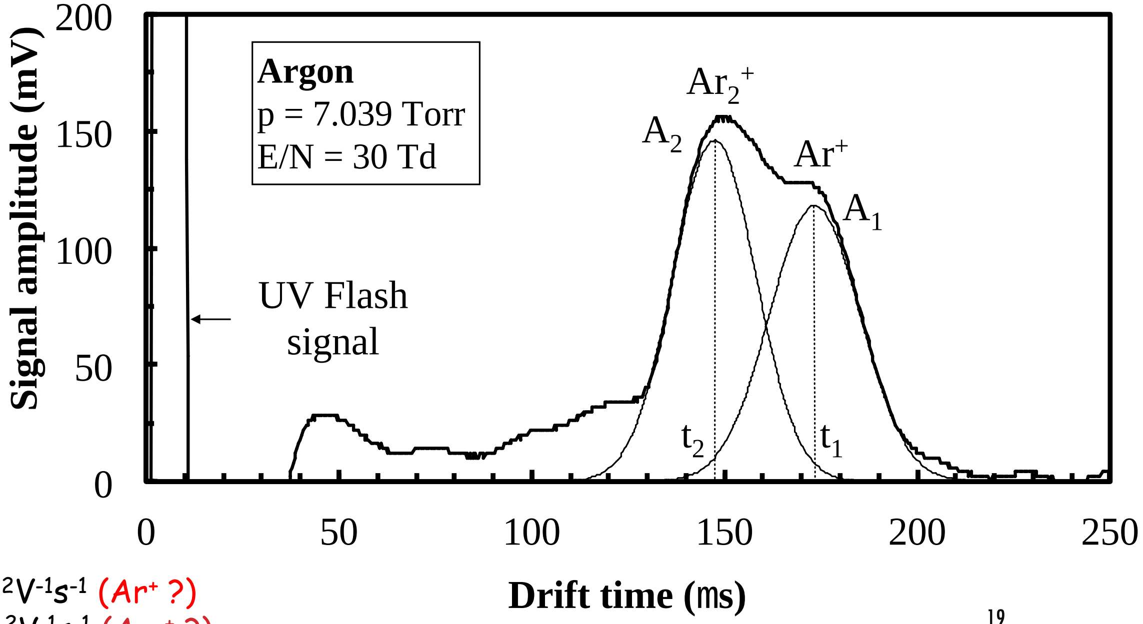
- Subtract the background to the signal
- Identify possible peaks
- Fit Gaussian curves to the spectrum obtained

peaks centroids

⬇

average drift time of the ion's distribution (t_{drift})

$$v_{\text{d}} = \frac{x_{drift}}{t_{drift}} \Rightarrow K = \frac{v_{\text{d}}}{E}$$



K_{01} = 1.57 $cm^2V^{-1}s^{-1}$ (Ar^+ ?)
K_{02} = 1.92 $cm^2V^{-1}s^{-1}$ (Ar_2^+ ?)

ION IDENTIFICATION PROCESS

Identification of candidate ions

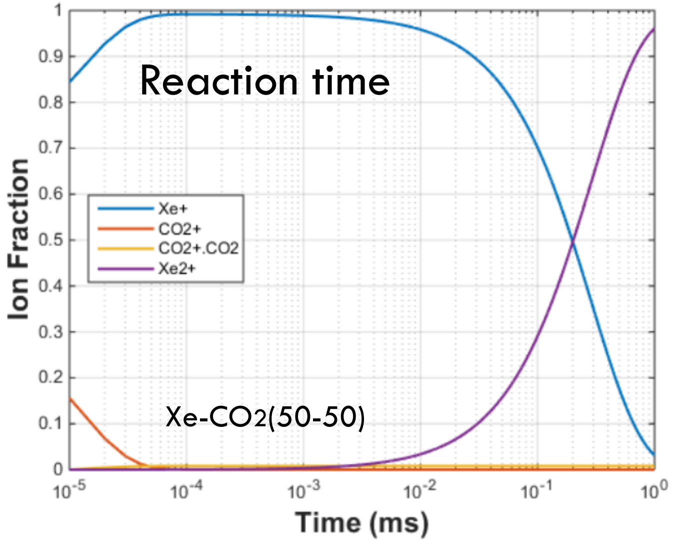
- GEM Voltage
- Possible Reactions
  - Cross Section
  - Reaction Rates

Most Probable Candidates

Table 4.13: Summary of possible reactions and respective rate constants or cross section for electron impact ionization at 20 eV (references on the last column).

A.F.V Cortez *2018*

Reaction	Rate Const. (*cm^3·s^{-1} or **cm^6·s^{-1})	Cross Sec. (10^{-16} cm^2)	Ref.
$e^- + Xe \rightarrow Xe^+ + 2e^-$	-	2.43 ± 0.12	[167]
$Xe^+ + Xe \rightarrow Xe + Xe^+$	2.5×10^{-10} *	-	[199]
$Xe^+ + 2Xe \rightarrow Xe_2^+ + Xe$	$2.0 \pm 0.2\times10^{-31}$ **	-	[169]
$e^- + CO_2 \rightarrow CO_2^+ + 2e^-$	-	0.452 ± 0.032	[200]
$CO_2^+ + CO_2 \rightarrow CO_2 + CO_2^+$	$3.7 \pm 0.37\times10^{-10}$ *	-	[190]
$CO_2^+ + CO_2 + M \rightarrow CO_2^+.CO_2 + M$	$2.1 \pm 0.3\times10^{-28}$ **	-	[191]
$CO_2^+ + Xe \rightarrow Xe^+ + CO_2$	$6.0 \pm 1.8\times10^{-10}$ *	-	[201]



Identification of expected mobility

- Estimate the influence of the predecessor ion on the overall mobility observed experimentally
- Langevin Limit (formula)
- Blanc’s law (mixtures)

Compare with experimental results

Theoretical Values = Experimental Values

EXPERIMENTAL RESULTS – XENON

IONIZATION

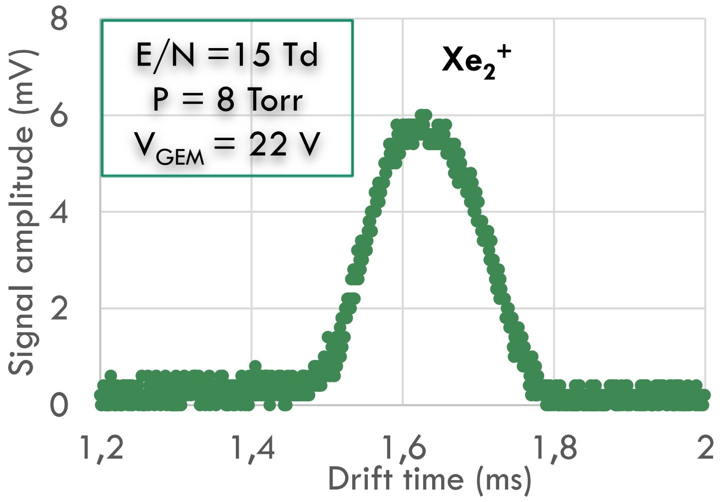
$e^- + Xe \rightarrow Xe^+ + 2e^-$

Above threshold
12.1 eV

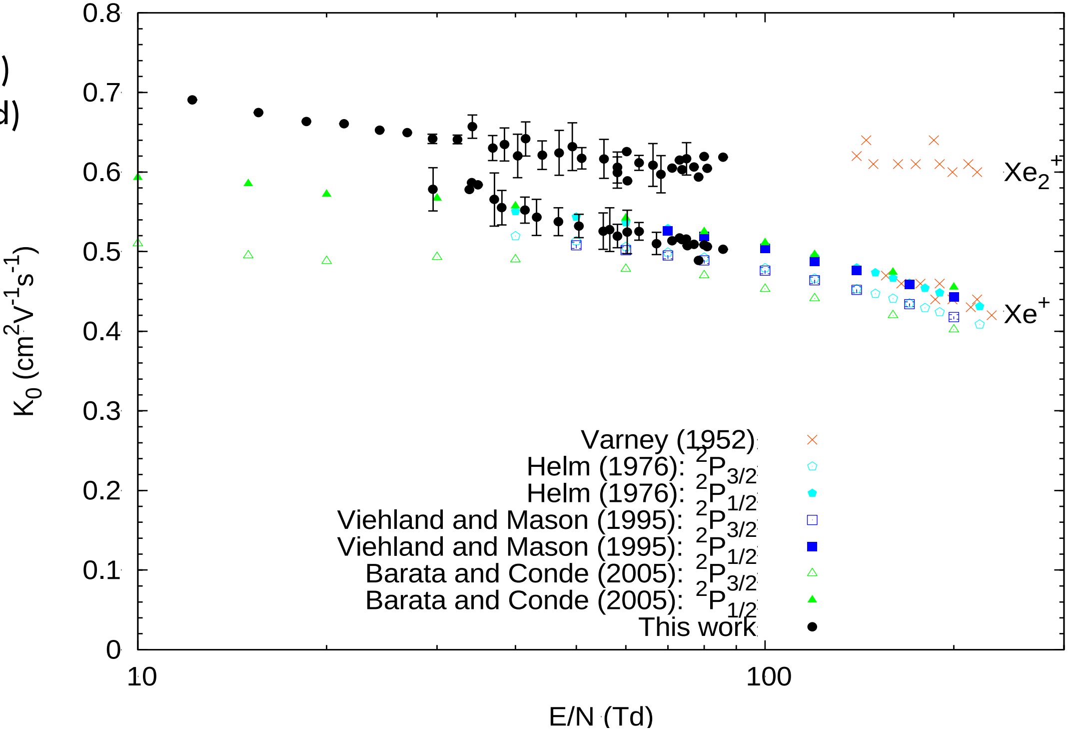
Appearance Energy
Xe^+ - 12.1 eV

Ion mobility in pure Xe

- One peak present (below 30 Td)
- Two peaks present (above 30 Td)



P.N.B. Neves *et al.* 2009



K_{01} ~ 0.578 $cm^2V^{-1}s^{-1}$ **Xe^+**

K_{02} ~ 0.642 $cm^2V^{-1}s^{-1}$ **Xe_2^+**

REACTIONS

$Xe^+ + Xe \rightarrow Xe + Xe^+$

$$k = 2.5 \times 10^{-10}\, {cm^3}/{s}$$

(delays the atomic ions)

$Xe^+ + 2Xe \rightarrow Xe_2^+ + Xe$

$$k = 2.0 \times 10^{-31}\, {cm^6}/{s}$$

$$\tau = 75.2\ \mu s\ (\mathrm{LP} - 8\ \mathrm{Torr})$$
$$\tau = 8.3\ ns\ (\mathrm{AP} - 760\ \mathrm{Torr})$$

EXPERIMENTAL RESULTS – CARBON DIOXIDE

Appearance Energies

$CO2^+$ 13.8 eV
CO^+ 19.5 eV
O^+ 19.1 eV

IONIZATION

$e^- + CO_2 \rightarrow CO_2^+ + 2e^-$

Above threshold 13.8 eV

$$\begin{aligned} e^- + CO_2 &\rightarrow CO_2^+ + 2e^- && 84.7\% \\ &\rightarrow CO^+ + O + 2e^- && 3.7\% \\ &\rightarrow O^+ + CO + 2e^- && 5.4\% \end{aligned}$$

Above 19.5 eV*

Ion mobility in pure CO_2

- One peak present

REACTIONS

$$CO_2^+ + CO_2 \rightarrow CO_2 + CO_2^+$$

$$k = 3.7 \times 10^{-10}\, {cm^3}/{s}$$

(delays the atomic ions)

$$CO_2^+ + CO_2 + M \rightarrow CO_2^+.CO_2 + M$$

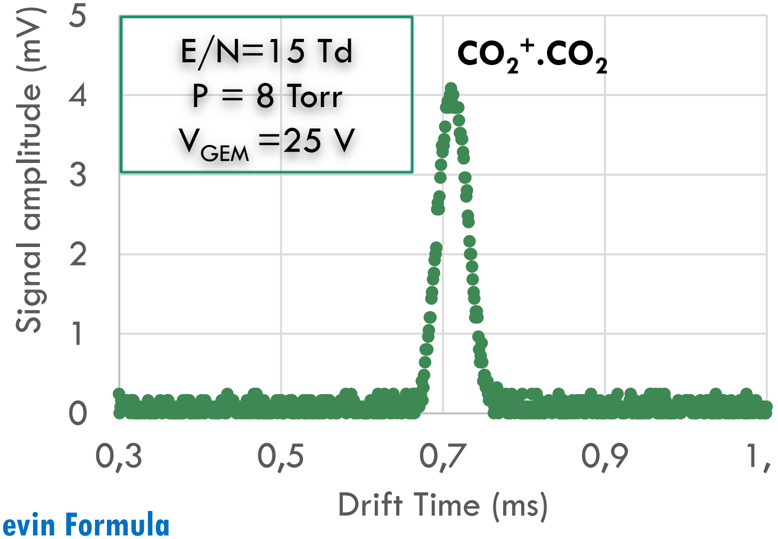
$$k = 2.1 \times 10^{-28}\, {cm^6}/{s}$$

(Cluster formation)

$$\tau = 71.6\, ns\ (LP - 8\ Torr)$$

$$\tau = 7.9\, ps\ (AP - 760\ Torr)$$

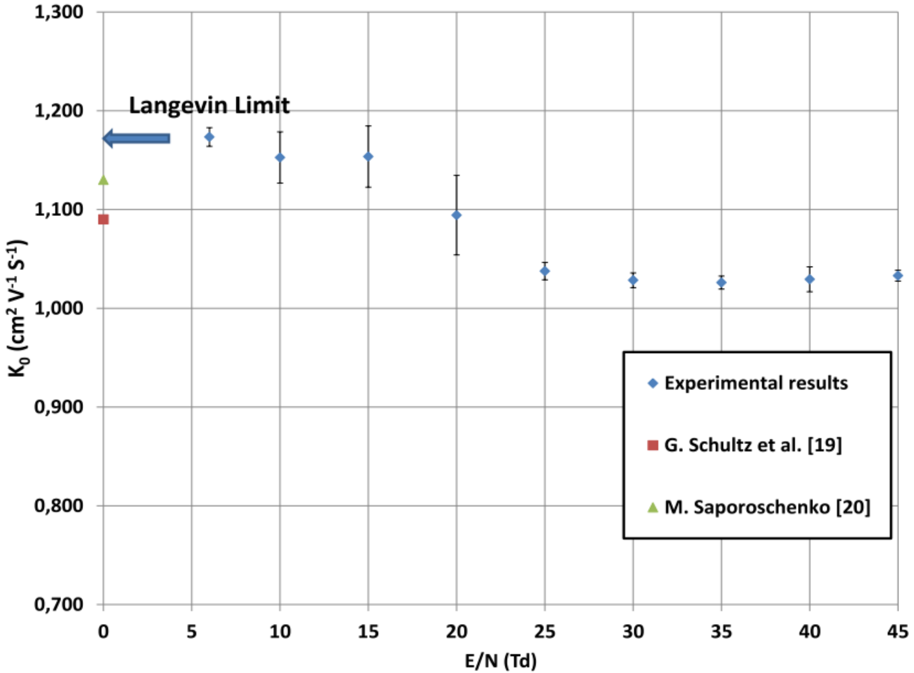
Typical spectrum



Langevin Formula

$1.17\ cm^2V^{-1}s^{-1} \neq 0.97\ cm^2V^{-1}s^{-1}$

P.M.C.C. Encarnação *et al.* 2015



$K_{01} \sim 1.17\ cm^2V^{-1}s^{-1}$ $CO_2^+ CO_2$

* values obtained from ionization cross sections for electron impact of 25 eV

EXPERIMENTAL RESULTS – Xe-CO2

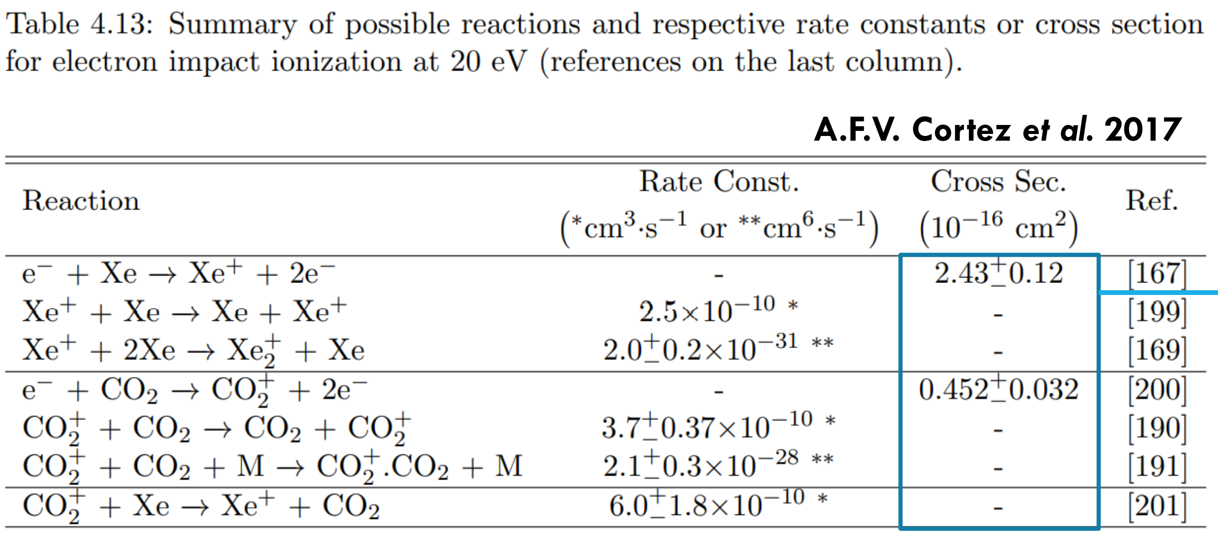


Table 4.13: Summary of possible reactions and respective rate constants or cross section for electron impact ionization at 20 eV (references on the last column).

A.F.V. Cortez *et al.* 2017

Reaction	Rate Const. (*cm^3·s^{-1} or **cm^6·s^{-1})	Cross Sec. (10^{-16} cm^2)	Ref.
$e^- + Xe \rightarrow Xe^+ + 2e^-$	-	2.43±0.12	[167]
$Xe^+ + Xe \rightarrow Xe + Xe^+$	2.5×10^{-10} *	-	[199]
$Xe^+ + 2Xe \rightarrow Xe_2^+ + Xe$	$2.0\pm0.2\times10^{-31}$ **	-	[169]
$e^- + CO_2 \rightarrow CO_2^+ + 2e^-$	-	0.452±0.032	[200]
$CO_2^+ + CO_2 \rightarrow CO_2 + CO_2^+$	$3.7\pm0.37\times10^{-10}$ *	-	[190]
$CO_2^+ + CO_2 + M \rightarrow CO_2^+.CO_2 + M$	$2.1\pm0.3\times10^{-28}$ **	-	[191]
$CO_2^+ + Xe \rightarrow Xe^+ + CO_2$	$6.0\pm1.8\times10^{-10}$ *	-	[201]

Ionization probability for Xe atoms is about 5 times higher than for CO2

Xe ions will be preferencially produced down to 15% Xe.

Considering a general reaction…

$Rg + Rg^+ \rightarrow X^+ + Y$

We can determine the reaction time:

$$\tau = \frac{1}{k[R_g]}$$

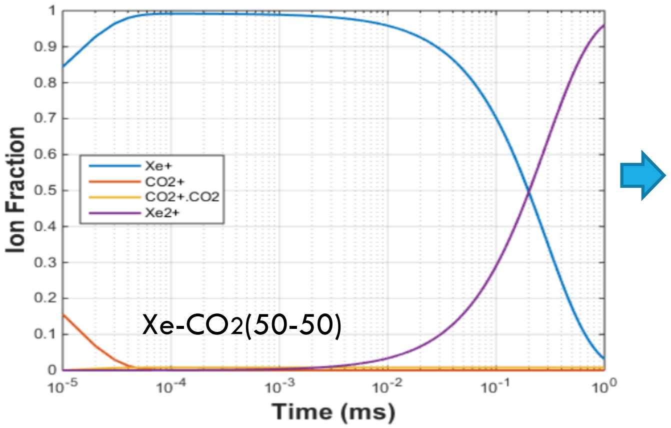
where

k - rate constant
P - Pressure
$N = 2.45 \times 10^{19}\ cm^{-3}$

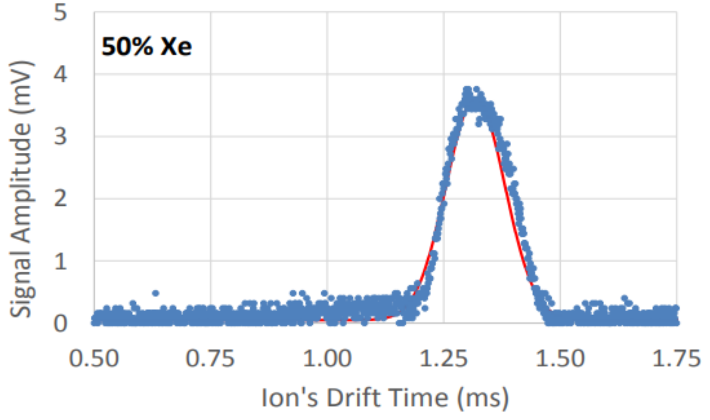
$$[R_g] = N\frac{P}{P_{Atm}}$$

$$\frac{[Rg^+]}{[Rg^+]_0} = e^{-\frac{t}{\tau}}$$

Variation of the concentration of a specific ion in a mixture.

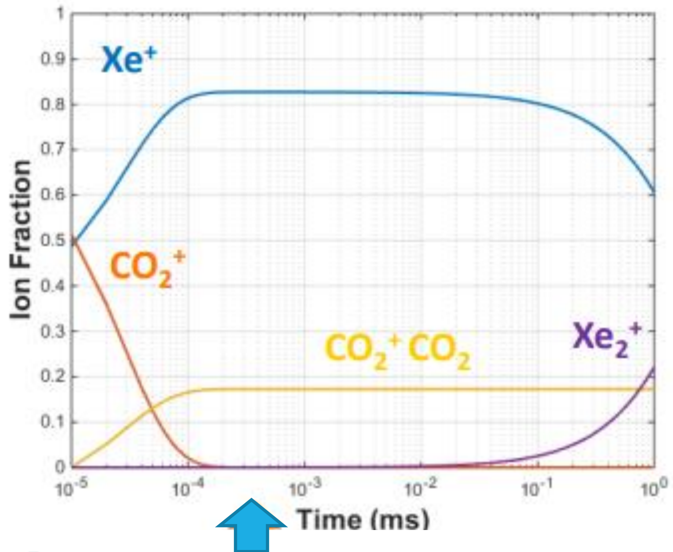


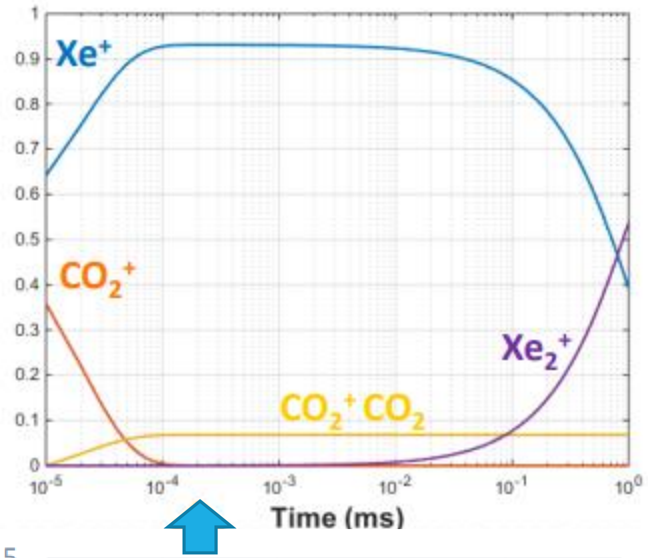
Identification of the final ion

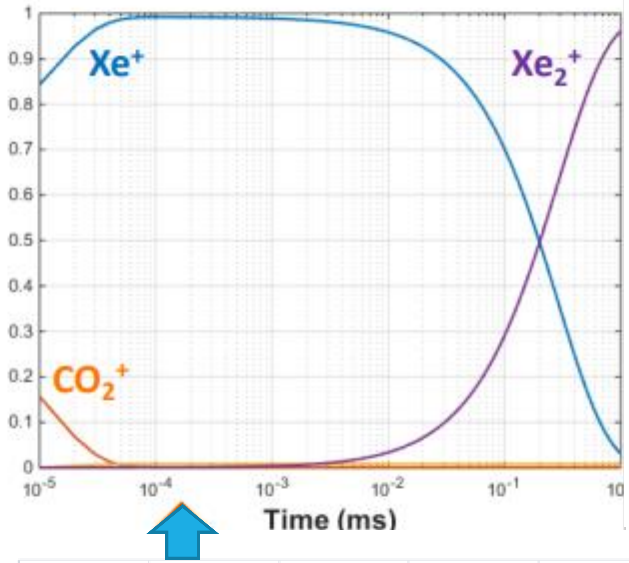


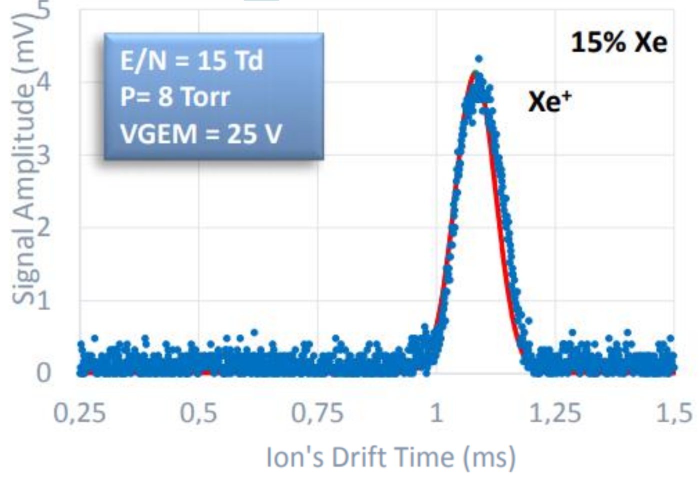
EXPERIMENTAL RESULTS – Xe-CO_2

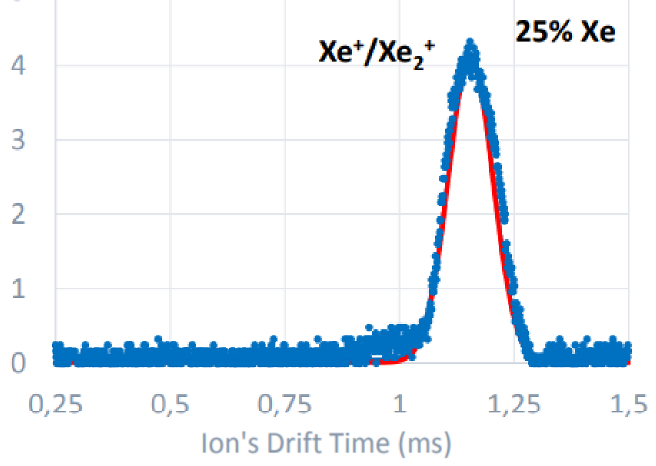
A.F.V. Cortez *et al.* 2017

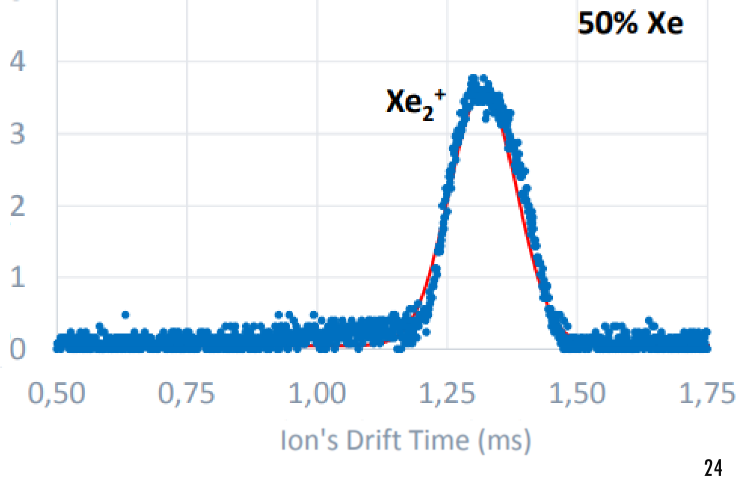




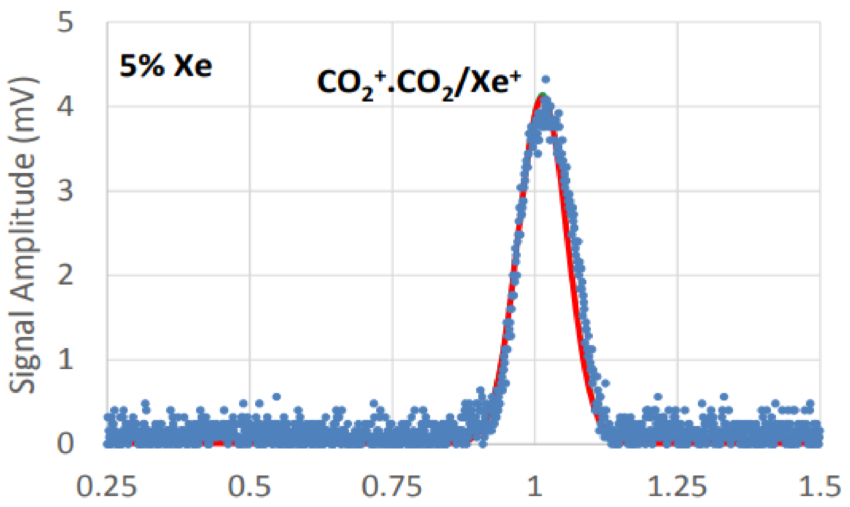






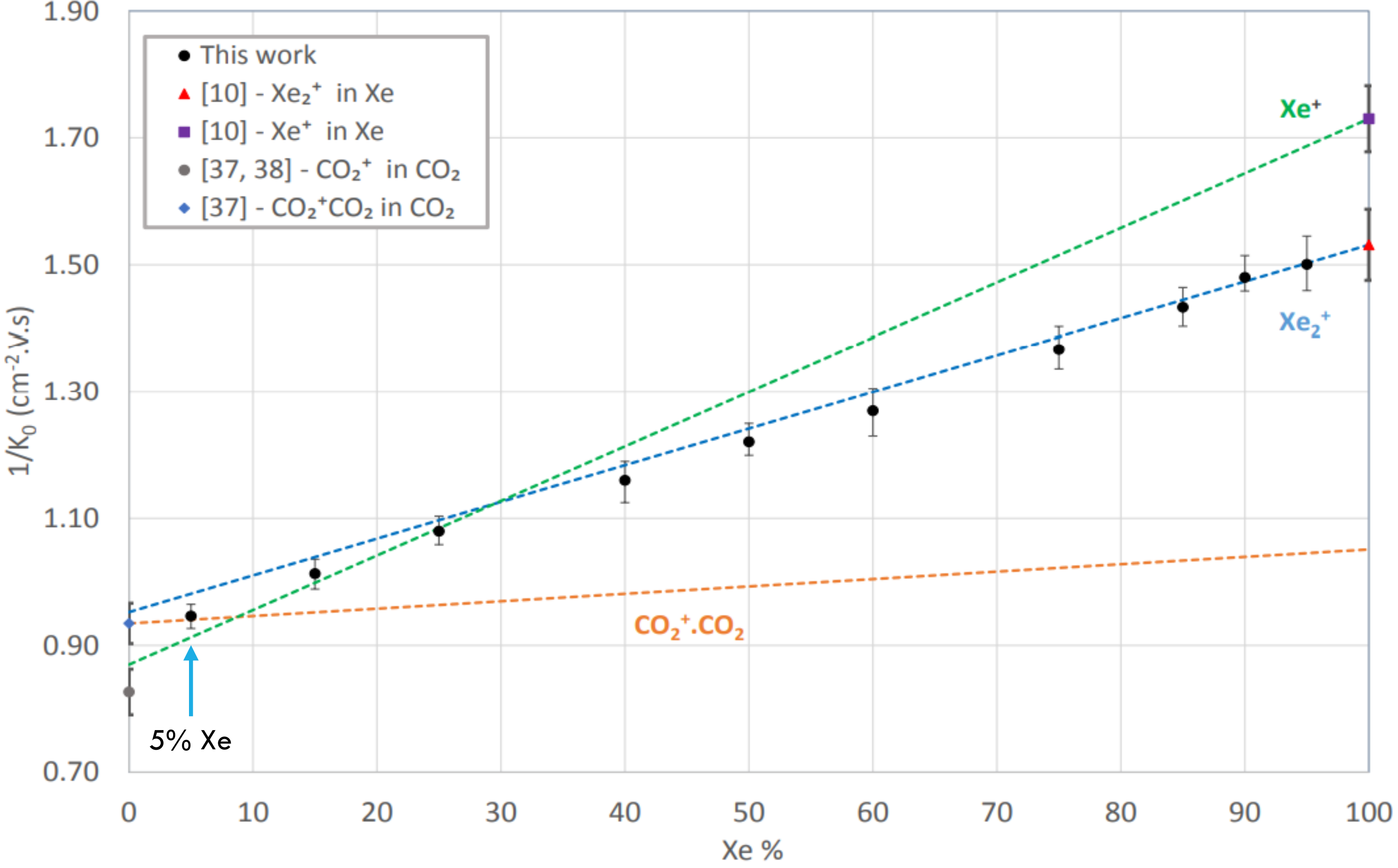


EXPERIMENTAL RESULTS – Xe-CO_2



- **Ions** move **slightly faster** and the signal **amplitude slightly increases** with the presence of **CO_2** between 95 and 5% Xe;
- Only one peak is observed expected to be from Xe ions;
- Behaviour well described by Blanc's law following the trend for Xe_2^+ for relevant mixtures.

A.F.V. Cortez *et al.* 2017



CHALLENGES AND FUTURE PROSPECTS

GRAN SASSO SCIENCE INSTITUTE
SCHOOL OF ADVANCED STUDIES
Scuola Universitaria Superiore

VALIDITY OF LANGEVIN THEORY

Cases where Langevin's theory fails?

- Large molecules;
- Atoms/molecules weakly polarizable;

Polarization Limit

$$K_{pol} \propto \frac{1}{\sqrt{\alpha\mu}}$$

Elastic Limit

$$K_{elast} \propto \frac{1}{d^2\sqrt{\mu}}$$

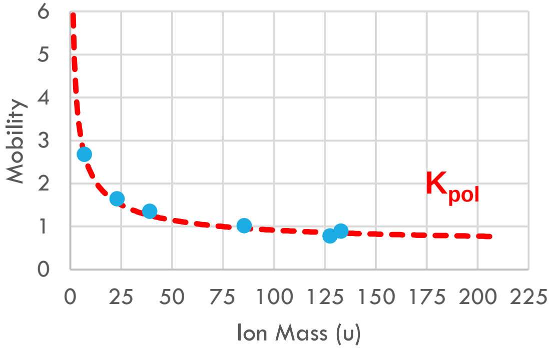
Problem is that ***d**** is not known with precision.

How to surpass Langevin's Theory limitations?

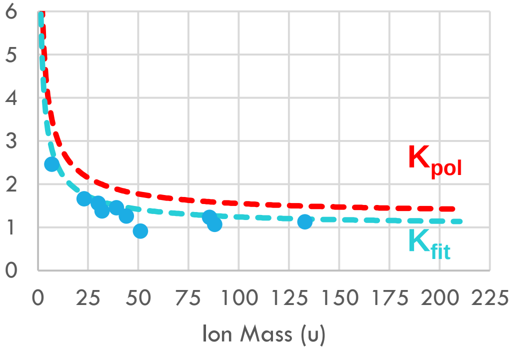
- Fitting the experimental mass-mobility data we can obtain better estimates, a good example is carbon dioxide. **A.F.V. Cortez *et al.* 2017**

*sum of the ion and gas radii

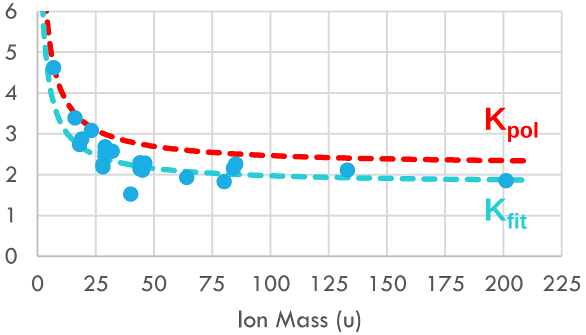
Xenon



Carbon Dioxide



Argon



Data taken from

A.F.V. Cortez 2018
Y. Kalkan *et al.* 2015

NEGATIVE ION MOBILITY

M.A.G. Santos 2018

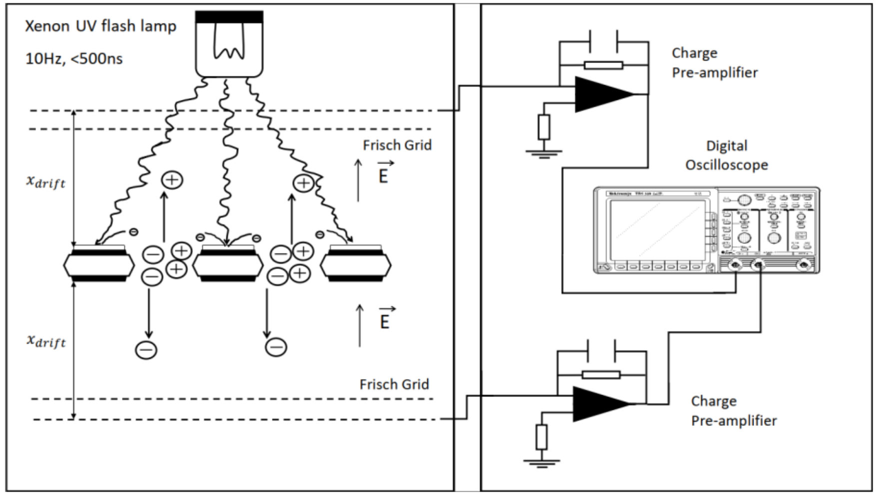
Opportunity

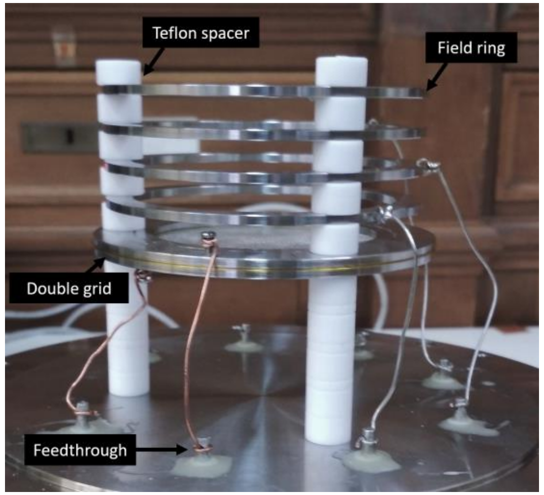
In a conventional Time Projection Chamber (TPC), the information is carried by electrons which have large transverse diffusion ➙ This limits the amount of information that can be collected from a given track (tracking capability).

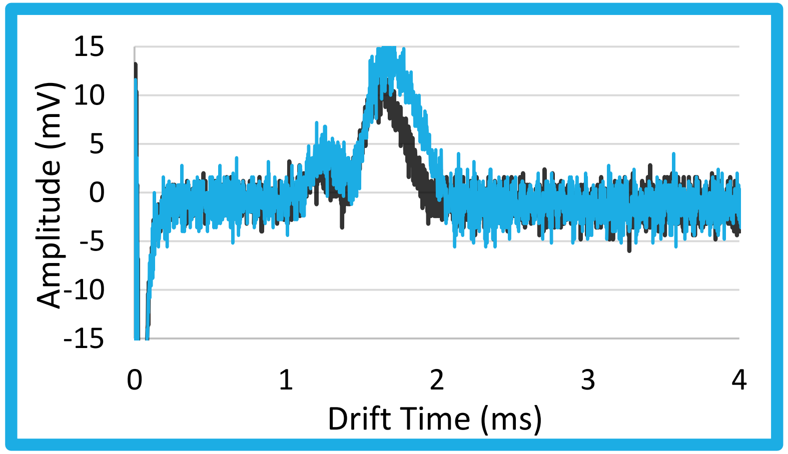
What lies ahead…

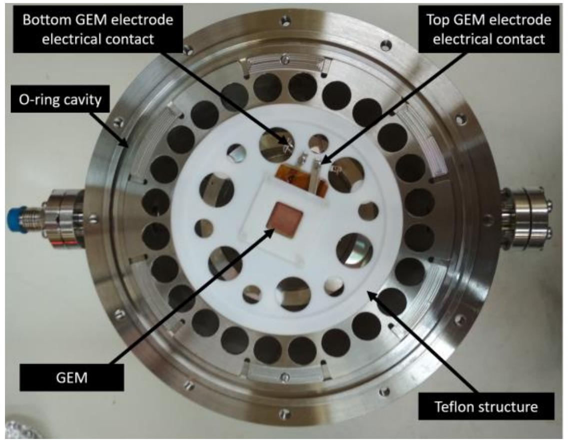
In a Negative Ion TPC, the ions carry the information. Negative ions have much lower transverse diffusion which leads to much better spatial resolutions (but also imply a lower rate).

These studies lead to 2 common CERN/RD51 projects:
- ➙ 'Measurement and calculation of ion mobility of some gas mixtures of interest'
- ➙ 'Study of negative ion mobility and ion diffusion for Negative Ion TPCs'









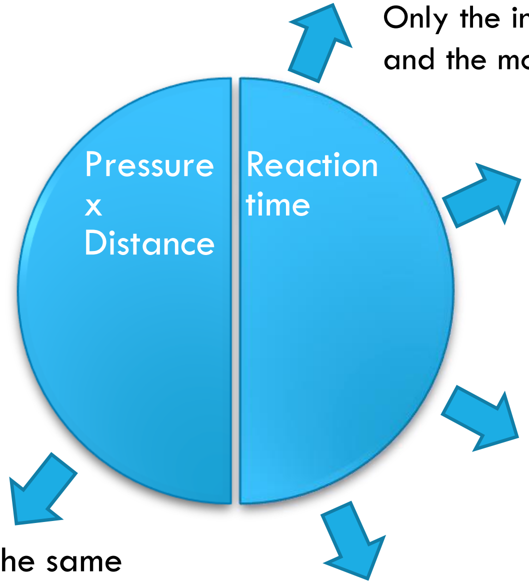
HIGH PRESSURE ION MOBILITY

How to move from low pressure to high pressure?

Key differentiating factors:

- Reaction time (τ)
- Cluster formation
  (pressure dependent)
- Impurities

Low pressure measurements tend to be more susceptible to the influence of impurities.



Pressure x Distance

Reaction time

If $\tau \ll t_{drift}$
Only the initial ion will be observed and the mobility is not affected

If $\tau \geq t_{drift}$
Both ions will be present but won’t be possible to distinguish them in the time spectra.

If $\tau < t_{drift}$
Only the final ion will be present.

If $\tau \gg t_{drift}$
Only the final ion will be observed and the mobility is not affected

How to determine the true mobility of the ions?

Enables to mimic the same conditions at high pressure

May prove to be na interesting approach as lowering the pressure might allow to study faster reactions and study the Effect of high E/N or the equivalente high effective temperature.

Main limitation:

Reactions that might take place or are favored at higher pressures

SUMMARY

SUMMARY

- Importance of ion mobility in the development of gas radiation detectors
  - Detector design (dimensioning, design of gating devices)
  - Performance (signal formation, rate capability, spatial resolution, aging and discharges)
- Discussed the effect of several processes and mechanisms on ion mobility
  - Electric field
  - Gas density
  - Chemical reactions (resonant charge transfer, cluster formation and impurities)
- Techniques used on ion identification and how to take advantage from low pressure ion drift chambers
- Explored the experimental measurements performed in Coimbra
- Addressed some of the main challenges and talked about future prospects
  - Validity of Langevin Theory
  - Mobility of negative ions
  - High pressure

ACKNOWLEDGEMENTS

A special thank you to Diego Gonzalez Diaz (IGFAE) and Paul Colas (CEA Saclay) for the invitation to present this topic in this workshop. This work would not be possible without the contribution of so many, in particular Rob Veenhof (RD51/CERN).

- CERN/RD51 Collaboration – Common Projects - ‘Measurement and calculation of ion mobility of some gas mixtures of interest’. Participating institutions:
- CERN/RD51 Collaboration – Common Projects - ‘Study of negative ion mobility and ion diffusion for Negative Ion TPCs’. Participating institutions:

THANK YOU!

GSSI
GRAN SASSO SCIENCE INSTITUTE
SCHOOL OF ADVANCED STUDIES
Scuola Universitaria Superiore

REFERENCES

- P. Langevin, **Une formule fondamentale de théorie cinetique**, Annal. Chimie Physique 5 (1905);
- A. Blanc, **Recherches sur le mobilités des ions dans les gaz**, J. Phys. Theor. Appl. 7 (1908);
- E.W. McDaniel and L.A. Viehland, **Transport of Slow Ions in Gases: Experiment, Theory, and Applications**, Physics Reports 5-6 (1984);
- K. Hiraoka, G. Nakajima, S. Shoda, **Determination of the stabilities of CO2+(C02)n and O2+(CO2)n, clusters with n=1-6**, Chem. Phys. Let. 146 (6) (1988);
- E.W. McDaniel, J.B.A. Mitchell and M.E. Rudd, **Atomic collisions — heavy particle projectiles**, Wiley, (1993);
- W. Blum and L. Rolandi, **Particle Detection with Drift Chambers**, Springer-Verlag, Berlin, Germany, (1994);
- G.F. Knoll, **Radiation detection and measurements**, John Wiley and Sons, Inc., New York, U.S.A., (2000);
- P.N.B. Neves *et al.* 2009, **Experimental measurement of the mobilities of atomic and dimer Ar, Kr, and Xe ions in their parent gases**, J. Chem. Phys. **133**, 124316 (2010) ;
- F. Sauli, **Gaseous Radiation Detectors: Fundamentals and Applications**, Cambridge Monographs on Particle Physics, Nuclear Physics and Cosmology, Cambridge University Press, (2014);
- G.A. Eiceman, Z. Karpas and H.H.J. Hill, **Ion Mobility Spectrometry**, third ed., CRC Press — Taylor & Francis Group, (2014);
- Y. Kalkan et al. 2015, **Cluster ions in gas-based detectors**, 2015 JINST **10** P07004;
- P.M.C.C Encarnação *et al.* 2015, **Experimental ion mobility measurements in Ar-CO2 mixtures**, 2015 JINST 9 P07008;
- A.F.V. Cortez *et al.* 2017, **Experimental ion mobility measurements in Xe-CO2 mixtures**, 2017 JINST 12 P06012;
- A. Deisting, C. Garabatos and A. Szabo, **Ion mobility measurements in Ar-CO2, Ne-CO2, and Ne-CO2-N2 mixtures, and the effect of water contents**, Nucl. Instrum. Meth. A 904 (2018);
- M.A.G. Santos, **Development of a Dual-Polarity Ion Drift Chamber and Study of ion transport properties in gaseous mixtures of interest**, MSc.Thesis, University of Coimbra, Portugal, (2018).
- A.F.V. Cortez, **Novel Techniques for High Pressure Noble Gas Radiation Detectors**, Ph.D. Thesis, University of Coimbra, Portugal, (2018).

Relevant oral presentations:

- R. Veenhof, **Which ions are producing the signals ?**, oral presentation, RD51 Collab. Meeting June 2020;
- R. Veenhof, **Cluster Ions**, oral presentation, RD51 Collab. Mini-week, December 2014;