Ion transport in CO_2-N_2 mixtures

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LIP Coimbra

1 Basic Concepts

2 Experimental Setup and Working Principle

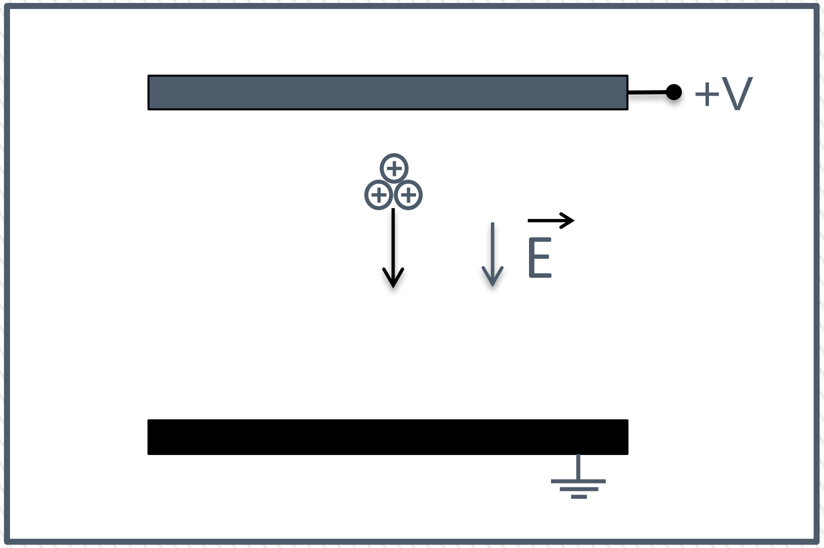
3 Ion Identification Process

4 Experimental results in:

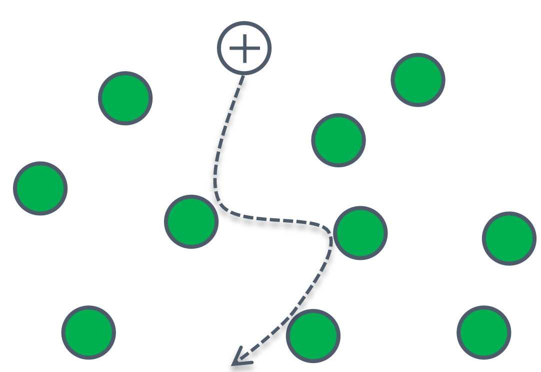
- a CO_2, N_2
- b CO_2-N_2

Basics

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

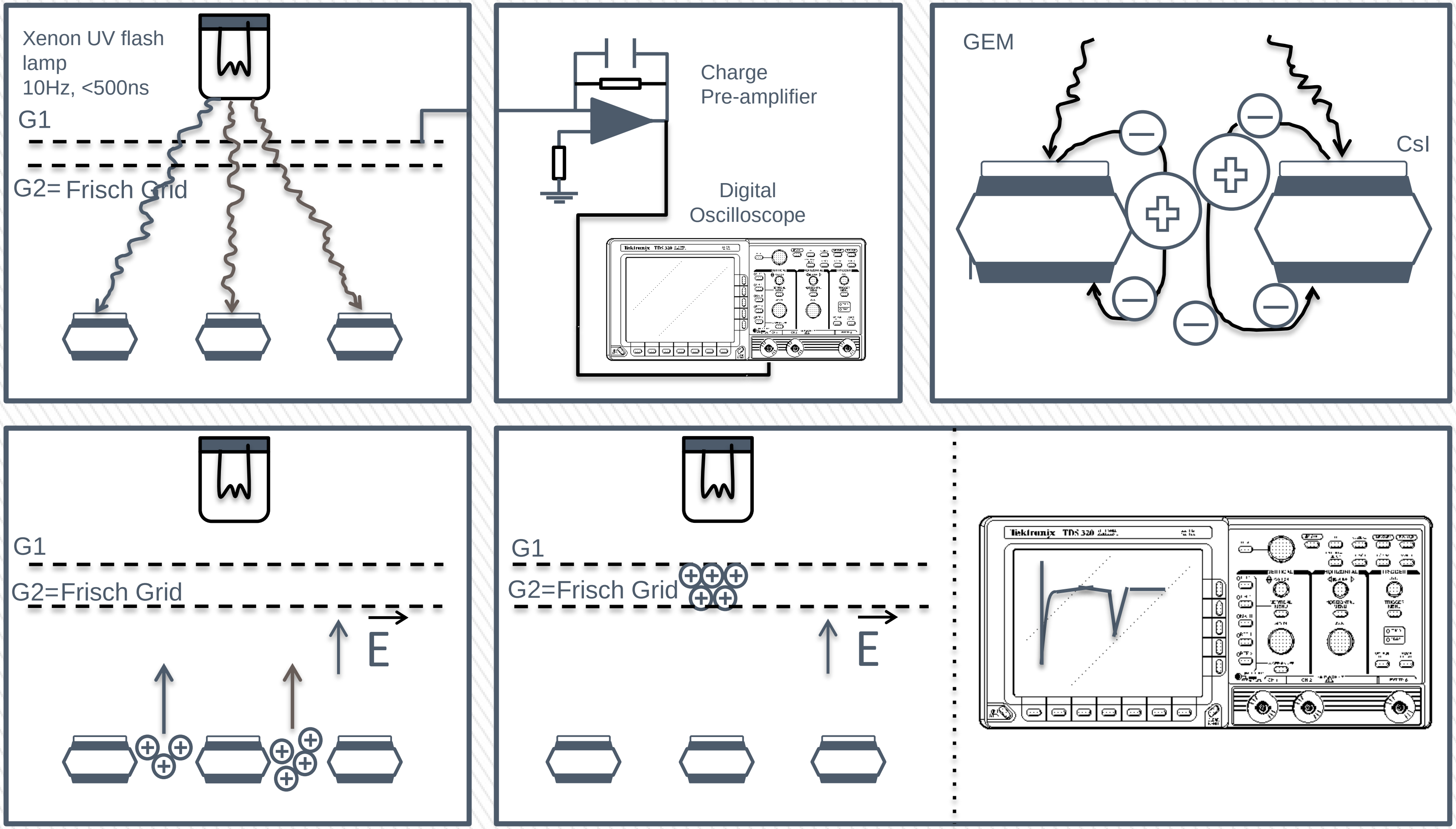
Blanc's Law

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

f_1, f_2– molar fraction of gas 1, 2

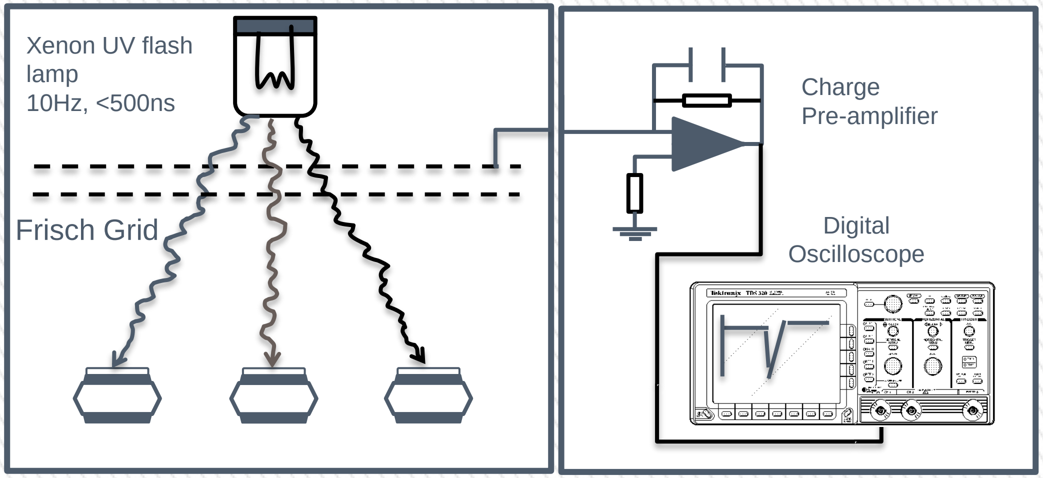
K_{0g1}, K_{0g2} – ion mobility in the gas 1 and 2

Experimental Setup and Working Principle



(Neves, Conde and Távora, 2007)

Experimental Setup and Working Principle

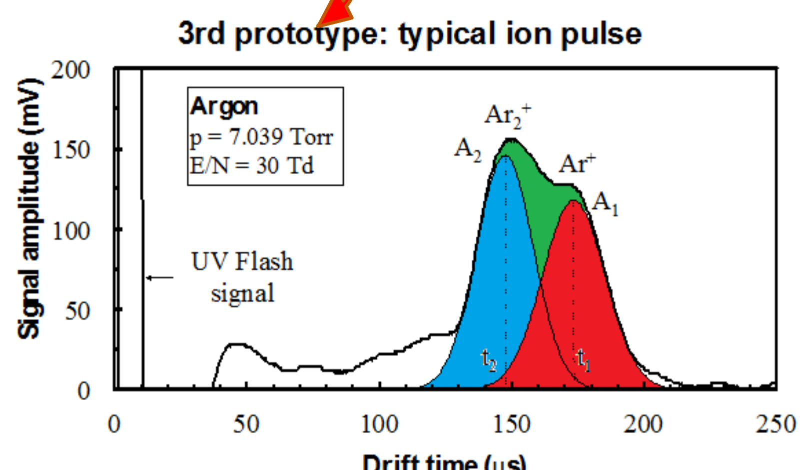


- Subtract the background to the signal
- Identify possible peaks
- Fit Gaussian curves to the peaks obtained

Peaks centroids

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

$$v_{\mathrm{d}} = \frac{x_{drift}}{t_{drift}} \rightarrow K = \frac{v_{\mathrm{d}}}{E}$$



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

Selection of Candidate ions

+

Calculation of expected mobility

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

Comparison with experimental results

Theoretical Values = Experimental Values

Match?

Experimental Results: CO_2

Ionization

above 19.5 eV

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

Above 13.8 eV

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

$\rightarrow CO^+ + \frac{1}{2}O_2 + 2e^-$

$\rightarrow O^+ + CO + 2e^-$

Appearance Energies

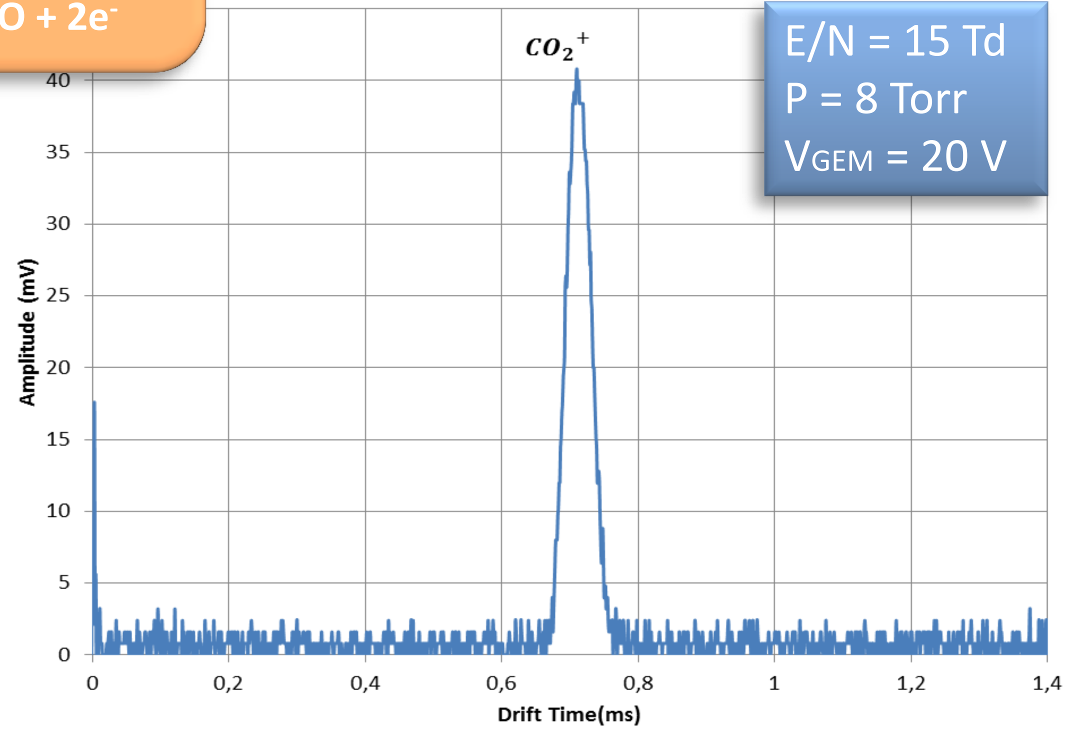
CO_2^+	**13.8 eV**
CO^+	**19.5 eV**
O^+	**19.1 eV**

Secondary Reactions

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

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

$O^+ + CO_2 \rightarrow O_2^+ + CO$



E/N = 15 Td
P = 8 Torr
VGEM = 20 V

P.M.C.C. Encarnação, 2015, JINST

Experimental Results: CO_2

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

Good agreement with earlier reported works:

1. **W. T. Huntress et al. :** $1.23\ cm^2V^{-1}s^{-1}$
2. **G. Schultz et al. :** $1.09\ cm^2V^{-1}s^{-1}$

Langevin Formula

$1.82\ cm^2V^{-1}s^{-1}$

$\neq$

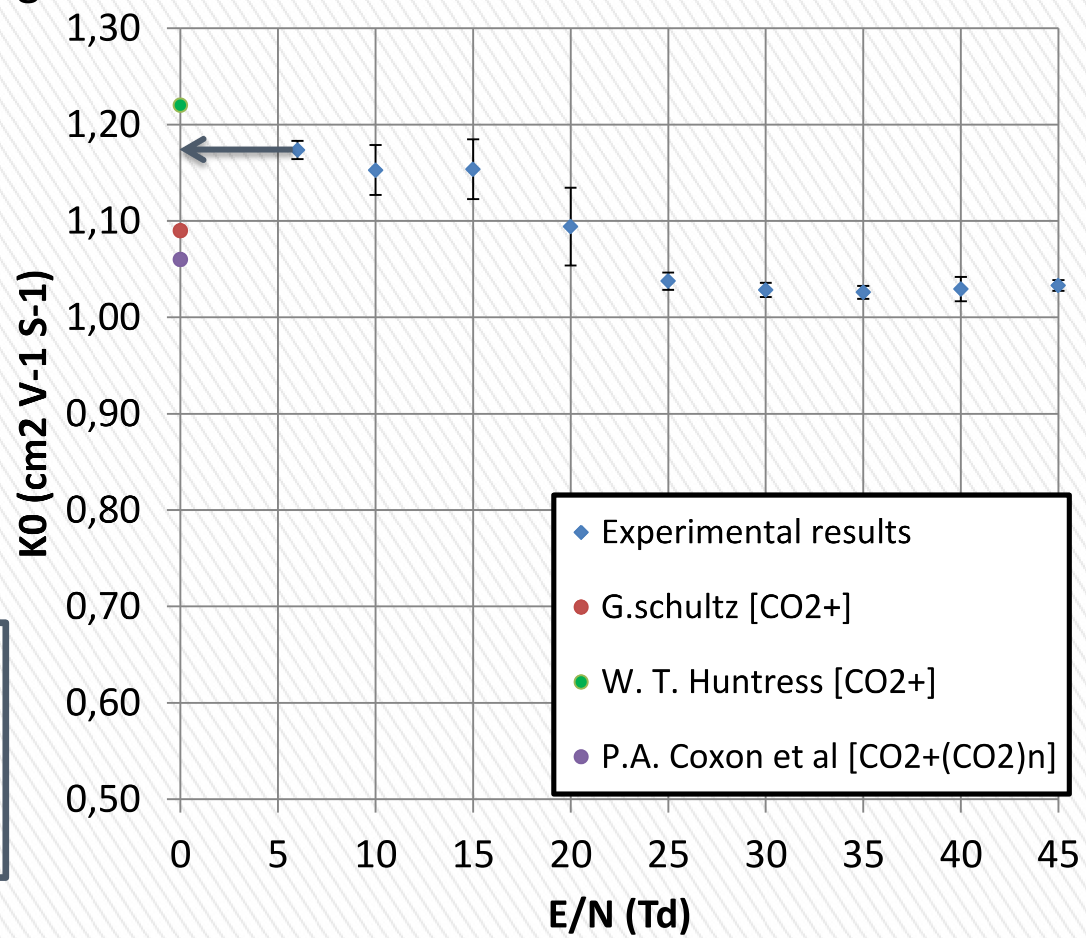
Extrapolated Value (E/N→0)

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

Charge Transfer Process

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

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



Experimental Results: N_2

Ionization

$N_2 + e \rightarrow N_2^{+} + e$

Above threshold 15,6 eV

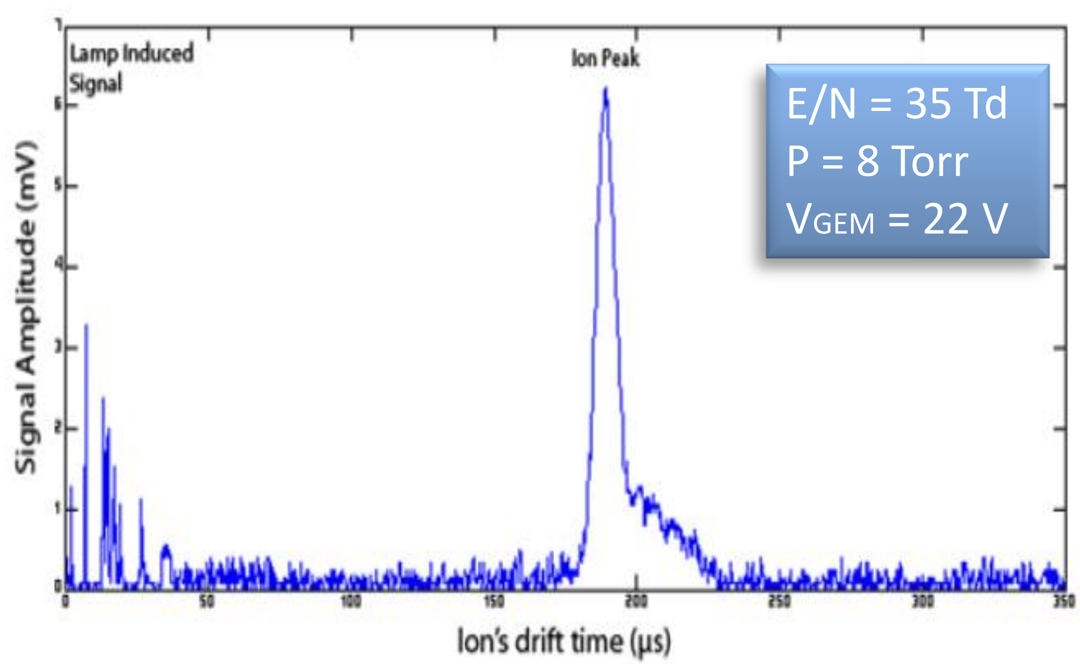
Appearance Energies

N_2^{+}	15,6 eV
N_3^{+}	21,1 eV
N^{+}	24,2 eV

Secondary Reactions

$N_2^{+} + 2N_2 \rightarrow N_4^{+} + N_2 + 0{,}87$ eV

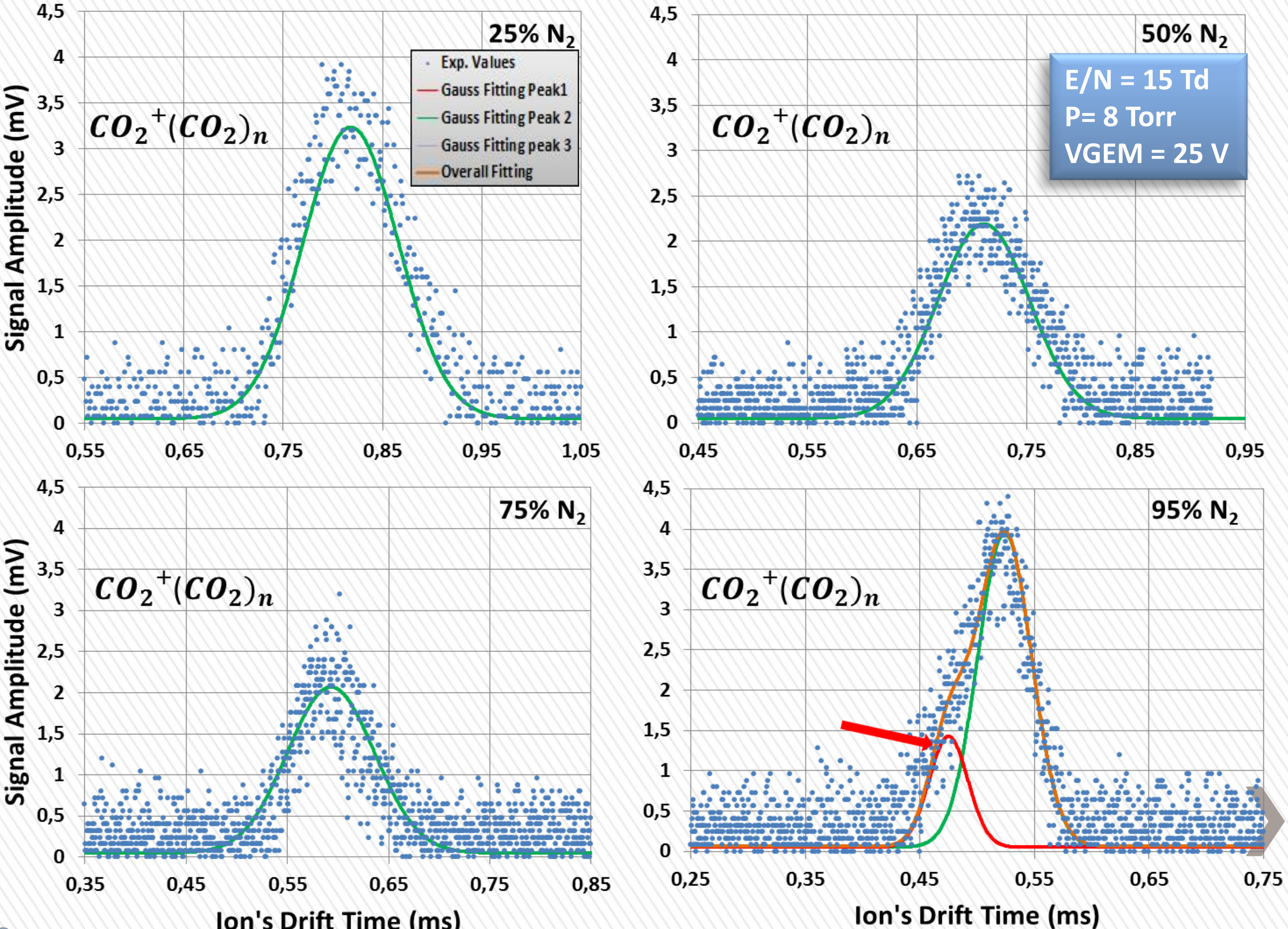
Rate constant $\rightarrow 5\text{X}10^{-29} cm^6 s^{-1}$



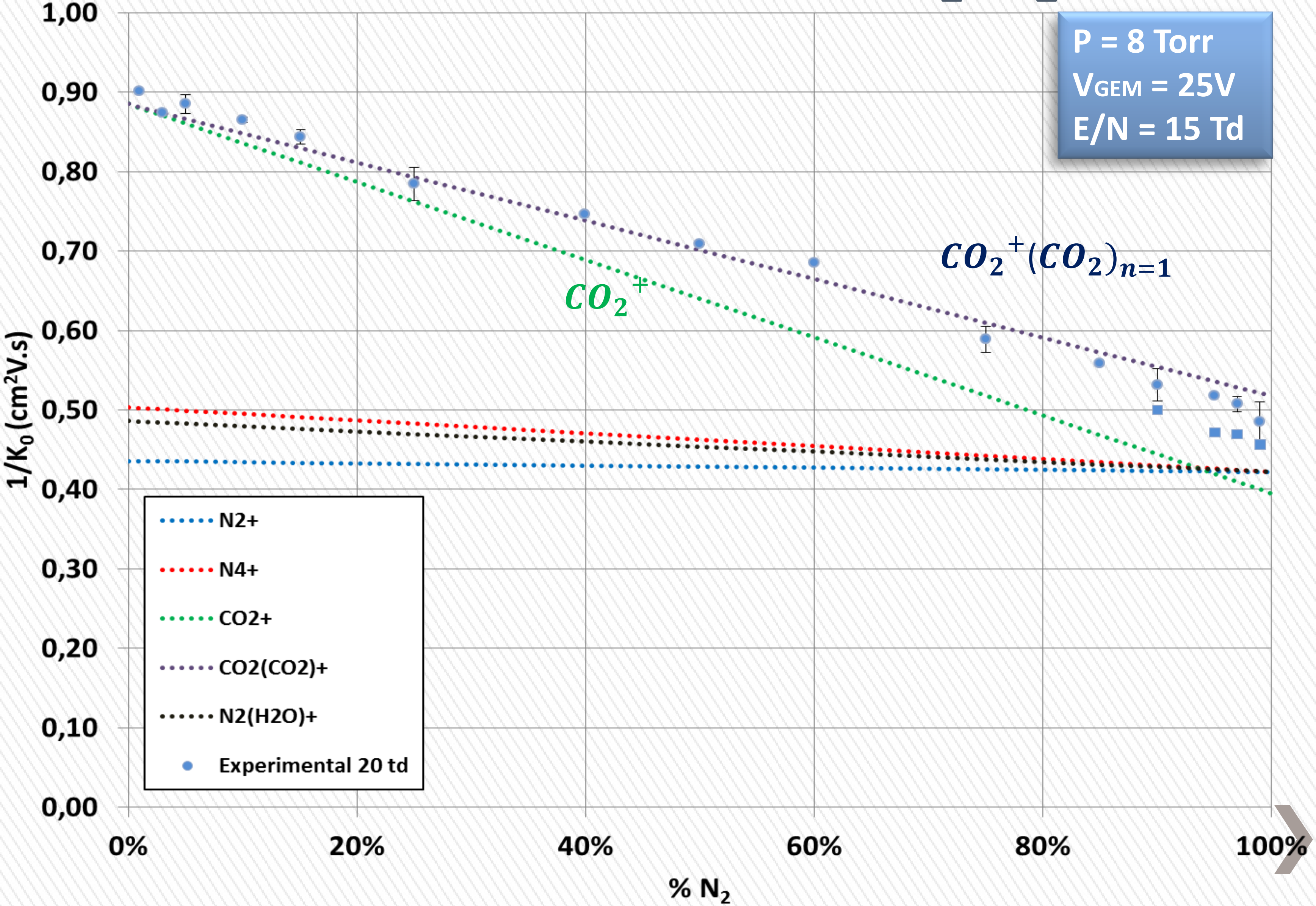
$K_{01} = 2{,}37\ cm^2V^{-1}s^{-1}\ (N_4^{+})$

A.N.C. Garcia, 2012, JINST

Experimental Results: CO_2-N_2



Experimental Results: CO_2-N_2



Experimental Results: CO_2-N_2

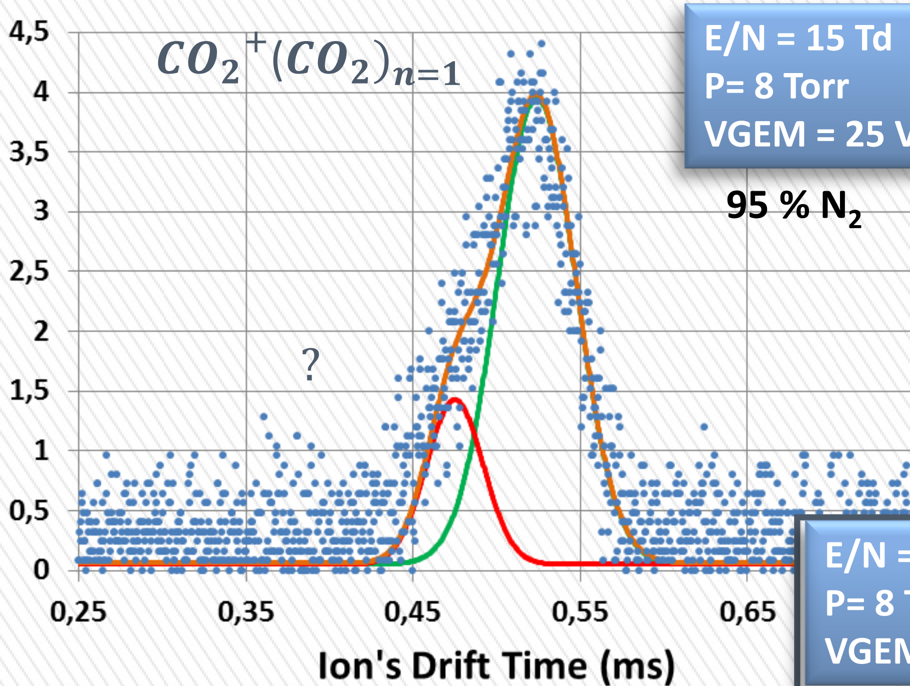
Direct Ionization	Cross Section (25V) (10^{-16} cm^2)	Final Ion
$CO_2 + e \rightarrow CO_2^+ + e$	0,969	CO_2^+
$CO_2 + e \rightarrow CO^+ + 1/2O_2 + e$	0,0279	CO^+
$CO_2 + e \rightarrow O^+ + CO + e$	0,0419	O^+
$N_2 + e \rightarrow N_2^+ + e$	13,5	N_2^+

E/N = 20 Td
P= 8 Torr (95% N_2 5% CO_2)
VGEM = 25 V

Secondary Reactions	Rate Constant $cm^3.s^{-1}$ or $cm^6.s^{-1}$	Final Ion
$N_2^+ + CO_2 \rightarrow N_2 + CO_2^+$	8E-10	CO_2^+
$N_2^+ + 2N_2 \rightarrow N_2 + N_4^+$	5E-29	N_4^+
$CO_2^+ + CO_2 + M \rightarrow CO_2.CO_2^+ + M$	2,1E-28	$CO_2CO_2^+$
$CO^+ + CO_2 \rightarrow CO_2^+ + CO$	3,7E-10	CO_2^+

K_{01} ~ 1,93±0,04 $cm^2V^{-1}s^{-1}$
(CO_2 $(CO_2)^+$)
K_{02} ~ 2,12±0,19 $cm^2V^{-1}s^{-1}$
?

Experimental Results: CO_2-N_2

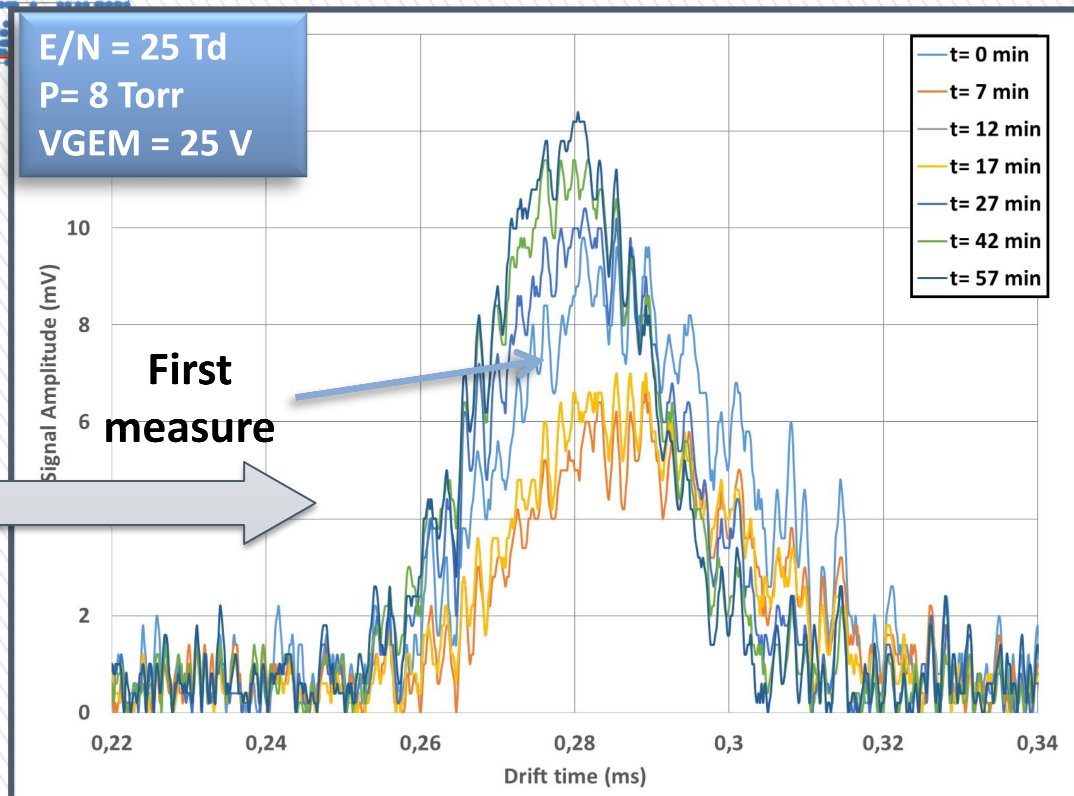


E/N = 15 Td
P= 8 Torr
VGEM = 25 V

Is the first peak caused by impurities?

- The signal appears only for voltage in VGEM higher than 25V.
- After 7 min (orange line), the both peaks (main and bump) of the signal decreases suggesting it isn't caused by impurities.

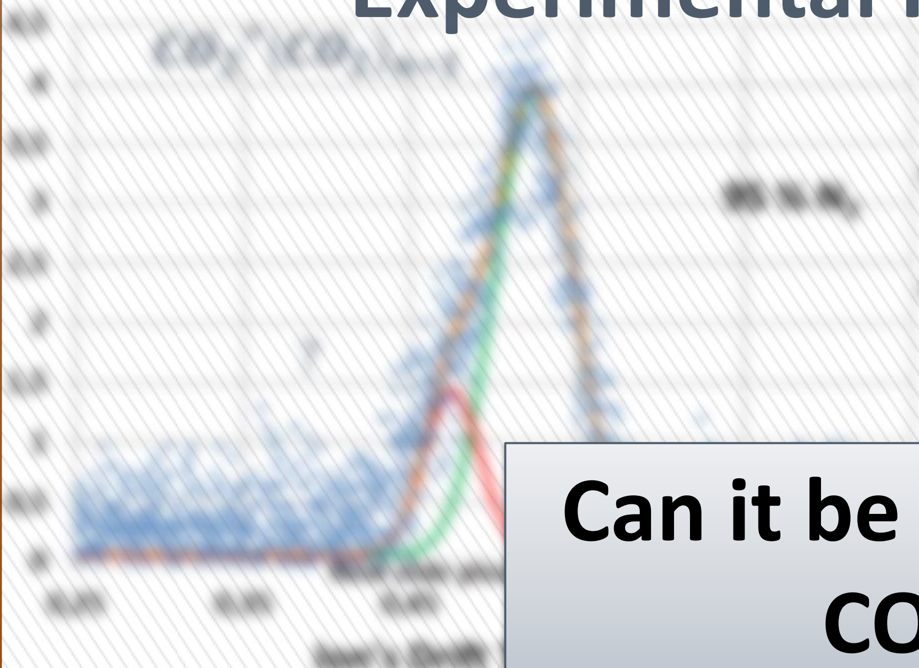
E/N = 25 Td
P= 8 Torr
VGEM = 25 V

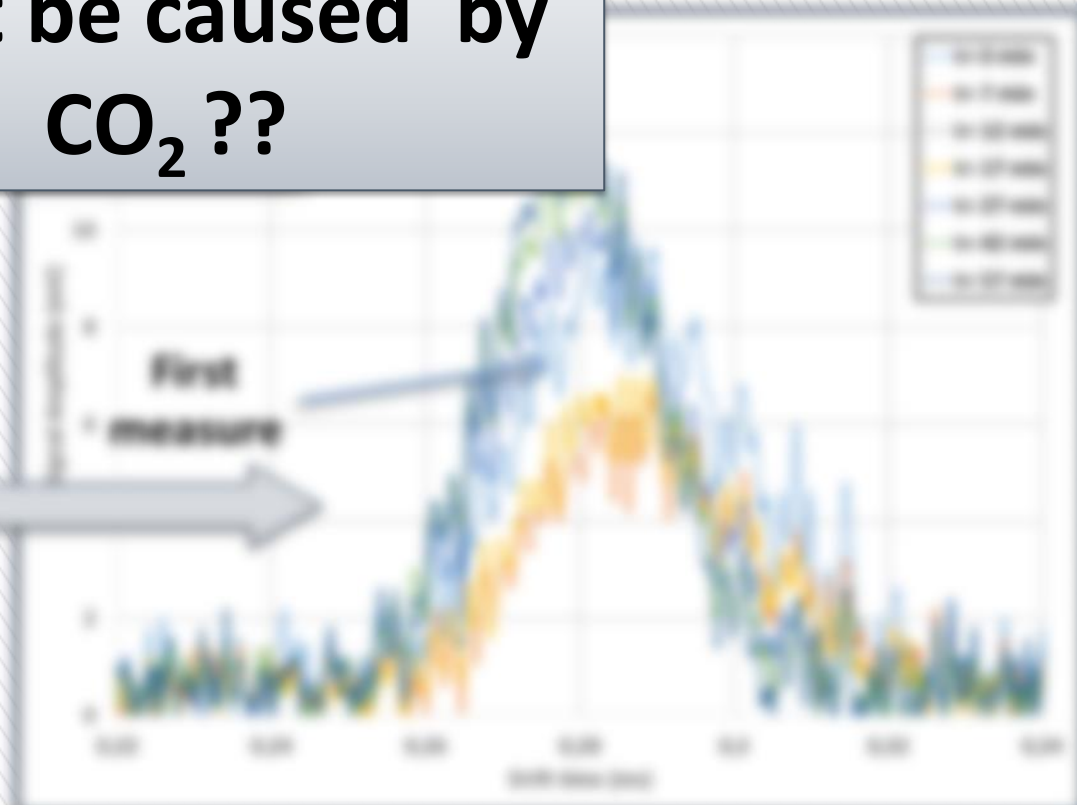


Causes:

- Gas purity (99,99997%) (HP)
- Outgassing process (LP)
- Contribution of the GEM

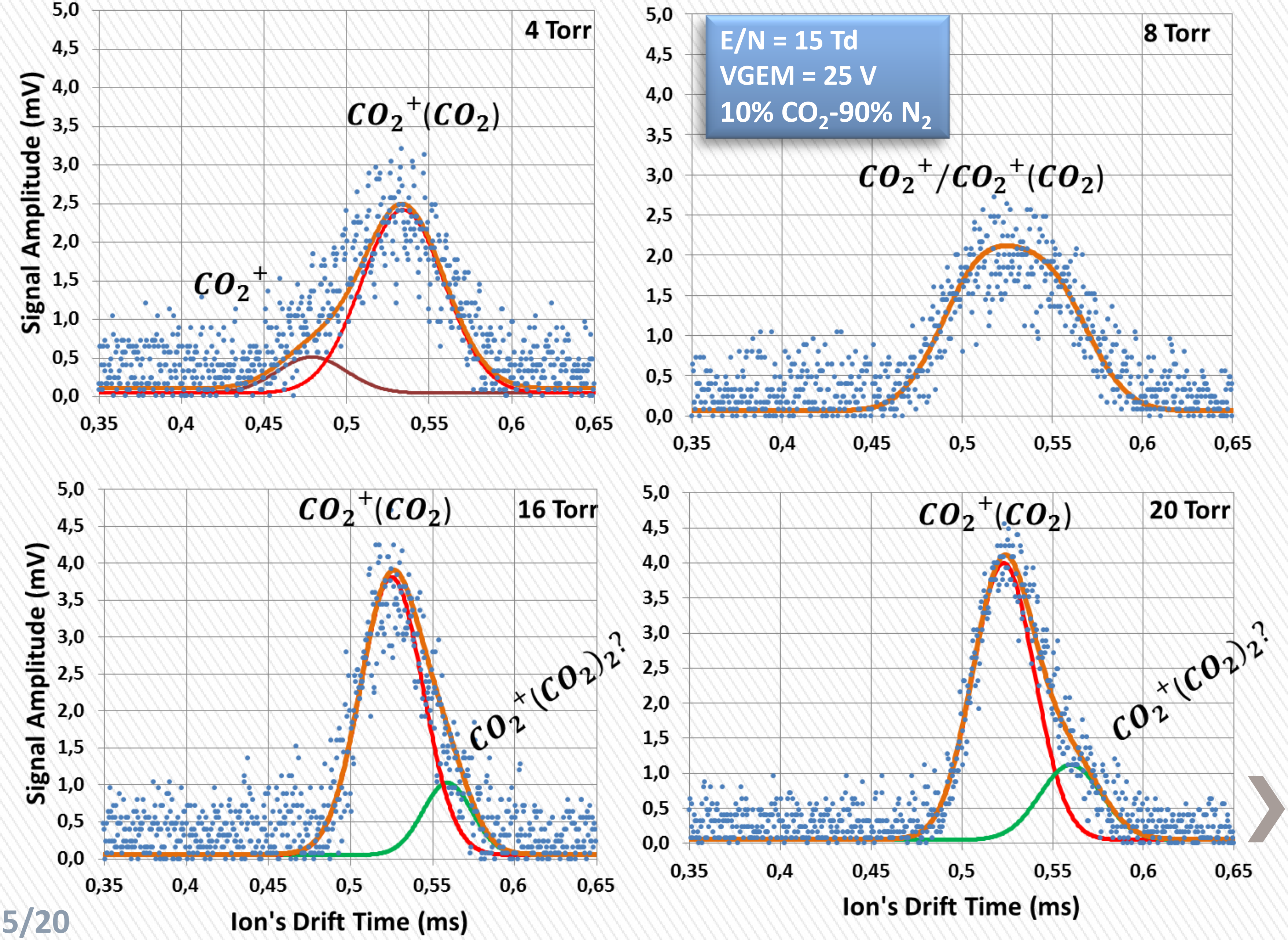
Experimental Results: CO_2-N_2





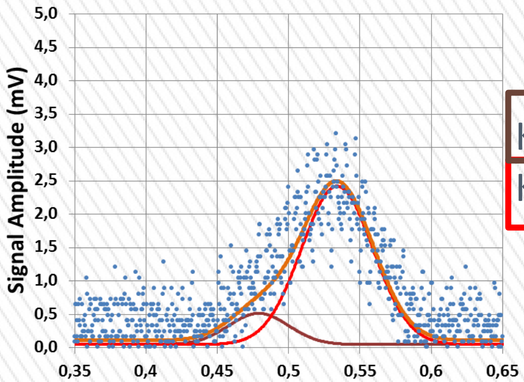
Can it be caused by CO_2 ??

Experimental Results: CO_2-N_2



Ion mobility of CO_2^+, $CO_2^+.(CO_2)$ and $CO_2^+.(CO_2)_2$

Study for 90% N_2/10% CO_2



Exp. Values

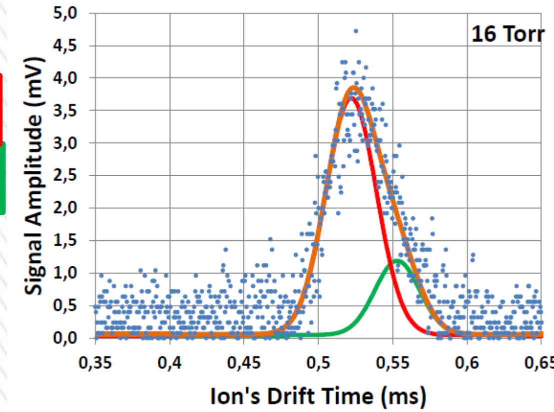
K_{01} = 2,11 $cm^2.V^{-1}.s^{-1}$

K_{02} = 1,90 $cm^2.V^{-1}.s^{-1}$

Exp. Values

K_{01} = 1,95 $cm^2.V^{-1}.s^{-1}$

K_{02} = 1,85 $cm^2.V^{-1}.s^{-1}$

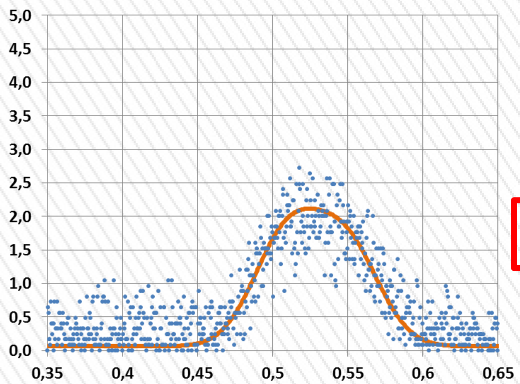


Blanc's law

$K_{01(CO2+)}$ = 2,26 $cm^2.V^{-1}.s^{-1}$

$K_{02(CO2+.CO2)}$ = 1,81 $cm^2.V^{-1}.s^{-1}$

$K_{02(CO2+.(CO2)2)}$ = 1,72 $cm^2.V^{-1}.s^{-1}$



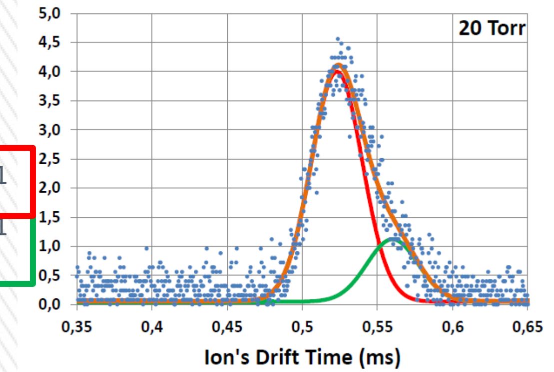
Exp. Values

K_{01} = 1,95 $cm^2.V^{-1}.s^{-1}$

Exp. Values

K_{01} = 1,94 $cm^2.V^{-1}.s^{-1}$

K_{02} = 1,84 $cm^2.V^{-1}.s^{-1}$



Three peaks were found

K_{01} = 2,11 $cm^2.V^{-1}.s^{-1}$

K_{02} = 1,95 $cm^2.V^{-1}.s^{-1}$

K_{03} = 1,84 $cm^2.V^{-1}.s^{-1}$

Ion mobility of CO_2^+, $CO_2^+.(CO_2)$ and $CO_2^+.(CO_2)_2$

Study for 90% $N_2/10\%\ CO_2$

Ions originated via N_2

1) N_2^+ charge transfer to CO_2

$k = 8{,}0 \times 10^{-10}\ cm^3 s^{-1}$

$$N_2^+ + CO_2 = N_2 + CO_2^+ \Rightarrow \frac{d[CO_2^+]}{dt} = k[N_2^+][CO_2] \Rightarrow t = \frac{1}{k[CO_2]}$$

2) N_4^+ formation

$k = 5{,}0 \times 10^{-29}\ cm^6 s^{-1}$

$$N_2^+ + 2N_2 = N_4^+ + N_2 \Rightarrow \frac{d[N_4^+]}{dt} = k[N_2^+]][CO_2]^2 \Rightarrow t = \frac{1}{k[N_2]^2}$$

Ions originated via CO_2

3) CO_2^+ Resonant charge transfer

$k = 3{,}7 \times 10^{-10}\ cm^3 s^{-1}$

$$CO_2^+ + CO_2 = CO_2 + CO_2^+ \Rightarrow \frac{d[CO_2^+]}{dt} = k[CO_2^+][CO_2] \Rightarrow t = \frac{1}{k[CO_2]}$$

4) Cluster formation

$k = 2{,}1 \times 10^{-28}\ cm^6 s^{-1}$

$$CO_2^+ + CO_2 + M = CO_2^+.CO_2 + M \Rightarrow \frac{d[CO_2^+.CO_2]}{dt} = k[CO_2^+][CO_2][N_2] \Rightarrow t = \frac{1}{k[CO_2][N_2]}$$

Ion mobility of CO_2^+, $CO_2^+.(CO_2)$ and $CO_2^+.(CO_2)_2$

Study for 90% $N_2/10\%$ CO_2

Reaction 1) N_2^+ charge transfer to CO_2

$N_2^+ + CO_2 = N_2 + CO_2^+$

Reaction 2) N_4^+ formation

$N_2^+ + 2N_2 = N_4^+ + N_2$

Reaction 3) CO_2^+ Resonant charge transfer

$CO_2^+ + CO_2 = CO_2 + CO_2^+$

Reaction 4) Cluster formation

$CO_2^+ + CO_2 + M = CO_2^+.CO_2 + M$

$K_{01"CO2+"} = 2{,}02\ cm^2.V^{-1}.s^{-1}$

$K_{02"CO2+.CO2"} = 1{,}94\ cm^2.V^{-1}.s^{-1}$

$K_{03"CO2+.(CO2)2"} = 1{,}84\ cm^2.V^{-1}.s^{-1}$

May give a clue on the origin of the bump!

Originated by N_2 | **Originated by CO_2**

Reaction time (us)	Reaction 1) Main Ion CO_2^+	Reaction 2) Main Ion N_4^+	Reaction 3) Main Ion CO_2^+	Reaction 4) Main Ion $CO_2^+.CO_2$
4 Torr	0,913	13,2	0,191	30,0
8 Torr	0,457	3,30	0,095	7,06
16 Torr	0,228	0,824	0,048	1,77
20 Torr	0,183	0,527	0,038	1,13

Present Status and Future Work

- Pursuit the investigation of the mobility of ions in different gas mixtures of practical use (if you have any suggestions feel free to contact us).
  - In the scope of the RD51 common project submitted with GSI (Germany), Uludag Univ. (Turkey) and VECC (India).

    Ar-CO_2 (was concluded and a paper published)
    Ne-CO_2 / CO_2-N_2 (to be published)
    Ne-N_2
    Ne-CO_2-N_2 (only prelimary results)
    Ar-CF_4
    Ne-CF_4

- Optimization of the detector:
  Variable Drift Distance (Already started -redesigning)
  Higher Pressure
  →
  - Rate constant influence
  - Study lighter ions (H_2)
  - Water influence on the ion's mobility
  - (...)

- Study of improved ion-neutral interaction models

- A special thank to FCT-Fundação para a Ciência e Tecnologia for supporting this work through the National funds in the frame of the Project QREN n.4825, Rad for Life

and to

- CERN/RD51 Collaboration – Common Projects - ‘Measurement and calculation of ion mobility of some gas mixtures of interest’. Participating institutions:

GSI (Germany)
Laboratory of Instrumentation and Experimental Particle Physics – LIP-Coimbra (Portugal)
Üludag University (Turkey) and VECC (India)

Thank you!

Universidade de Coimbra

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

Candidate ions identification

GEM Voltage

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

Rg (pure)

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

Reaction Time

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

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

- Identification the possible ions present.

Possible Reactions

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

Universal decay law

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

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

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

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

- Identification the possible ions present.

Select Most Probable Ions

Ion mobility results comparison