ION MOBILITY MEASUREMENT IN GASES

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LABORATÓRIO DE INSTRUMENTAÇÃO E FÍSICA EXPERIMENTAL DE PARTÍCULAS

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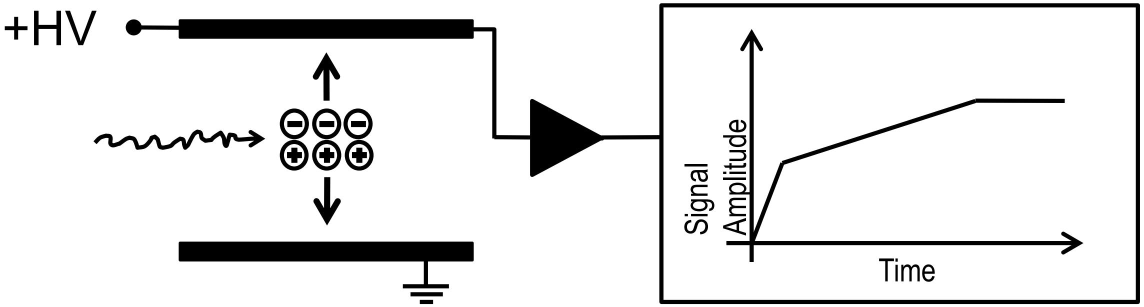
LIP

INTEREST AND APPLICATIONS

Gaseous Radiation Detectors



Ion Mobility Spectrometry

Technique that aims at identifying ionized molecules in a gas based on their mobility in a carrier buffer gas.

High Energy Physics

NEXT experiment: HPXe TPC

$^{136}Xe \rightarrow {}^{136}Ba^{++} + 2e$

K_0: Ba^{++}, Ba^{+}, Xe^{+}, Xe_2^{+}, …

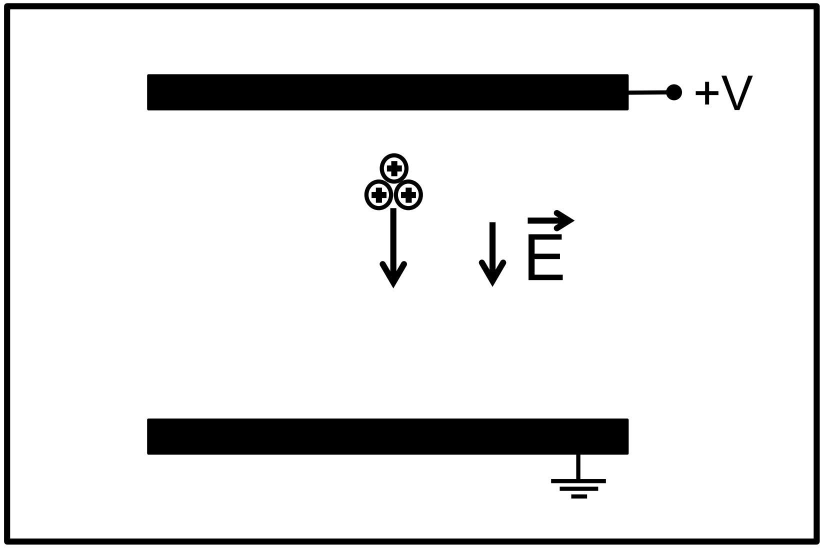
OUTLINE

- **Basic concepts**
- **Experimental Setup**
  - GEM: The Key to Ion Mobility Measurements
  - Working Principle
  - Results and Discussion
    - Ion Mobility Measurements in Rare Gases
      - Results: Ar, Kr, Xe
    - Ion Mobility Measurements in Gaseous Mixtures
      - Results: Xe-$N_{2,}$ Ar-C_2H_6
    - Discussion
      - Ion Identification Process
      - Limitations: Impurities
      - Limitations: Space-Charge Effects

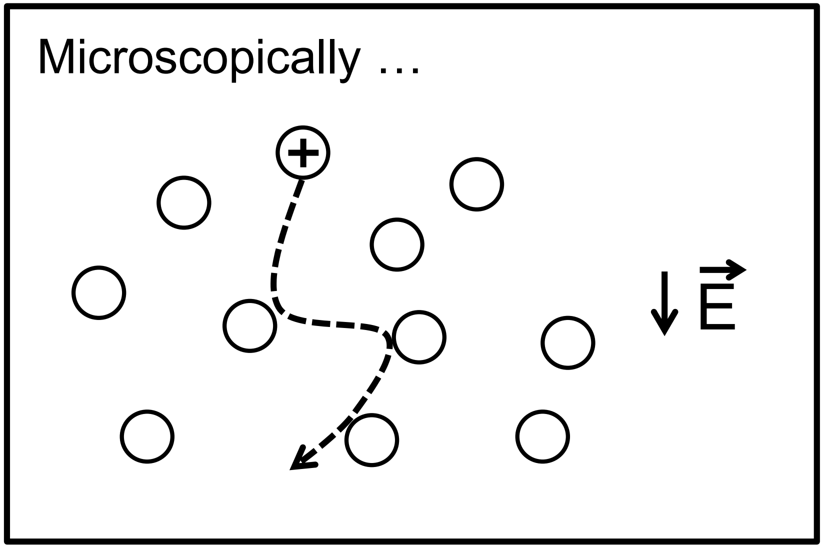
- **Conclusions**

BASIC CONCEPTS

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



Microscopically …



Drift velocity

$$v_d = KE$$

E- Electric Field
K-Ion Mobility

Reduced Mobility

$$K_0 = KN/N_0$$

N – Gas number density
N_0–Loschmidt Number

Langevin Limit

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

μ – reduced mass
α – neutral polarizability

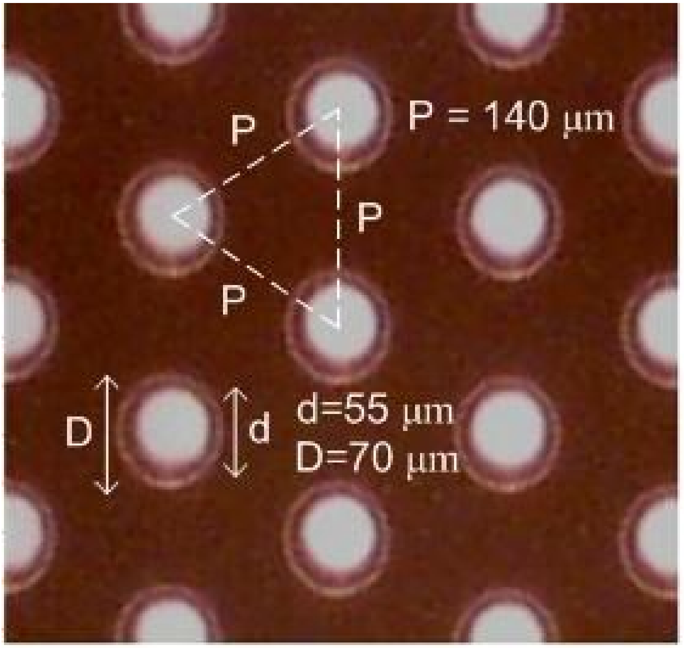
Blanc's Law

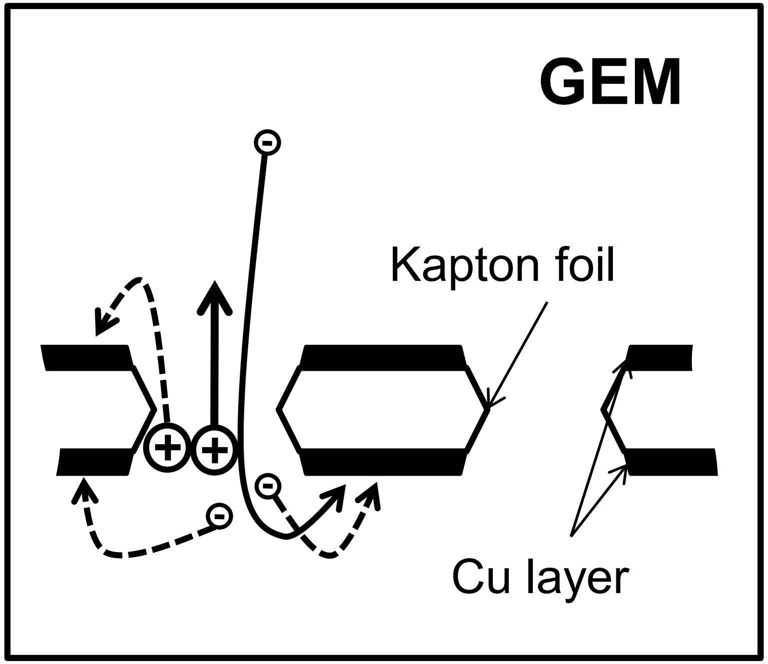
$$\frac{1}{K_{0mix}} = \frac{f_1}{K_{0g1}} + \frac{f_2}{K_{0g2}}$$

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

GEM: THE KEY TO THE ION MOBILITY MEASUREMENTS

Inventor: Fabio Sauli, CERN, 1997



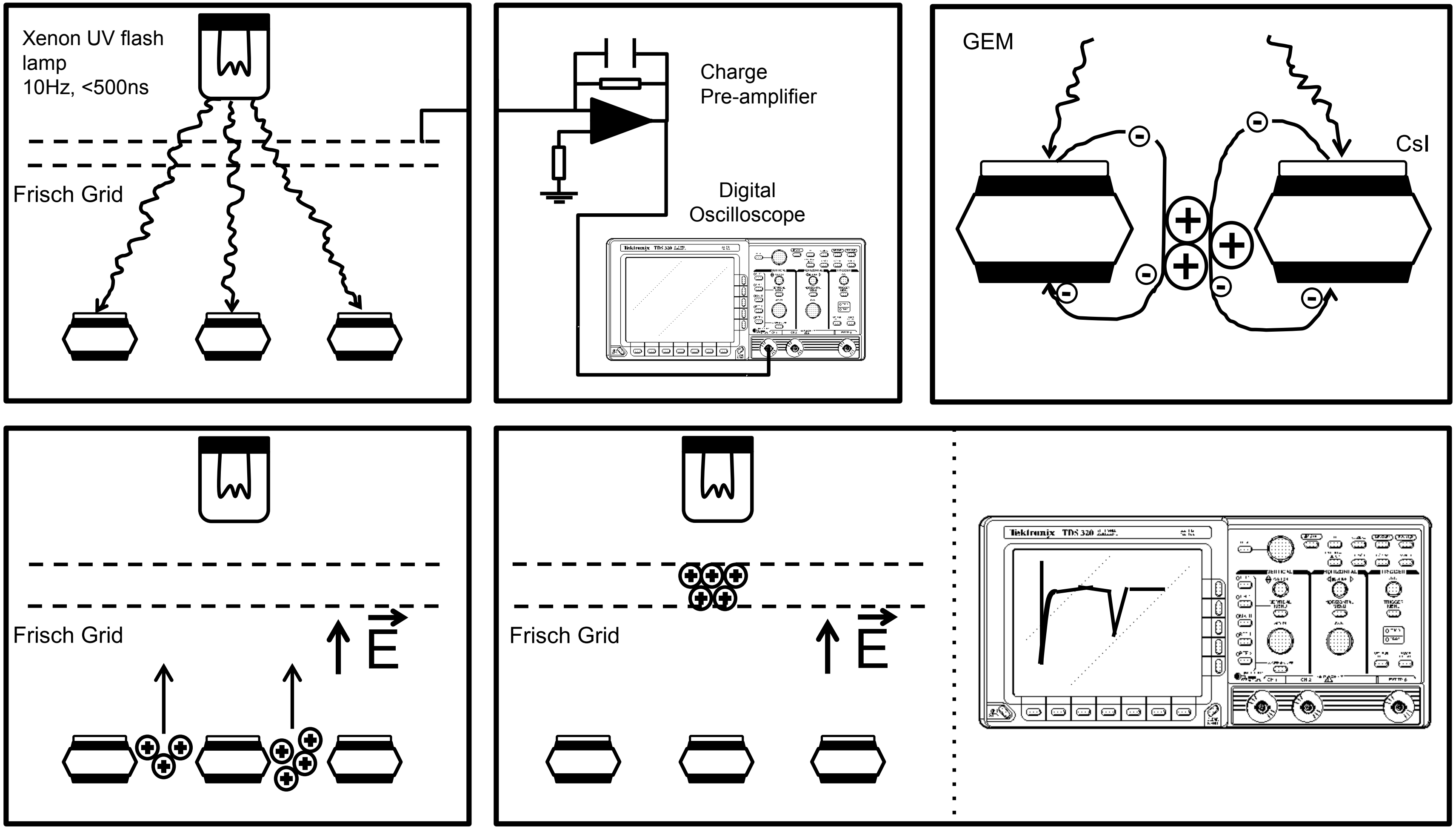


Ion source

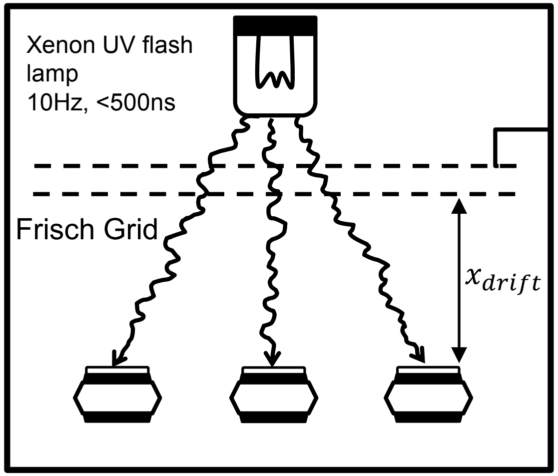
- Allows to limit the variety of ions produced by changing the voltage across the GEM.
- Ions' initial position is known with great accuracy.

EXPERIMENTAL SETUP: WORKING PRINCIPLE

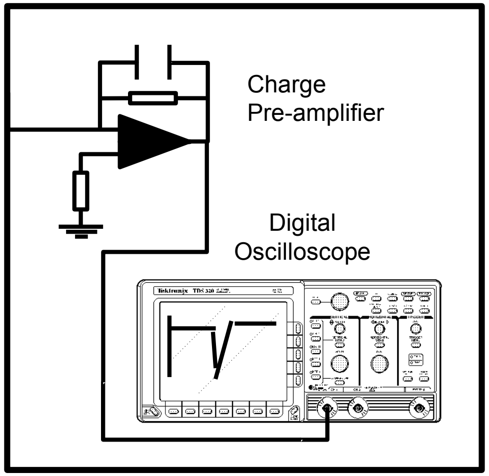
(Neves, Conde and Távora, 2007)



EXPERIMENTAL SETUP: WORKING PRINCIPLE



$x_{drift} = 4.273$ cm



After the signal and the background were recorded…

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

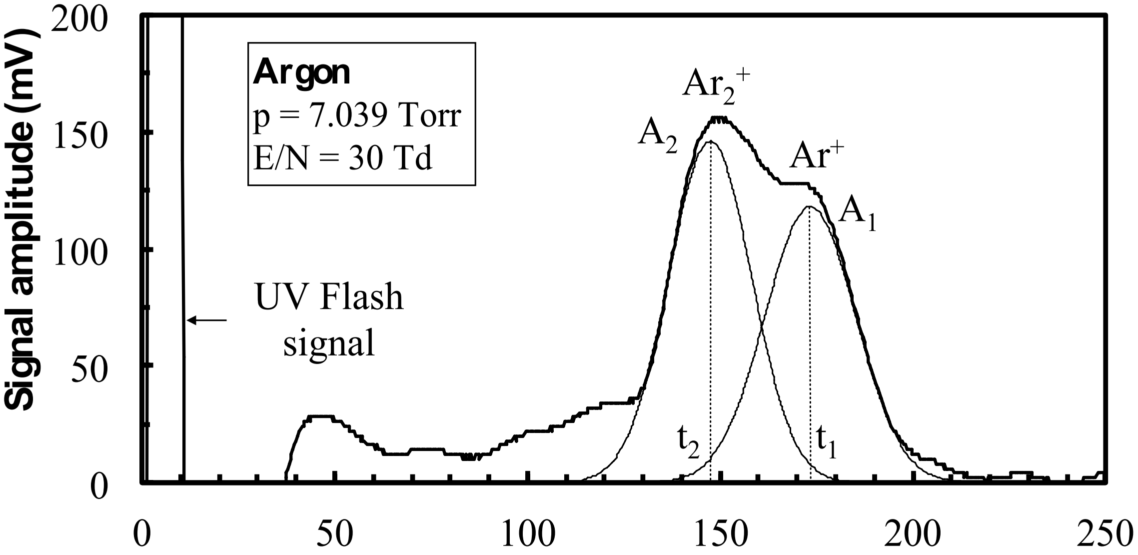
peaks centroids

⬇

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

$$v_d = \frac{x_{drift}}{t_{drift}} \Rightarrow K = \frac{v_d}{E}$$

prototype: typical ion pulse

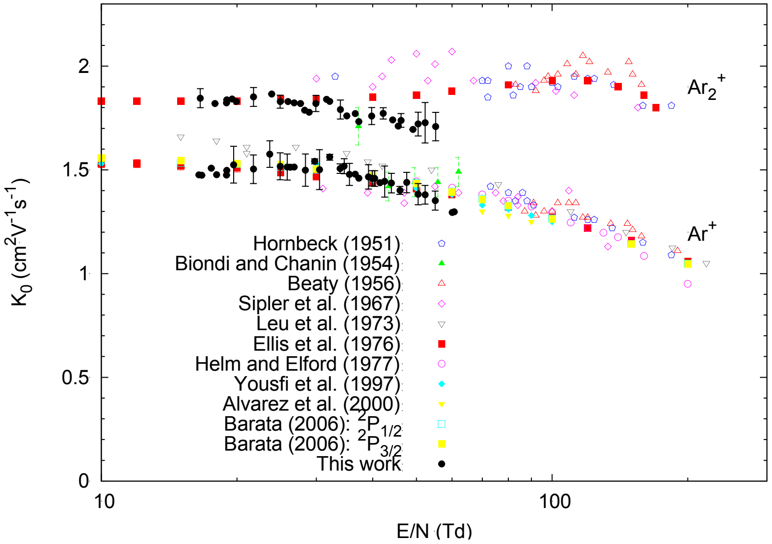


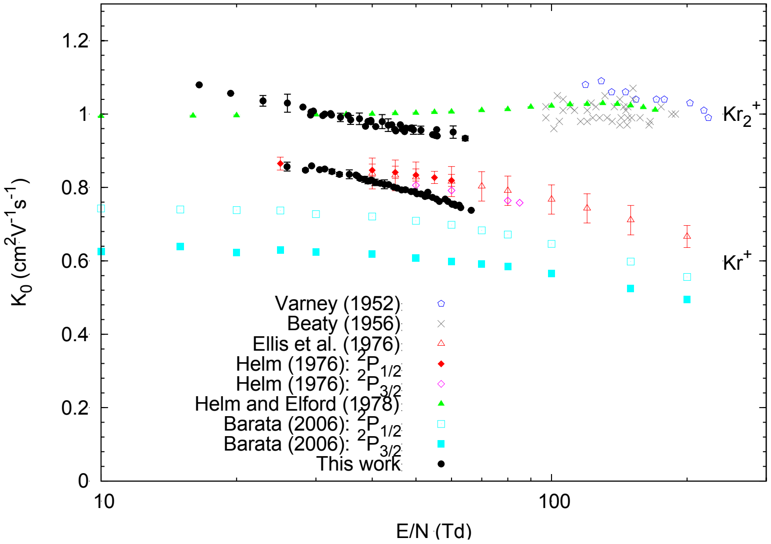
$K_{01} = 1.57\ cm^2V^{-1}s^{-1}$ (Ar^+ ?)

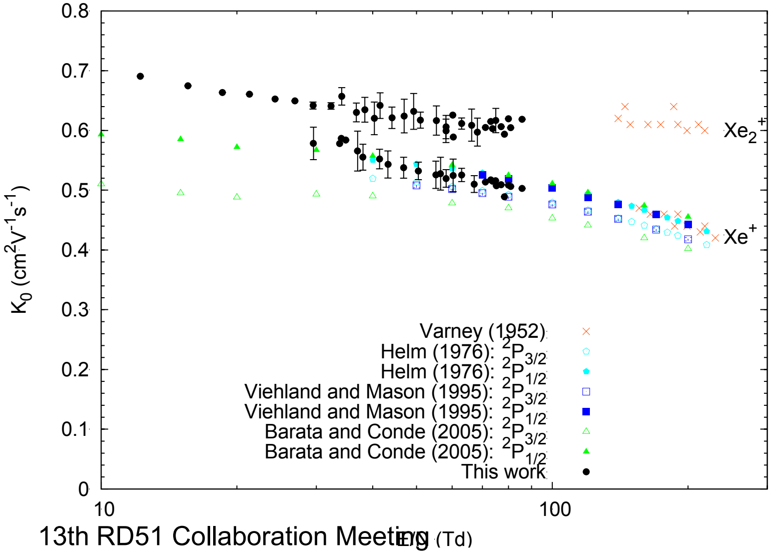
$K_{02} = 1.92\ cm^2V^{-1}s^{-1}$ (Ar_2^+ ?)

ION MOBILITY MEASUREMENTS

(Neves, Conde and Távora, 2011; Neves et al., 2011)

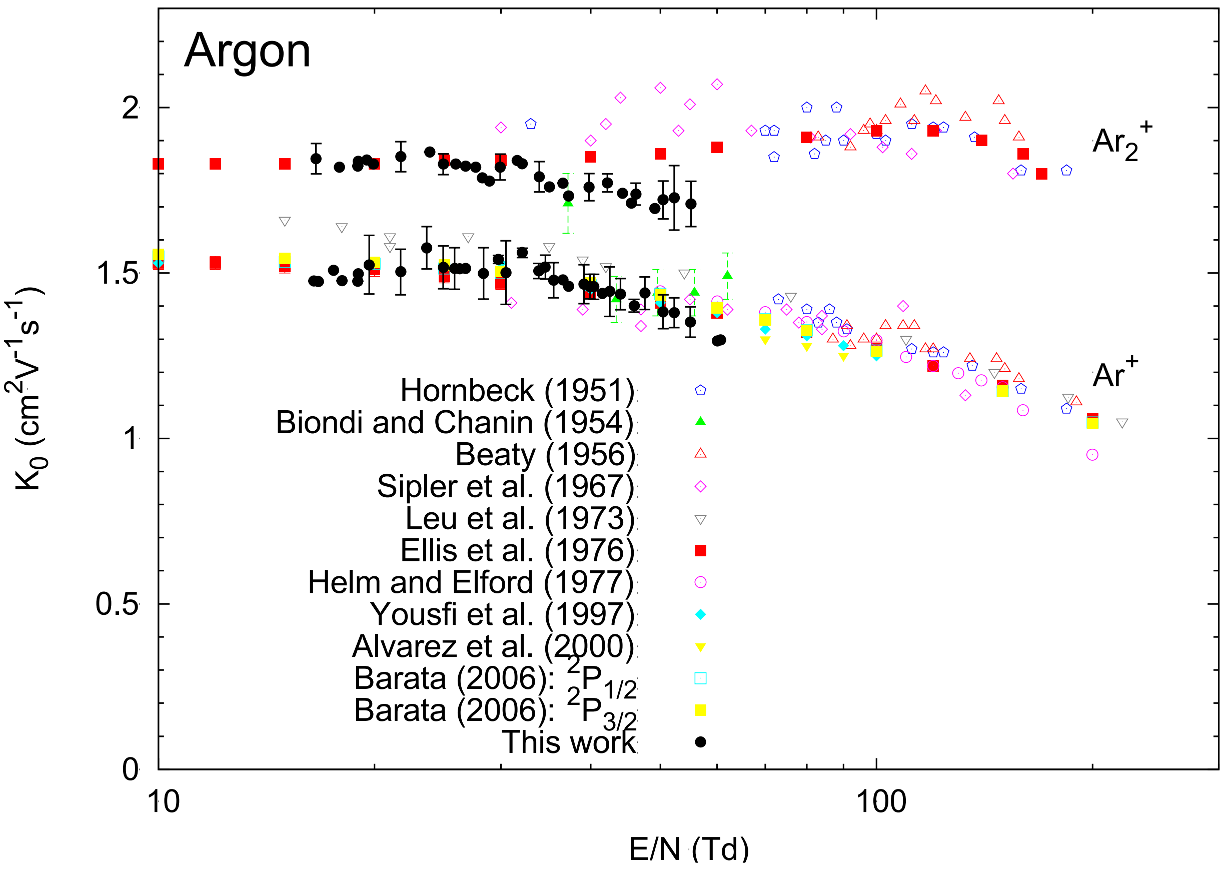






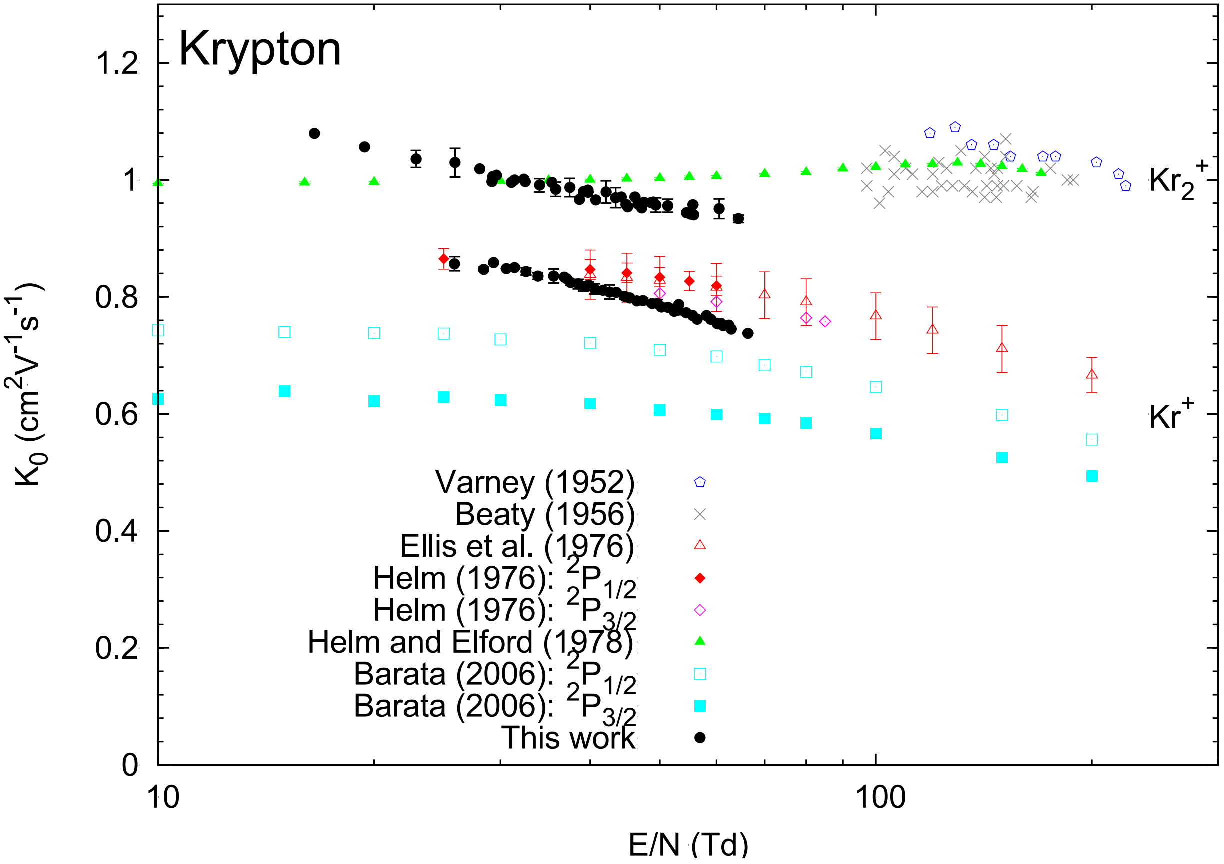
RESULTS: ION MOBILITY

(Neves, Conde and Távora, 2010; Neves et al., 2011)



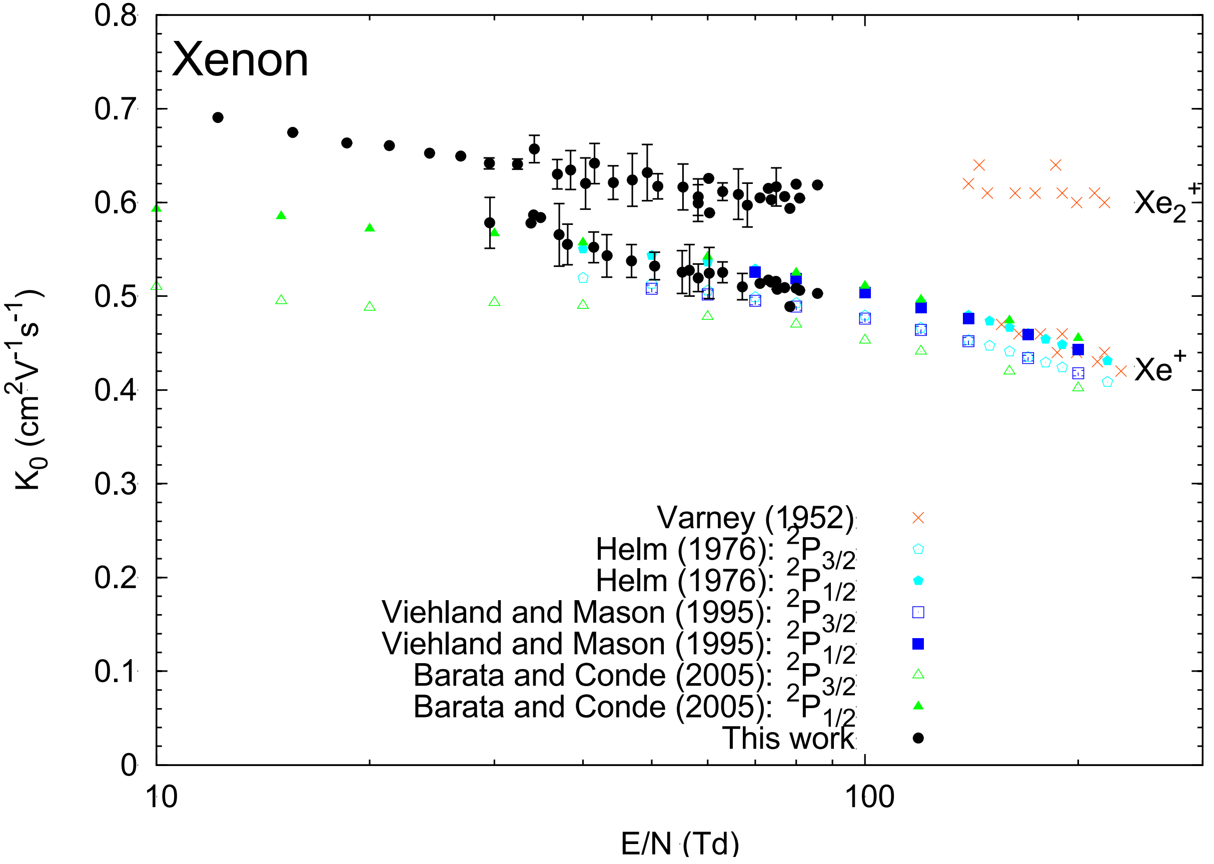
RESULTS: ION MOBILITY

(Neves, Conde and Távora, 2010; Neves et al., 2011)



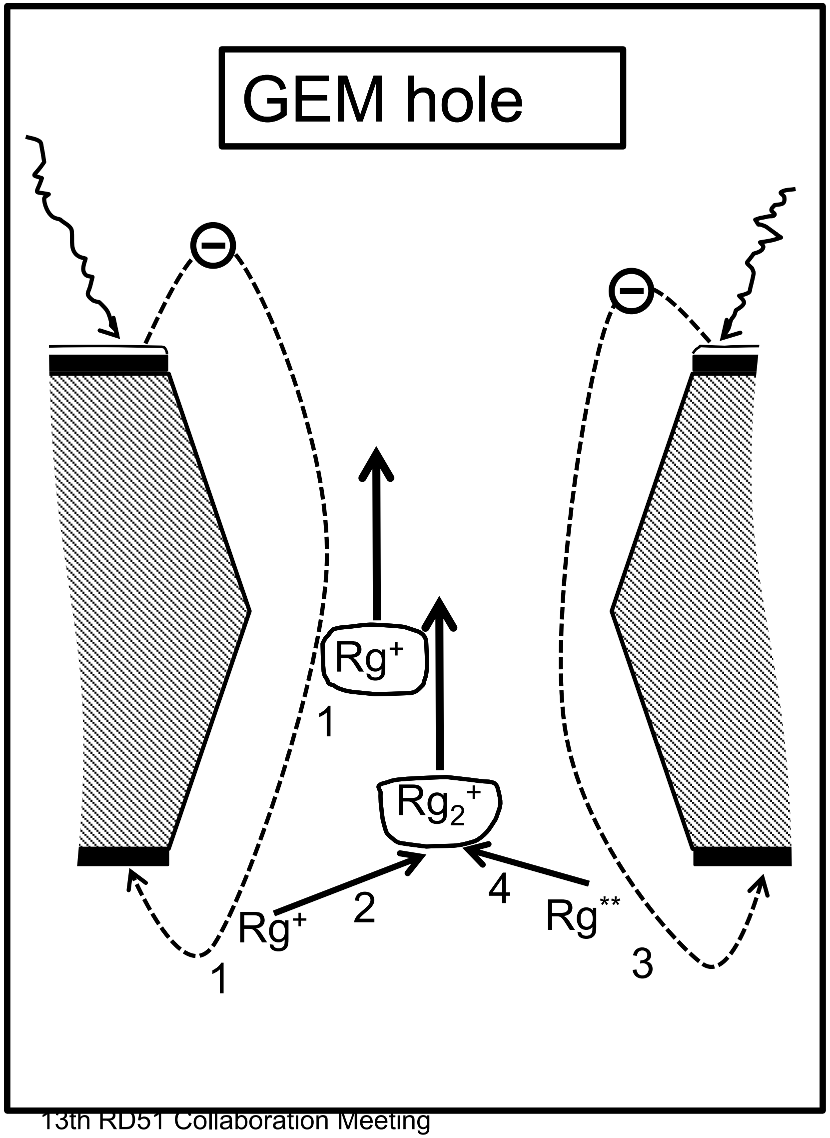
RESULTS: ION MOBILITY

(Neves, Conde and Távora, 2010; Neves et al., 2011)



LOOKING INSIDE THE GEM

The origin of the atomic and dimer rare gas ions...



Reactions

(1) $e + Rg -> Rg^{+} + 2e$
(Ionization)

(2) $e + Rg -> Rg^{**} + e$
(Excitation)

(3) $Rg^{+} + 2Rg -> Rg_2^{+} + Rg$
(3-body reaction)

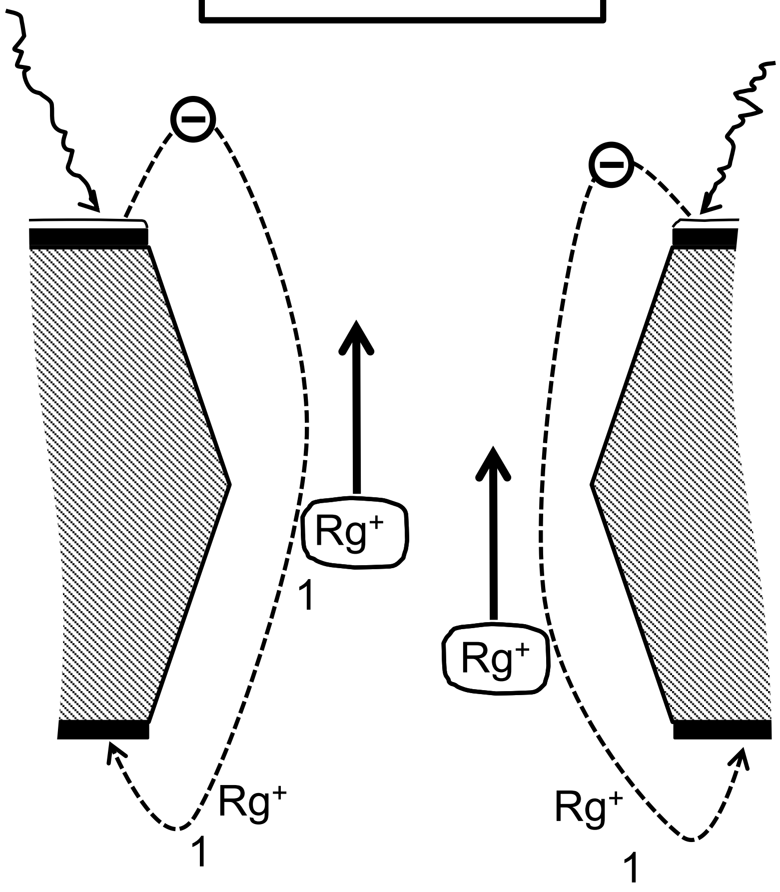
(4) $Rg^{**} + Rg -> Rg_2^{+} + e$
(Associative Reaction)

$Rg^{+} + Rg -> Rg + Rg^{+}$
(Charge Transfer)

LOOKING INSIDE THE GEM

The origin of the atomic and dimer rare gas ions...

GEM hole



Reactions

While the atomic rare gas ions have one common origin...

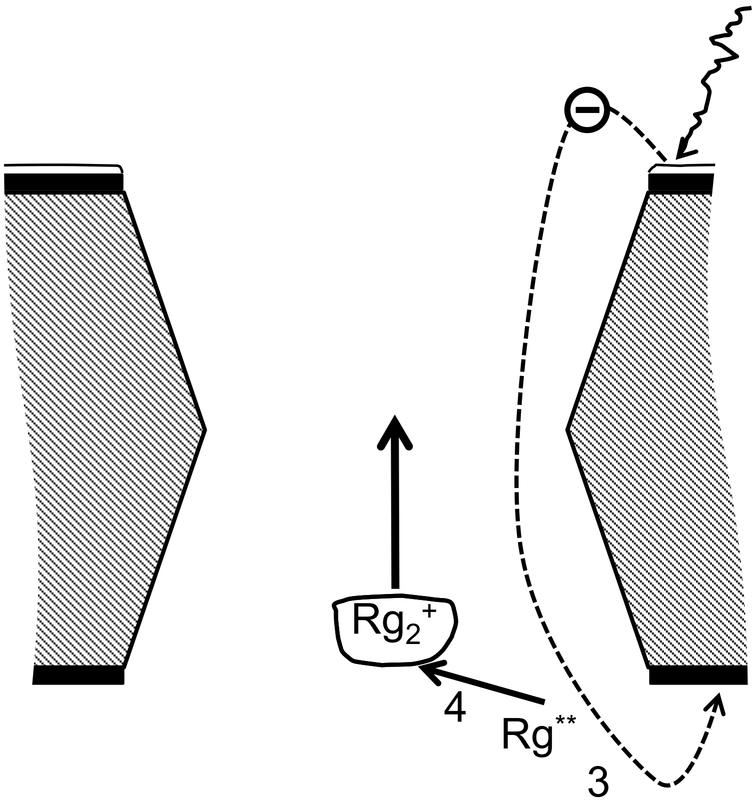
(1) $e + Rg \rightarrow Rg^{+} + 2e$
(Ionization)

the dimer rare gas ions have two distinct origins...

LOOKING INSIDE THE GEM

The origin of the dimer rare gas ions...

GEM hole



Reactions

For pressures below 1 Torr the dominant process is..

(3) $e + Rg \rightarrow Rg^{**} + e$ (Excitation)

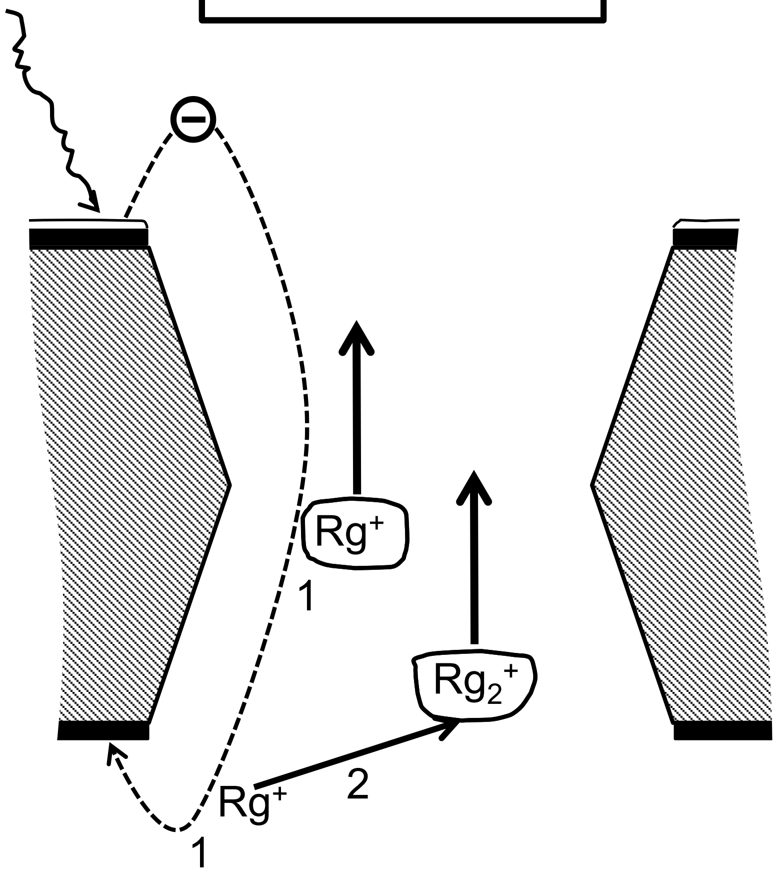
(4) $Rg^{**} + Rg \rightarrow Rg_2^+ + e$ (Associative Reaction)

Hornbeck-Molnar process

LOOKING INSIDE THE GEM

The origin of the dimer rare gas ions...

GEM hole



Reactions

At our working pressures (higher than 6 Torr) the reactions responsible for the appearance of the observed ions are..

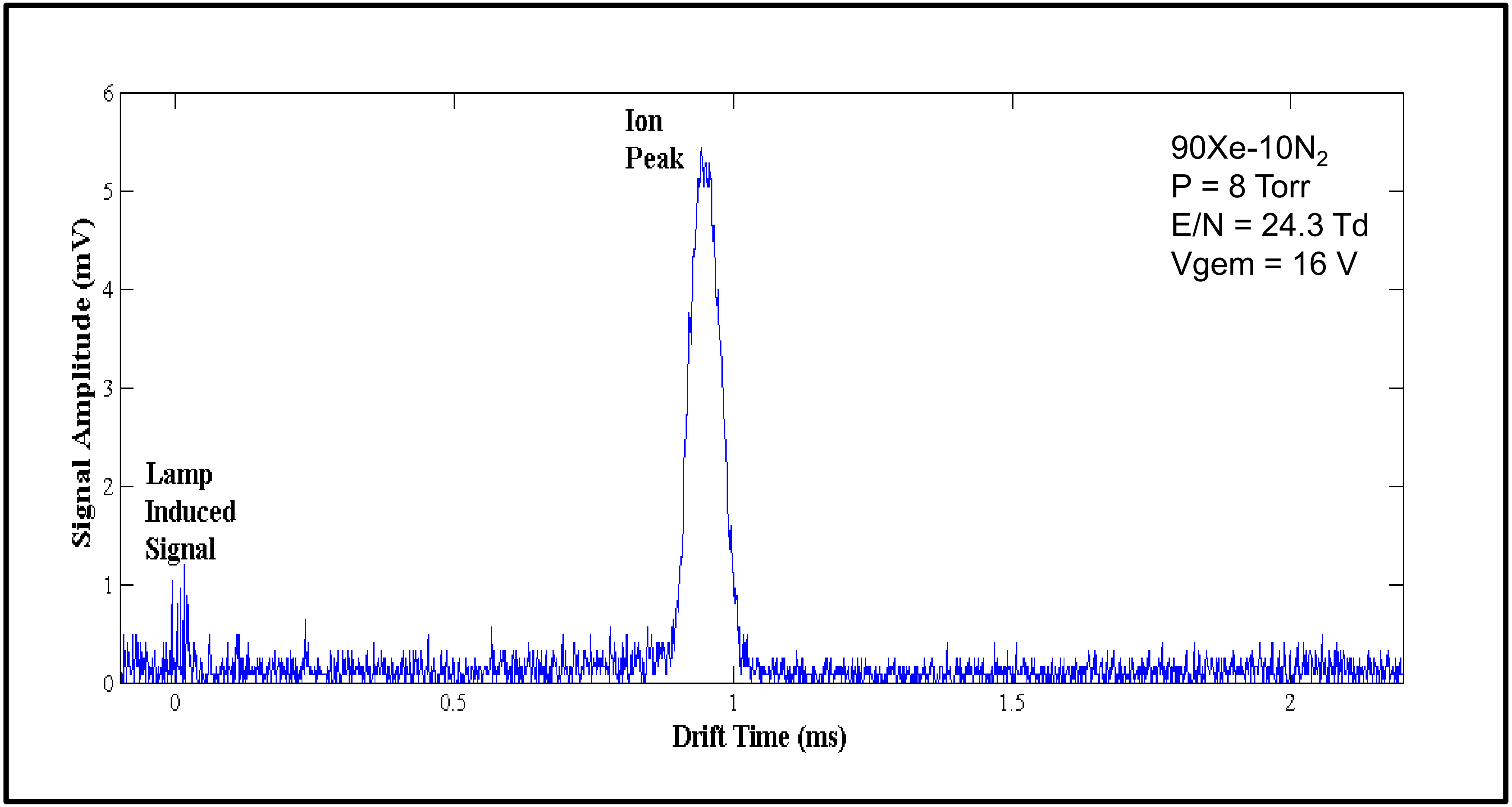
(1) $e + Rg \rightarrow Rg^+ + 2e$
(Ionization)

(2) $Rg^+ + 2Rg \rightarrow Rg_2^+ + Rg$
(3-body reaction)

ION IDENTIFICATION: XE-N_2

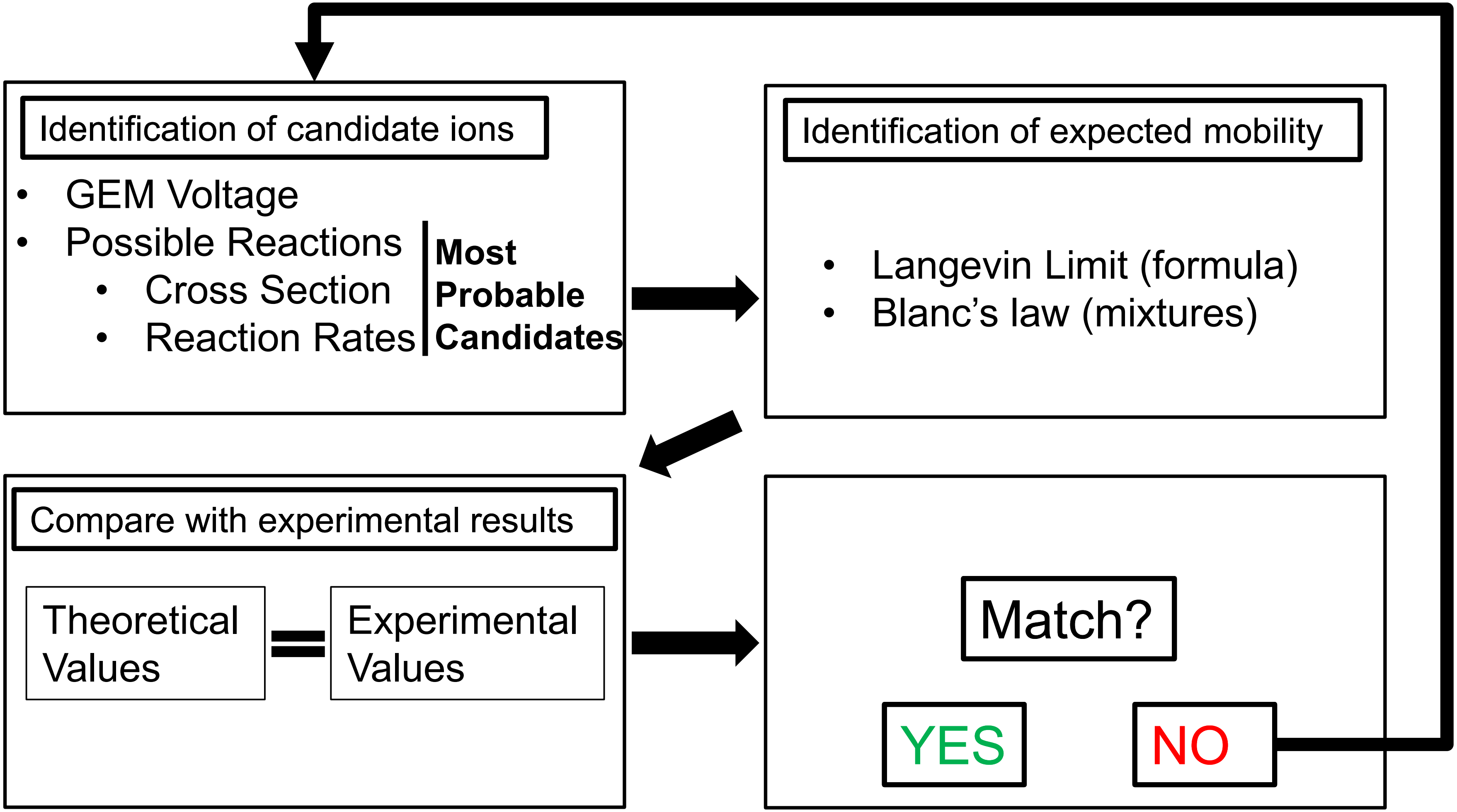
EXAMPLE 2

Xe-N2 was studied for the NEXT Experiment…



Which ion are we observing?

ION IDENTIFICATION PROCESS



Identification of candidate ions

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

Most Probable Candidates

Identification of expected mobility

- Langevin Limit (formula)
- Blanc's law (mixtures)

Compare with experimental results

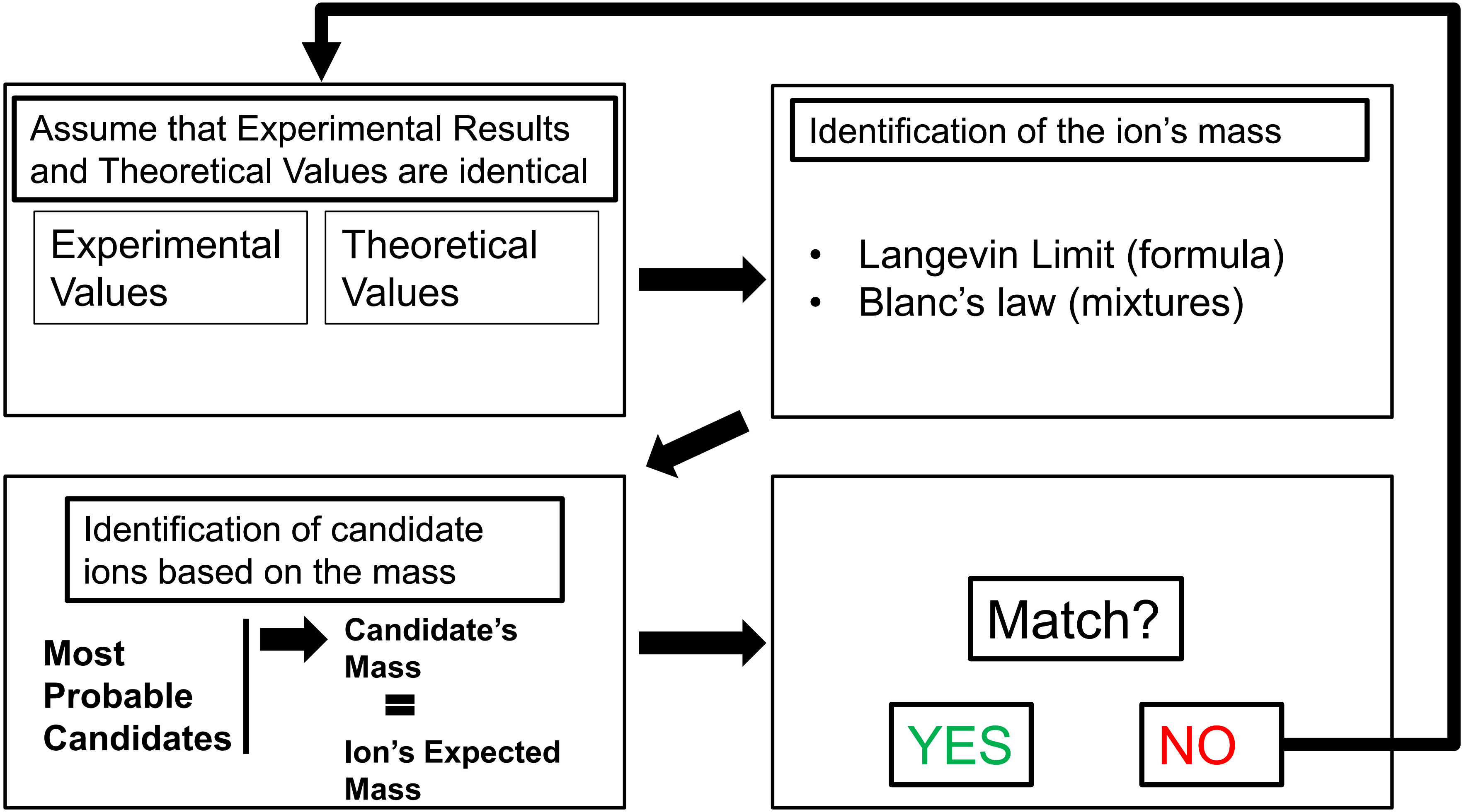
Theoretical Values = Experimental Values

Match?

YES

NO

ION IDENTIFICATION PROCESS



Assume that Experimental Results and Theoretical Values are identical

Experimental Values

Theoretical Values

Identification of the ion's mass

- Langevin Limit (formula)
- Blanc's law (mixtures)

Identification of candidate ions based on the mass

Most Probable Candidates

Candidate's Mass

=

Ion's Expected Mass

Match?

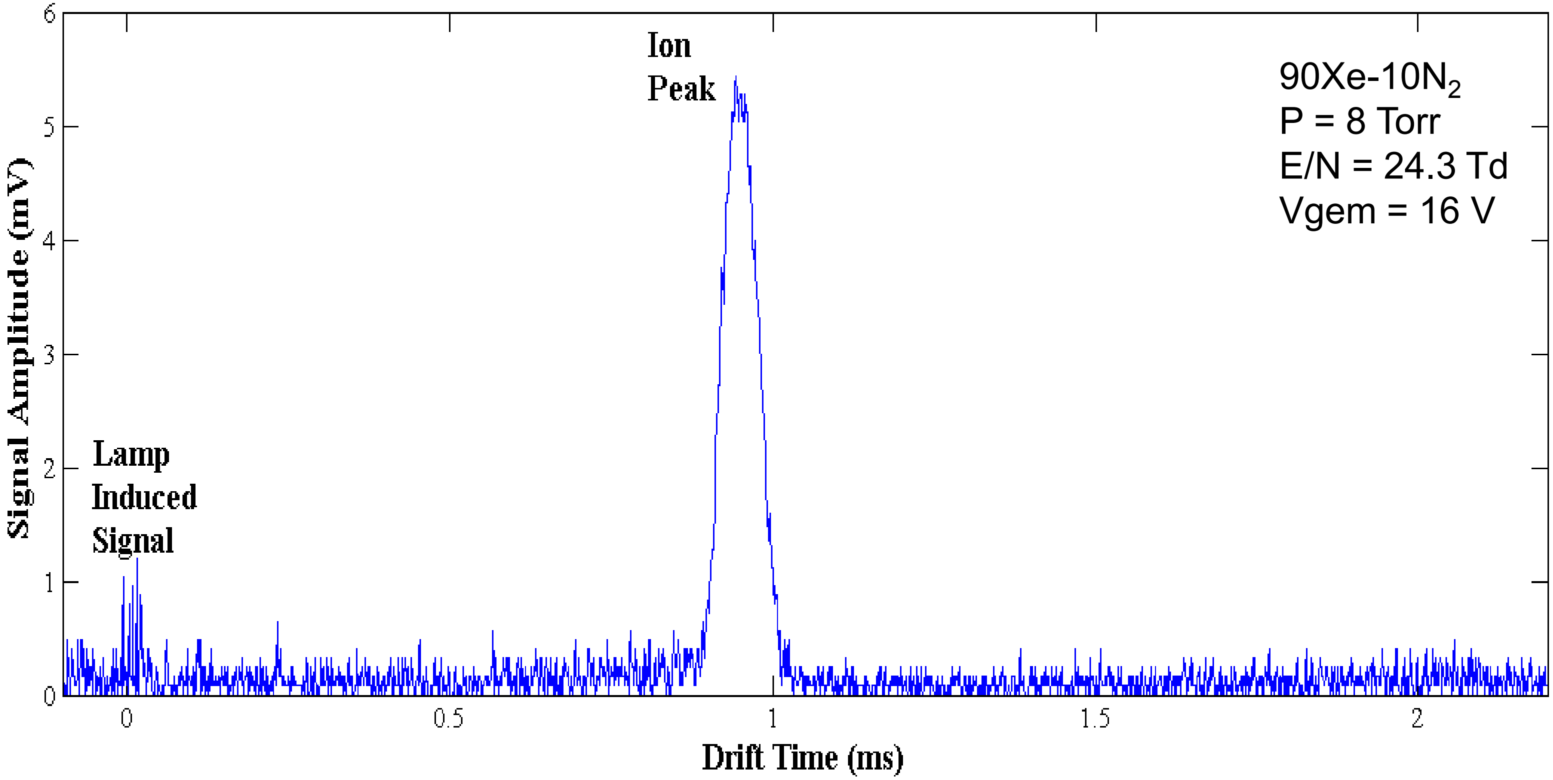
YES

NO

ION IDENTIFICATION: XE-N_2

EXAMPLE 2

Xe-N2 was studied for the NEXT Experiment…

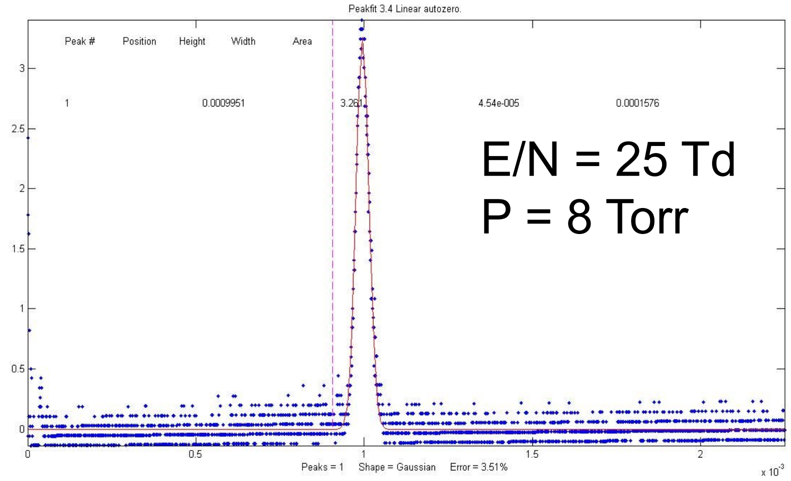


Which ion are we observing?

RESULTS XE-N_2

EXAMPLE 2

Xe



E/N = 25 Td
P = 8 Torr

(Ionization)

Xe + e -> Xe^+ + 2e

(Reactions)

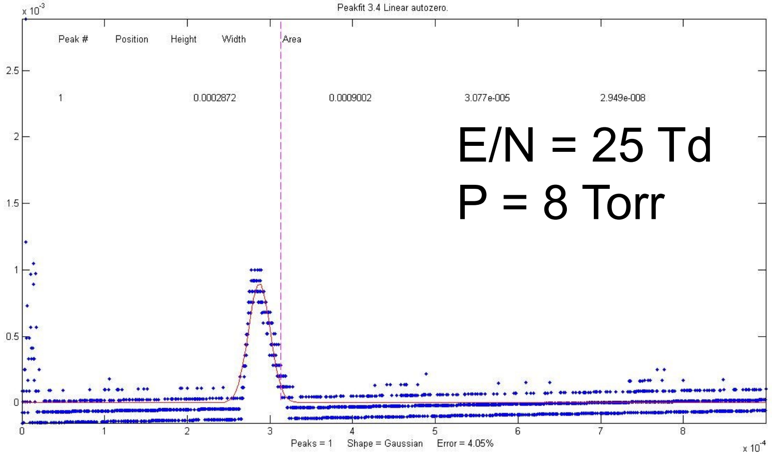
Xe^+ + 2Xe -> Xe_2^+ + Xe

Xe^+ + Xe -> Xe + Xe^+

For Vgem = 14.5 V

K_{01} ~ 0.654 $cm^2V^{-1}s^{-1}$
(Xe_2^+ ?)

N_2



E/N = 25 Td
P = 8 Torr

(Ionization)

N_2 + e -> N_2^+ + 2e

(Reactions)

N_2^+ + $2N_2$ -> N_4^+ + N_2

For Vgem = 20 V

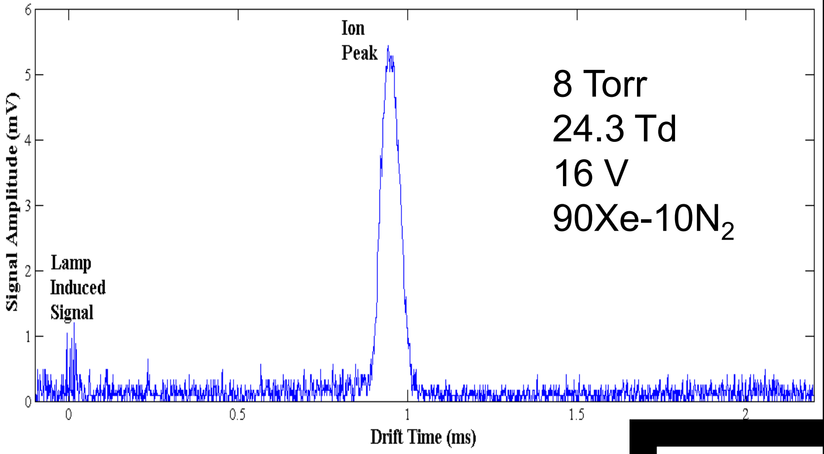
K_{01} ~ 2.350 $cm^2V^{-1}s^{-1}$
(N_4^+ ?)

The dissociative energy of the N_4^+ is much larger than the kinetic energy of the ion under the low reduced electric field.

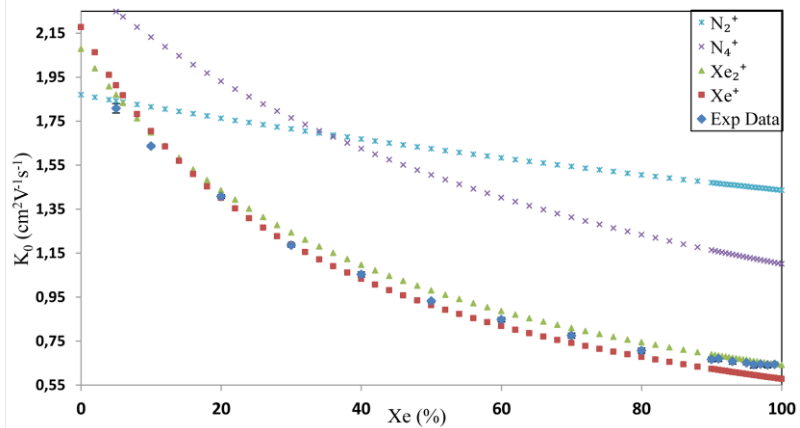
DISCUSSION: XE-N_2

EXAMPLE 2

Results



8 Torr
24.3 Td
16 V
90Xe-10N_2



K_0 ~ 0.685 $cm^2V^{-1}s^{-1}$ (Xe_2^+ ?)

Discussion

Possible ion candidates

Xe^+ , Xe_2^+ , N_2^+ and N_4^+

Blanc's Law with **Langevin limit**

K_0 ~ 1.570 $cm^2V^{-1}s^{-1}$ (N_2^+ ?)
K_0 ~ 1.210 $cm^2V^{-1}s^{-1}$ (N_4^+ ?)
K_0 ~ 0.590 $cm^2V^{-1}s^{-1}$ (Xe^+ ?)
K_0 ~ 0.690 $cm^2V^{-1}s^{-1}$ (Xe_2^+ ?)

Same Product
Xe_2^+
(Charge Transfer Reaction)

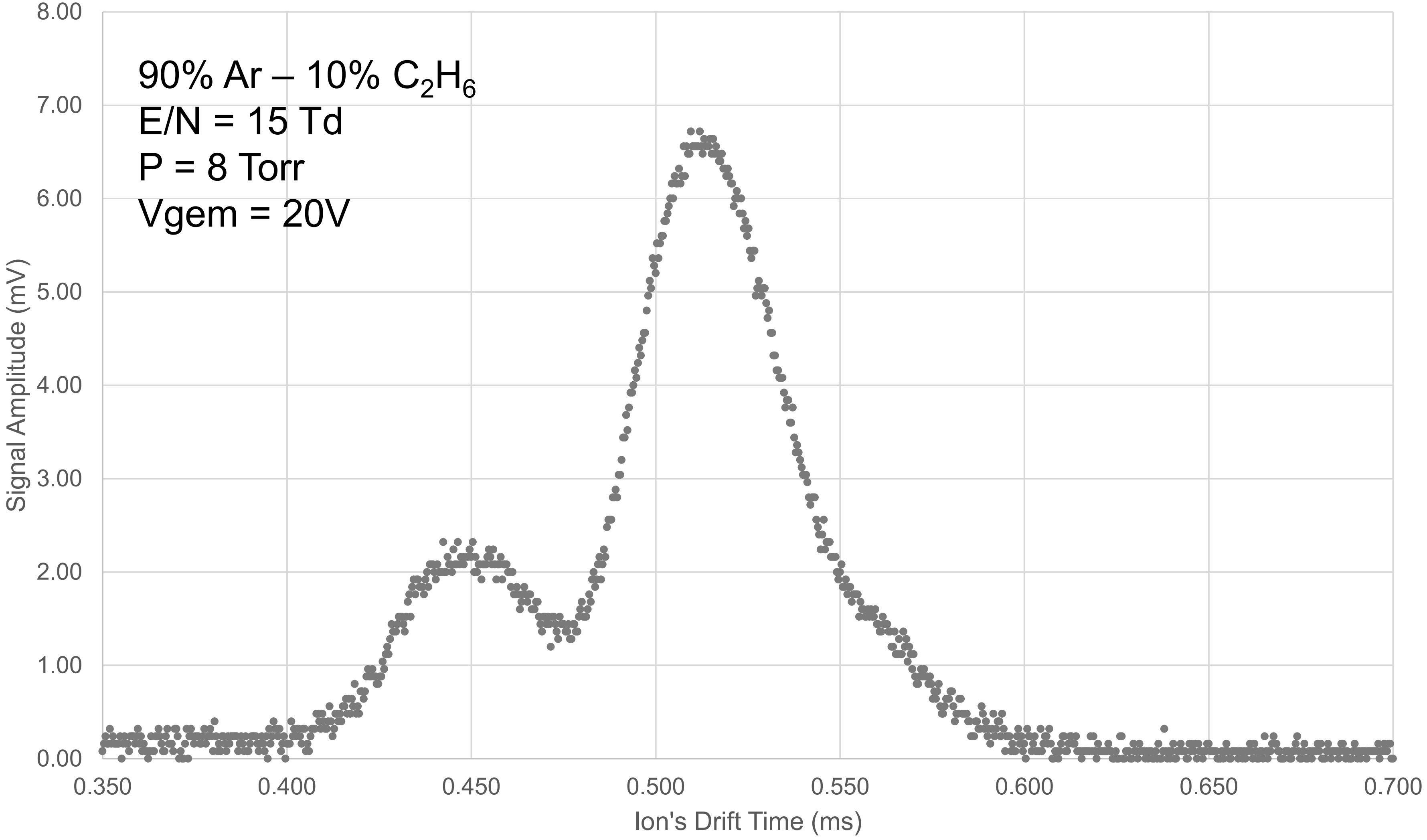
$N_2^+ + Xe \rightarrow Xe^+ + N_2$

Prevents the appearance of N_2^+ and N_4^+.

Match

ION IDENTIFICATION: AR-C_2H_6

EXAMPLE 1

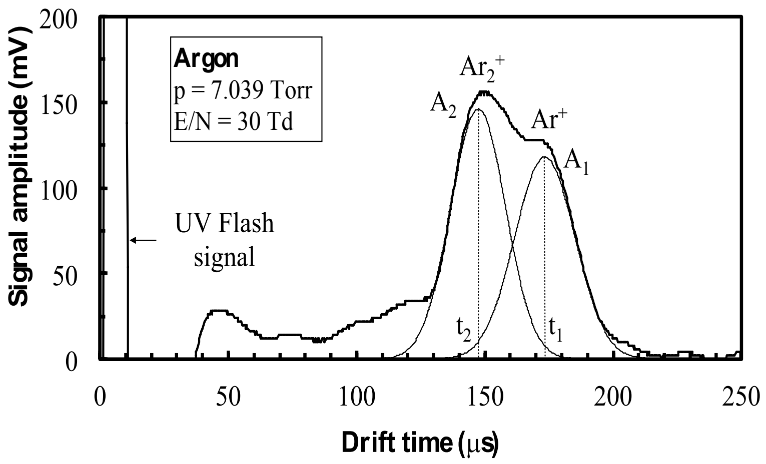


Which ions are we observing?

RESULTS AR-C_2H_6

EXAMPLE 1

Ar



For Vgem = 20 V

(Ionization)

$Ar + e \rightarrow Ar^+ + 2e$

(Reactions)

$Ar^+ + 2Ar \rightarrow Ar_2^+ + Ar$

$Ar^+ + Ar \rightarrow Ar + Ar^+$

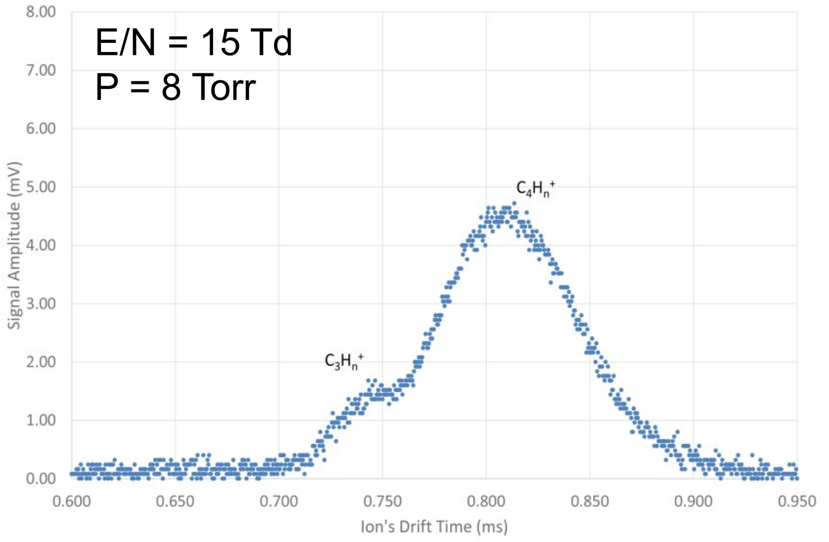
$K_{01} \sim 1.57\ cm^2V^{-1}s^{-1}$

(Ar^+ ?)

$K_{02} \sim 1.92\ cm^2V^{-1}s^{-1}$

(Ar_2^+ ?)

C_2H_6



For Vgem = 20 V

(Ionization)

$C_2H_6 + e \rightarrow C_2H_6^+ + e$	0.15
$\rightarrow C_2H_5^+ + H + e$	0.11
$\rightarrow C_2H_4^+ + H_2$	0.44
$\rightarrow C_2H_3^+ + H + H_2$	0.12
$\rightarrow C_2H_2^+ + 2H_2$	0.07
$\rightarrow CH_3^+ + CH_3$	0.03

$K_{01} \sim 2.57\ cm^2V^{-1}s^{-1}$

(C_3H_n ?)

$K_{02} \sim 2.44\ cm^2V^{-1}s^{-1}$

($C_4H_n^+$?)

C_2H_6

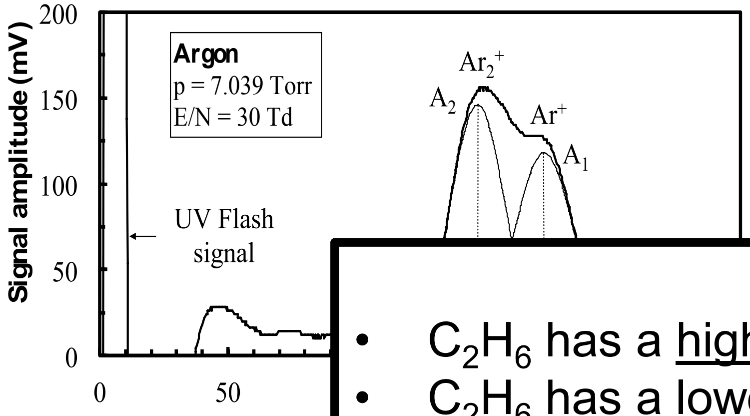
$\rightarrow$ $C_3H_n^+$ (n: 7,8,9)

$C_4H_n^+$ (n: 7,9,10,12)

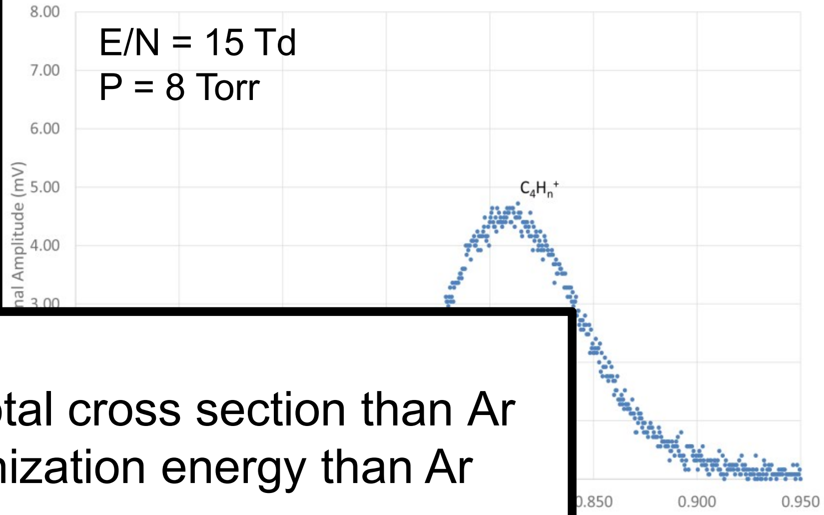
RESULTS AR-C_2H_6

EXAMPLE 1

Ar



C_2H_6



- C_2H_6 has a <u>higher</u> total cross section than Ar
- C_2H_6 has a <u>lower</u> ionization energy than Ar

For Vgem = 20 V

(Ionization)

$Ar + e \rightarrow Ar^+ + 2e$

(Reactions)

$Ar^+ + 2Ar \rightarrow Ar_2^+ + Ar$

$Ar^+ + Ar \rightarrow Ar + Ar^+$

K_{01} ~ 1.57 $cm^2V^{-1}s^{-1}$
(Ar^+ ?)

K_{02} ~ 1.92 $cm^2V^{-1}s^{-1}$
(Ar_2^+ ?)

For Vgem = 20 V

(Ionization)

$$C_2H_6 + e \begin{array}{ll} \rightarrow C_2H_6^+ + e \\ \rightarrow C_2H_5^+ + H + e \\ \rightarrow C_2H_4^+ + H_2 \\ \rightarrow C_2H_3^+ + H + H_2 \\ \rightarrow C_2H_2^+ + 2H_2 \\ \rightarrow CH_3^+ + CH_3 \end{array} \begin{bmatrix} 0.15 \\ 0.11 \\ 0.44 \\ 0.12 \\ 0.07 \\ 0.03 \end{bmatrix} \Rightarrow \begin{array}{l} C_2H_6 \\ C_3H_n^+ \text{ (n: 7,8,9)} \\ C_4H_n^+ \text{ (n: 7,9,10,12)} \end{array}$$

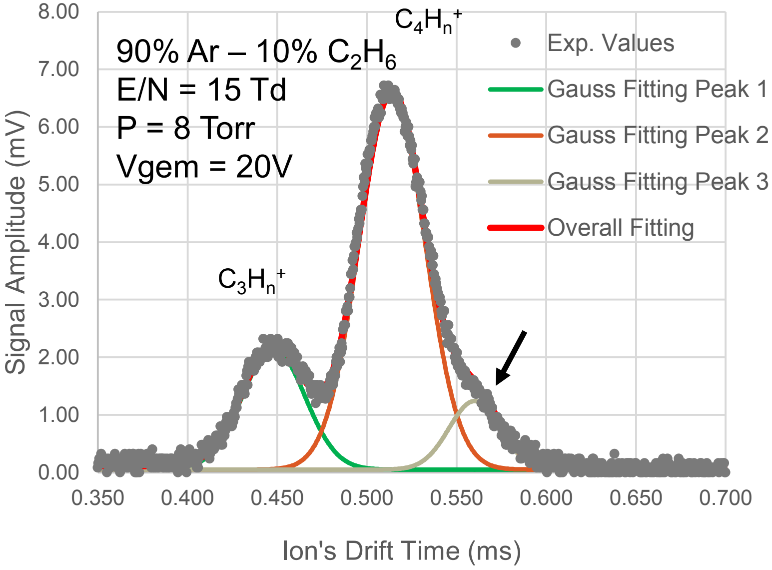
K_{01} ~ 2.57 $cm^2V^{-1}s^{-1}$
(C_3H_n ?)

K_{02} ~ 2.44 $cm^2V^{-1}s^{-1}$
($C_4H_n^+$?)

DISCUSSION: AR-C_2H_6

EXAMPLE 1

Results



K_{01} ~ 2.37 $cm^2V^{-1}s^{-1}$ ($C_3H_n^+$?)
K_{02} ~ 2.07 $cm^2V^{-1}s^{-1}$ ($C_4H_n^+$?)
K_{02} ~ 1.91 $cm^2V^{-1}s^{-1}$ ($C_5H_{11}^+$?)

Discussion

(Charge Transfer Reaction)

$Ar^+ + C_2H_6 \rightarrow C_2H_5^+ + Ar$ 0.08
$\rightarrow C_2H_4^+ + Ar$ 0.22
$\rightarrow C_2H_3^+ + Ar$ 0.42
$\rightarrow C_2H_2^+ + Ar$ 0.23
$\rightarrow CH_3^+ + Ar$ 0.05

Prevents the formation of Ar_2^+.

Same Ion Products
Different Distribution

Blanc's Law with **Langevin limit**

K_{01} = 2.27 $cm^2V^{-1}s^{-1}$ ($C_3H_n^+$)
K_{02} = 2.10 $cm^2V^{-1}s^{-1}$ ($C_4H_n^+$)
K_{02} = 2.03 $cm^2V^{-1}s^{-1}$ ($C_5H_{11}^+$)

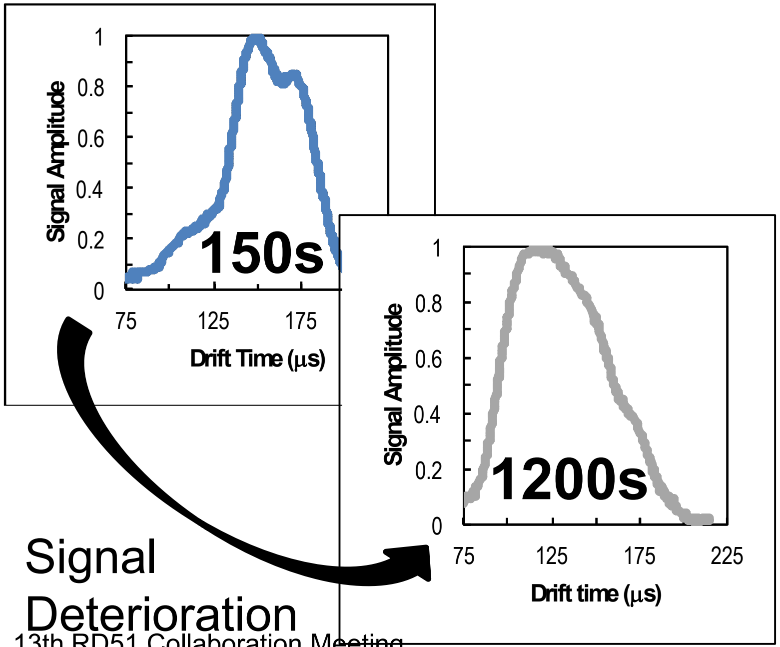
Match

ION MOBILITY STUDY LIMITATIONS: IMPURITIES

Impurities

- Gas purity (99,999%) (HP)
- Outgassing process (LP)

(mainly H_2O)

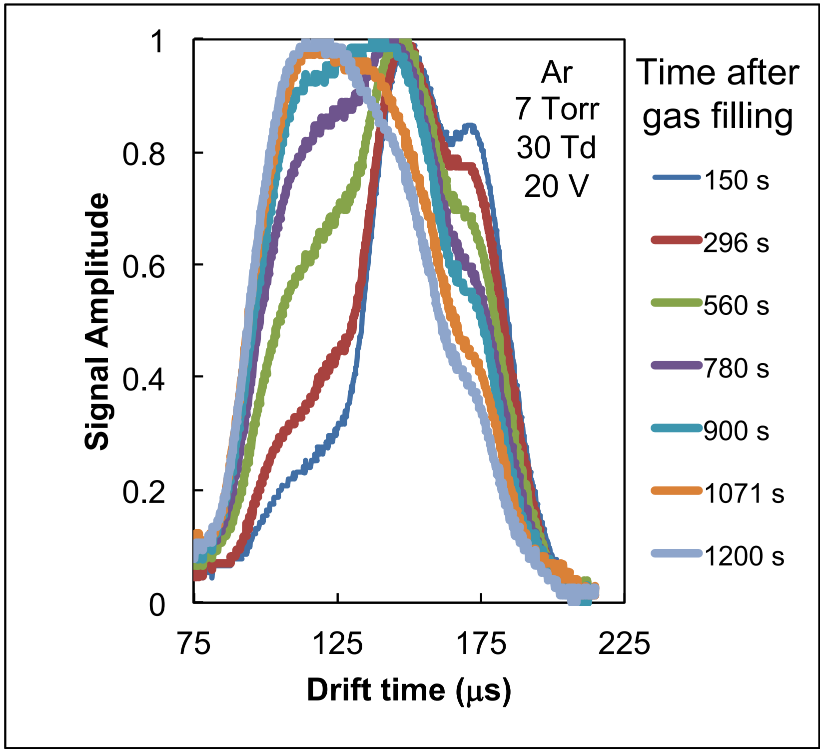


Signal Deterioration

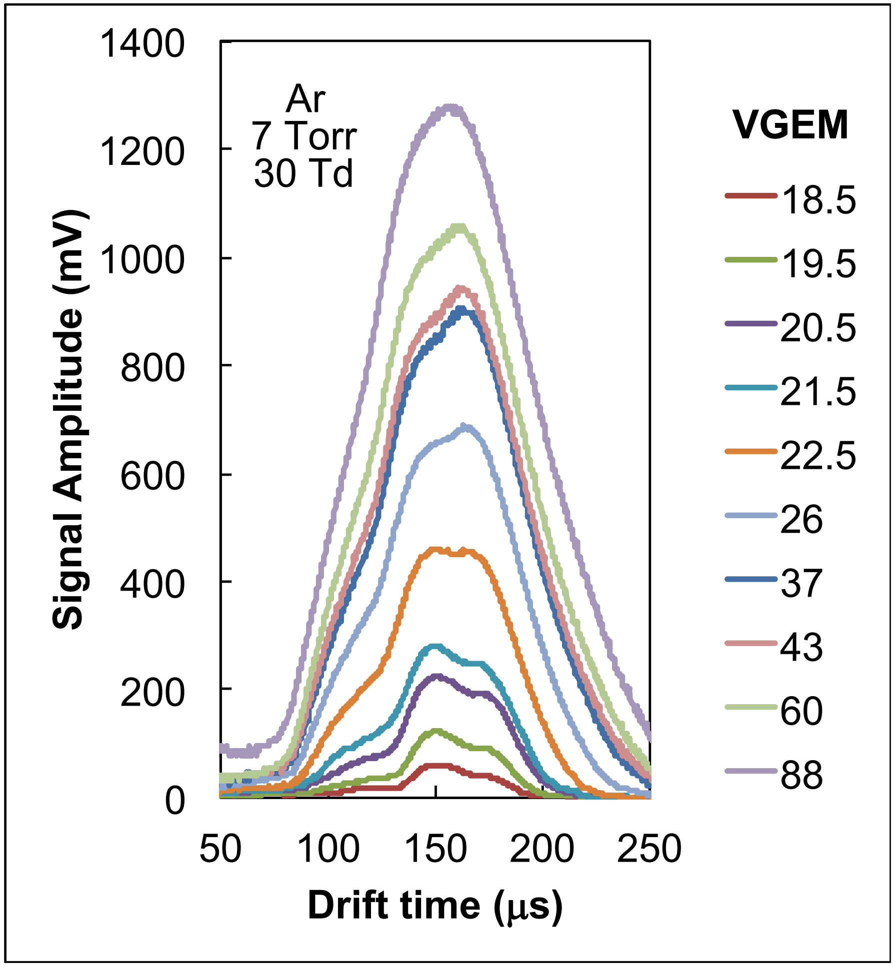
Reduced Electric Field

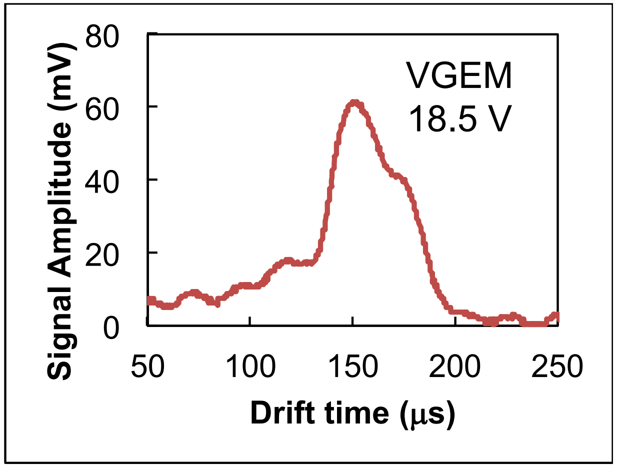
- For low E/N values.

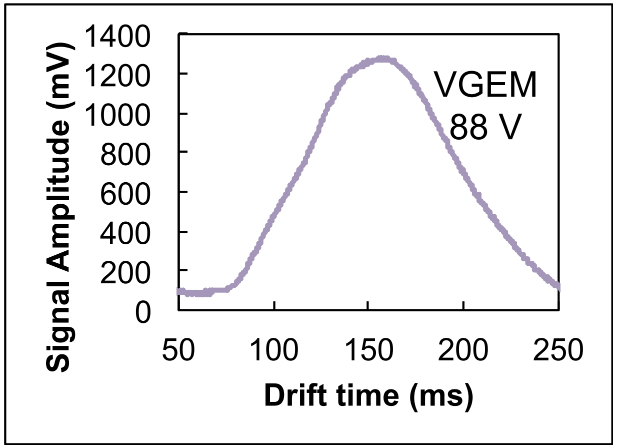
Increasing probability of collision with Impurity Molecules



ION MOBILITY STUDY LIMITATIONS: SPACE-CHARGE EFFECTS







CONCLUSIONS

- This technique has allowed us to make **ion mobility measurements** in several gases.
- This technique may also be used to measure some **reaction rate constants (although not presented)**.
- A GEM is used to produce the ions. The **ions' initial position** is known with great precision. The number and type of ions can be controlled by **varying the GEM voltage**.
- Although this technique doesn't provide **direct identification** of the ions, using a different method we were able to identify the group of ions present.
- **Impurities** and **space-charge** effects have to be taken into consideration when analyzing the experimental results.

- This work was supported by FCT through the following projects

  CERN/FP/123613/2011 - Prof. Dr. João Barata

  CERN/FP/116392/2010 - Prof. Dr. Rui Marques

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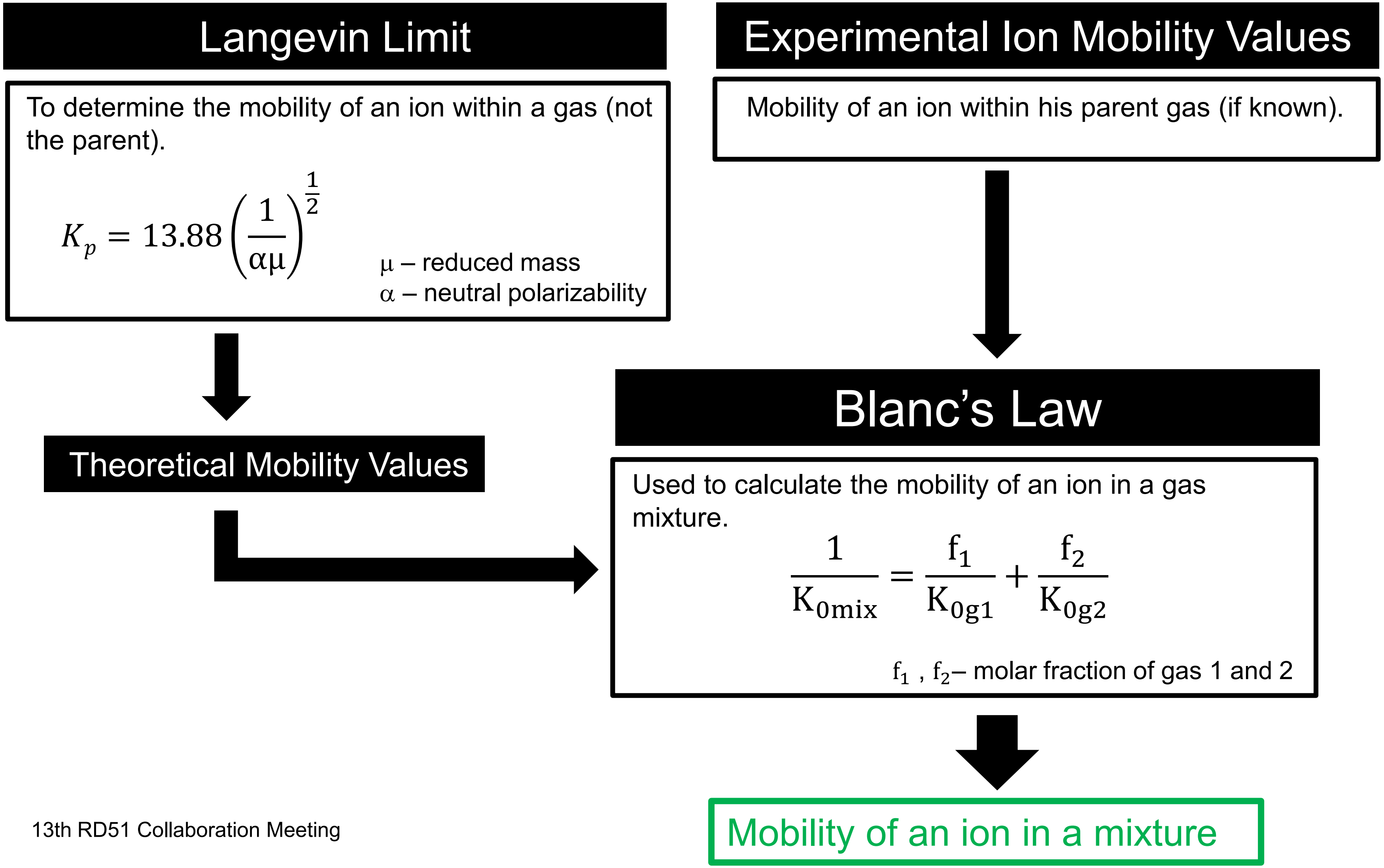
Thank you!

MIXING LANGEVIN LIMIT WITH BLANC'S LAW



Langevin Limit

To determine the mobility of an ion within a gas (not the parent).

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

μ – reduced mass
α – neutral polarizability

Theoretical Mobility Values

Experimental Ion Mobility Values

Mobility of an ion within his parent gas (if known).

Blanc's Law

Used to calculate the mobility of an ion in a gas mixture.

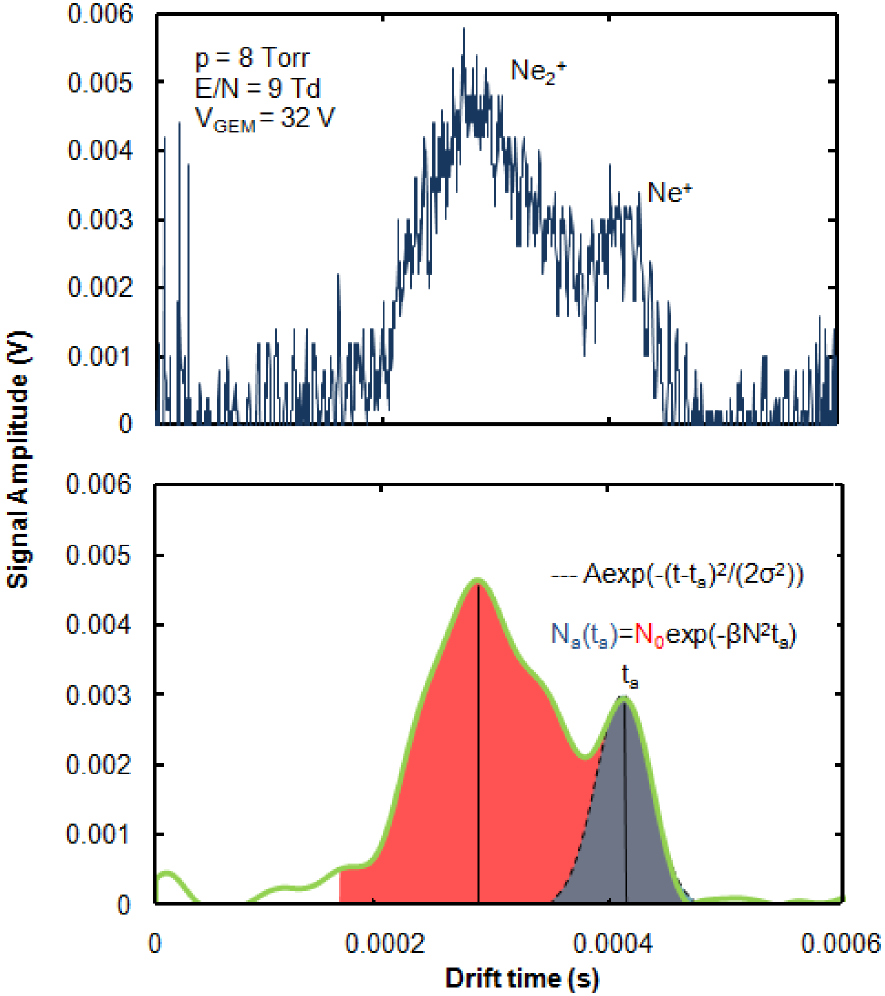
$$\frac{1}{K_{0mix}} = \frac{f_1}{K_{0g1}} + \frac{f_2}{K_{0g2}}$$

f_1 , f_2– molar fraction of gas 1 and 2

Mobility of an ion in a mixture

REACTION RATE MEASUREMENTS

$$Rg^+ + 2Rg \overset{\beta}{\text{->}} Rg_2^+ + Rg$$



$Rg^+ + 2Rg \text{ -> } Rg_2^+ + Rg$

$d[Rg^+]/dt= -\beta[Rg^+][Rg]^2$

$[Rg+](t)=[Rg+](0)\exp(-\beta N^2 t)$

$[Rg^+](t)$ is proportional to the area of the atomic ion gaussian.

[Rg+](0) is proportional to the total area.

Depends on:
- Temperature

RESULTS: REACTION RATE

$$Rg^+ + 2Rg \xrightarrow{\beta} Rg_2^+ + Rg$$

Ne: $\beta = (5.6 \pm 0.1)\mathrm{x}10^{-32}\ \mathrm{cm}^6\mathrm{s}^{-1}$

Ar: $\beta = (1.2 \pm 0.2)\mathrm{x}10^{-31}\ \mathrm{cm}^6\mathrm{s}^{-1}$

Kr: $\beta = (2.1 \pm 0.9)\mathrm{x}10^{-31}\ \mathrm{cm}^6\mathrm{s}^{-1}$

Xe: $\beta = (1.5 \pm 0.2)\mathrm{x}10^{-31}\ \mathrm{cm}^6\mathrm{s}^{-1}$

(Neves, Conde and Távora, 2010)

CANDIDATE IONS IDENTIFICATION

GEM Voltage

- Maximum energy gained by electrons.
- Primary ions possible to be formed.

Rg (pure)

$Rg + e \rightarrow Rg^+ + 2e$

Possible Reactions

Ions formed through reactions of the primary ions with neutral atoms or molecules from the medium.

Reaction Time

Used to calculate the mobility of an ion in a gas mixture.

$$\tau = \frac{1}{kN}$$

- Identification the possible ions present.

Universal decay law

Used to calculate the variation of the concentration of a specific ion in a mixture.

$$Rg + Rg^+ \xrightarrow{k} X^+ + Y$$

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

$$\frac{[\mathrm{X}^+]}{[\mathrm{X}^+]_0} = 1 - \frac{[\mathrm{Rg}^+]}{[\mathrm{Rg}^+]_0}$$

- Identification the possible ions present.

Select Most Probable Ions