

Ion transport

Simulating ion motion

- ▶ Lines found in most Garfield++ avalanche programs:

```
// Load the ion mobilities.
```

```
gas->LoadIonMobility("/afs/cern.ch/user/r/rjd/GemGain/Charge/mob_Ar_Ar+");
```

- ▶ What do they do ?
- ▶ Why are they often inappropriate ?

The importance of 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.
- ▶ Hence we better know the basics of ions:
 - ▶ *which ions* are produced in the avalanche ?
 - ▶ *which ions* generate the signal ?
 - ▶ *how fast* do the ions move ?
 - ▶ are they subject to *diffusion* ?

Mobility

- ▶ The velocity with which ions move is usually expressed in the form of a mobility:

- ▶ v_D : drift velocity

$$v_D = K E$$

- ▶ K : mobility

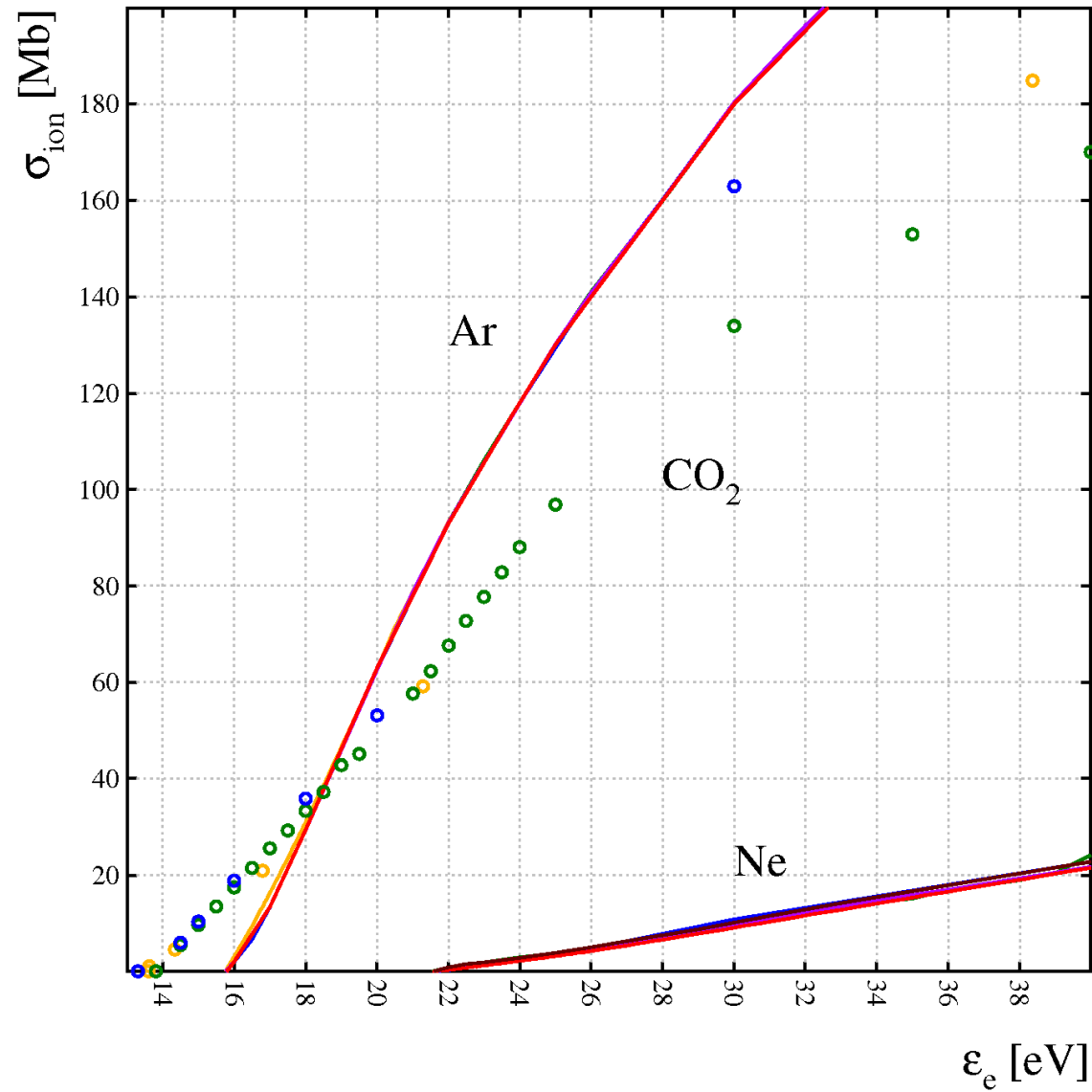
- ▶ E : electric field

- ▶ Reason: for moderate fields, the mobility is approximately constant.

Electron-impact cross sections

- ▶ CO_2^+ and Ar^+ compete.
- ▶ Ne^+ has higher threshold and is produced less.

[Pure gases, data from LXcat]



Avalanche products

▶ Ar^+ dominates in Ar-CO_2 ,

CO_2^+ and Ne^+ in Ne-CO_2

Title:arco2.eps

Creator:HIGZ Version 1.29/04

CreationDate:2014/12/18 03.08

CreationDate:2014/12/18 03.08

Title:neco2.eps

Creator:HIGZ Version 1.29/04

CreationDate:2014/12/18 04.04

CreationDate:2014/12/18 04.04

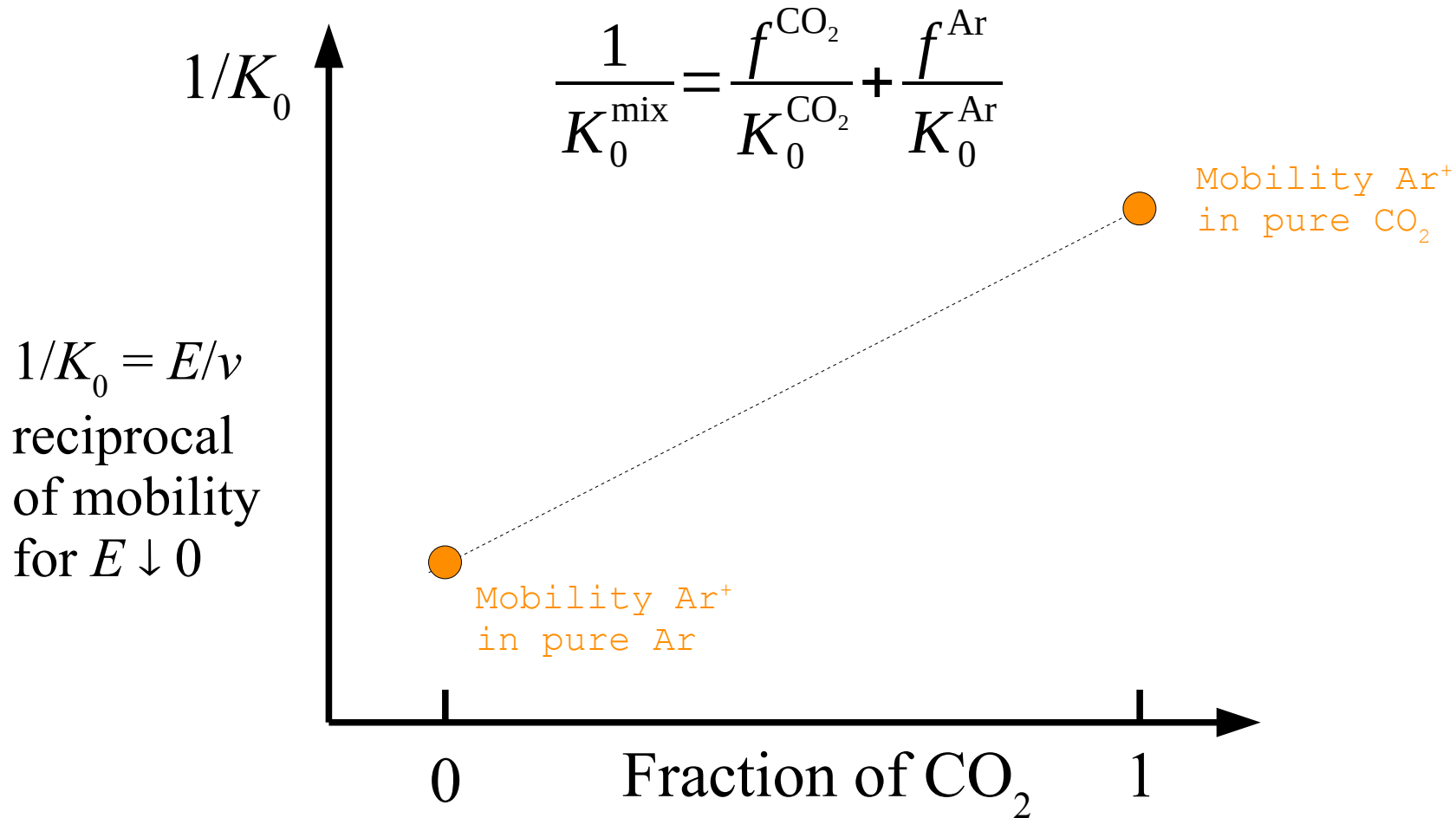
Avalanche products in Ar-CO₂

- ▶ This tells us that avalanches primarily produce Ar⁺ ions.
- ▶ Does this mean that the signals are generated by Ar⁺ ions ?
Maybe.
- ▶ If so, we need the **mobility of Ar⁺ in Ar-CO₂ mixtures.**
- ▶ This can in principle be calculated with Blanc's law.

Avalanche products in Ne-CO₂

- ▶ This tells us that avalanches produce mostly CO₂⁺ ions and a few Ne⁺ ions.
- ▶ Does this mean that the signals are generated by CO₂⁺ and Ne⁺ ions ? Maybe.
- ▶ If so, we need the **mobility of CO₂⁺ and Ne⁺ in Ne-CO₂ mixtures.**
- ▶ This can in principle be calculated with Blanc's law.

Blanc's mobility interpolation



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

Known & unknown mobilities

▶ Known mobilities:

- ▶ Ar^+ in Ar, Ne^+ in Ne,
- ▶ Ar_2^+ in Ar, Ne_2^+ in Ne,
- ▶ CO_2^+ in Ar, CO_2^+ in Ne.

▶ Not published:

- ▶ Ar^+ in CO_2 , Ne^+ in CO_2 .

why ?

▶ Published, but controversial:

- ▶ CO_2^+ in CO_2 .

can you guess why ?

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

► Noble gas ion mobilities are well known:

Title:

Creaf

CreationDate:2007/07/20 15.20

CreationDate:2007/07/20 15.20

Ar

CreationDate:2007/07/20 15.20

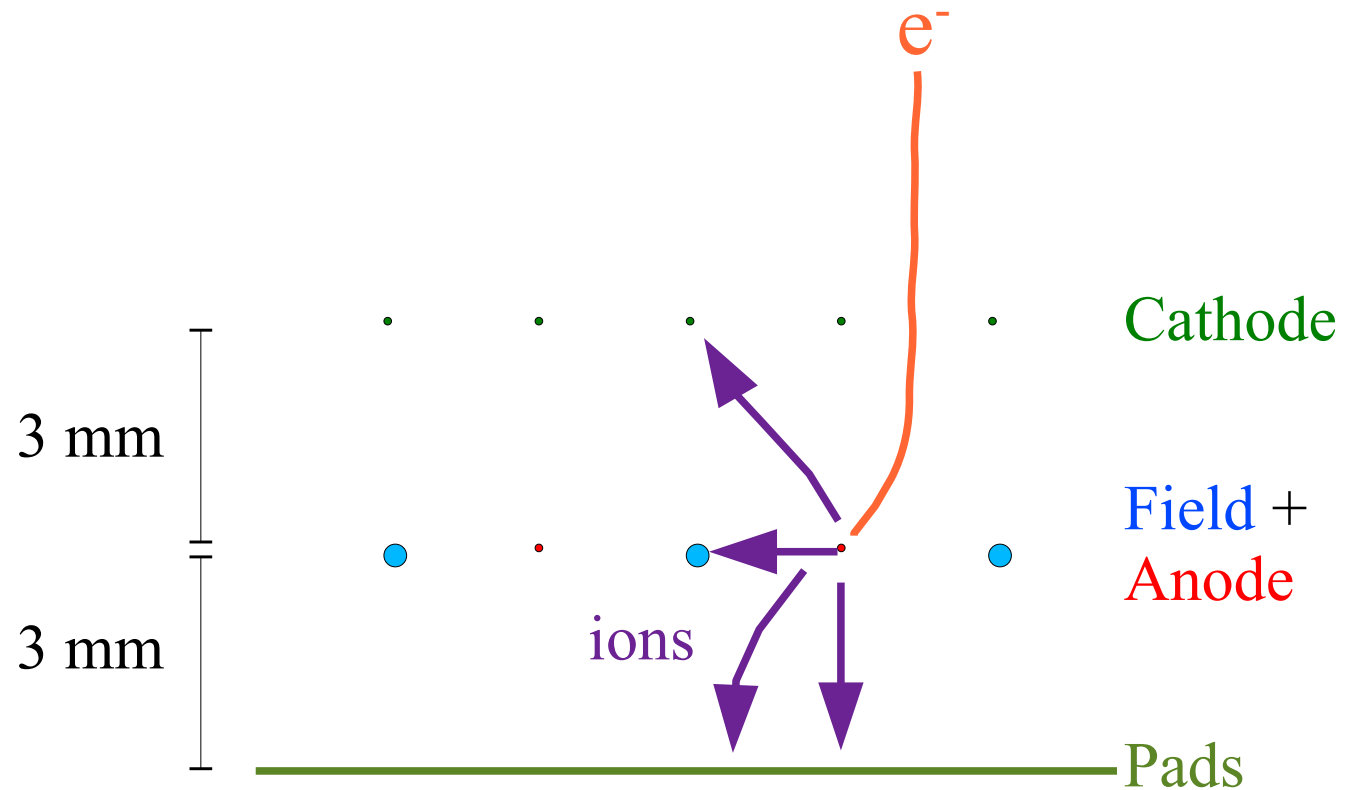
CreationDate:2007/07/20 15.20

Ne

HW Ellis *et al.*, At. data nucl.
data tables **17** (1976) 177-210
(compilation)

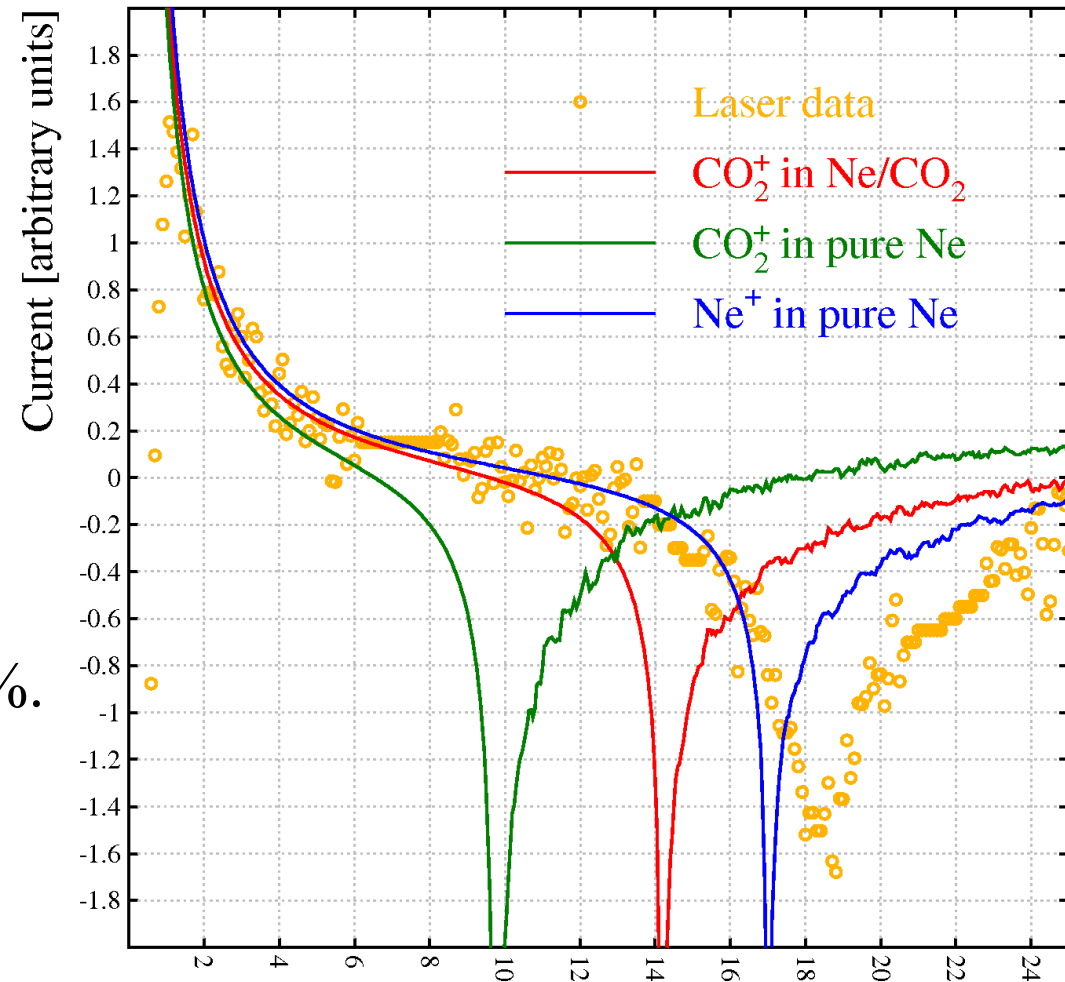
Ion induced signals

- ▶ Current induced on the pads of a TPC by ions moving from the anode wires to the pads and the field wires:



Signals in Ne-CO₂

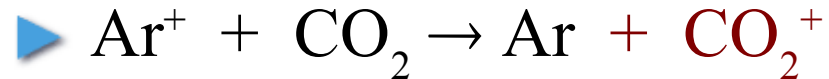
- ▶ Ne⁺ in Ne comes nearest to the measurements ...
- ▶ we've used it for years ...
- ▶ but does it make sense ?
- ▶ NA49 TPC: Ne 90 % CO₂ 10 %.
[Data: Rainer Renfordt]



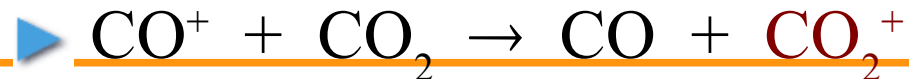
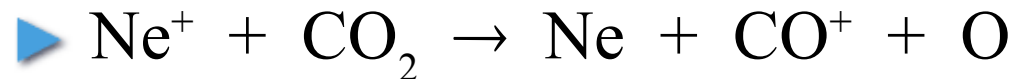
Time taken by an ion from anode wire to field wire [μs]

Principal reactions involving CO₂

▶ Ar⁺: charge exchange, $\tau \approx 0.85$ ns



▶ Ne⁺: charge transfer in 2-steps, $\tau \approx 8$ ns



▶ CO₂: 3-body association, 7-20 ps



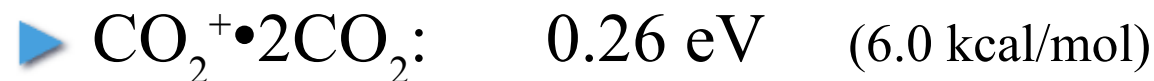
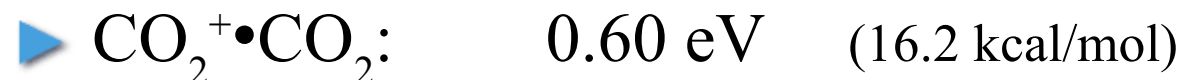
Situating cluster ions

- ▶ 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

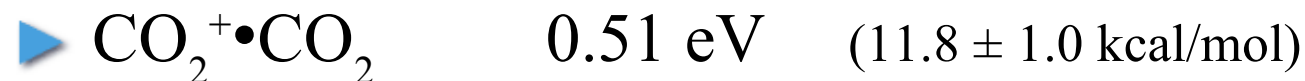
[B.M. Smirnov, "Cluster Ions and Van Der Waals Molecules," CRC press]

Binding energy of CO₂ cluster ions

▶ Binding energy:



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



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

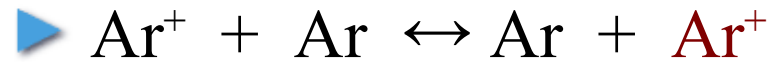
(Conversion: 1 kcal/mole = 0.043 eV)

Life cycle of $\text{CO}_2^+\bullet(\text{CO}_2)_n$

- ▶ $\text{CO}_2^+\bullet\text{CO}_2$ has a dissociation energy of 0.6 eV far above thermal energies at 1 bar. It is a so-called long-lived cluster:
 - ▶ calculated lifetime = 5 ns
 - [B.M. Smirnov, “Cluster Ions and Van Der Waals Molecules,” CRC press]
- ▶ much longer than the formation time $\tau = 7\text{-}20$ ps via 3-body association in 10 % CO_2 with Ar + CO_2 as “helpers”.
- ▶ Any isolated CO_2^+ rapidly binds again.
- ▶ $\text{CO}_2^+\bullet(\text{CO}_2)_n$ probably lives shorter but will recombine. The cluster size n will therefore fluctuate at the ns time scale.

Reactions of Ar⁺ and Ne⁺

▶ Resonant charge exchange: (why does this matter ?)



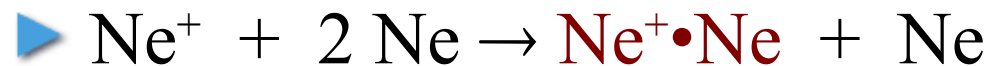
▶ $k = 4.6 \cdot 10^{-10} \text{ cm}^3/\text{s}$, $\tau \approx 100 \text{ ps}$ (for $N_{\text{Ar}} = 2.45 \cdot 10^{19}/\text{cm}^3$)

▶ Ar₂⁺ dimer formation:



▶ $k = 2.3 \pm 0.1 \cdot 10^{-31} \text{ cm}^6/\text{s}$, $\tau \approx 7 \text{ ns}$

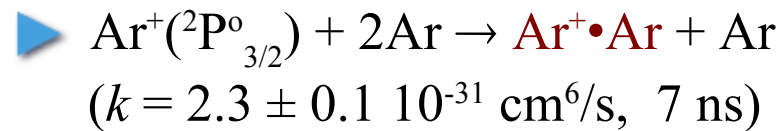
▶ Ne₂⁺ dimer formation:



▶ $k = 0.6 \cdot 10^{-31} \text{ cm}^6/\text{s}$

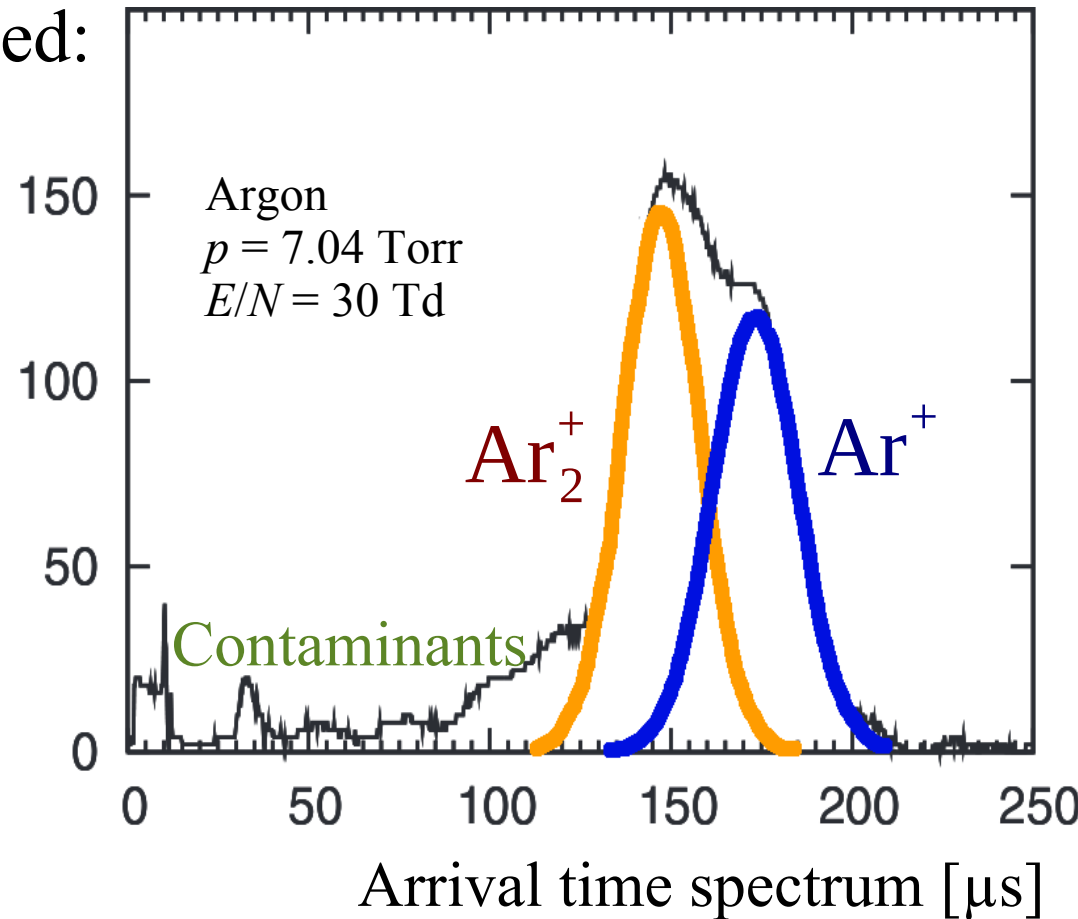
Ions drifting in pure Ar

► In pure Ar dimers are formed:



► Note: dimers move *faster* than ions due to $\text{Ar} \leftrightarrow \text{Ar}^+$ resonant charge exchange

[PNB Neves et al. 10.1063/1.3497651]



Thermal collision frequency

- ▶ Mean relative velocity (μ = reduced mass):

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

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

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

- ▶ Combine with the number density to get collision time:

$$\tau = \frac{1}{N \sigma \bar{v}_{\text{rel}}} = \frac{k_{\text{B}}T}{p} \frac{1}{\sigma \bar{v}_{\text{rel}}} = \frac{1}{p \sigma} \sqrt{\frac{\pi \mu k_{\text{B}}T}{8}} \approx 45 \text{ ps}$$

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 [$1/\text{cm}^3$];
- ▶ The proportionality factor k is called **rate constant**:
 - ▶ rate = k [cm^3/s] N_B [$1/\text{cm}^3$].
 - ▶ The reaction time τ is the reciprocal of the rate.

3-body reactions

- ▶ Reactions resulting in a bound state, require the evacuation of excess energy & momentum
 - ▶ via internal degrees of freedom (rotation, vibration ...), or
 - ▶ via a 3-body reaction, with helpers.
- ▶ The rate constant in 3-body reactions has the unit of cm^6/s .
- ▶ Example 1: $\text{Ar}^+ + \text{Ar} + \text{Ar} \rightarrow \text{Ar}^+\cdot\text{Ar} + \text{Ar}$
 - ▶ $k = 2.3 \cdot 10^{-31} \text{ cm}^6/\text{s}$, assuming $N \approx 2.45 \cdot 10^{19}/\text{cm}^3$
 - ▶ rate = $k N^2 = 1.3 \cdot 10^8/\text{s}$, $\tau = 7 \text{ ns}$
- ▶ Example 2: $\text{CO}_2^+ + \text{CO}_2 + \text{CO}_2 \rightarrow \text{CO}_2^+\cdot\text{CO}_2 + \text{CO}_2$
 - ▶ $k = 2.4 \cdot 10^{-28} \text{ cm}^6/\text{s}$
 - ▶ rate = $k N^2 = 1.4 \cdot 10^{11}/\text{s}$, $\tau = 7 \text{ ps}$

mathematica

- ▶ Start from the number of Ar^+ and CO_2^+ produced in the avalanche.
- ▶ Calculate evolution of Ar^+ , CO_2^+ , $\text{CO}_2^+\cdot\text{CO}_2$ clusters and Ar_2^+ dimers.

```
Clear[nAr, nAr2, nCO2, ncl]
evol = DSolve[
  {nAr'[x] == -(rArAr2 + rArCO2) nAr[x],
    nAr[0] == n0Ar,

    nAr2'[x] == rArAr2 nAr[x],
    nAr2[0] == 0,

    nCO2'[x] == rArCO2 nAr[x] - rCO2cl nCO2[x],
    nCO2[0] == n0CO2,

    ncl'[x] == rCO2cl nCO2[x],
    ncl[0] == 0},

  {nAr[x], nAr2[x], ncl[x], nCO2[x]},
  x];
CForm[%]
```

Evolution in Ar-CO₂ (93-7)

- ▶ Initial ions:
 - ▶ Ar⁺ →
 - ▶ CO₂⁺
 - ▶ Ar₂⁺
 - ▶ CO₂⁺ →
 - ▶ CO₂⁺.CO₂

Title:timeevolarco2-93-7.eps:

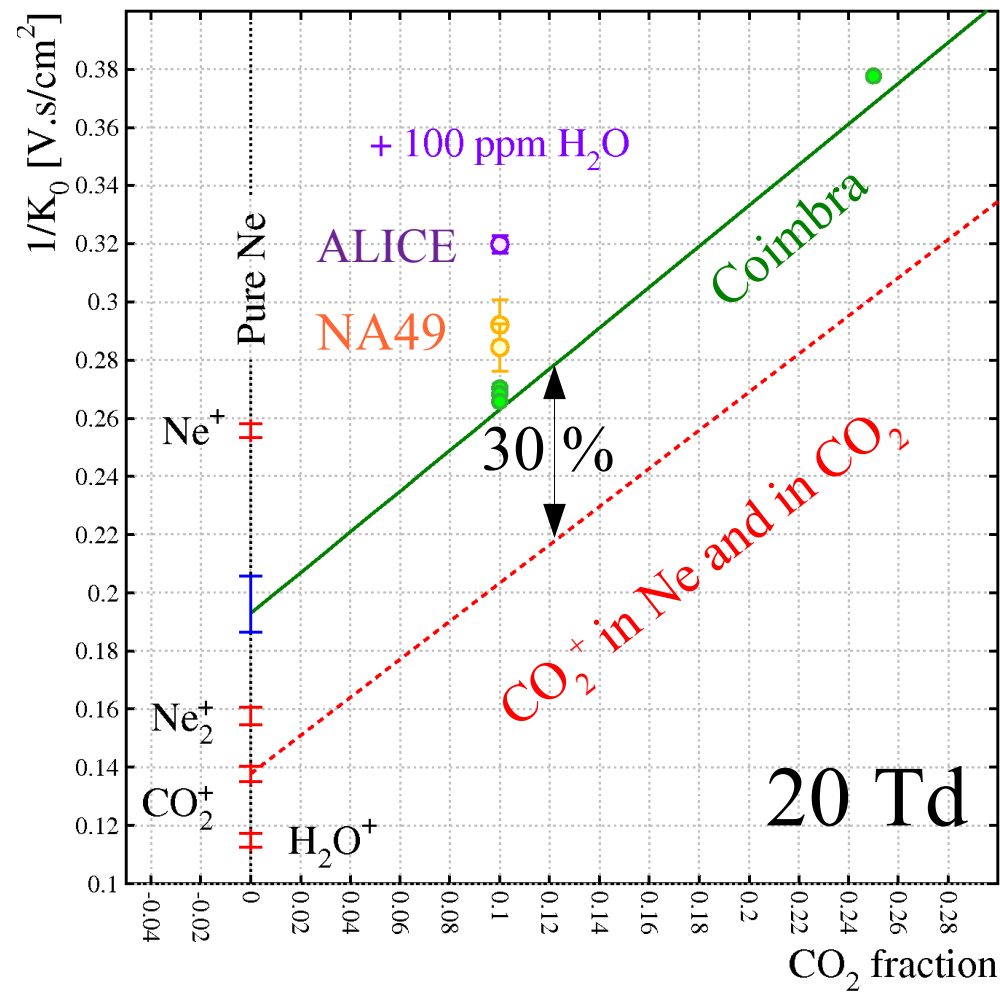
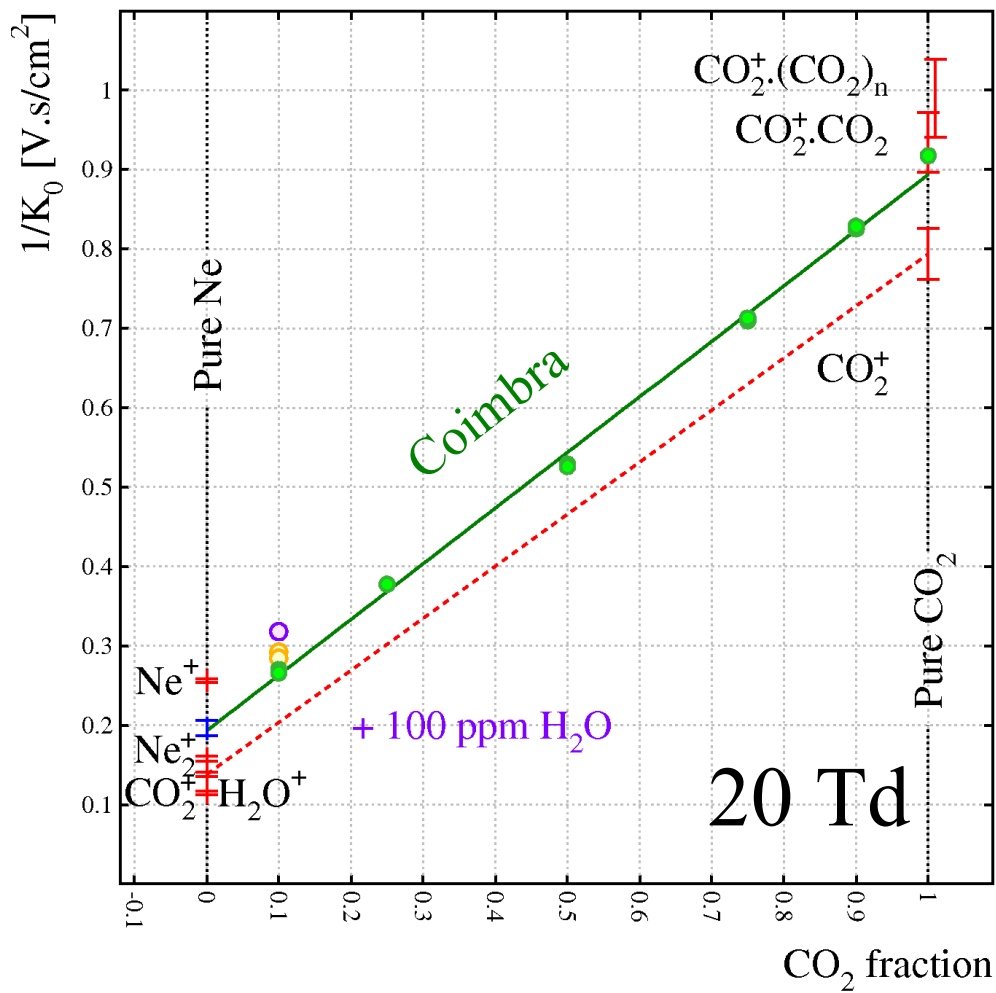
Creator:ROOT Version 6.18/04

CreationDate:Mon Jan 13 12:37:34 2020

CreationDate:Mon Jan 13 12:37:34 2020

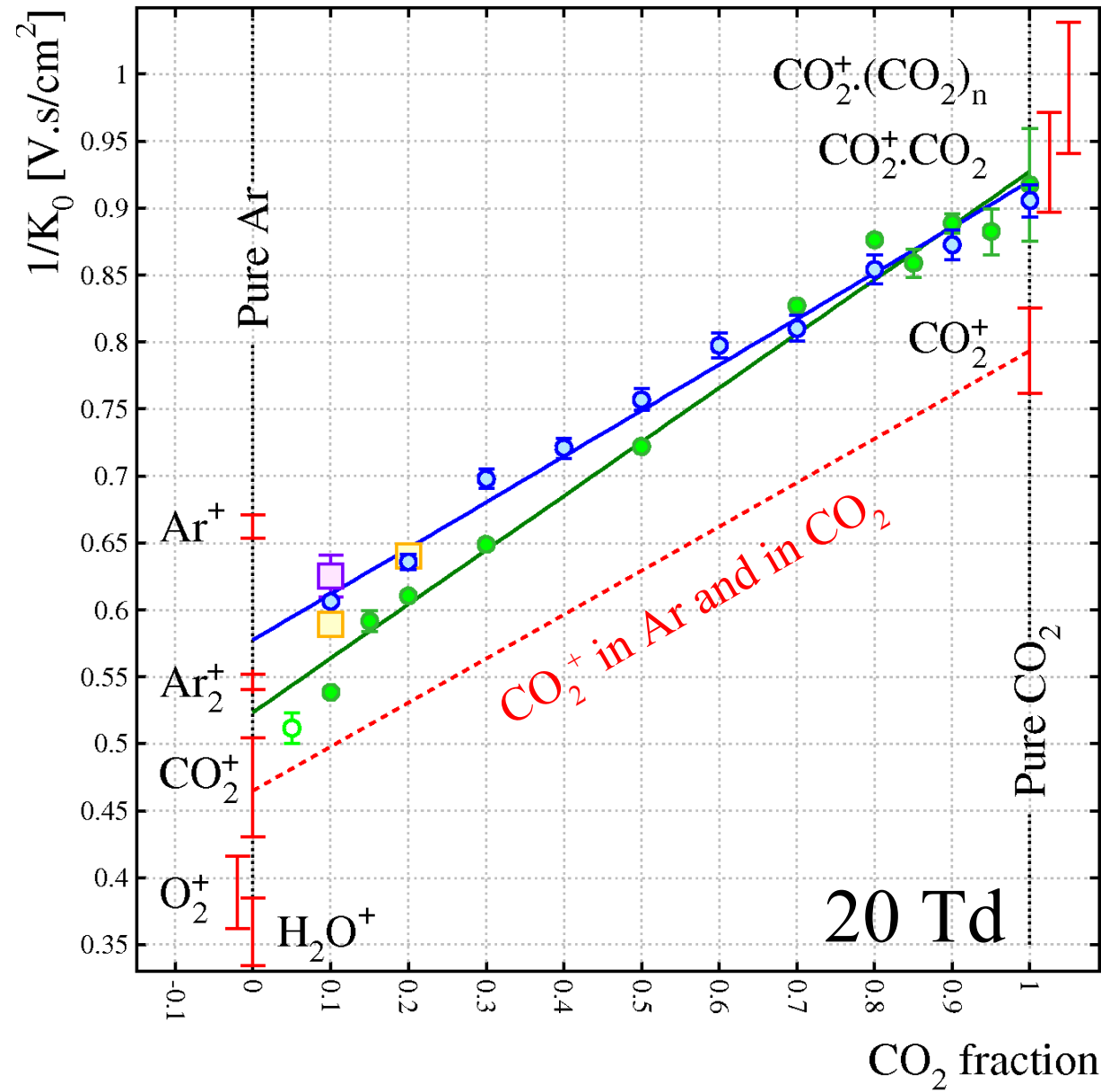
Blanc diagram for Ne-CO₂

► Like in Ar-CO₂, CO₂⁺ forms clusters in Ne-CO₂.



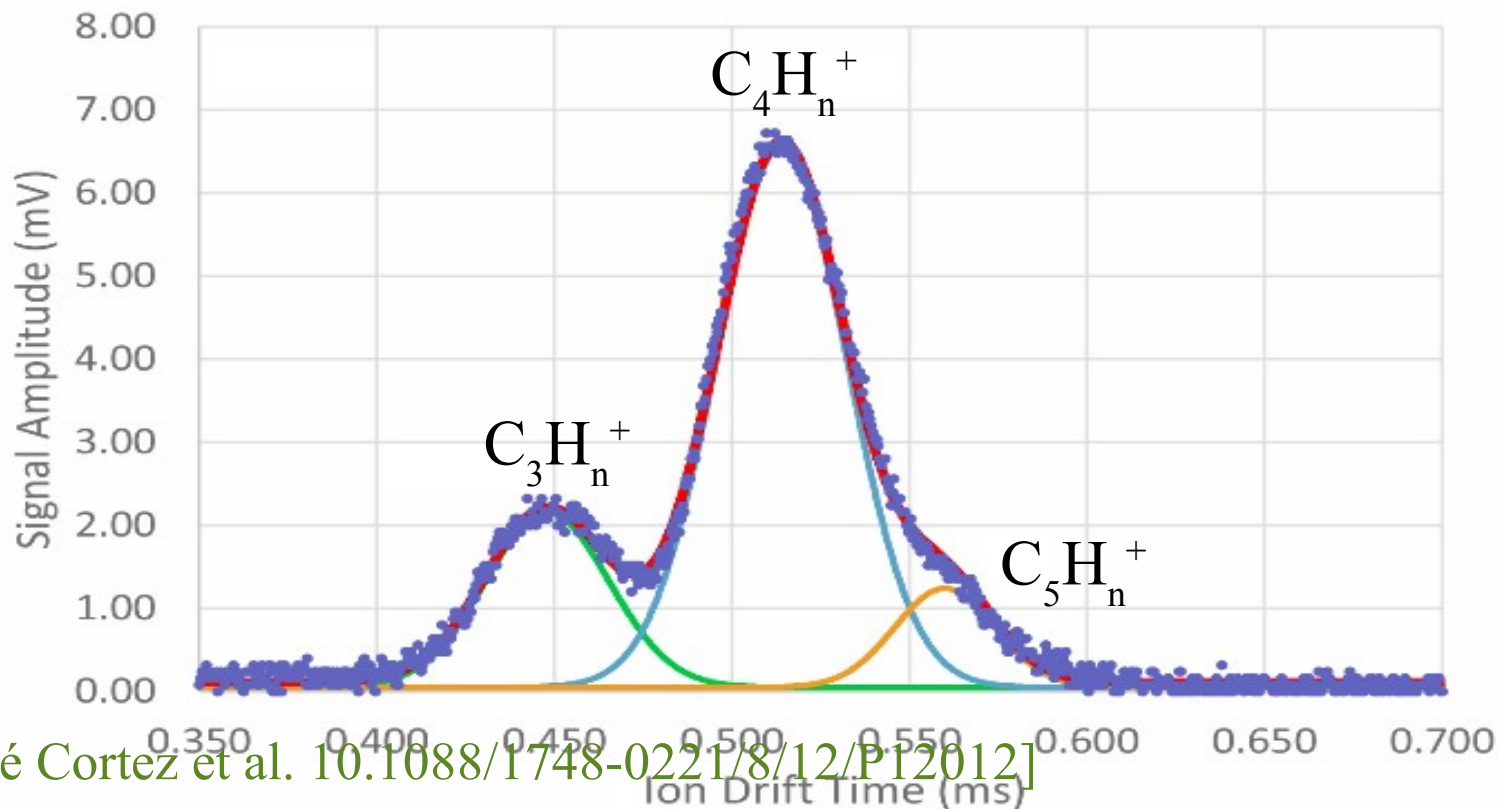
Blanc diagram for Ar-CO₂

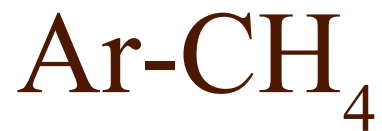
- ▶ **Coxon:** pure CO₂
- ▶ **Schultz:** 1 atm
- ▶ **Coimbra:** 0.01 atm, smaller clusters ?
- ▶ **NA49:** 1 atm
- ▶ **ALICE:** 1 atm, water clusters ?



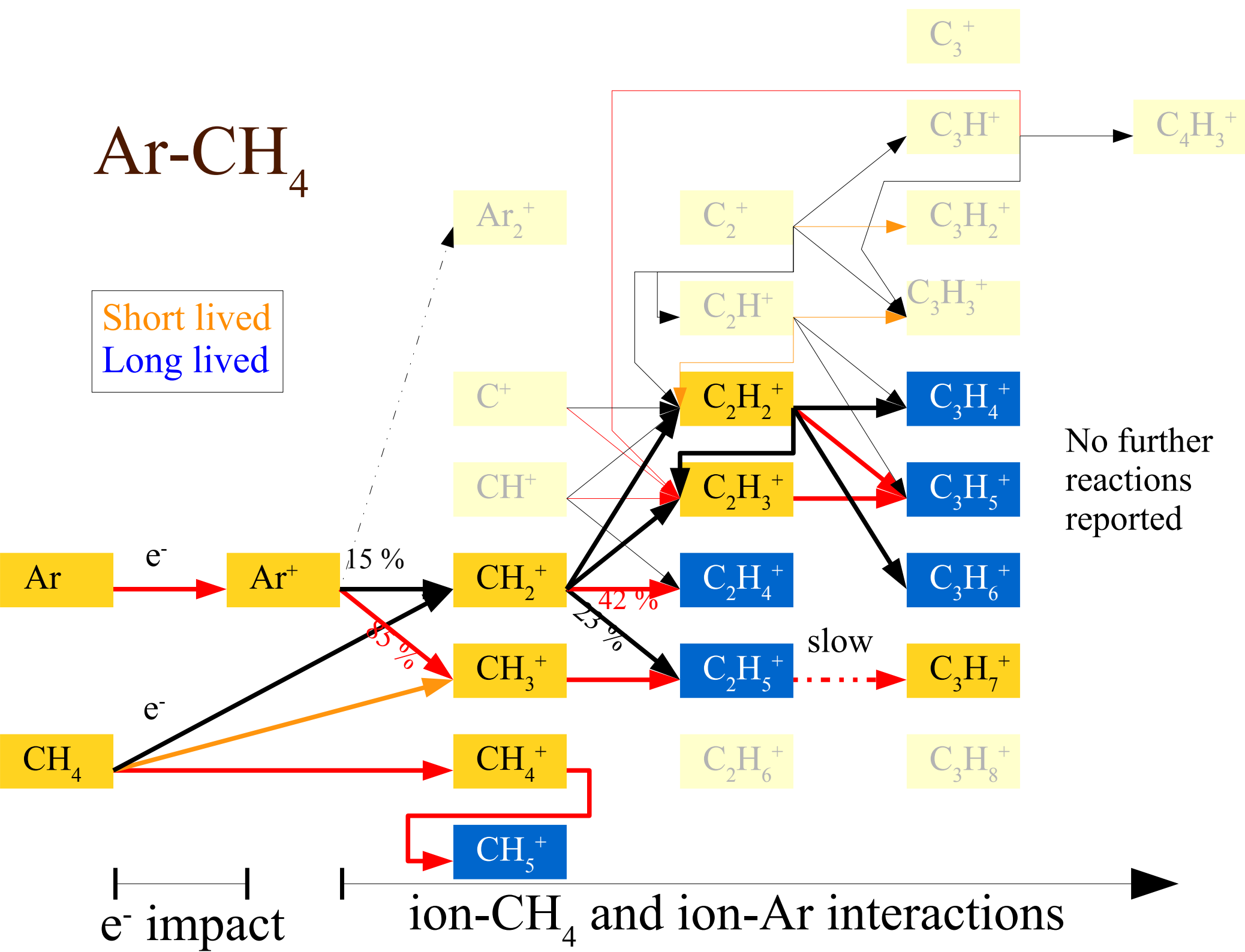
How about alkanes ?

- ▶ Ar 90 % - C₂H₆ 10 %, at low pressure.
- ▶ Expect Ar⁺ or C₂H₆⁺ but ... none are seen – why ?





Short lived
Long lived



Avalanche ions in Ar-CO₂-CH₄ (90-7-3)

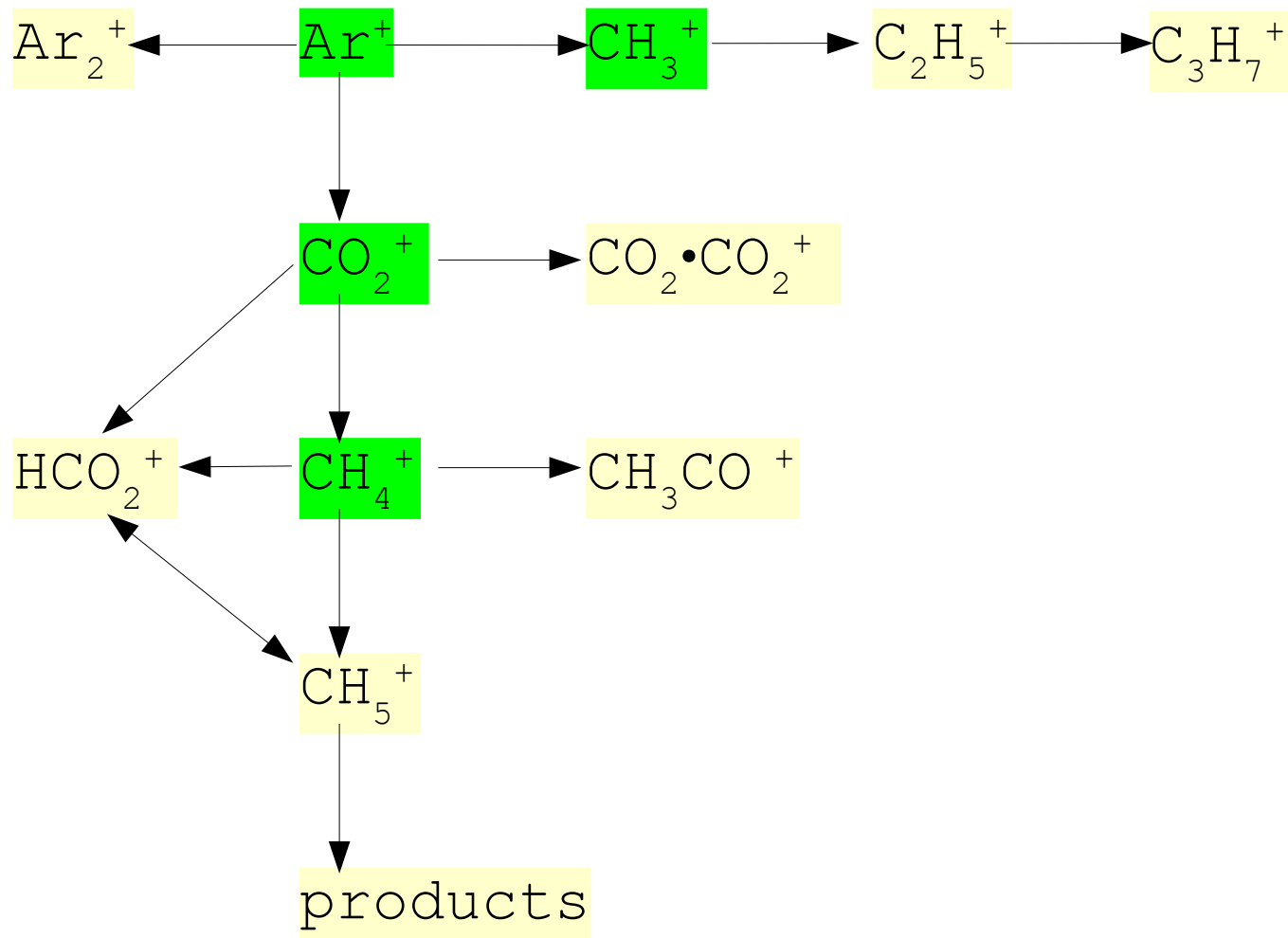
	Ion	Energy [eV]	Rate [GHz]	Fraction
Ar	Ar ⁺	15.75961	53.73	88.3 %
CO ₂	CO ₂ ⁺	13.776	3.119	5.1 %
	CO ₂ ^{+*}	17.314	0.3758	
	CO ₂ ^{+*}	18.077	0.2218	
	O ⁺	19.07	0.1324	
	CO ⁺	19.47	0.1525	
CH ₄	CH ₄ ⁺	12.65	1.959	3.2 %
	CH ₃ ⁺	14.25	1.115	1.8 %
	CH ₂ ⁺	15.2	0.07018	

Magboltz 11.2bis,
 $E = 100$ kV/cm
1 atm, 20 C

Reactions in Ar-CO₂-CH₄

▶ Ar ⁺ + Ar + M	→ Ar ₂ ⁺ + M	100 %	$k = 2.3 \cdot 10^{-31}$	± 10 %
▶ Ar ⁺ + CO ₂	→ CO ₂ ⁺ + Ar	100 %	$k = 5 \cdot 10^{-10}$	± 10 %
▶ Ar ⁺ + CH ₄	→ CH ₃ ⁺ + Ar + H	85 %	$k = 1.1 \cdot 10^{-9}$	± 10 %
▶	→ CH ₂ ⁺ + Ar + H ₂	15 %		
▶ CO ₂ ⁺ + CO ₂ + M	→ CO ₂ •CO ₂ ⁺ + M	100 %	$k = 2.4 \cdot 10^{-28}$	
▶ CO ₂ ⁺ + CH ₄	→ CH ₄ ⁺ + CO ₂	25 %	$k = 1.1 \cdot 10^{-9}$	± 10 %
▶	→ HCO ₂ ⁺ + CH ₃	75 %		
▶ CH ₃ ⁺ + CH ₄	→ C ₂ H ₅ ⁺ + H ₂	100 %	$k = 1.1 \cdot 10^{-9}$	± 10 %
▶ C ₂ H ₅ ⁺ + CH ₄	→ C ₃ H ₇ ⁺ + H ₂	100 %	$k = 1 \cdot 10^{-14}$	± 10 %
▶ CH ₄ ⁺ + CH ₄	→ CH ₅ ⁺ + CH ₃	100 %	$k = 1.15 \cdot 10^{-9}$	± 10 %
▶ CH ₅ ⁺ + CH ₄	→ products	100 %	$k = 3 \cdot 10^{-11}$	± 30 %
▶ CH ₄ ⁺ + CO ₂	→ HCO ₂ ⁺ + CH ₃	99 %	$k = 9.6 \cdot 10^{-10}$	± 10 %
▶	→ CH ₃ CO ⁺ + OH	1 %		
▶ CH ₅ ⁺ + CO ₂	→ HCO ₂ ⁺ + CH ₄	100 %	$k = 4 \cdot 10^{-11}$	± 10 %
▶ HCO ₂ ⁺ + CH ₄	→ CH ₅ ⁺ + CO ₂	100 %	$k = 6 \cdot 10^{-10}$	± 15 %

Reaction chains



Evolution in Ar-CO₂-CH₄ (90-7-3)

▶ Initial ions:



Title:timeevolarco2ch4-90-7-3.eps:

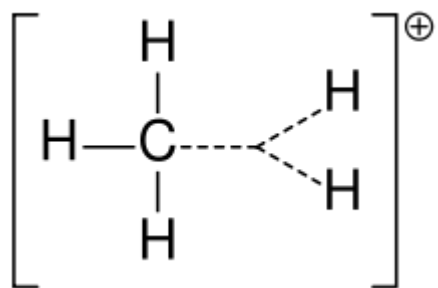
Creator:ROOT Version 6.18/04

CreationDate:Sun Jan 12 22:21:08 2020

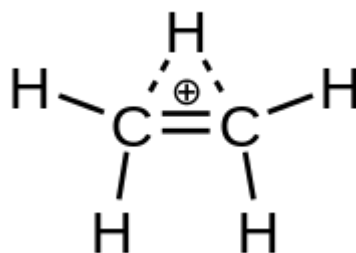
CreationDate:Sun Jan 12 22:21:08 2020

Products after 10 ns

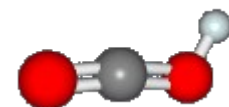
- ▶ $\text{C}_2\text{H}_5^+ \rightarrow \text{C}_3\text{H}_7^+$ slow reaction, $k = 1 \cdot 10^{-14}$
 [Hiraoka & Kebarle <https://doi.org/10.1063/1.431116>]
- ▶ $\text{CH}_5^+ \rightarrow$ “products” slow reaction, $k = 3 \cdot 10^{-11}$
- ▶ $\text{CO}_2 \cdot \text{CO}_2^+ \rightarrow$ grows to $n = 3-4$, reacts with CH_4 to HCO_2^+ ?
 [Y. Kalkan et al. 2015 JINST 10 P07004]
- ▶ $\text{Ar}^+ \rightarrow \text{Ar}_2^+$ drifts faster than Ar^+
- ▶ $\text{HCO}_2^+ \rightarrow \text{CH}_5^+$ HCO_2^+ decays at $k = 6 \cdot 10^{-10}$



methanium



ethenium



protonated
carbon diox

Summary ions

- ▶ Avalanches ionise the constituent gases, and the initial ions undergo a staggering sequence of reactions.
 - ▶ In Ar-CO₂ and Ne-CO₂ mixtures, the signal ions are CO₂⁺•(CO₂)_n clusters;
 - ▶ water forms larger clusters, further reducing the mobility;
 - ▶ pure noble gases form dimers, Ar₂⁺, Ne₂⁺ 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;
 - ▶ CH₄ leads to exotic molecules.
- ▶ There is room for these in this field.

Overview

- ▶ Xe-CH₄
 - ▶ CH₅⁺, C₂H₅⁺, C₃H₇⁺, Xe₂⁺
- ▶ Xe-C₂H₆
 - ▶ C₃H_n⁺, C₄H_n⁺, Xe₂⁺
- ▶ Xe-CO₂-C₂H₆
 - ▶ C₂H₄⁺, C₂H₅⁺, C₂H₆⁺, XeC₂H₆⁺, CO₂•CO₂⁺
- ▶ Xe-CF₄
 - ▶ CF₃⁺, Xe₂⁺
- ▶ Xe-CF₄-CO₂
 - ▶ Xe⁺, Xe₂⁺, CF₃⁺, CO₂•CO₂⁺
- ▶ Ar-CH₄
 - ▶ CH₅⁺, C₂H₄⁺, C₂H₅⁺, C₃H₄⁺, C₃H₅⁺, C₃H₆⁺, C₃H₇⁺, Ar₂⁺
- ▶ Ar-C₂H₆
 - ▶ C₃H_n⁺, C₄H_n⁺, Ar₂⁺
- ▶ Ar-iC₄H₁₀
 - ▶ C₄H₁₀⁺, C₈H_n⁺, C₁₂H_m⁺
- ▶ Ar-CF₄
 - ▶ CF₃⁺
- ▶ Ar-CO₂
 - ▶ CO₂•CO₂⁺, Ar₂⁺
- ▶ Ar-CO₂-CH₄
 - ▶ C₂H₅⁺, CH₅⁺, CO₂•CO₂⁺, Ar₂⁺, HCO₂⁺, CH₃⁺
- ▶ Ne-CF₄
 - ▶ CF₃⁺
- ▶ Ne-CO₂
 - ▶ CO₂•CO₂⁺, Ne₂⁺
- ▶ N₂
 - ▶ N₂•N₂⁺
- ▶ C₂H₆
 - ▶ C₂H₄⁺, C₃H₅⁺, C₃H₇⁺, C₃H₈⁺, C₃H₉⁺, C₄H₉⁺, C₄H₁₀⁺, C₄H₁₂⁺
- ▶ Xe-N₂
 - ▶ Xe⁺, Xe₂⁺
- ▶ iC₄H₁₀
 - ▶ C₈H_n⁺, C₁₂H_m⁺

Not used

Ionisation potentials

▶ Xe:	12.129843 eV
▶ Ar:	15.759 eV
▶ Ne:	21.56454 eV

▶ CO₂: 13.777 eV

▶ CH₄: 12.61 eV

▶ C₂H₆: 11.52 eV

▶ C₃H₈: 10.94 eV

▶ *i*C₄H₁₀: 10.68 eV

▶ *n*C₄H₁₀: 10.53 eV

▶ C₂H₅: 8.4 eV

▶ CH₅: 8.3 eV ?

▶ HCO₂: 8.3 eV ?

▶ C₃H₇: 7.5 eV

Cluster mobility in Ar-CO₂ & Ne-CO₂

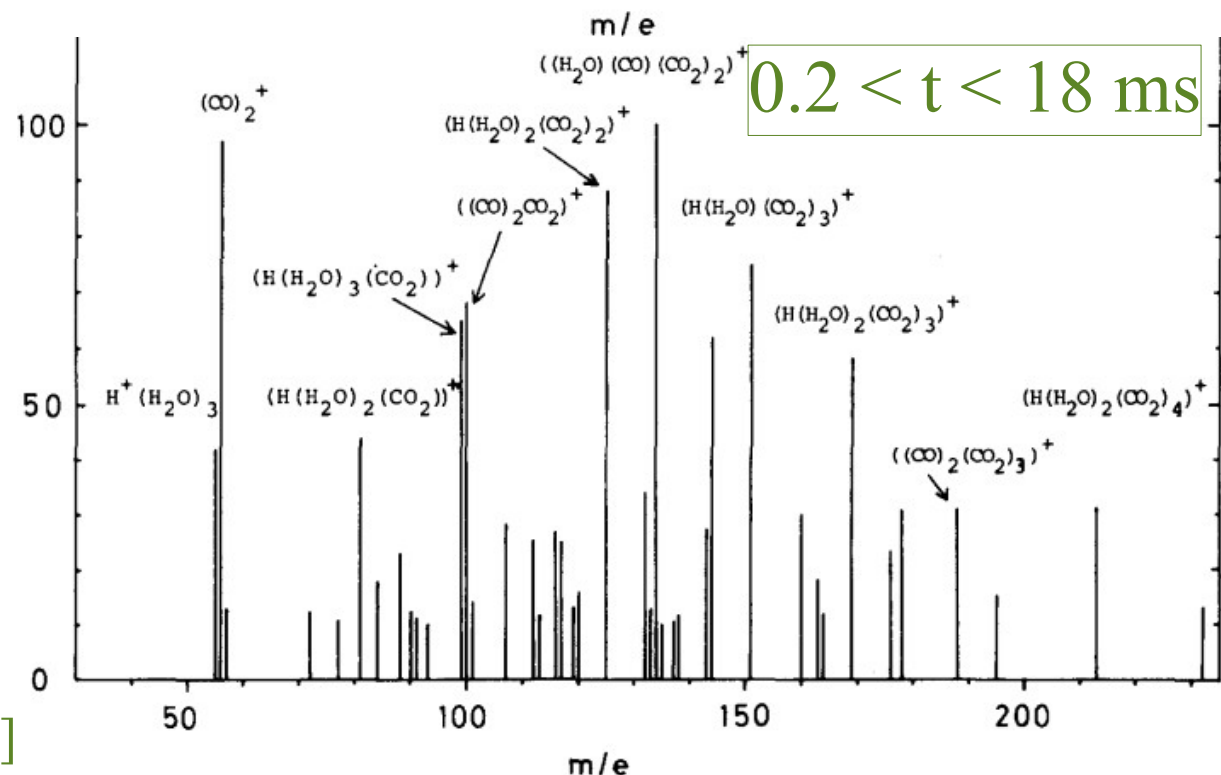
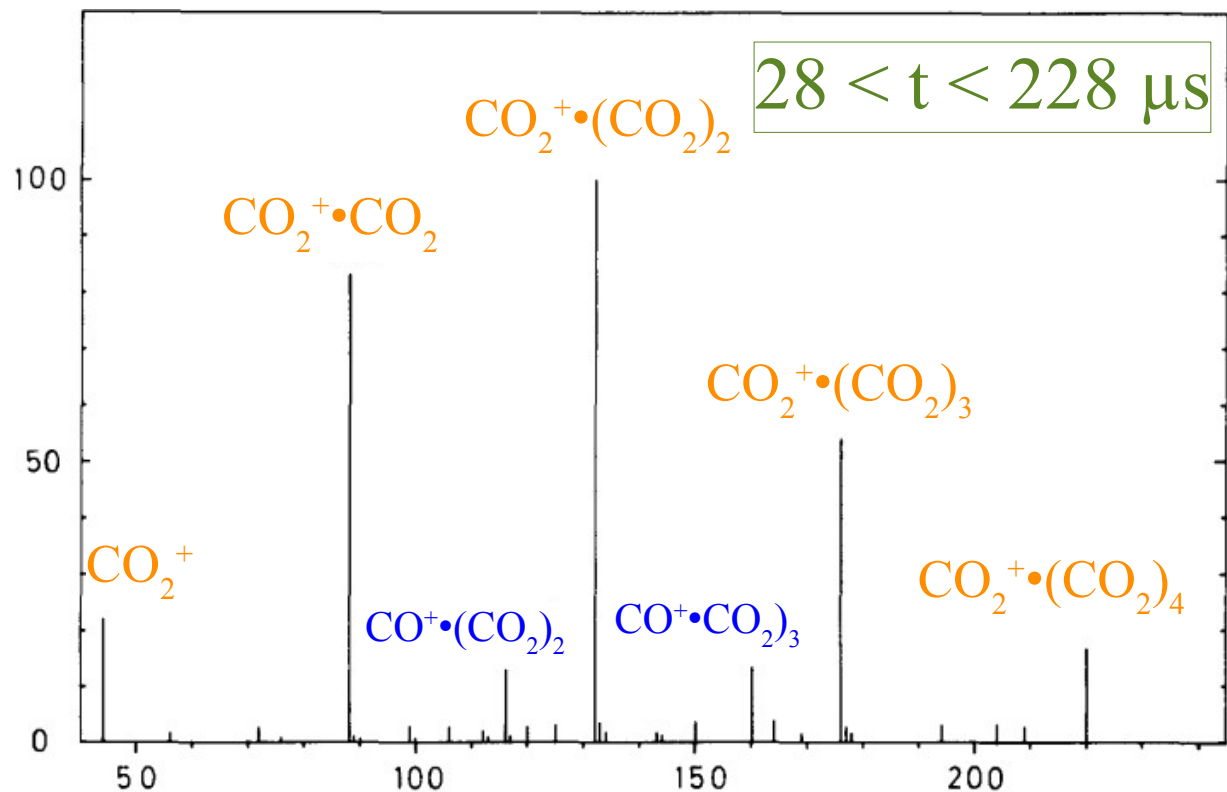
- ▶ One needs as ingredients:
 - ▶ the Blanc interpolation formula;
 - ▶ the mobility of the ions in the pure gases.
- ▶ There are measurements of:
 - ▶ Ar⁺ in Ar, Ne⁺ in Ne,
 - ▶ CO₂⁺ in Ar and in Ne;
 - ▶ CO₂⁺, CO₂⁺•CO₂ and CO₂⁺•(CO₂)_n in CO₂.
- ▶ But we have not found measurements of:
 - ▶ mobility of CO₂⁺•(CO₂)_n neither in Ar nor in Ne;
 - ▶ we can get an idea from the mass-mobility relation.

CO₂ at 1 bar

► At 1 bar clusters are observed to emerge and then decay:

► Until 200 μs:
 $\text{CO}_2^+ \cdot (\text{CO}_2)_n$ and
 $\text{CO}^+ \cdot (\text{CO}_2)_n$

► Later: *only* clusters from contaminants, e.g. H₂O, OH ...



Experimental check

- ▶ Remains showing that experiments indeed observe $\text{CO}_2^+ \cdot (\text{CO}_2)_n$ and not CO_2^+ .
- ▶ This we do by comparing:
 - ▶ measured mobility as function of mix, with
 - ▶ mobility of CO_2^+ , Ar^+ and Ne^+ from literature.

Avalanche products & by-products

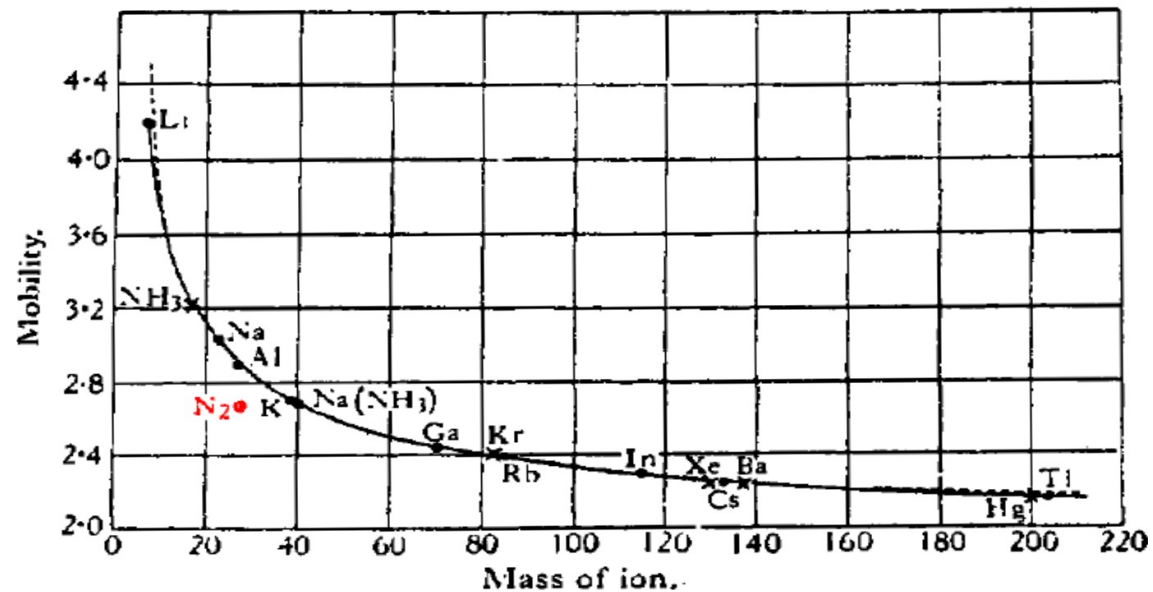
▶ At very low pressure, there are traces of O^+ , C^+ and CO^+ :



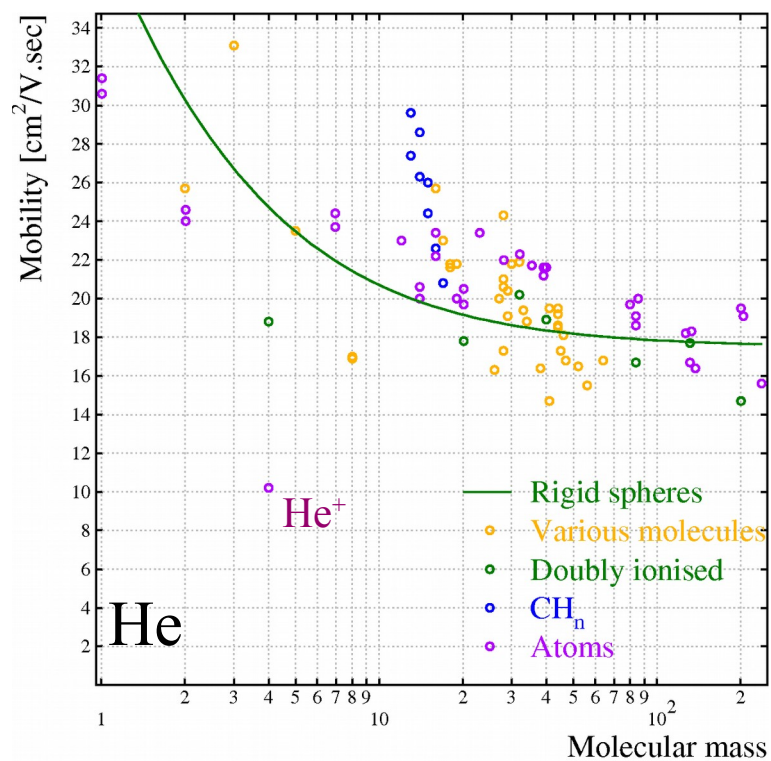
▶ These traces probably also exist at higher pressure, but they disappear rapidly, except the cluster and O_2^+ .

[H.W. Ellis et al., J. Chem. Phys. **64** (1976) 3935-3941, 10.1063/1.432024]

He, Xe, N₂



[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.]



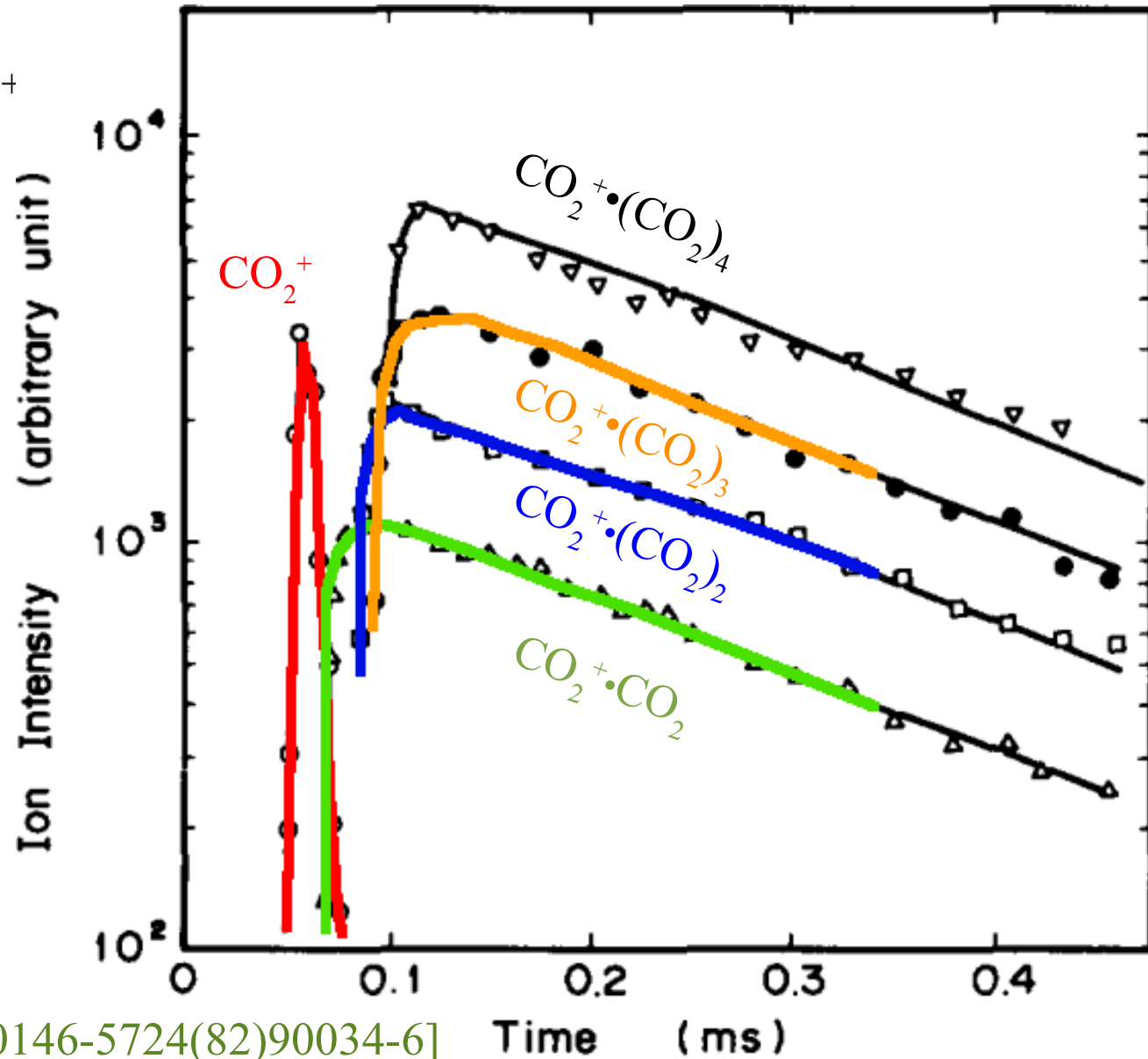
Title:mobmassXe.eps
 Creator:HIGZ Version 1.29/04
 CreationDate:2015/12/12 19.44
 CreationDate:2015/12/12 19.44

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 CO₂⁺;
- ▶ in nearly pure Ne, there could be some Ne₂⁺.
- ▶ Instead, we obtained $CO_2^+ \bullet CO_2$.

CO₂ at 1 atm: cluster (dis)appearance

- ▶ Not clear why CO₂⁺ forms at $t > 50 \mu\text{s}$.
- ▶ Clusters with CO₂⁺ ion core form by $t = 100 \mu\text{s}$.
- ▶ React with contaminants $\tau \sim 190 \mu\text{s}$.

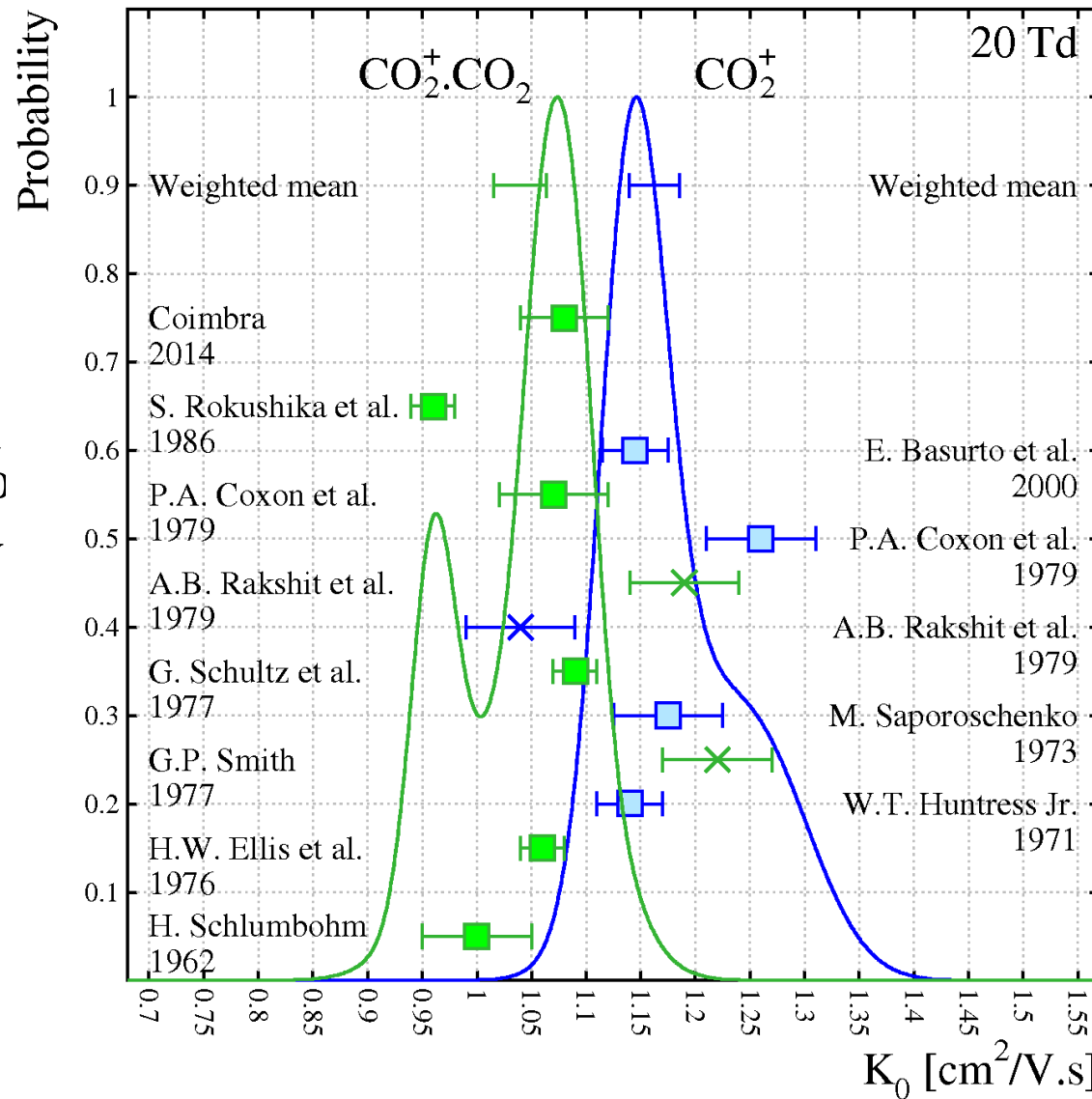


Life cycle of $\text{CO}_2^+\bullet(\text{CO}_2)_n$

- ▶ $\text{CO}_2^+\bullet\text{CO}_2$ has a dissociation energy of 0.6 eV far above thermal energies at 1 bar. It is a so-called long-lived cluster:
 - ▶ calculated lifetime = 5 ns
 - [B.M. Smirnov, “Cluster Ions and Van Der Waals Molecules,” CRC press]
- ▶ much longer than the formation time $\tau = 7\text{-}20$ ps via 3-body association in 10 % CO_2 with $\text{Ar} + \text{CO}_2$ as “helpers”.
- ▶ Any isolated CO_2^+ rapidly binds again.
- ▶ $\text{CO}_2^+\bullet(\text{CO}_2)_n$ probably lives shorter but will recombine. The cluster size n will therefore fluctuate at the ns time scale.

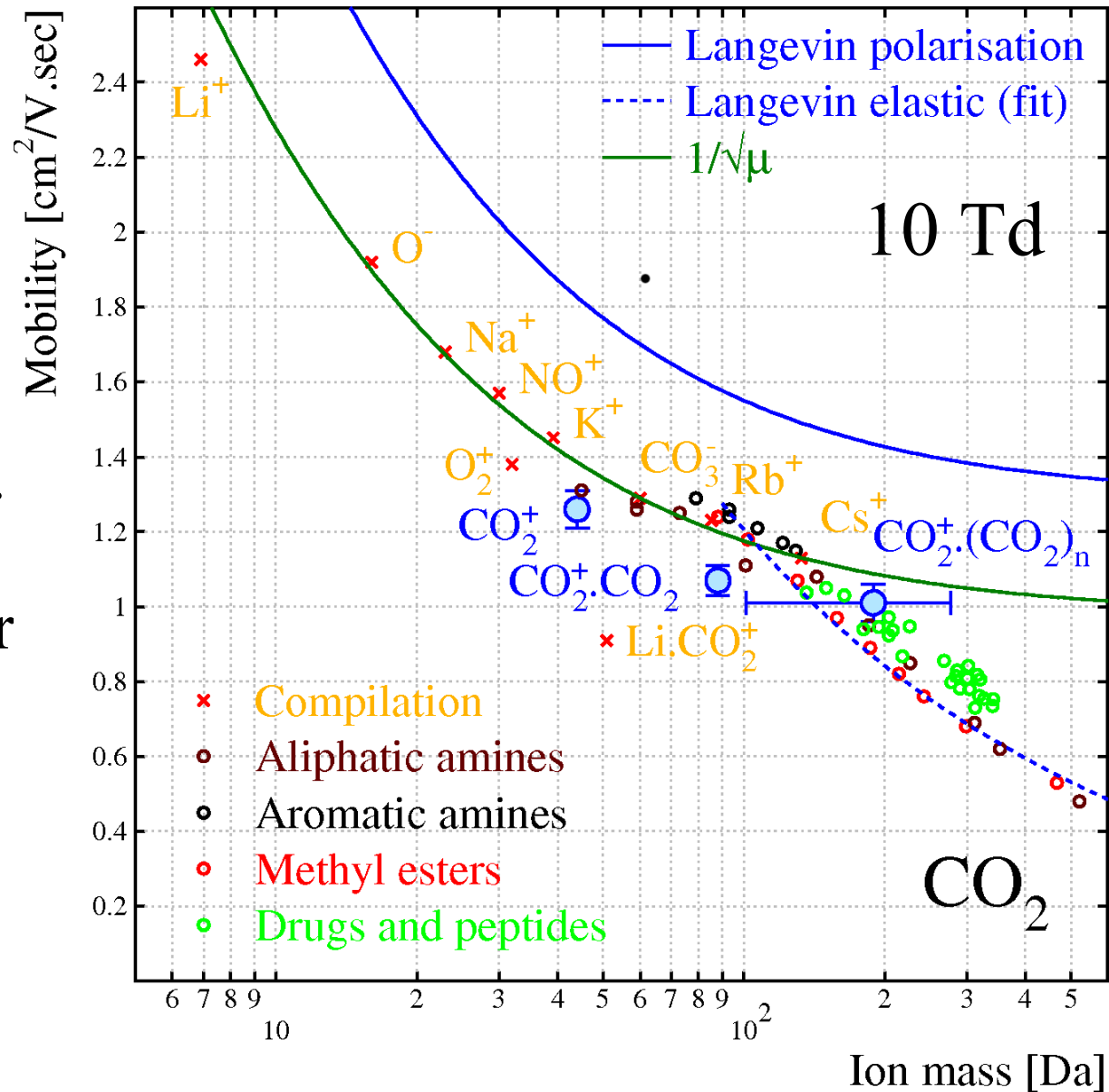
Mobility of CO_2^+ and $\text{CO}_2^+\cdot(\text{CO}_2)_n$ in CO_2

- ▶ At atmospheric pressure, one almost inevitably measures $\text{CO}_2^+\cdot\text{CO}_2$ or $\text{CO}_2^+\cdot(\text{CO}_2)_n$.
- ▶ Cluster mobility 10-15 % smaller than ion mobility
- ▶ Two measurements exist of clusters with large n .

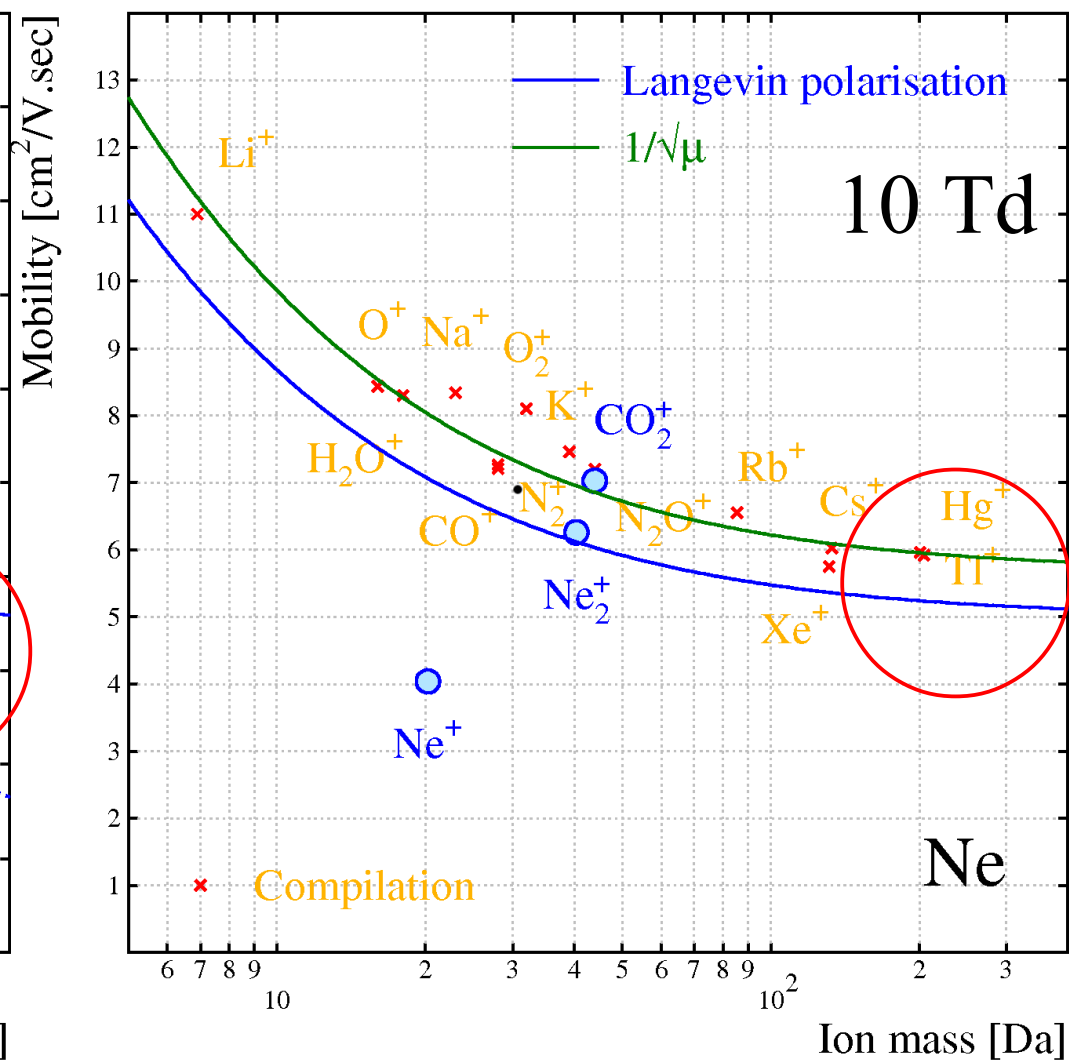
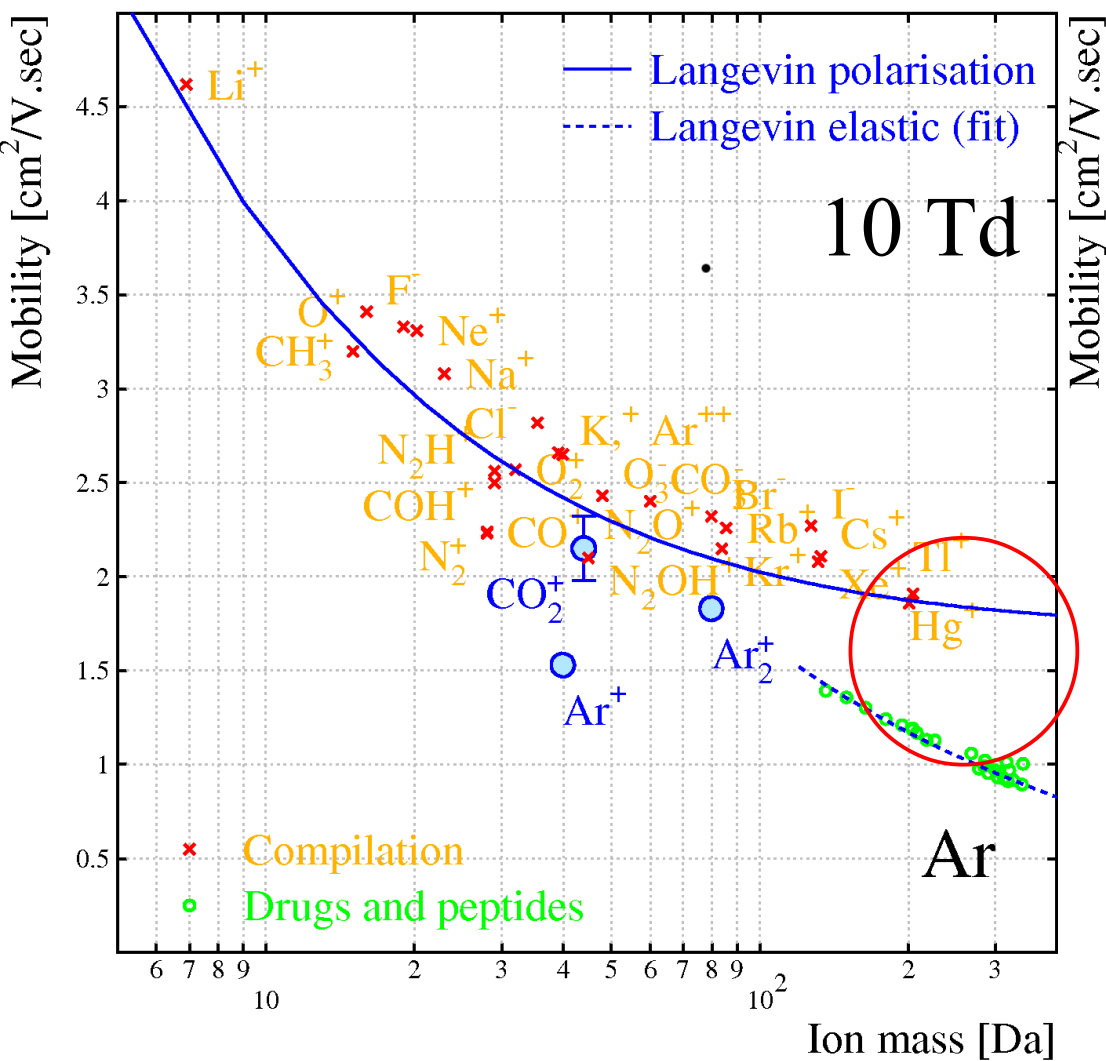


Mass-mobility in CO₂

- ▶ Langevin polarisation limit not appropriate for many ions.
- ▶ Langevin elastic limit can fit molecular ions.
- ▶ Uncertainty for cluster ion mobility.
- ▶ Little resonant charge exchange effect.



Mass-mobility in pure Ar and Ne



Atlas TRT signals

▶ Data:

- ▶ Xe-CO₂-CF₄ 70/10/20
- ▶ Straw tube
- ▶ $V_w = 1530$ V
- ▶ $r_w = 15$ μm , $r_t = 2$ mm

▶ Fit:

- ▶ $1/(t+t_0)$

Title:sigfit.eps

Creator:HIGZ Version 1.29/04

CreationDate:2017/09/18 20.15

CreationDate:2017/09/18 20.15

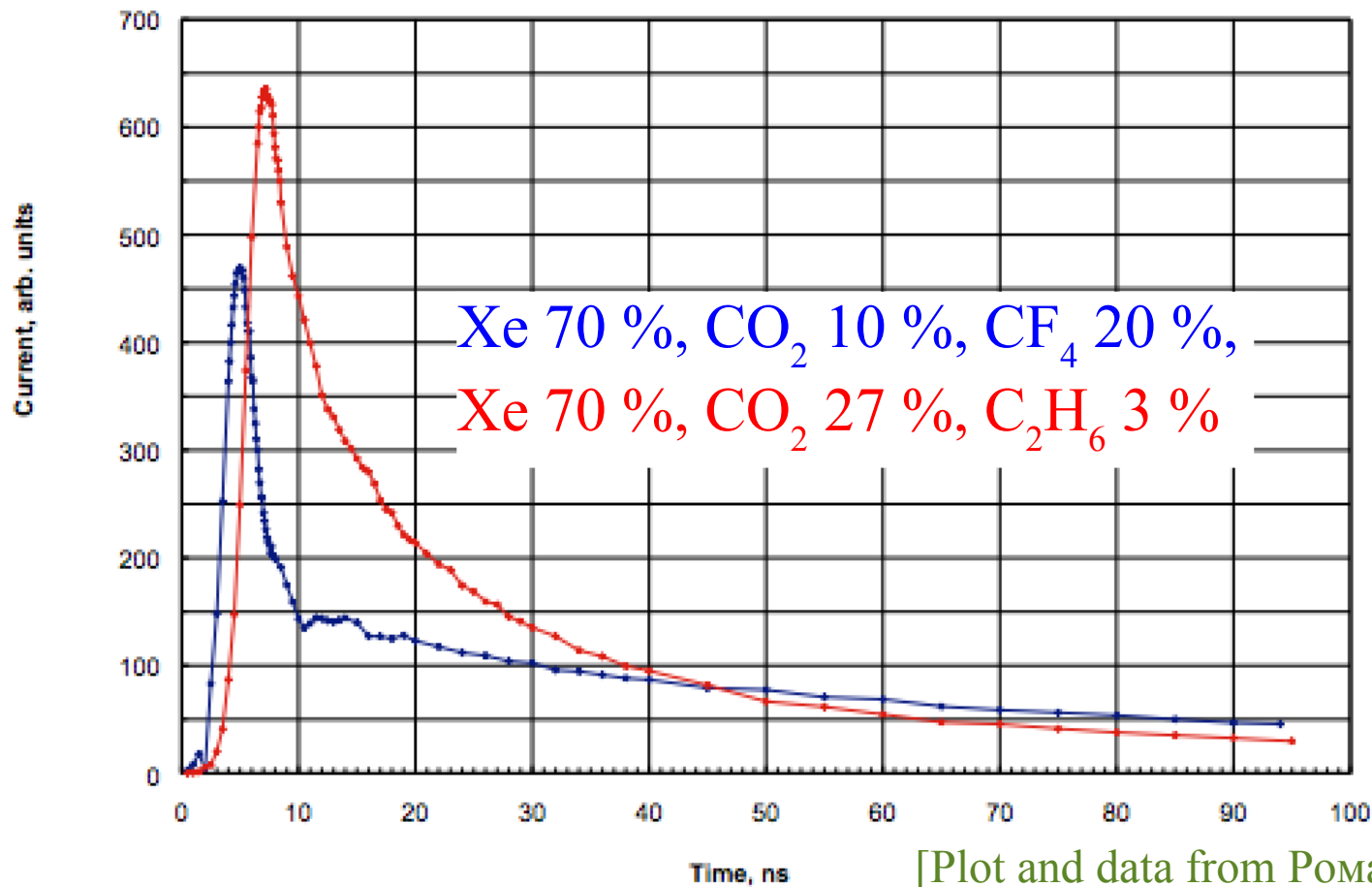
Electron signal

Ion tail

Time [ns]

Adding C_2H_6

- ▶ C_2H_6 makes the tail steeper and the mobility larger:



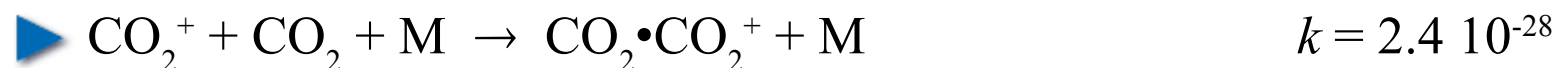
Ionisation potentials

- ▶ C_2H_6 : 11.52 eV
- ▶ $\text{Xe}^+(\text{}^2\text{P}_{3/2})$: 12.129843 eV
- ▶ $\text{Xe}^+(\text{}^2\text{P}_{1/2})$: 13.44 eV
- ▶ CO_2 : 13.776 eV
- ▶ CF_4 : 15.70 eV for CF_3^+ (main ionisation channel)
16.2 ± 0.1 eV for CF_4^+

Reactions in Xe-CO₂-CF₄



[A.P. Vitols and H.J. Oskam, Phys. Rev. A **8** (1973) 1860-1863.]



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



[V.G. Anicich and W.T. Huntress Jr., Astrophys. J. Suppl. **62** (1986) 553-672.]



Evolution of Xe-CO₂-CF₄ (70-10-20)

- ▶ Initial ion mix for 100 kV/cm;
- ▶ Xe⁺ and Xe₂⁺ dominate from 10 ns on, Xe_{*n*}⁺ for *n* > 2 are not shown: rates are not known.
- ▶ CF₃⁺ is an avalanche product; with its low IP, it does not react;
- ▶ CF₄⁺ is not produced, CF₄ has a high IP, is not attacked by ions.
- ▶ CO₂⁺ transfers to Xe⁺ and rapidly forms clusters.

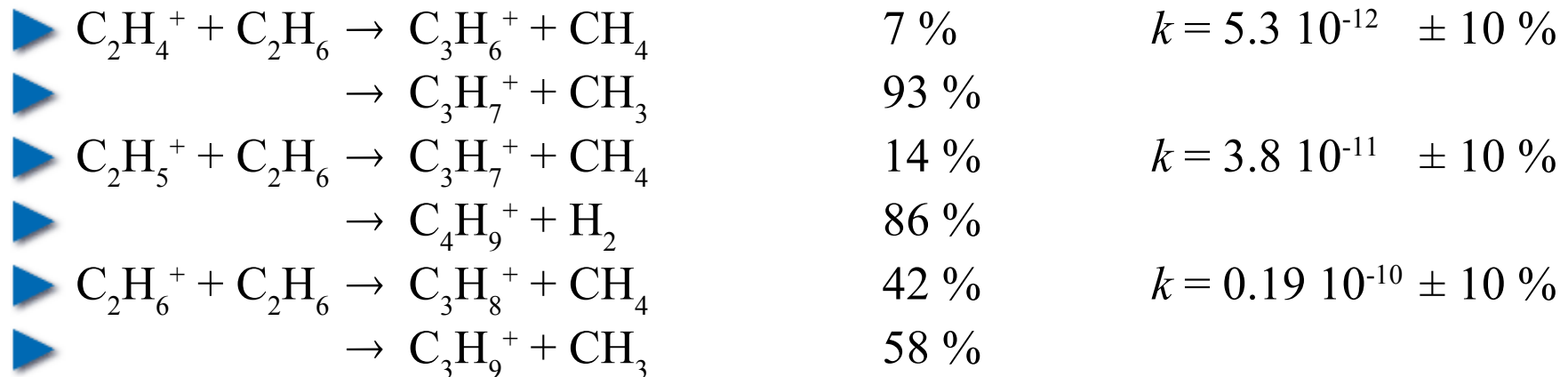
Title:timeevolxecf4co2.eps:

Creator:ROOT Version 6.04/02

CreationDate:Wed Sep 6 17:01:27 2017

CreationDate:Wed Sep 6 17:01:27 2017

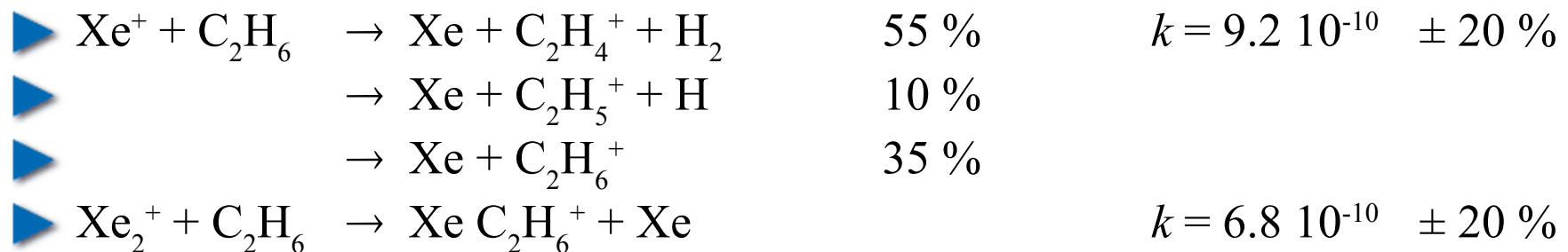
Reactions in Xe-C₂H₆



[V.G. Anicich and W.T. Huntress Jr., *Astrophys. J. Suppl.* **62** (1986) 553-672,
A.F.V. Cortez et al. 2013 JINST 8 P07013, J.M.C. Perdigoto et al. 2017 JINST 12 P09003]



[A.P. Vitols and H.J. Oskam, *Phys. Rev. A* **8** (1973) 1860-1863.]



[Kevin Giles et al., *J. Phys. B: At. Mol. Opt. Phys.* **22** (1989) 873-883.

N.G. Adams et al., *J. Phys. B: At. Mol. Phys.* **13** (1980) 3235-3246.]

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[%]

$$\left\{ \left\{ \begin{aligned} nC2H4[x] &\rightarrow \left(\left(1 - e^{-(rXeC2H4+rXeC2H5+rXeC2H6+rXeXe2)x} \right) n0Xe rXeC2H4 + \right. \\ &\quad \left. n0C2H4 (rXeC2H4 + rXeC2H5 + rXeC2H6 + rXeXe2) \right) / \\ &\quad (rXeC2H4 + rXeC2H5 + rXeC2H6 + rXeXe2), \\ nC2H5[x] &\rightarrow - \frac{\left(-1 + e^{-(rXeC2H4+rXeC2H5+rXeC2H6+rXeXe2)x} \right) n0Xe rXeC2H5}{rXeC2H4 + rXeC2H5 + rXeC2H6 + rXeXe2}, \end{aligned} \right. \right.$$

Evolution of $\text{Xe-C}_2\text{H}_6$ (97-3)

- ▶ Initial ion mix for 100 kV/cm;
- ▶ after 10 ns, the only Xe-related ion that remains is XeC_2H_6^+ which is made from Xe_2^+ ;
- ▶ the diagram does not show the C_3H_x^+ and C_4H_x^+ ions subsequently generated by C_2H_4^+ and C_2H_5^+ ;
- ▶ Xe_n^+ for $n > 2$ are not shown because the rates are not known.

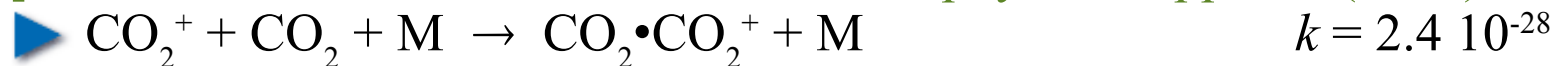
Title:timeevolutionxec2h6.eps
Creator:HIGZ Version 1.29/04
CreationDate:2017/09/06 16.02
CreationDate:2017/09/06 16.02

Reactions in Xe-CO₂-C₂H₆

▶ All reactions from Xe-C₂H₆ and in addition:



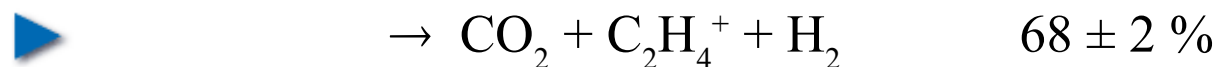
[V.G. Anicich and W.T. Huntress Jr., *Astrophys. J. Suppl.* **62** (1986) 553-672.]



[B.M. Smirnov, *Cluster Ions and Van Der Waals Molecules*]



[V.G. Anicich and W.T. Huntress Jr., *Astrophys. J. Suppl.* **62** (1986) 553-672.]



[Masaharu Tsuji, [10.1016/0168-1176\(94\)03996-8](https://doi.org/10.1016/0168-1176(94)03996-8)]

Evolution of $\text{Xe-CO}_2\text{-C}_2\text{H}_6$ (70-27-3)

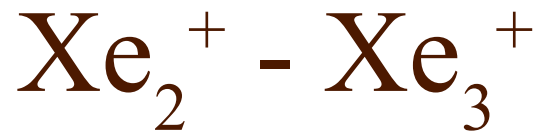
- ▶ Initial ion mix for 100 kV/cm;
- ▶ CO_2^+ rapidly forms clusters due to the large CO_2 fraction;
- ▶ CO_2 does not affect the dominance of C_xH_y over Xe.
- ▶ Xe_n^+ for $n > 2$ are not shown because rates are not known.

Title:timeevolxeco2c2h6.eps:

Creator:ROOT Version 6.04/02

CreationDate:Wed Sep 6 16:16:47 2017

CreationDate:Wed Sep 6 16:16:47 2017



- ▶ We have not found the rate constant for Xe_3^+ production in the literature, but H. Helm has measured [293 K]:

$$K_e = \frac{[\text{Xe}_2^+][\text{Xe}][\text{Xe}]}{[\text{Xe}_3^+][\text{Xe}]} = \frac{k_r}{k_f} = 2.8 \pm 0.5 \cdot 10^{18}$$

- ▶ where k_f is the rate coefficient for the transformation of Xe_2^+ to Xe_3^+ , and k_r the rate for the reverse reaction.
- ▶ Given that $[\text{Xe}_3^+] / [\text{Xe}_2^+] = 3.6 \pm 0.6 \cdot 10^{-19} N$, the ratio of concentrations is 9.7 ± 1.6 at 293 K, atmospheric pressure and zero field.

What have we learned ?

- ▶ After 10 ns, the ion with the lowest IP remains:
 - ▶ In Xe without C_2H_6 , this is Xe^+ and related;
 - ▶ if C_2H_6 is present, $C_xH_y^+$ dominates.
- ▶ In the long run, Xe^+ is likely to form Xe_n^+

Mobility and stability of small Xe_n^+

- ▶ Mobilities are known for the smallest Xe clusters;
- ▶ these are remarkably stable;
- ▶ ΔH for $n \geq 5$ clusters is nearly constant at ~ 0.1 eV.

Xe_n^+	Mass	$\mu (E = 0, T=300 \text{ K})$	$\Delta H \text{ } n-1 \rightarrow n$	References
	[Da]	[$\text{cm}^2/\text{V.s}$]	[eV]	
Xe^+	131.293	0.55	-	Helm, Viehland-Mason
Xe_2^+	262.586	0.61	1.05 (5 %)	NIST, Helm 1976
Xe_3^+	393.879	0.57	0.29 (5 %)	NIST, Helm 1976
Xe_4^+	525.172	?	0.26 (3 %)	NIST, Hiraoka
Xe_5^+	656.465	?	0.11 (5 %)	NIST, Hiraoka

[Ker]

Mobility of ions in Xe

- ▶ $E/N = 10$ Td,
extrapolated from higher E/N where needed (Xe^+).
- ▶ Polarisation limit
assuming $\alpha_{\text{Xe}} = 4.01$ D.
- ▶ Xe_2^+ and Xe_3^+ are below the
polarisation limit.

[From the H.W. Ellis et al. compilations
except Xe^+ and Xe_2^+ , which are from
P.N.B. Neves, 10.1063/1.3497651]

Title:mobmassXe.eps

Creator:HIGZ Version 1.29/04

CreationDate:2017/09/23 20.53

CreationDate:2017/09/23 20.53

Large Xe_n clusters

- ▶ Much larger clusters, with a size of 10^4 , have been observed.
- ▶ They are produced by “supersonic adiabatic expansion through a nozzle.”

Avalanche ions in Ar-CO₂-CH₄ (93-4-3)

	Ion	Energy [eV]	Rate [GHz]	Fraction
Ar	Ar ⁺	15.75961	56.65	91.1 %
CO ₂	CO ₂ ⁺	13.776	1.815	2.9 %
	CO ₂ ^{+*}	17.314	0.2250	
	CO ₂ ^{+*}	18.077	0.1261	
	O ⁺	19.07	0.08213	
	CO ⁺	19.47	0.08430	
CH ₄	CH ₄ ⁺	12.65	1.996	3.2 %
	CH ₃ ⁺	14.25	1.138	1.8 %
	CH ₂ ⁺	15.2	0.07641	

Magboltz 11.2bis,
 $E = 100$ kV/cm
1 atm, 20 C

Evolution in Ar-CO₂-CH₄ (93-4-3)

▶ Initial ions:



Title:timeevolarco2ch4-93-4-3-bis.eps:

Creator:ROOT Version 6.18/04

CreationDate:Mon Jan 13 21:09:11 2020

CreationDate:Mon Jan 13 21:09:11 2020