and...

Cluster Ions

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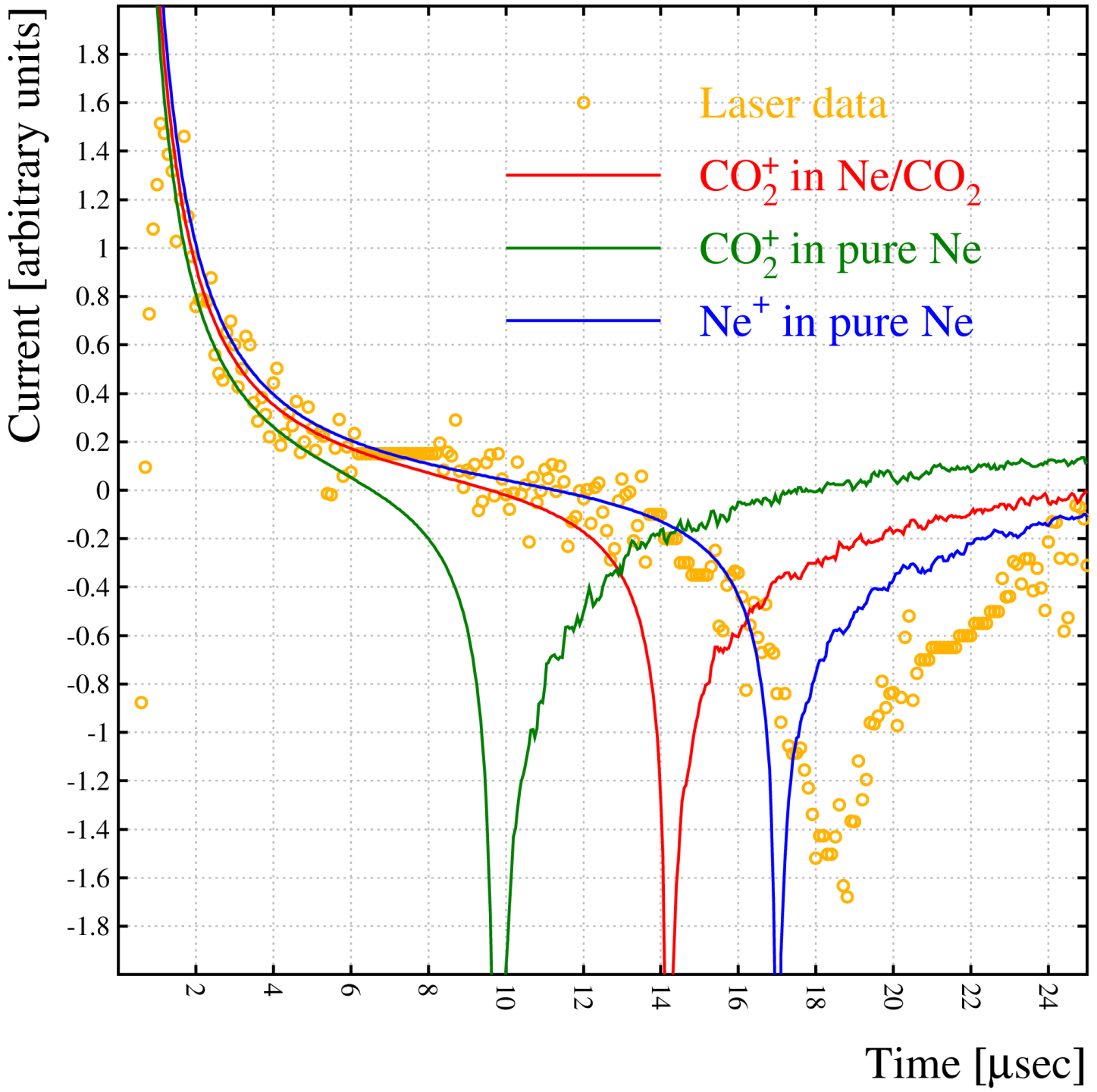
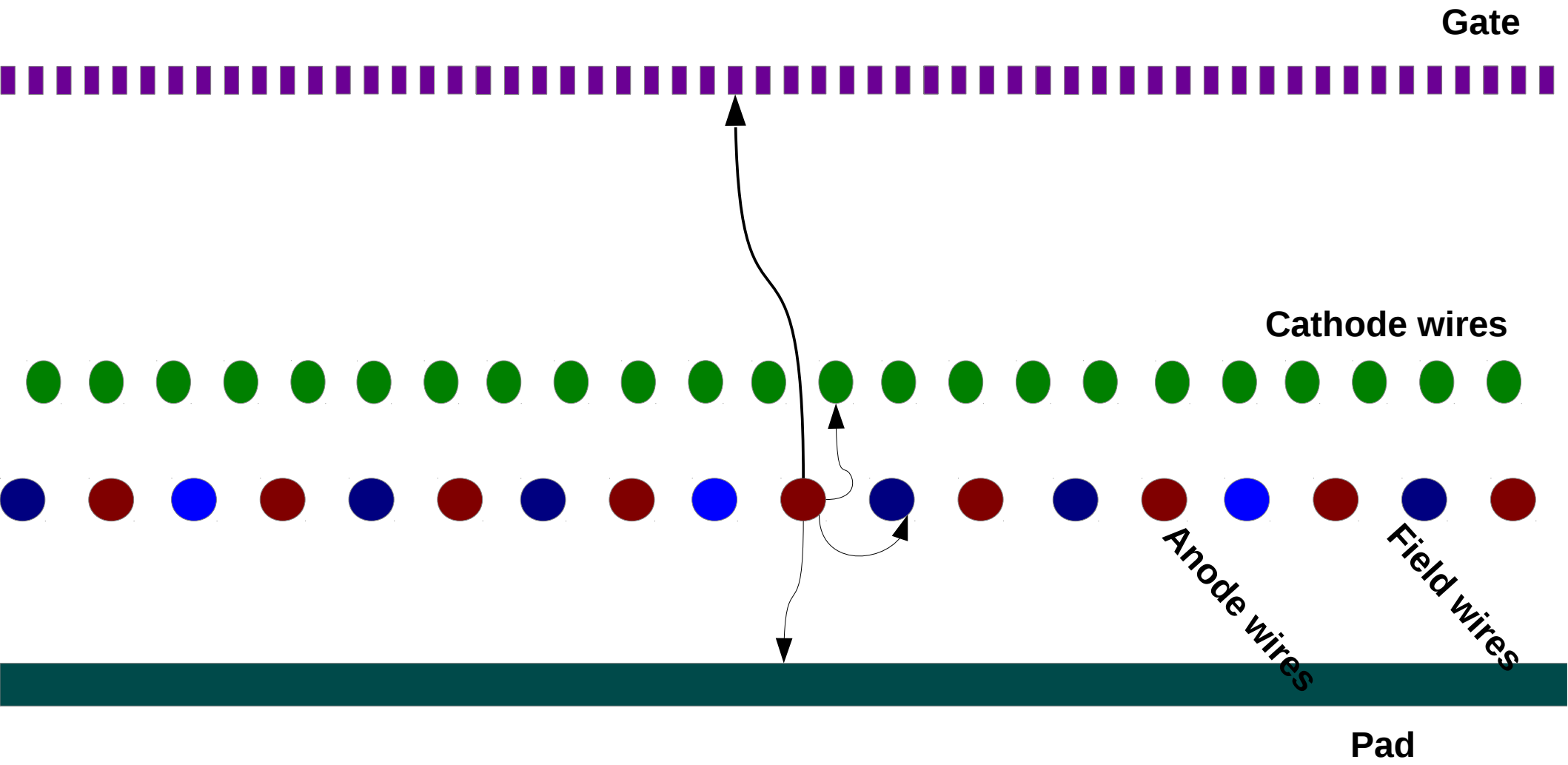
15th RD51 Collaboration Meeting, CERN, (16-20 March 2015)


Current [arbitrary units]
Time [μsec]
Laser data
CO_2^+ in Ne/CO_2
CO_2^+ in pure Ne
Ne^+ in pure Ne
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
2
4
6
8
10
12
14
16
18
20
22
24

TPC



How fast the Reactions ?

Atmospheric pressure and 10 % mixture

Ar^+ Reactions

$$Ar^+ + CO_2 \rightarrow Ar + CO_2^+ \qquad (k = 4.80 \pm 0.72\ 10^{-10}\ cm^3/s) \qquad \sim 0.85\ ns$$

$$Ar^+ + Ar + M \rightarrow Ar^+ \cdot Ar + M \qquad (k = 2.3 \pm 0.2\ 10^{-31}\ cm^6/s) \qquad \sim 8.9 \pm 0.8\ ns.$$

(Rate Cons. from Vincent G. Anicich (1993) and John Hornbeck (1951)

Ne^+ Reactions

$$Ne^+ + CO_2 \rightarrow CO^+ + O + Ne \qquad (k = 0.500 \pm 0.050\ 10^{-10}\ cm^3/s) \qquad \sim 8\ ns$$

$$CO^+ + CO_2 \rightarrow CO_2^+ + CO \qquad (k = 10.16 \pm 0.77\ 10^{-10}\ cm^3/s)$$

(Rate Cons. from V.G. Anicich and W.T. Huntress, Jr.(1986) and Boris M. Smirnov, (1992)

$$Ne^+ + Ne + M \rightarrow Ne^+ \cdot Ne + M \qquad (k = 0.6\ 10^{-31}\ cm^6/s)$$

(Rate Cons. from Boris M. Smirnov, (1992)

How fast the Reactions ?

CO_2^+ Reactions

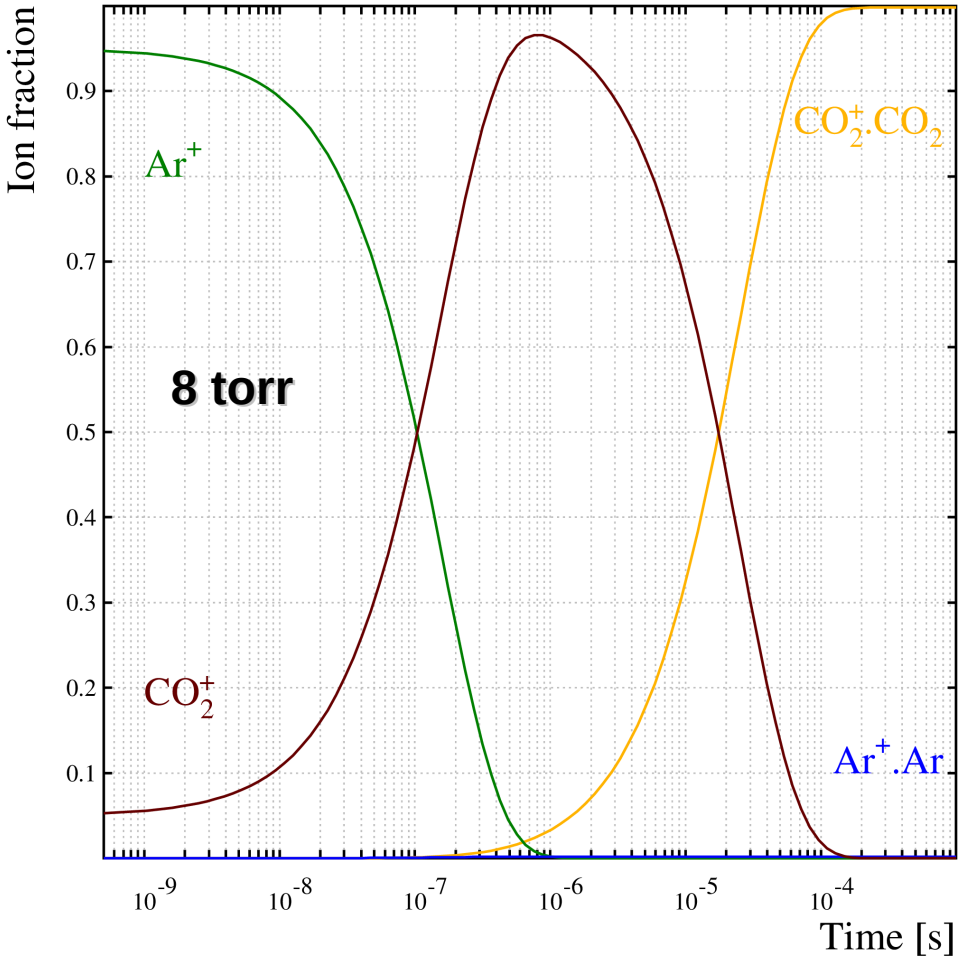
$$CO_2^+ + CO_2 + M \rightarrow CO_2^+ \cdot CO_2 + M \qquad (k = 2.4\ 10^{-28}\ cm^6/s) \qquad \sim 7 - 20\ ps$$

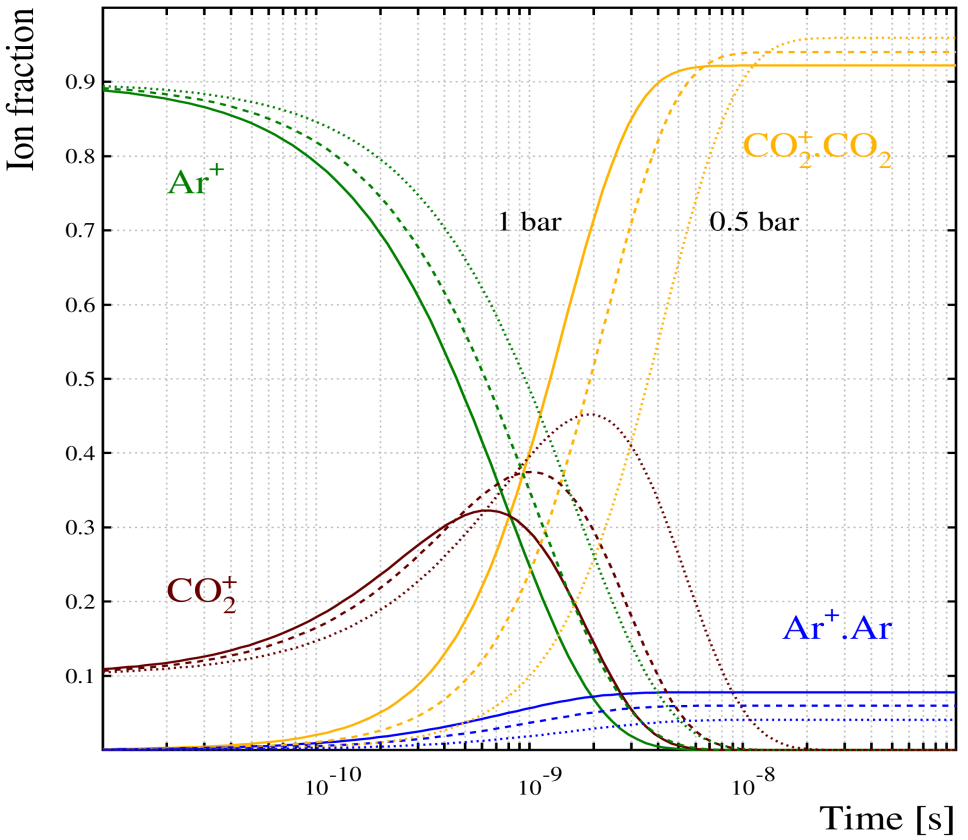
(Rate Cons. from Boris M. Smirnov, (1992)

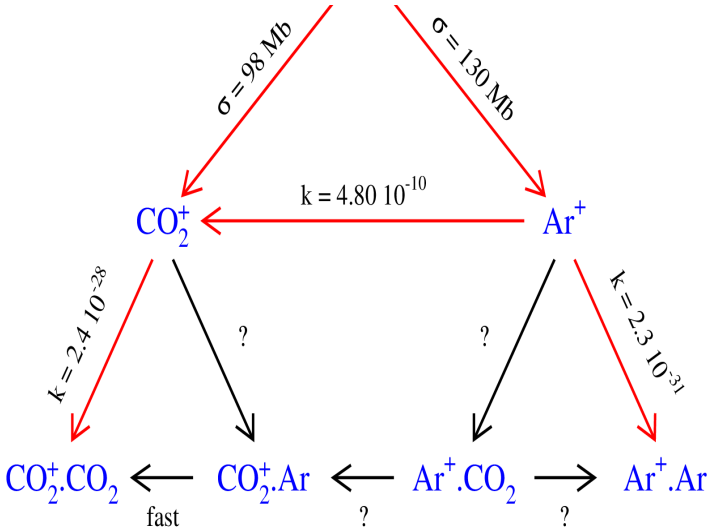
$$CO_2^+ + CO_2 \rightarrow CO_2 + CO_2^+ \qquad (k = 3.70 \pm 0.37\ 10^{-10}\ cm^3/s) \sim 110\ ps$$

Rate Cons. from Vincent G. Anicich (1993)

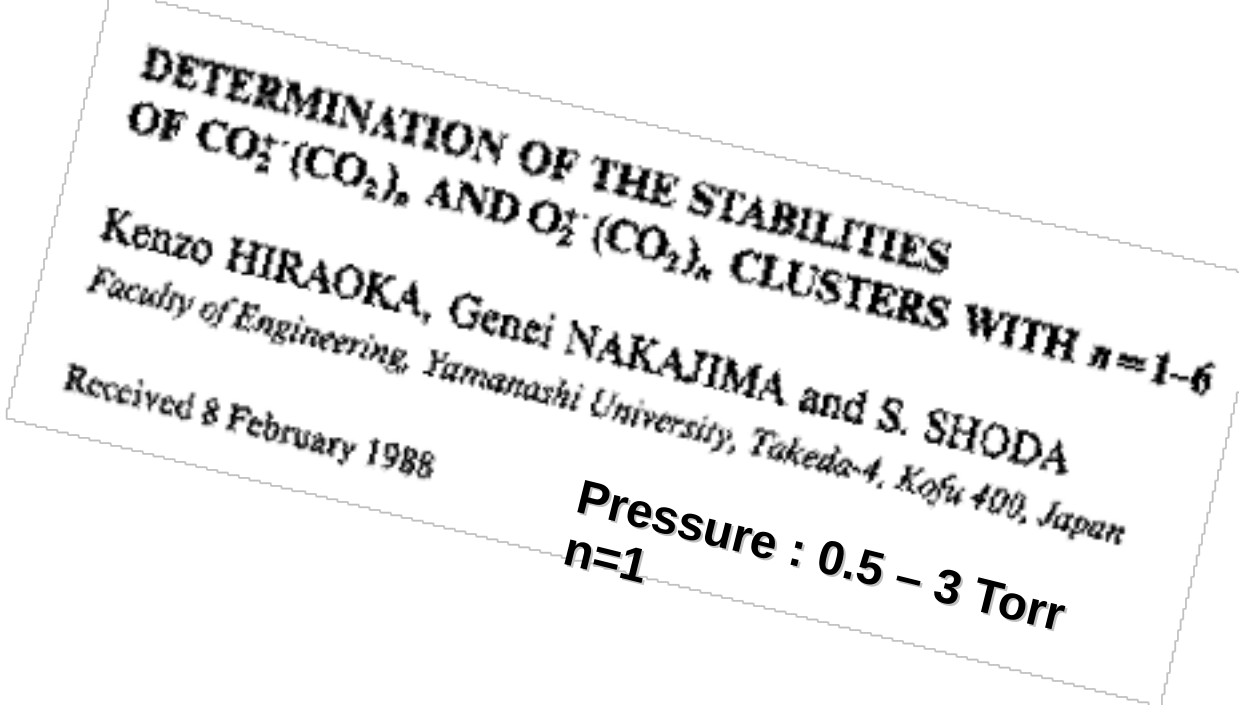
Clustering dynamics







Cluster size $CO_2^+ \cdot (CO_2)_n$



DETERMINATION OF THE STABILITIES OF $CO_2^+(CO_2)_n$ AND $O_2^-(CO_2)_n$ CLUSTERS WITH $n = 1$–6

Kenzo HIRAOKA, Genei NAKAJIMA and S. SHODA

Faculty of Engineering, Yamanashi University, Takeda-4, Kofu 400, Japan

Received 8 February 1988

Pressure : 0.5 – 3 Torr
n=1

Andreas J. Illies(1988)

The Cluster does not grow further at 300 K and low pressure (70 - 400 Pa).

H.W. Ellis et al. (1976)

n = 2-8 ($HCO^+.CO_2$)

At atmospheric pressure

Andreas J. Illies(1989)

n ≈ 4.3 (on 18 molecules)
~ Atmospheric pressure

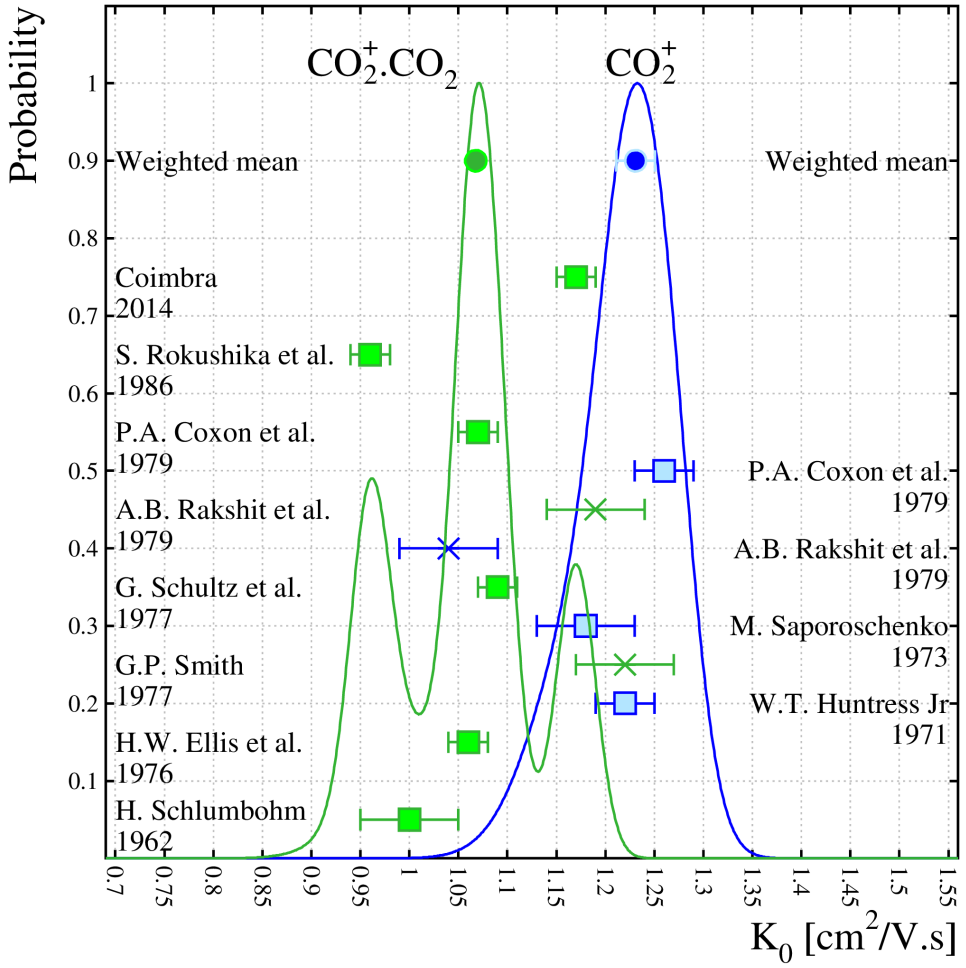
Y. Ikezoe et al. (1982)
N= 0-4
At low and atmospheric pressure

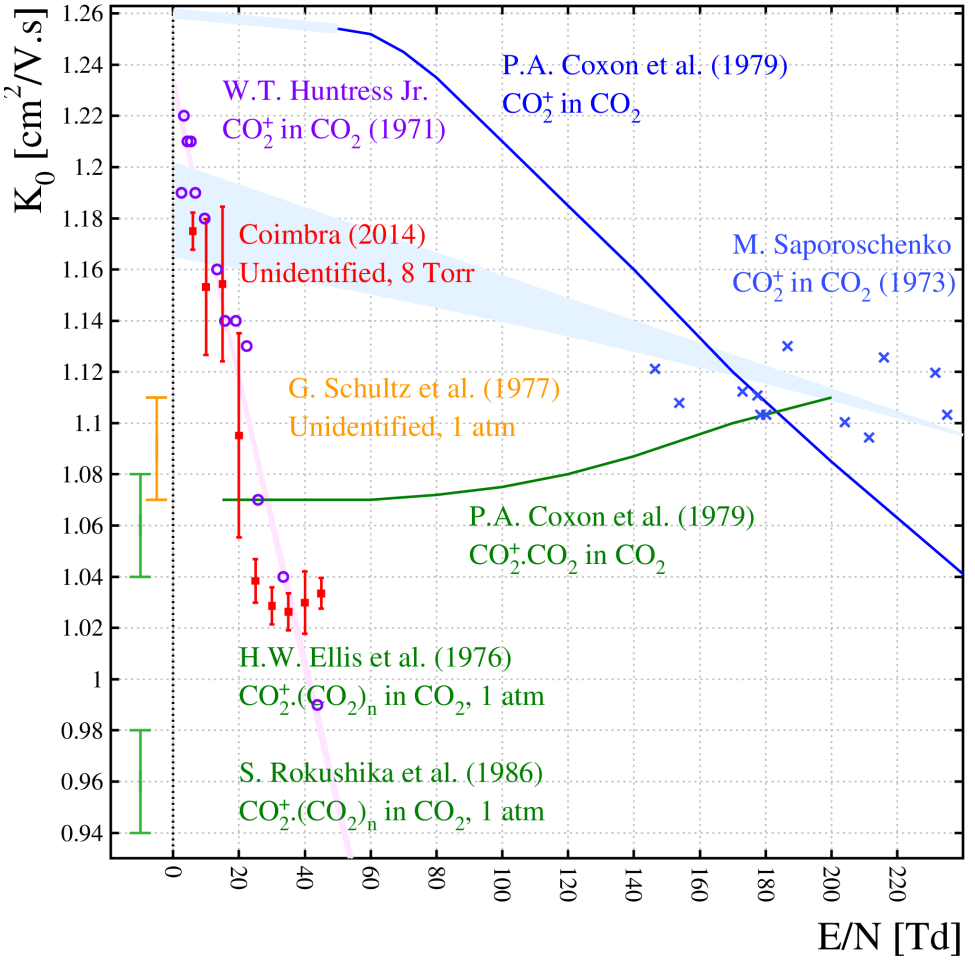
After a few microseconds there will be only :

*** CO_2CO2 Clusters**
*** Ar Dimers**
*** Ne Dimers**

We will estimate the mobilities of this object !

Mobilitiy of CO_2 and CO_2 clusters





CO_2^+ in CO_2

- **Clusters**
- $1.26 \pm 0.05\ \mathrm{cm}^2/\mathrm{V.s}$ at $p = 3.5$ - 13 Pa

P.A. Coxon and J.L. Moruzzi (1979)

Conflicting data S =2.2

$CO_2^+ \cdot (CO_2)_n$ in CO_2

1.07Â±0.04% cm2/V.s

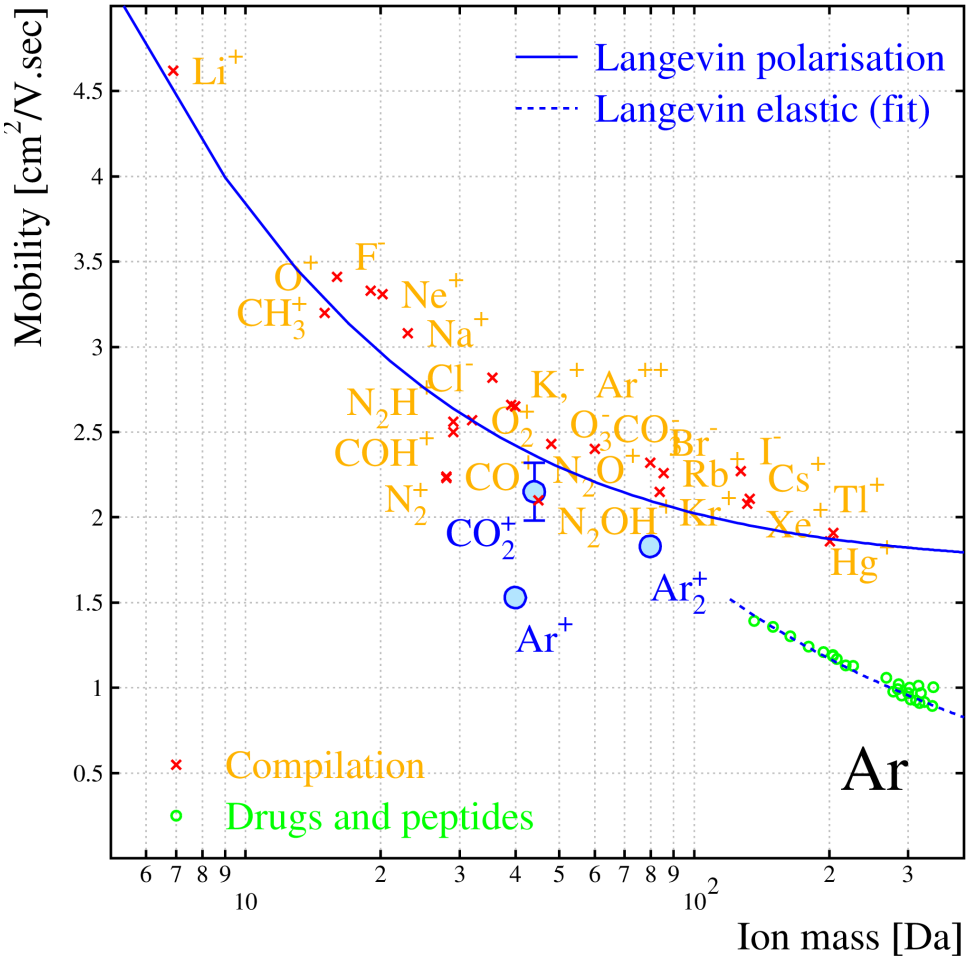
at 53-67 Pa

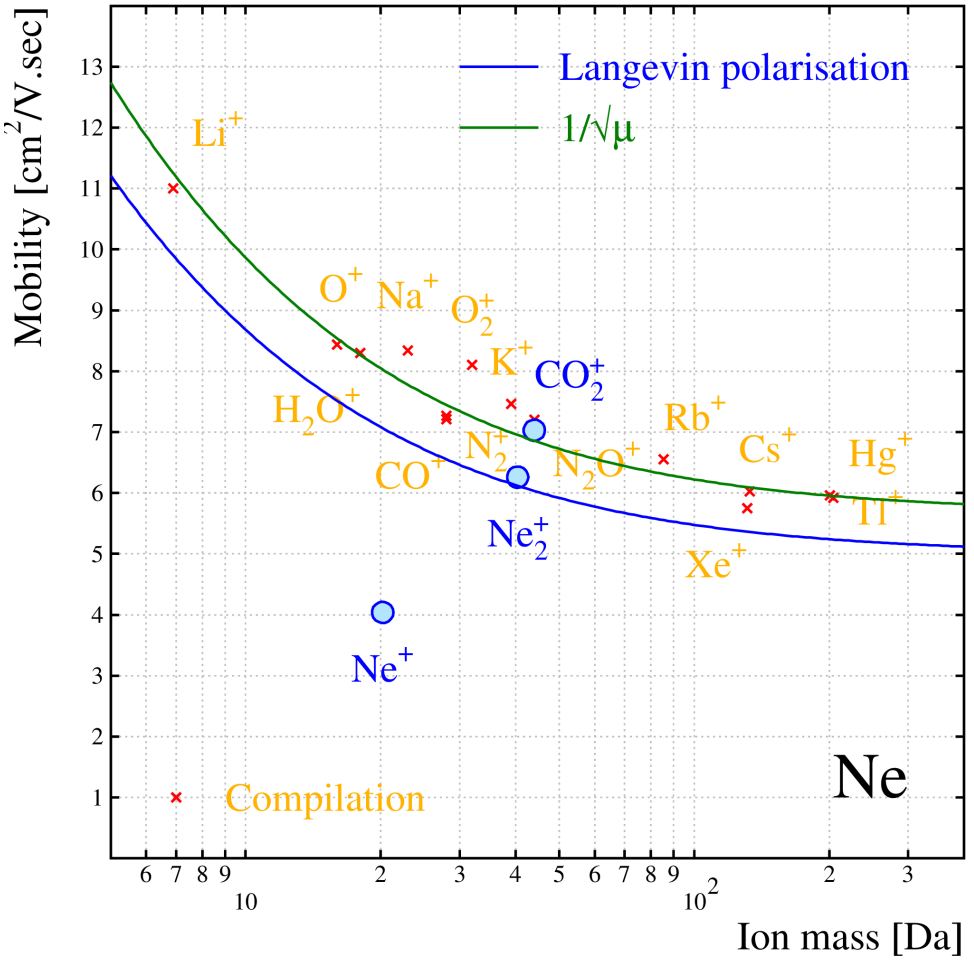
P.A. Coxon and J.L. Moruzzi (1979)

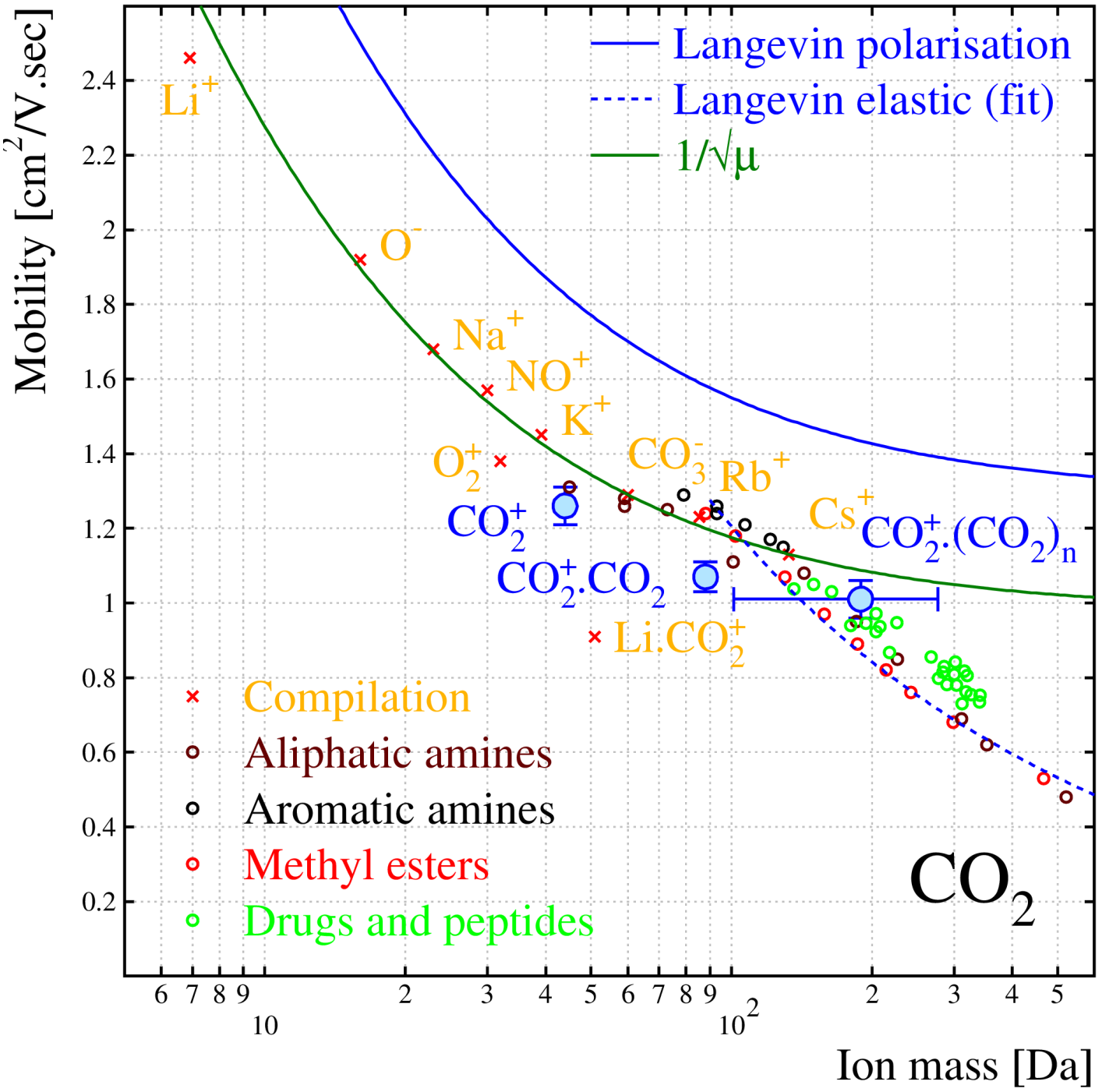
Compatible data S = 1.3

$CO_2^+ \cdot (CO_2)_n$ in Ar - Ne

No data


Mobility [cm²/V.sec]
Ion mass [Da]
Langevin polarisation
Langevin elastic (fit)
Compilation
Drugs and peptides
Ar
Li+
O+
F-
CH3+
Ne+
Na+
Cl-
K+
Ar++
N2H+
O2+
O3-
CO3-
COH+
Br-
I-
CO2+
N2+
N2O+
Rb+
Cs+
Tl+
N2OH+
Kr+
Xe+
Hg+
Ar2+
Ar+


Mobility [cm²/V.sec]
Ion mass [Da]
Langevin polarisation
1/√μ
Compilation
Ne
Li+
O+
Na+
O2+
K+
CO2+
H2O+
Rb+
N2+
N2O+
CO+
Cs+
Hg+
Tl+
Ne2+
Xe+
Ne+


Mobility [cm²/V.sec]
Ion mass [Da]
Langevin polarisation
Langevin elastic (fit)
1/√μ
Li+
O-
Na+
NO+
K+
O2+
CO3-
Rb+
Cs+
CO2+
CO2+.(CO2)n
CO2+.CO2
Li.CO2+
Compilation
Aliphatic amines
Aromatic amines
Methyl esters
Drugs and peptides
CO2

Data sources

NA49 TPC data from Rainer Renfordt (transit time between anode and field wire).

ALICE TPC data from Chilo, Marian, Christian Lippmann and Mesut (transit time between anode and cathode wire).

Coimbra data from Pedro Encarnação and André F.V. Cortez (20 Td uniform field between GEM and mesh, at 8 torr).

P.M.C.C. Encarnação et al., Experimental Ion Mobility measurements in Ar-CO_2 mixtures, Journal of Instrumentation 10 (2015) P01010 (20 Td uniform field between GEM and mesh, at 8 torr).

G. Schultz et al., Mobilities of positive ions in some gas mixtures used in proportional and drift chambers, Revue de Physique Appliquée (Paris) 12 (1977) 67–70 ($E/N \leq 20$ Td field between 2 wire meshes, at 1 atm).

Blanc's law : mobility in mixture

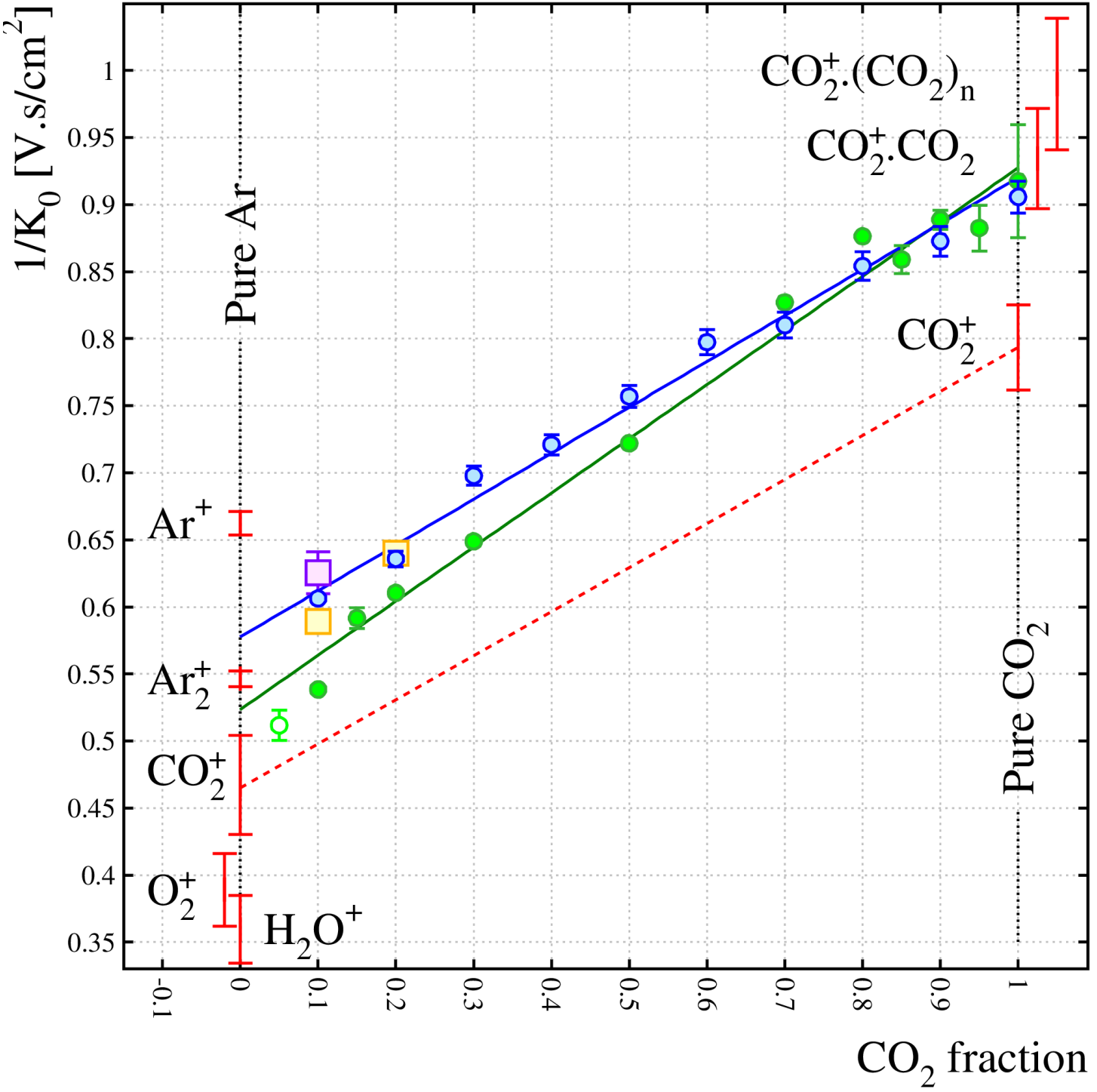
$$\frac{1}{K^0_{\text{mix}}} = \frac{f_1}{K^0_1} + \frac{f_2}{K^0_2}$$

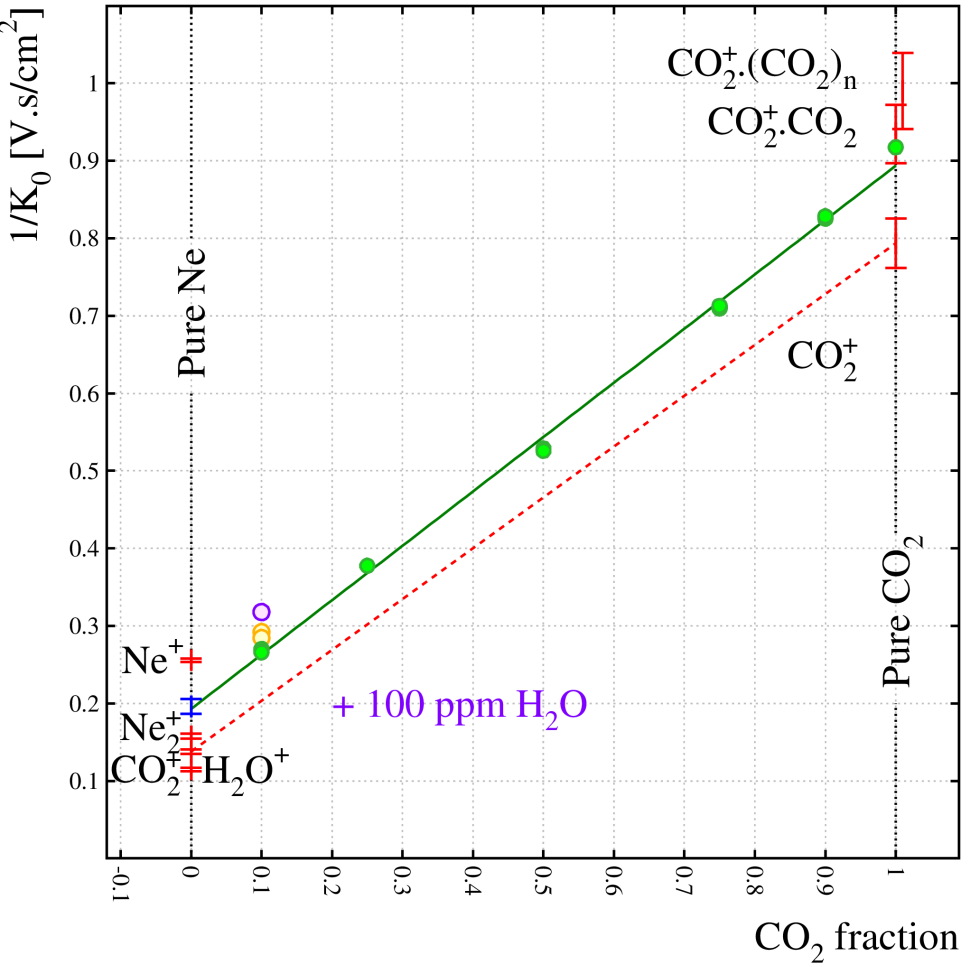
K^0: reduced mobility

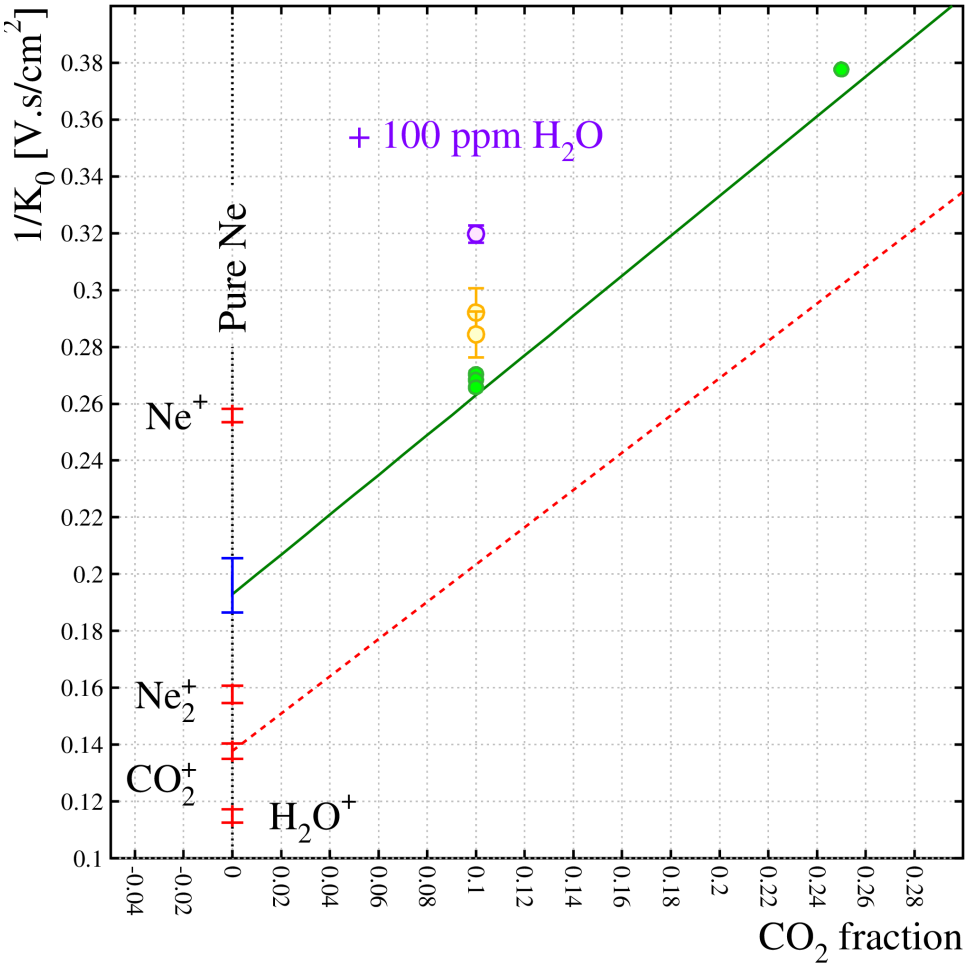
f_1 and f_2: molar fractions

if the component gases react between them : FAIL

If there is clustering in the gas : mobility will change


1/K0 [V.s/cm2]
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
Pure Ar
Pure CO2
CO2+.(CO2)n
CO2+.CO2
CO2+
Ar+
Ar2+
CO2+
O2+
H2O+
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
CO2 fraction


1/K0 [V.s/cm2]
Pure Ne
Pure CO2
CO2+.(CO2)n
CO2+.CO2
CO2+
Ne+
Ne2+
CO2+
H2O+
+ 100 ppm H2O
CO2 fraction


1/K0 [V.s/cm2]
Pure Ne
+ 100 ppm H2O
Ne+
Ne2+
CO2+
H2O+
CO2 fraction

Conclusions

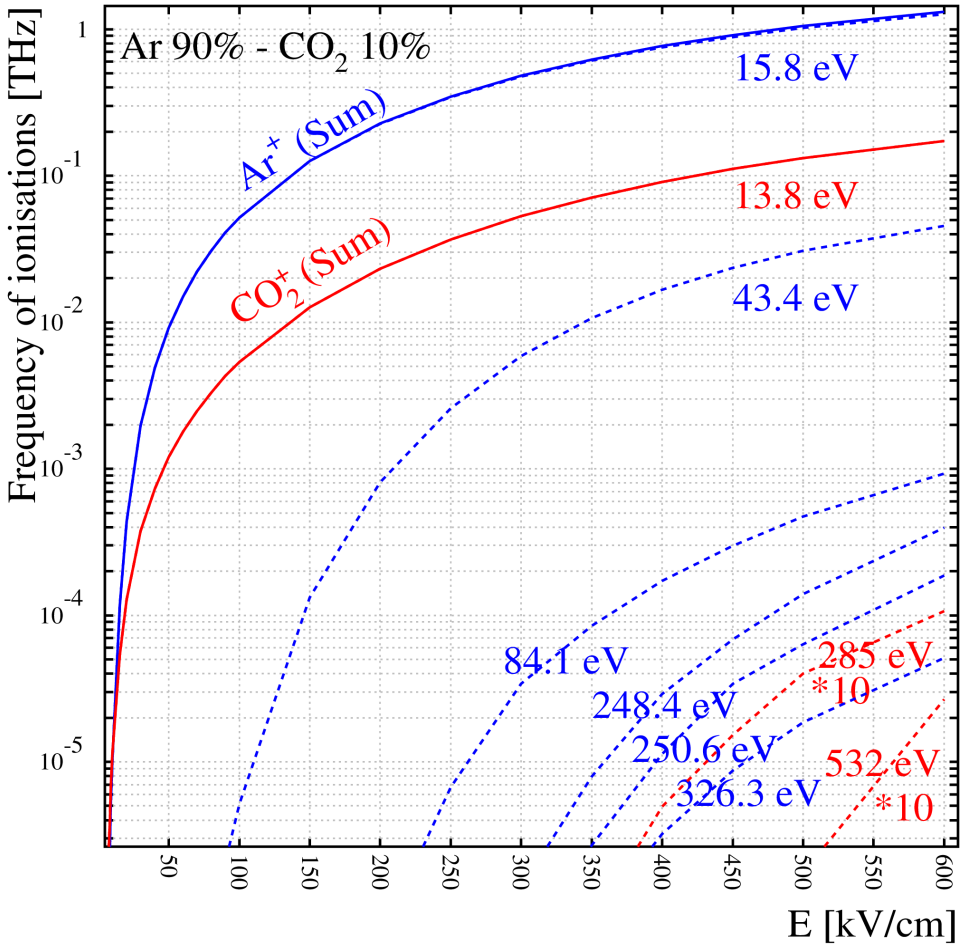
The signal ions are just $CO_2.(CO_2)$ clusters, they are not CO^+_2 or noble gas ions.

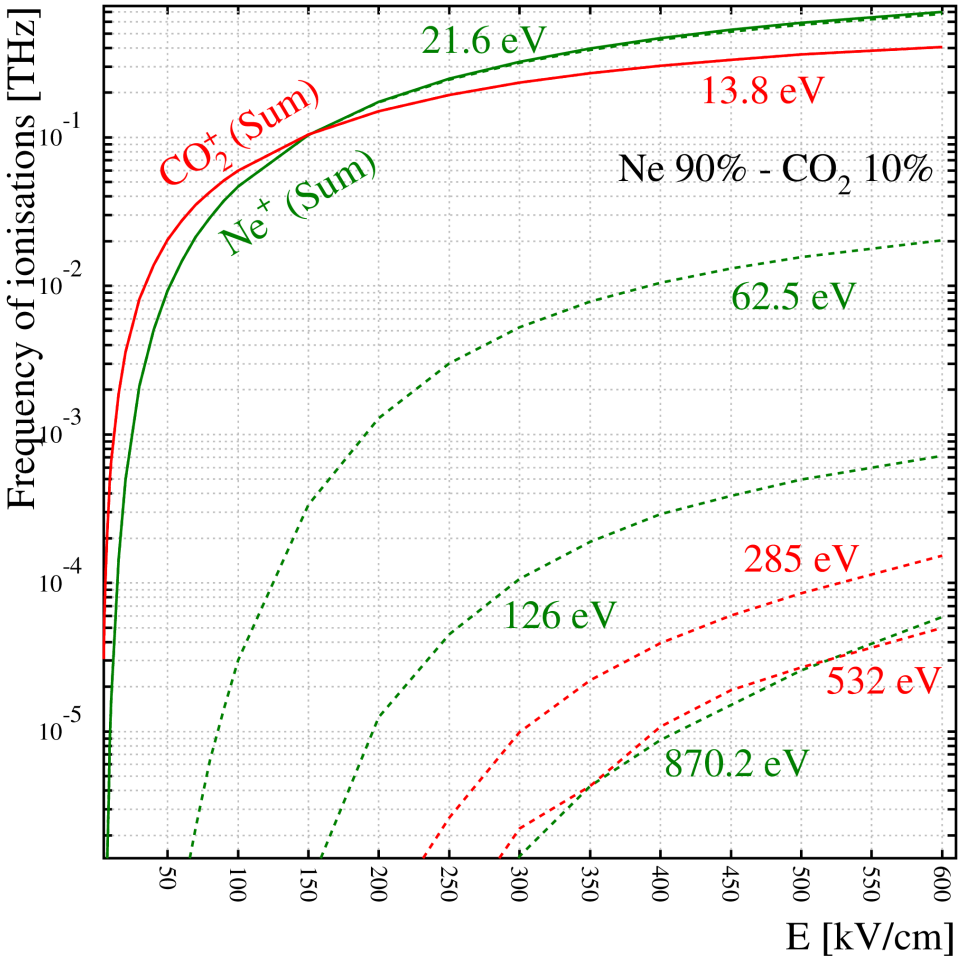
It is experimentally confirmed by the literature.

Cluster ions are heavier and slower than CO^+_2 ions.

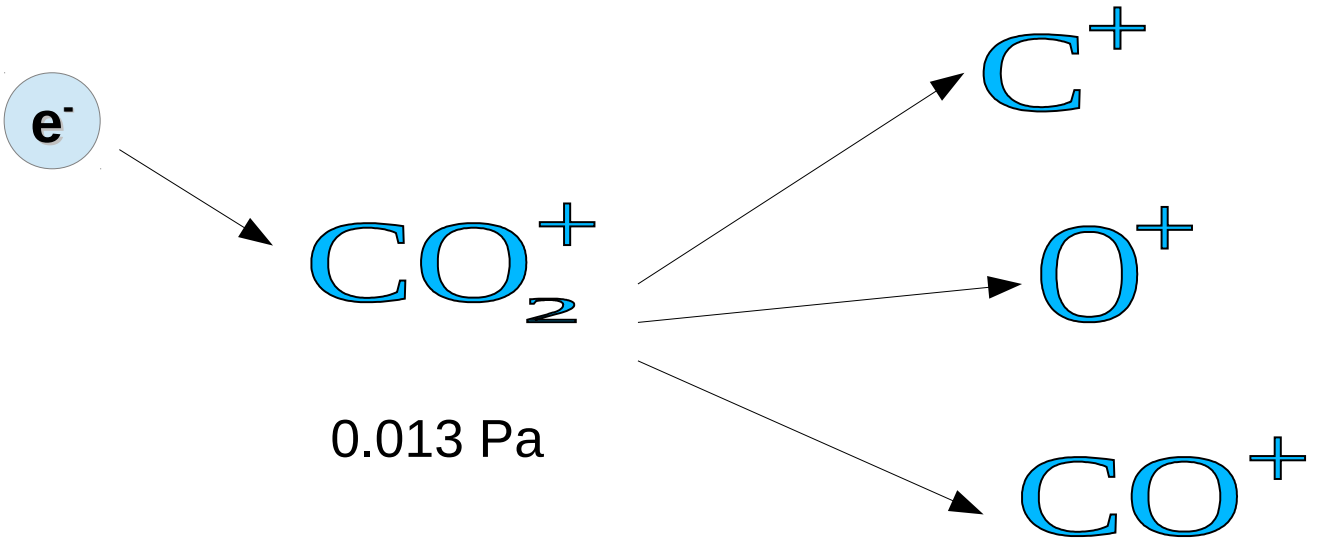
Mass spectrometry unavoidable !

Ionisation rates





Plots prepared by Özkan Şahin by using Magboltz 10.6



$$O^+ + CO_2 \rightarrow O_2^+ + CO \qquad (k = 1.03 \pm 0.10\ 10^{-9}\ cm^3/s)$$

$$O_2^+ + CO_2 + M \rightarrow O_2^+ \cdot CO_2 + M \qquad (k = 0.5 \pm 0.1\ 10^{-30}\ cm^6/s)$$

~300 ns

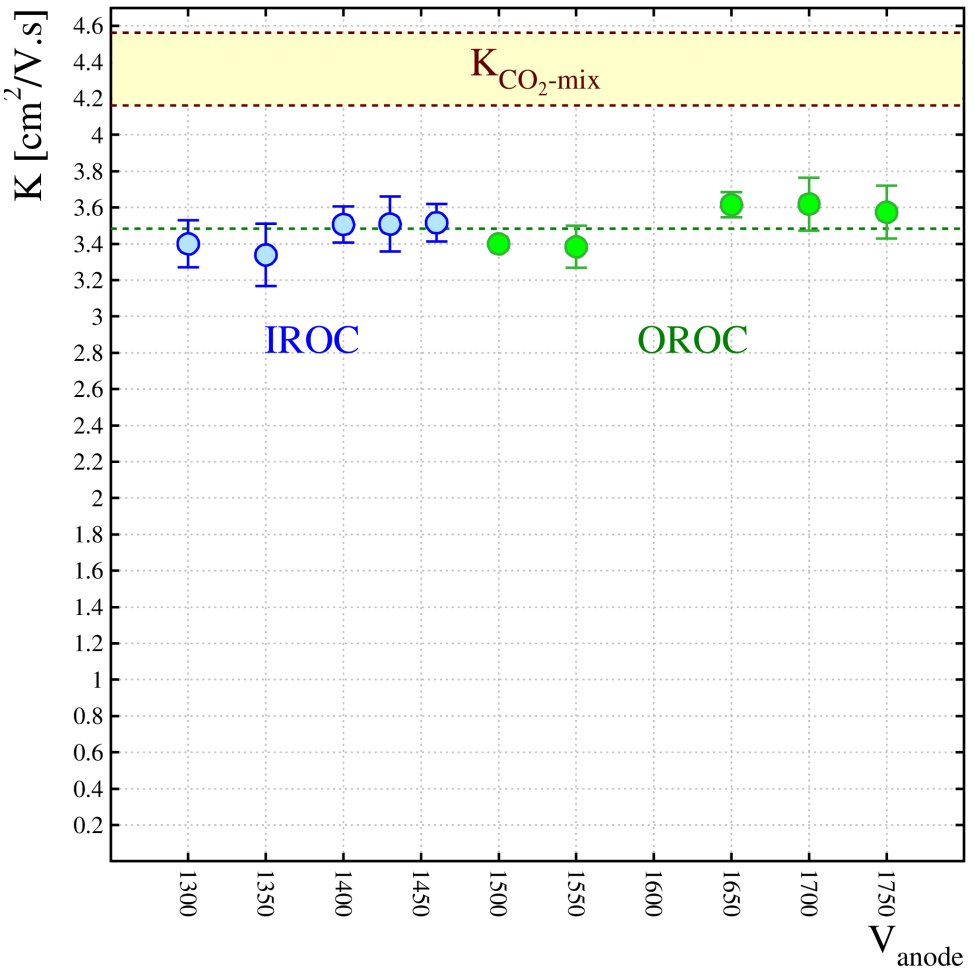
$$C^+ + CO_2 \rightarrow CO^+ + CO \qquad (k = 1.120 \pm 0.078\ 10^{-9}\ cm^3/s)$$

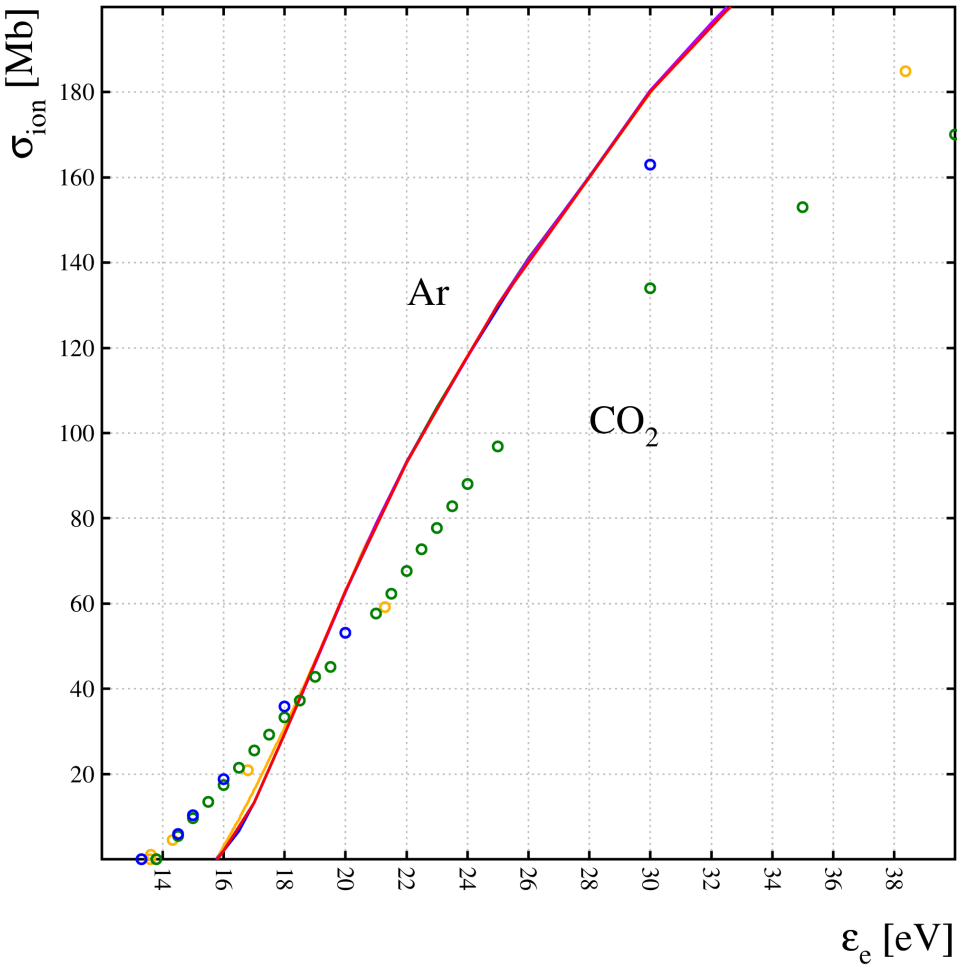
$$CO^+ + CO_2 \rightarrow CO_2^+ + CO \qquad (k = 1.020 \pm 0.075\ 10^{-9}\ cm^3/s)$$

~370 ps

(Rate Cons. from V.G. Anicich and W.T. Huntress,(1986) and Boris M. Smirnov, (1992)

TPC measurements




σion [Mb]
180
160
140
120
100
80
60
40
20
Ar
CO2
14
16
18
20
22
24
26
28
30
32
34
36
38
εe [eV]