

# 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* ?

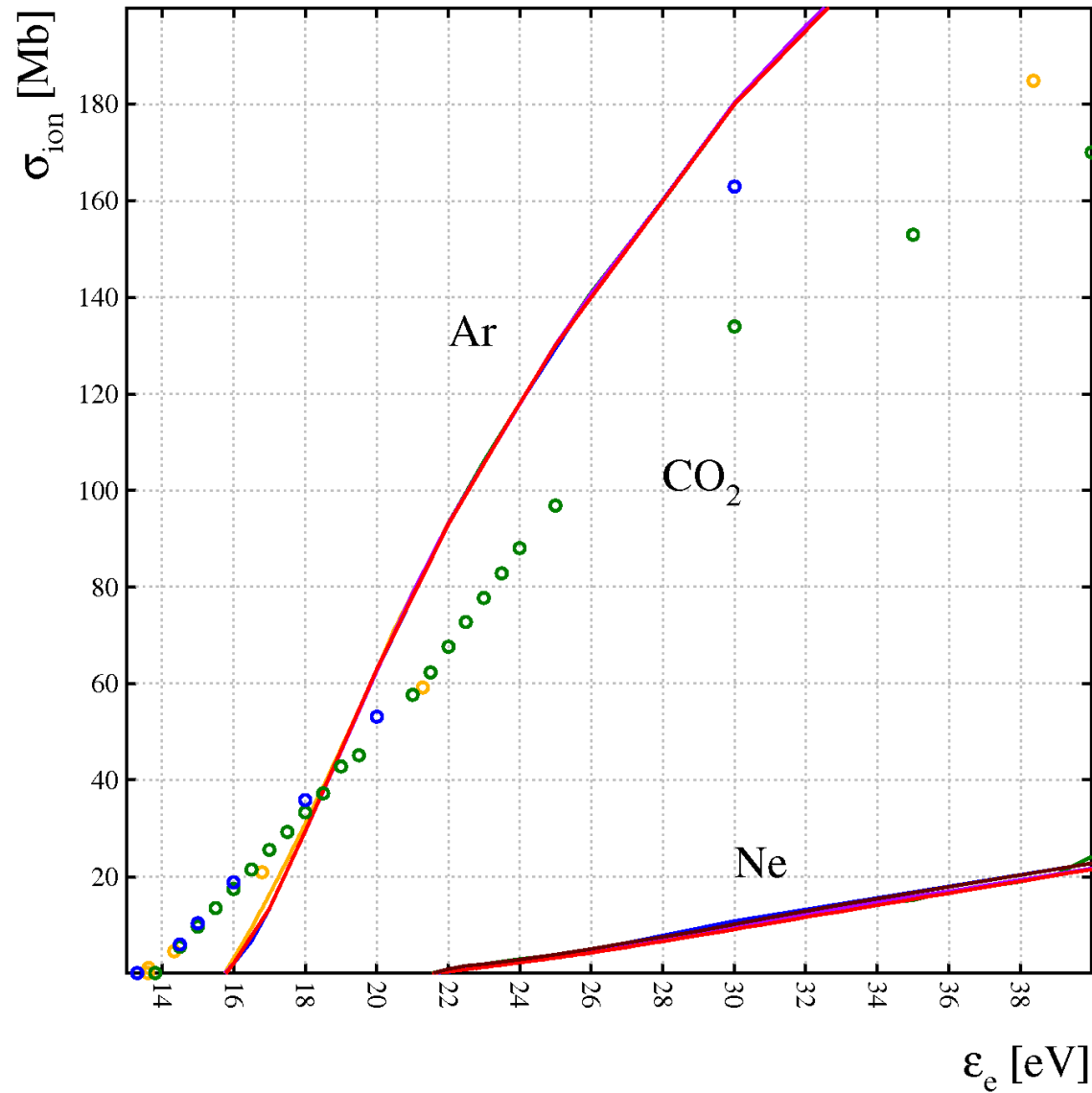
# Mobility

- ▶ The velocity with which ions move is usually expressed in the form of a mobility:
  - ▶  $v_D$ : drift velocity
  - ▶  $K$ : mobility  $v_D = K E$
  - ▶  $E$ : electric field
- ▶ Reason: for moderate fields, the mobility is approximately constant.

# Electron-impact cross sections

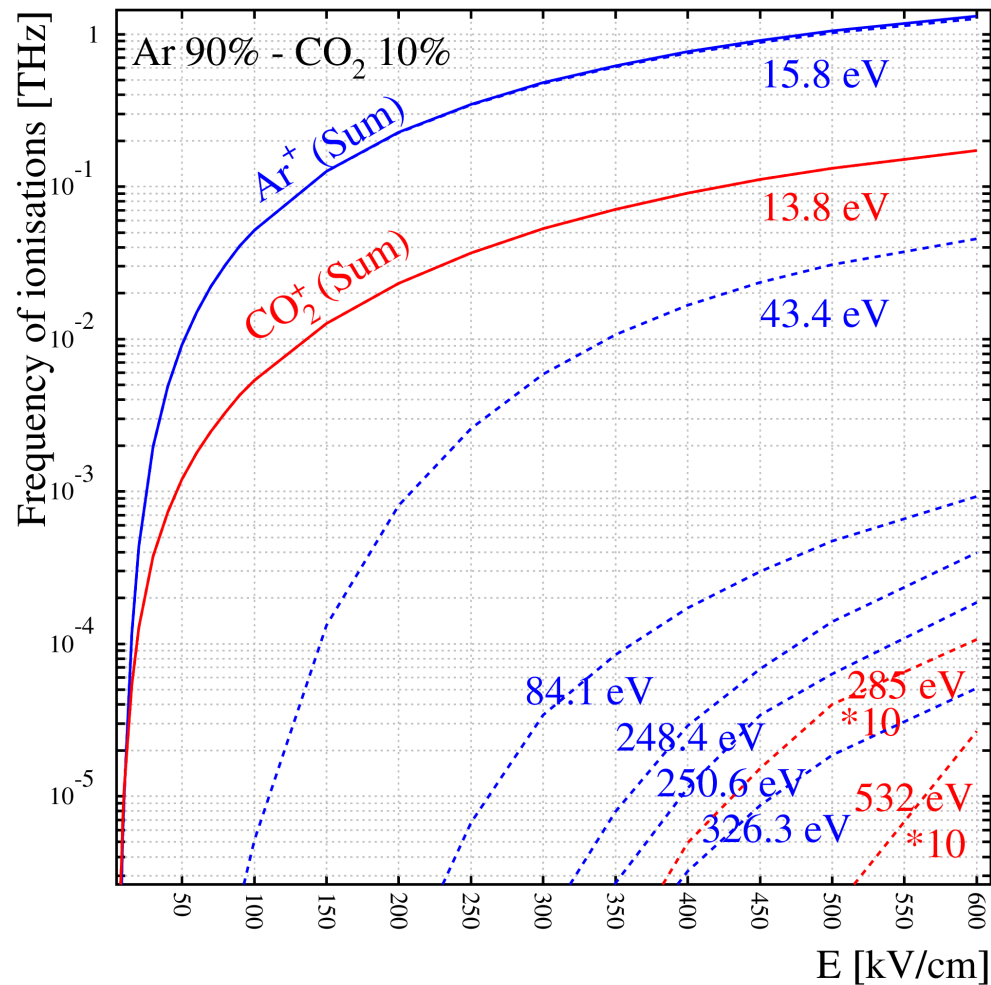
- ▶  $\text{CO}_2^+$  and  $\text{Ar}^+$  compete.
- ▶  $\text{Ne}^+$  has higher threshold and is produced less.

[Pure gases, data from LXcat]

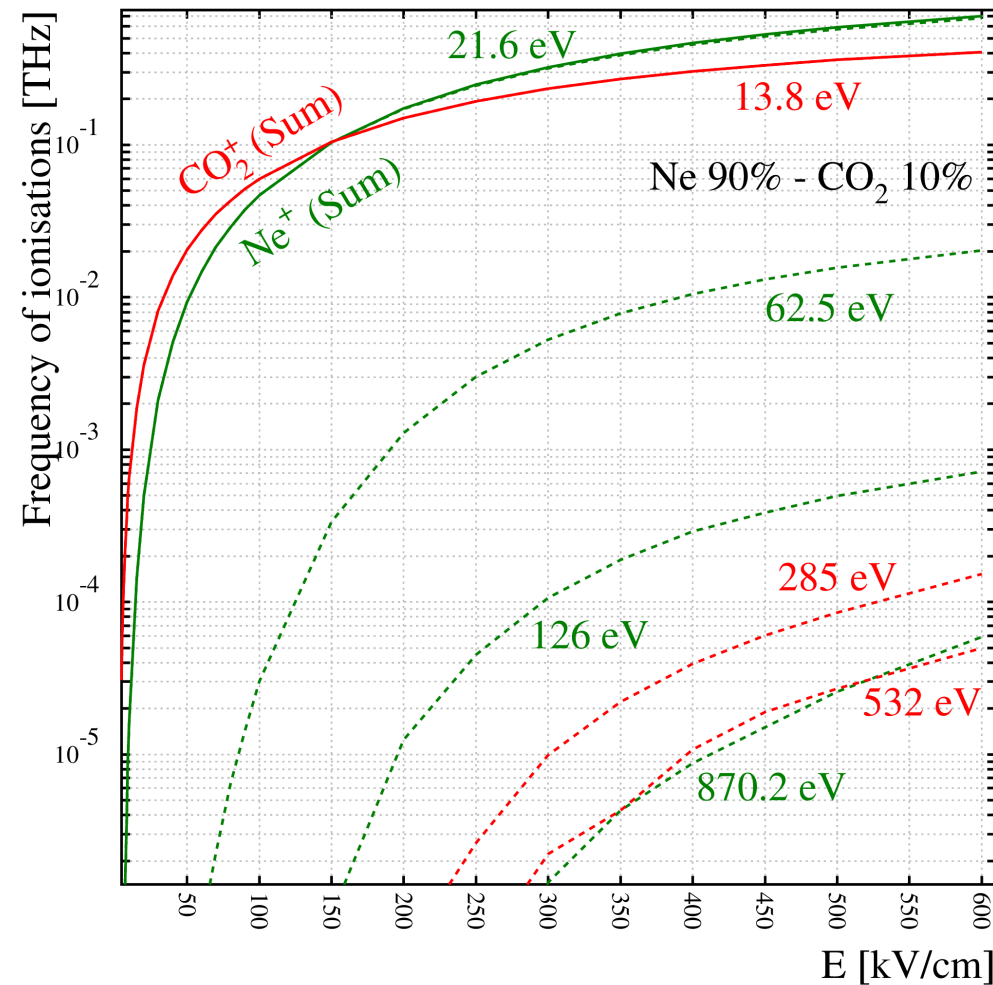


# Avalanche products

►  $\text{Ar}^+$  dominates in  $\text{Ar-CO}_2$ ,



$\text{CO}_2^+$  and  $\text{Ne}^+$  in  $\text{Ne-CO}_2$



# Avalanche products in Ar-CO<sub>2</sub>

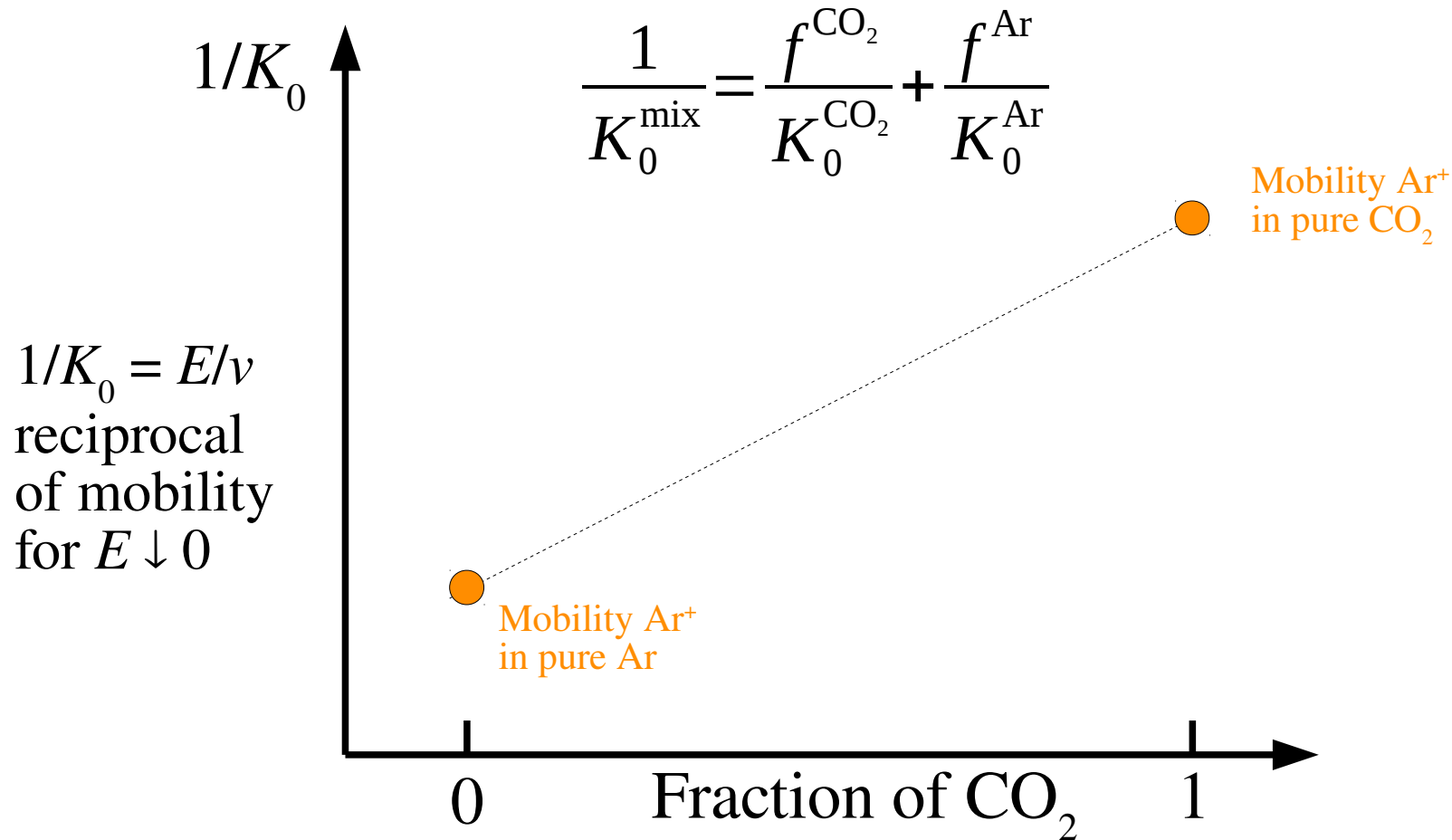
- ▶ This tells us that avalanches primarily produce Ar<sup>+</sup> ions.
- ▶ Does this mean that the signals are generated by Ar<sup>+</sup> ions ?  
Maybe.
- ▶ If so, we need the **mobility of Ar<sup>+</sup> in Ar-CO<sub>2</sub> mixtures.**
- ▶ This can in principle be calculated with Blanc's law.

# Avalanche products in Ne-CO<sub>2</sub>

- ▶ This tells us that avalanches produce mostly CO<sub>2</sub><sup>+</sup> ions and a few Ne<sup>+</sup> ions.
- ▶ Does this mean that the signals are generated by CO<sub>2</sub><sup>+</sup> and Ne<sup>+</sup> ions ? Maybe.
- ▶ If so, we need the **mobility of CO<sub>2</sub><sup>+</sup> and Ne<sup>+</sup> in Ne-CO<sub>2</sub> 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/jphysap:019080070082501]

# Known & unknown mobilities

## ▶ Known mobilities:

- ▶  $\text{Ar}^+$  in Ar,       $\text{Ne}^+$  in Ne,
- ▶  $\text{Ar}_2^+$  in Ar,       $\text{Ne}_2^+$  in Ne,
- ▶  $\text{CO}_2^+$  in Ar,       $\text{CO}_2^+$  in Ne.

## ▶ Not published:

- ▶  $\text{Ar}^+$  in  $\text{CO}_2$ ,       $\text{Ne}^+$  in  $\text{CO}_2$ .

why ?

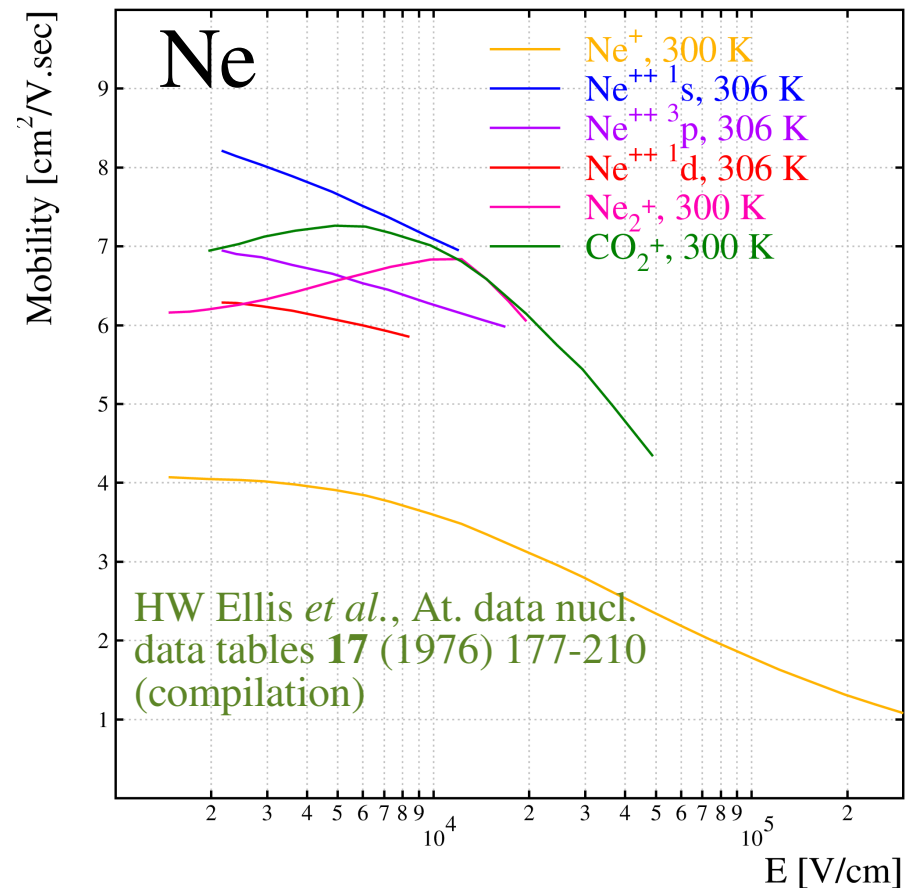
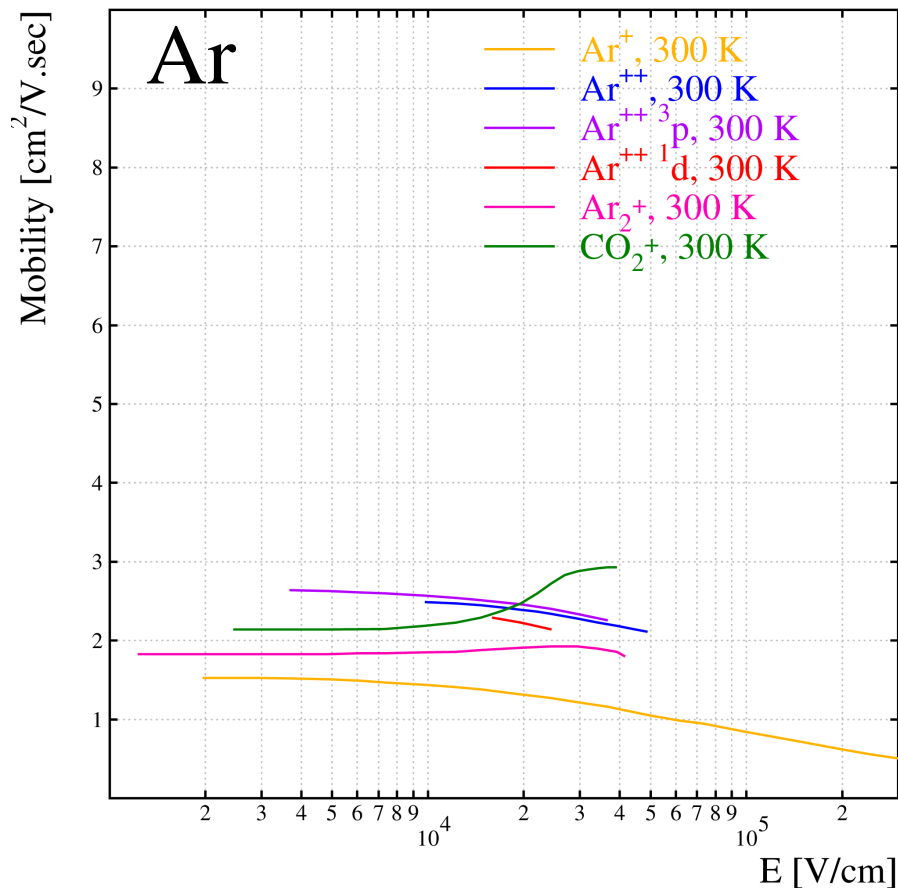
## ▶ Published, but controversial:

- ▶  $\text{CO}_2^+$  in  $\text{CO}_2$ .

can you guess why ?

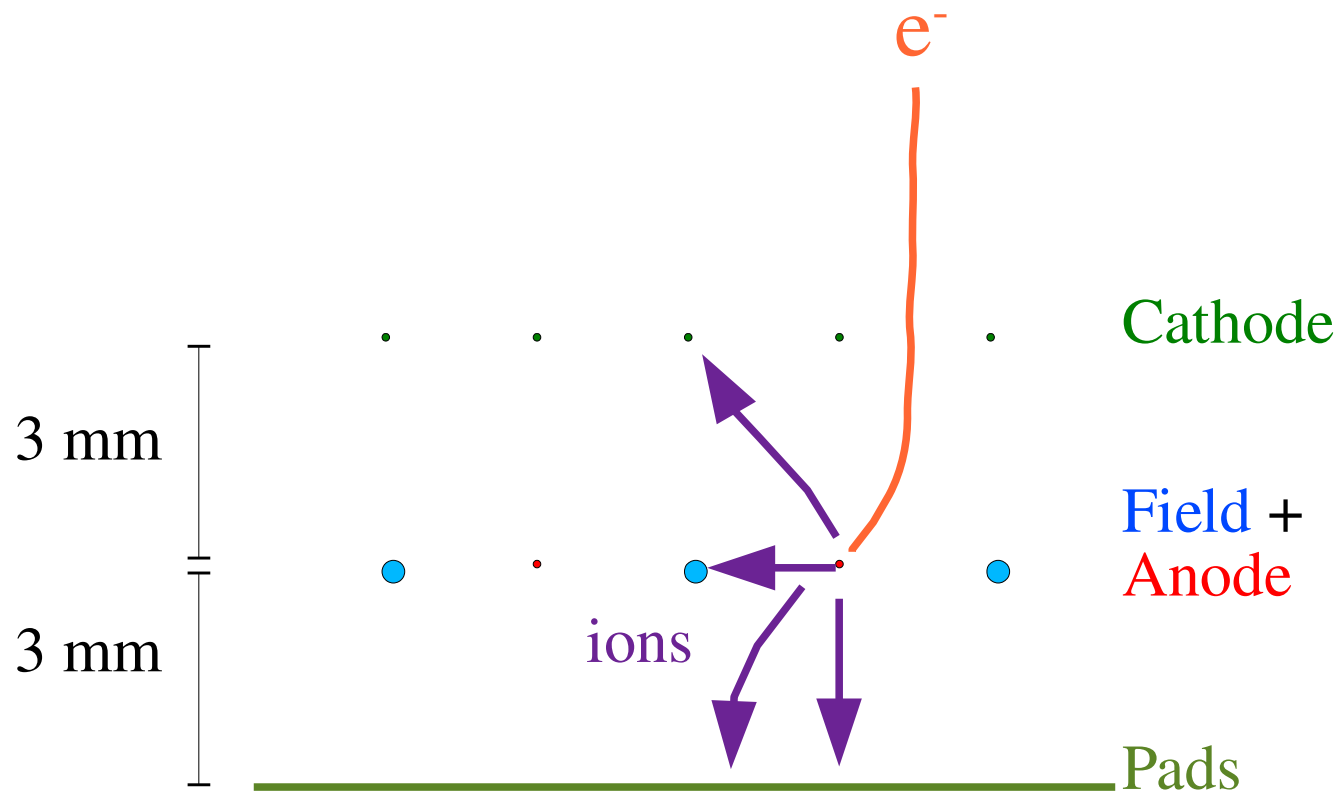
# Ar<sup>+</sup> and Ne<sup>+</sup> mobility $\equiv v_D(E) / E$

► Noble gas ion mobilities are well known:



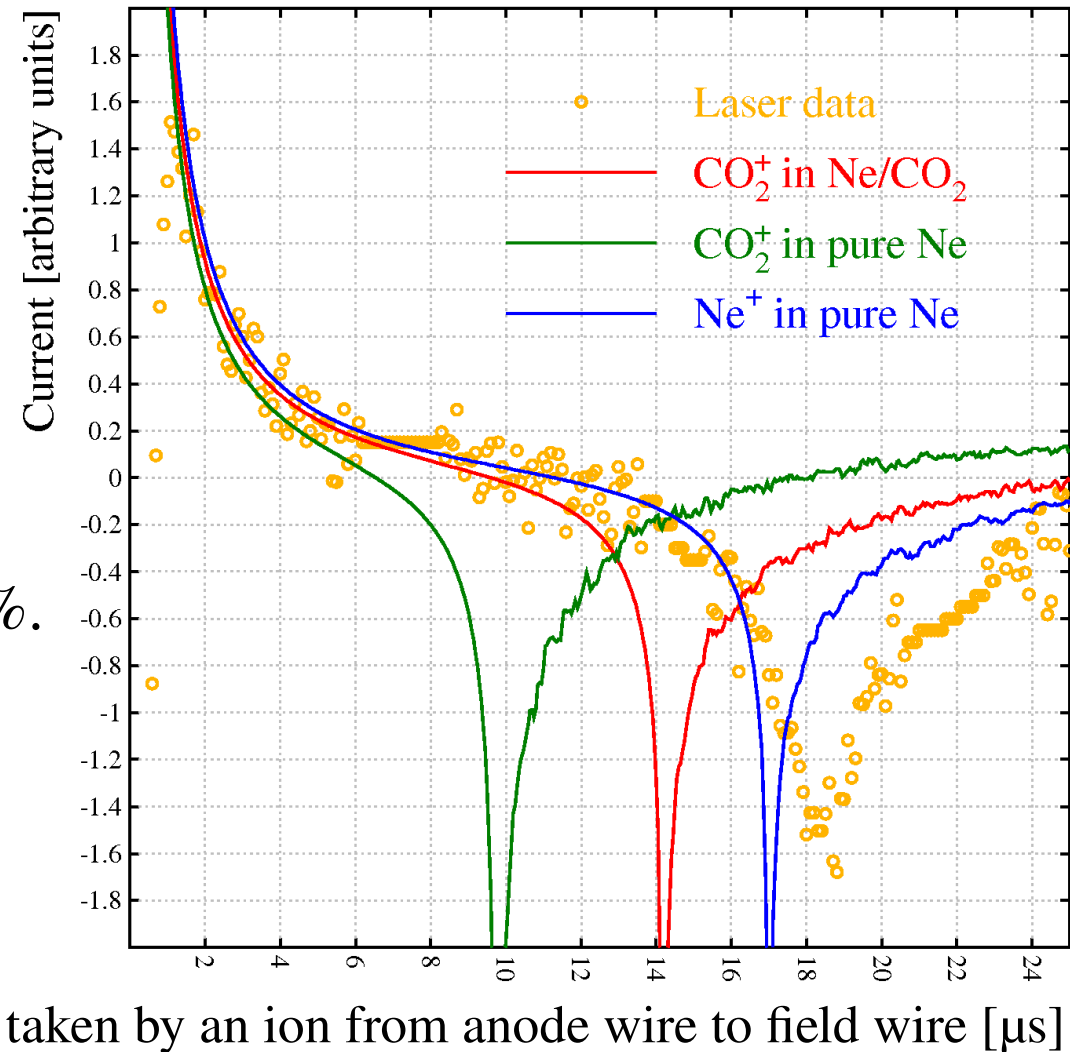
# Ion induced signals

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



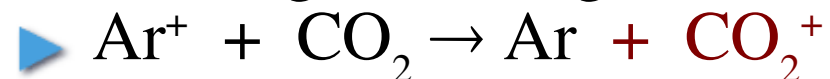
# Signals in Ne-CO<sub>2</sub>

- ▶ Ne<sup>+</sup> in Ne comes nearest to the measurements ...
- ▶ we've used it for years ...
- ▶ but does it make sense ?
- ▶ NA49 TPC: Ne 90 % CO<sub>2</sub> 10 %.  
[Data: Rainer Renfordt]

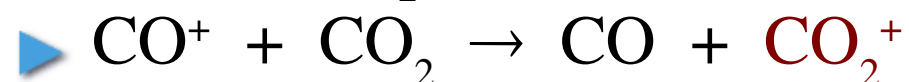
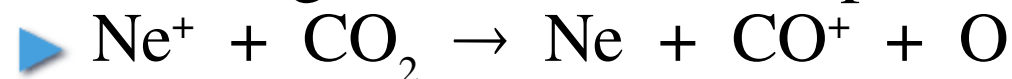


# Principal reactions involving CO<sub>2</sub>

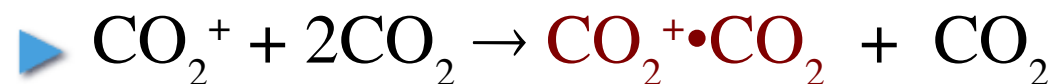
▶ Ar<sup>+</sup>: charge exchange,  $\tau \approx 0.85$  ns



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



▶ CO<sub>2</sub>: 3-body association, 7-20 ps



[For 10 % CO<sub>2</sub>, atmospheric pressure, room temperature]

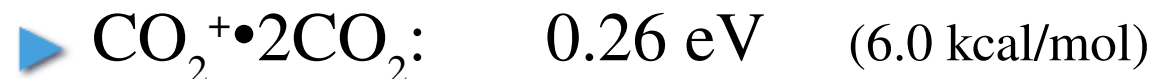
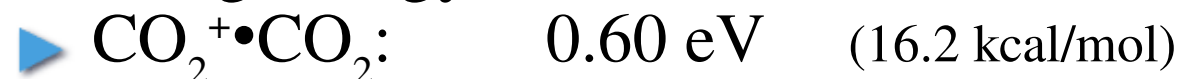
# Situating cluster ions

- ▶ 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

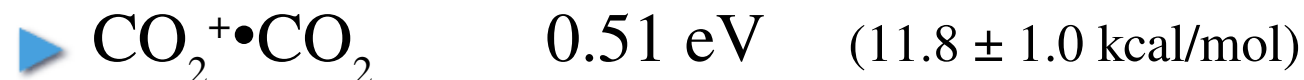
[B.M. Smirnov, "Cluster Ions and Van Der Waals Molecules," CRC press]

# Binding energy of CO<sub>2</sub> 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)

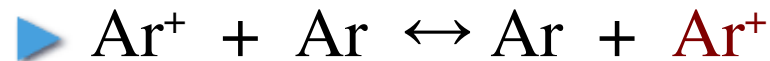


# Life cycle of $\text{CO}_2^+\bullet(\text{CO}_2)_n$

- ▶  $\text{CO}_2^+\bullet\text{CO}_2$  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 %  $\text{CO}_2$  with Ar +  $\text{CO}_2$  as “helpers”.
- ▶ Any isolated  $\text{CO}_2^+$  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<sup>+</sup> and Ne<sup>+</sup>

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



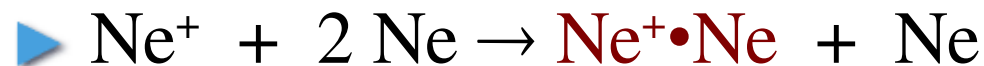
▶  $k = 4.6 \cdot 10^{-10} \text{ cm}^3/\text{s}$ ,  $\tau \approx 100 \text{ ps}$  (for  $N_{\text{Ar}} = 2.45 \cdot 10^{19}/\text{cm}^3$ )

▶ Ar<sub>2</sub><sup>+</sup> dimer formation:



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

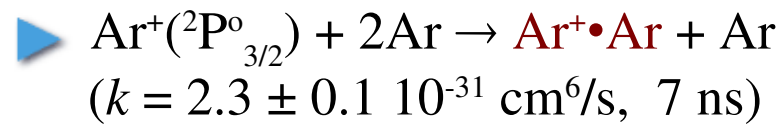
▶ Ne<sub>2</sub><sup>+</sup> dimer formation:



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

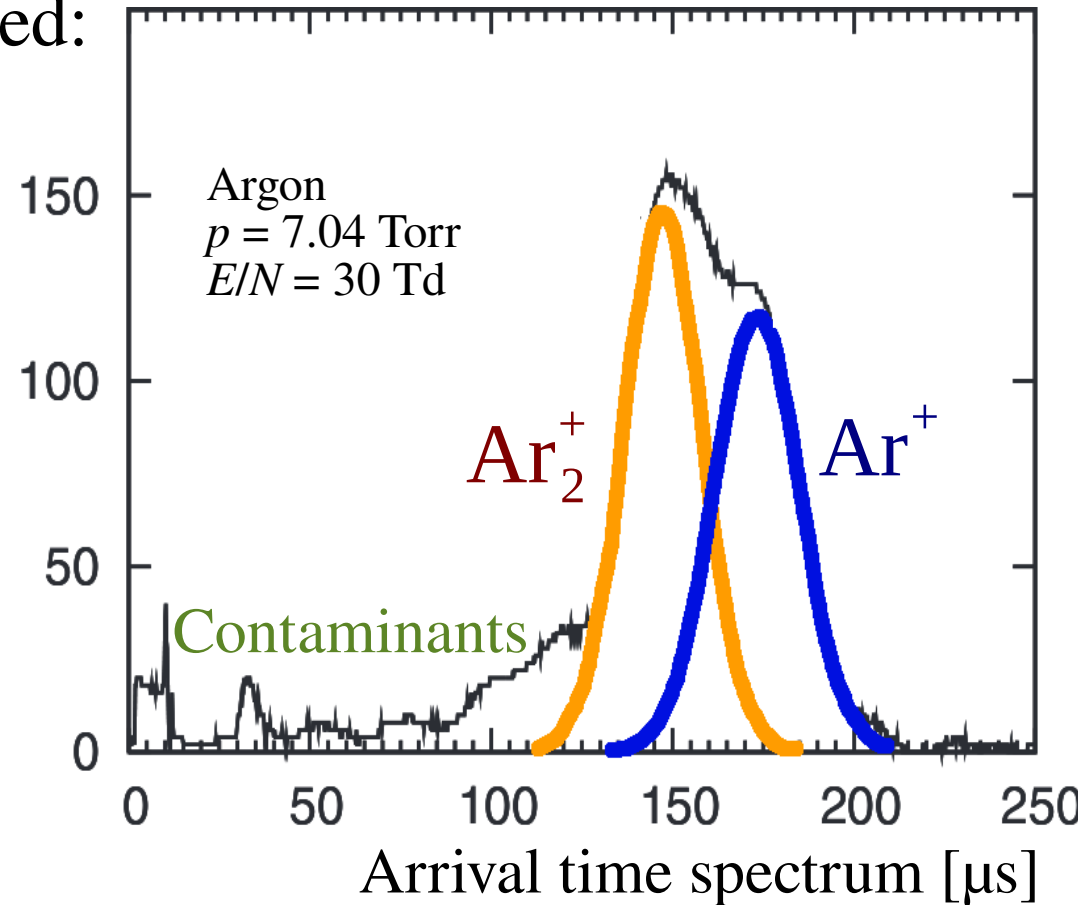
# Ions drifting in pure Ar

► 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 ( $\mu$  = reduced mass):

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

- ▶ Multiplying with the cross section  $\sigma$  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/cm<sup>3</sup>];
- ▶ The proportionality factor  $k$  is called **rate constant**:
  - ▶ rate =  $k$  [cm<sup>3</sup>/s]  $N_B$  [1/cm<sup>3</sup>].
  - ▶ The reaction time  $\tau$  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  $\text{cm}^6/\text{s}$ .
- ▶ Example 1:  $\text{Ar}^+ + \text{Ar} + \text{Ar} \rightarrow \text{Ar}^+\bullet\text{Ar} + \text{Ar}$ 
  - ▶  $k = 2.3 \cdot 10^{-31} \text{ cm}^6/\text{s}$ , 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:  $\text{CO}_2^+ + \text{CO}_2 + \text{CO}_2 \rightarrow \text{CO}_2^+\bullet\text{CO}_2 + \text{CO}_2$ 
  - ▶  $k = 2.4 \cdot 10^{-28} \text{ cm}^6/\text{s}$
  - ▶ rate =  $k N^2 = 1.4 \cdot 10^{11}/\text{s}$ ,  $\tau = 7 \text{ ps}$

# mathematica

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

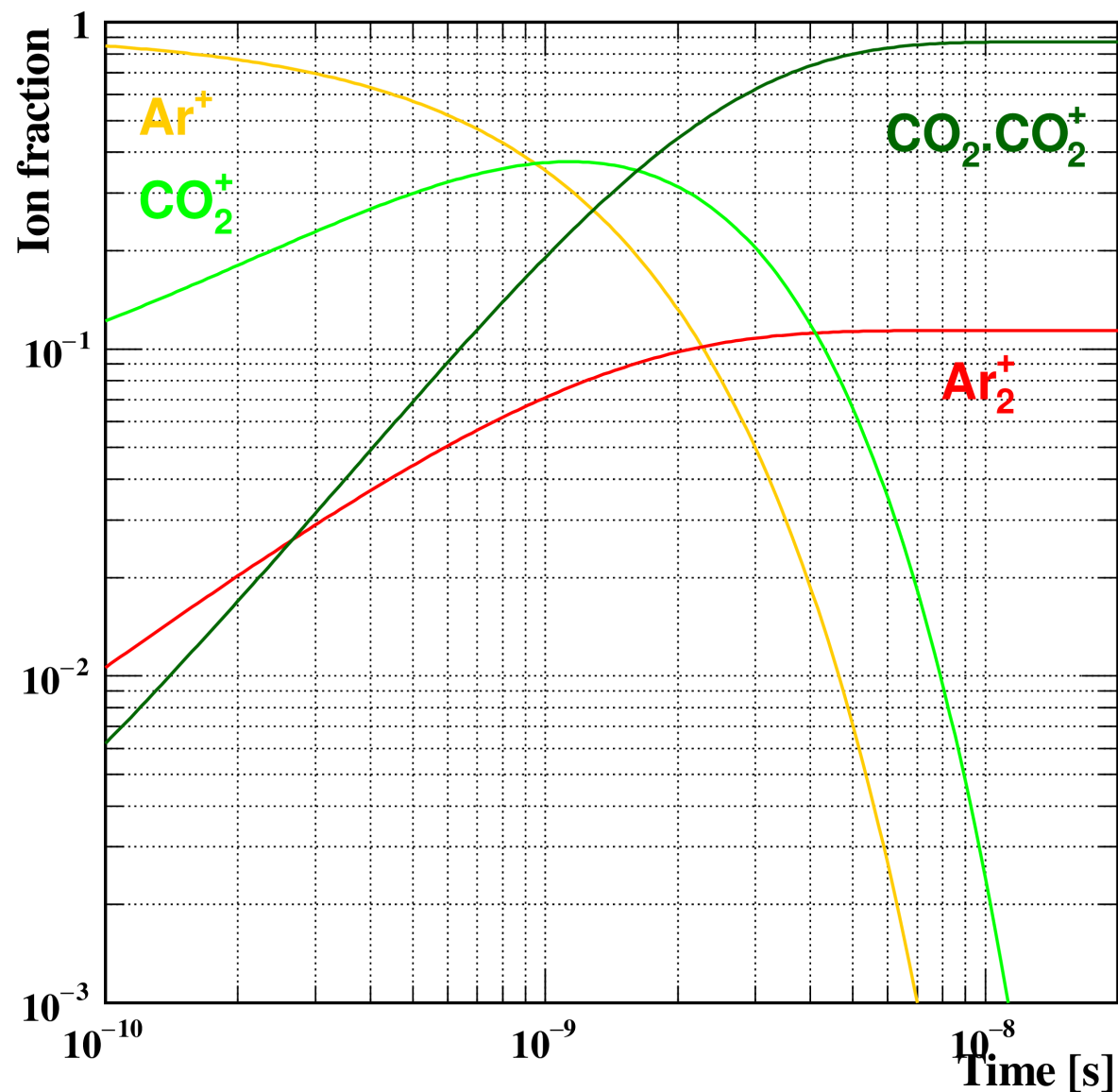
   nCO2'[x] == rArCO2 nAr[x] - rCO2cl nCO2[x],
   nCO2[0] == n0CO2,

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

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

# Evolution in Ar-CO<sub>2</sub> (93-7)

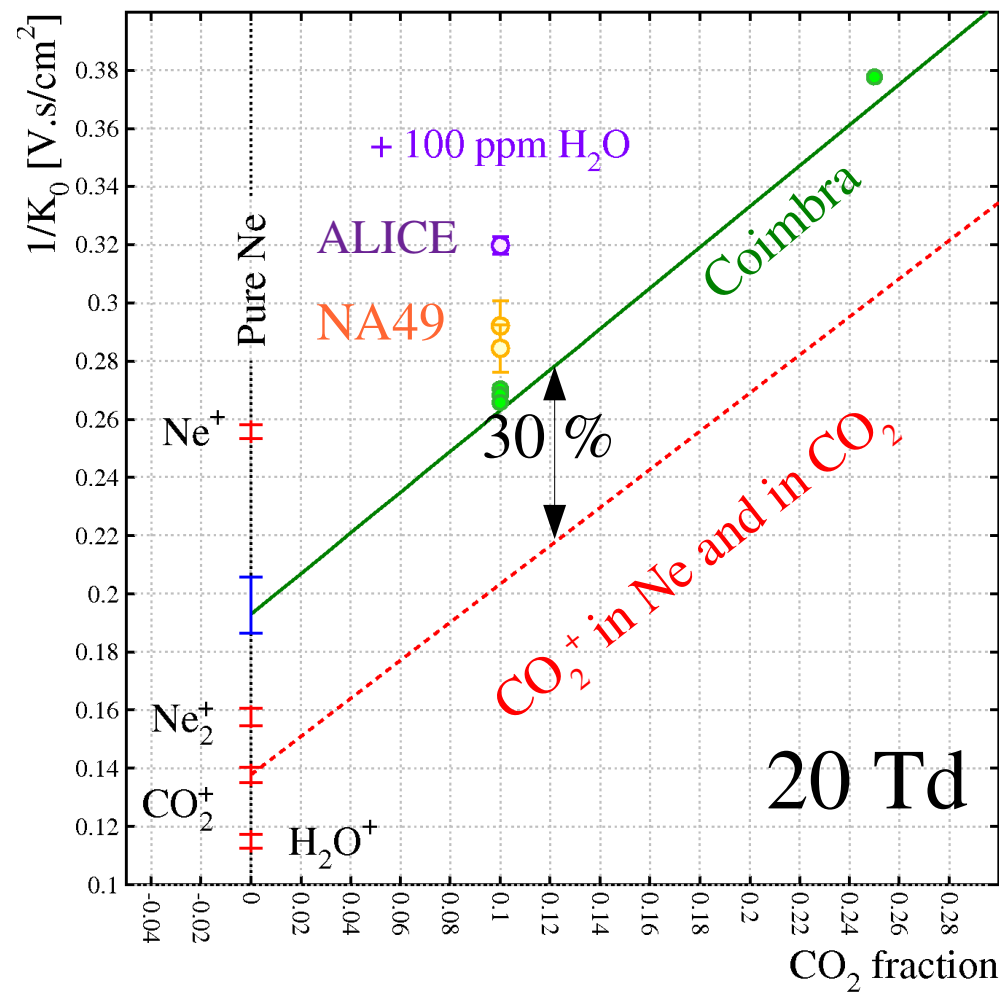
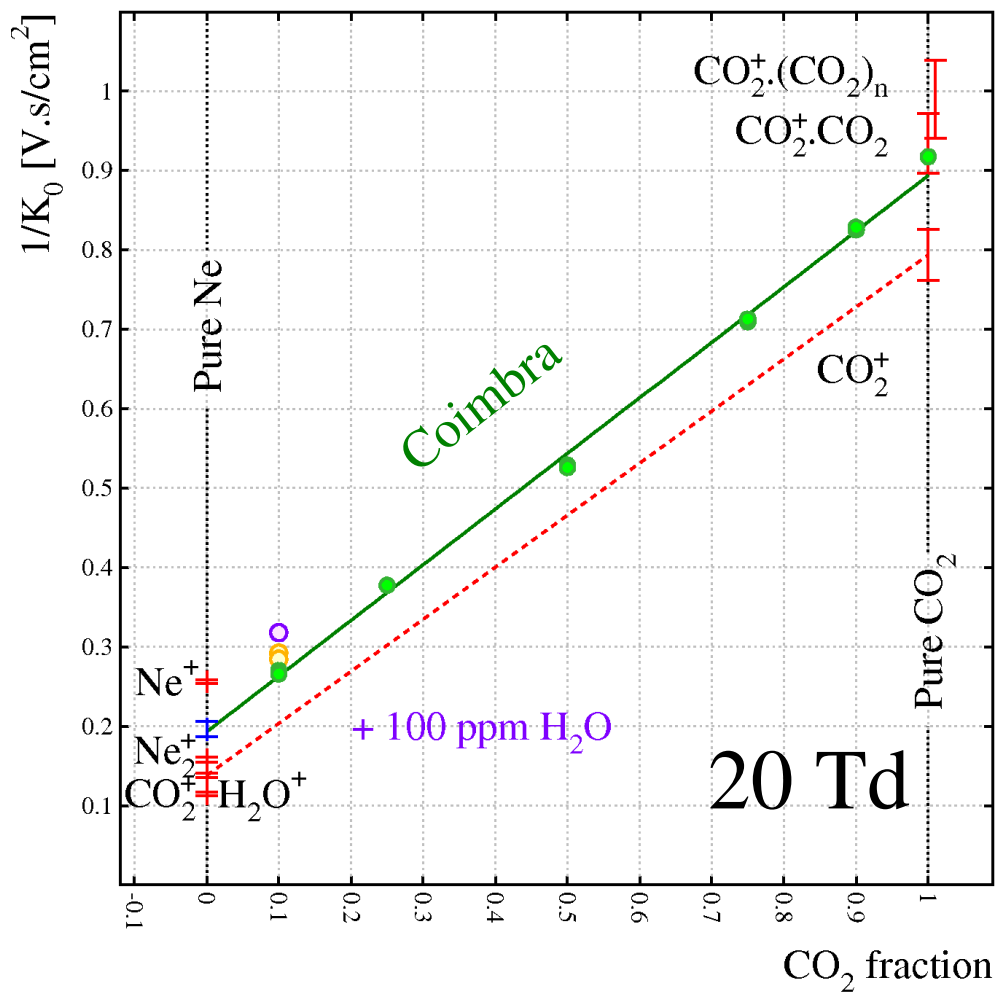
- ▶ Initial ions:
- ▶ Ar<sup>+</sup> →
  - ▶ CO<sub>2</sub><sup>+</sup>
  - ▶ Ar<sub>2</sub><sup>+</sup>
  - ▶ CO<sub>2</sub><sup>+</sup> →
  - ▶ CO<sub>2</sub><sup>+</sup>·CO<sub>2</sub>





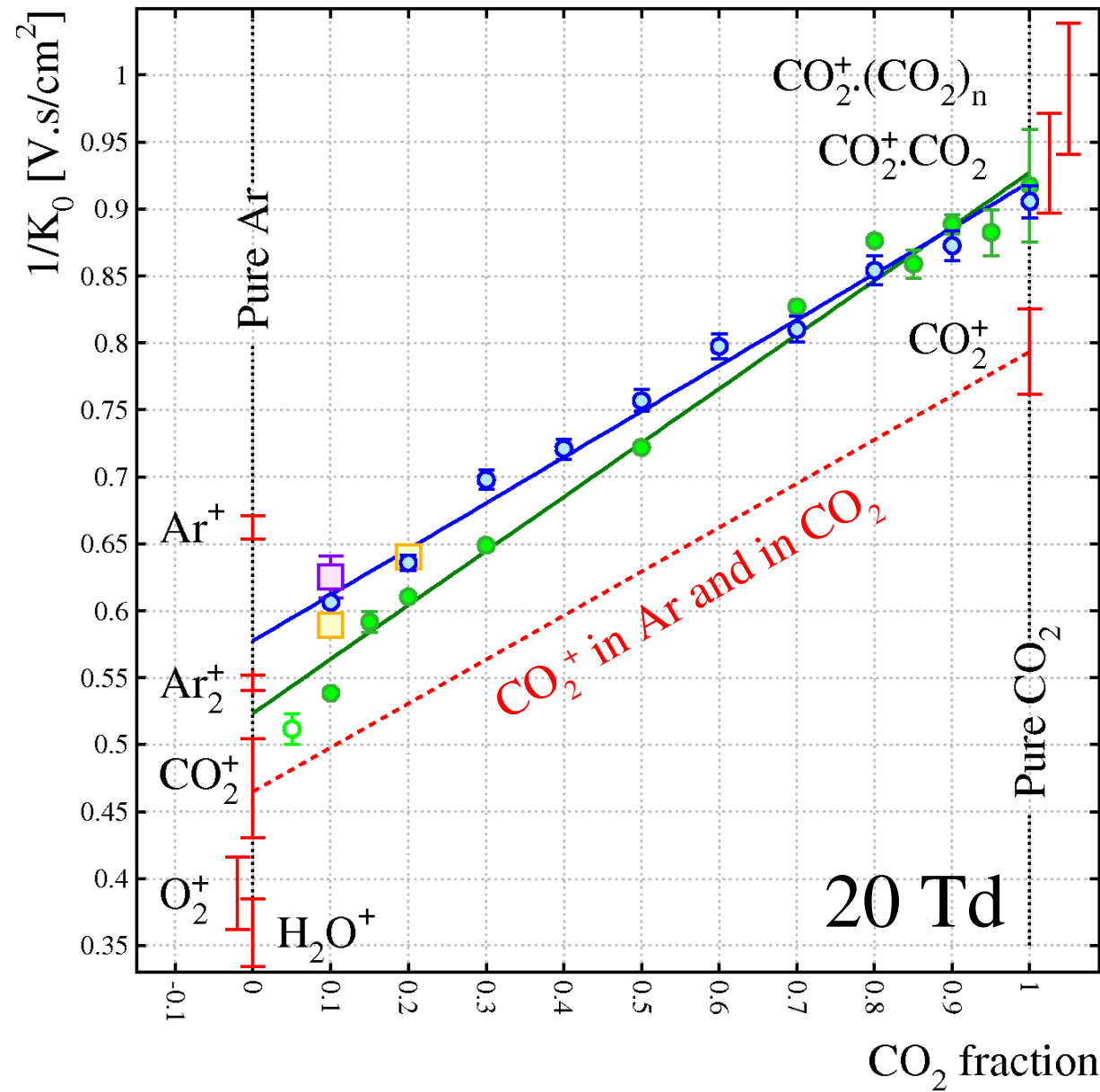
# Blanc diagram for Ne-CO<sub>2</sub>

- ▶ Like in Ar-CO<sub>2</sub>, CO<sub>2</sub><sup>+</sup> forms clusters in Ne-CO<sub>2</sub>.



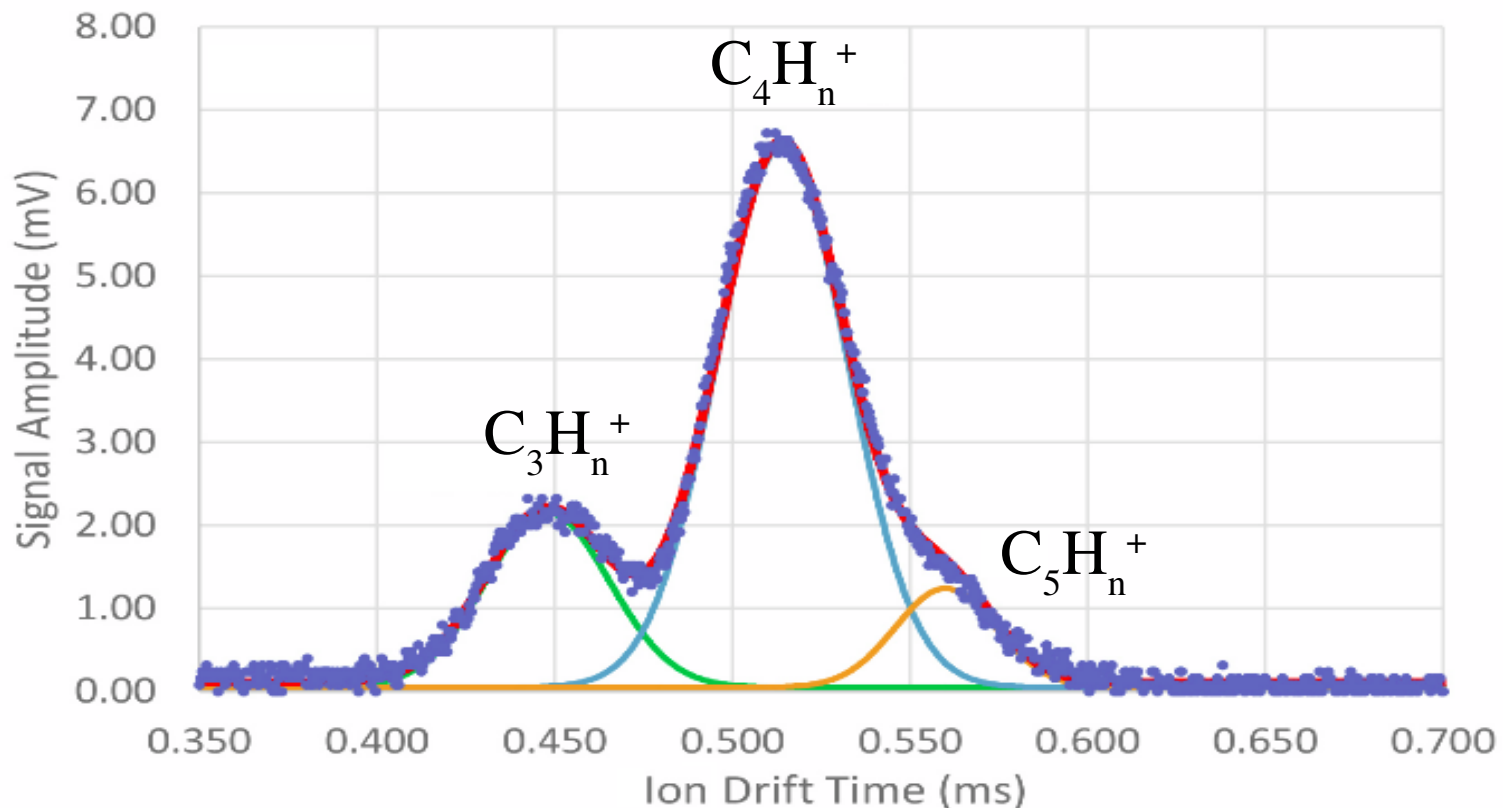
# Blanc diagram for Ar-CO<sub>2</sub>

- ▶ **Coxon:** pure CO<sub>2</sub>
- ▶ **Schultz:** 1 atm
- ▶ **Coimbra:** 0.01 atm, smaller clusters ?
- ▶ **NA49:** 1 atm
- ▶ **ALICE:** 1 atm, water clusters ?



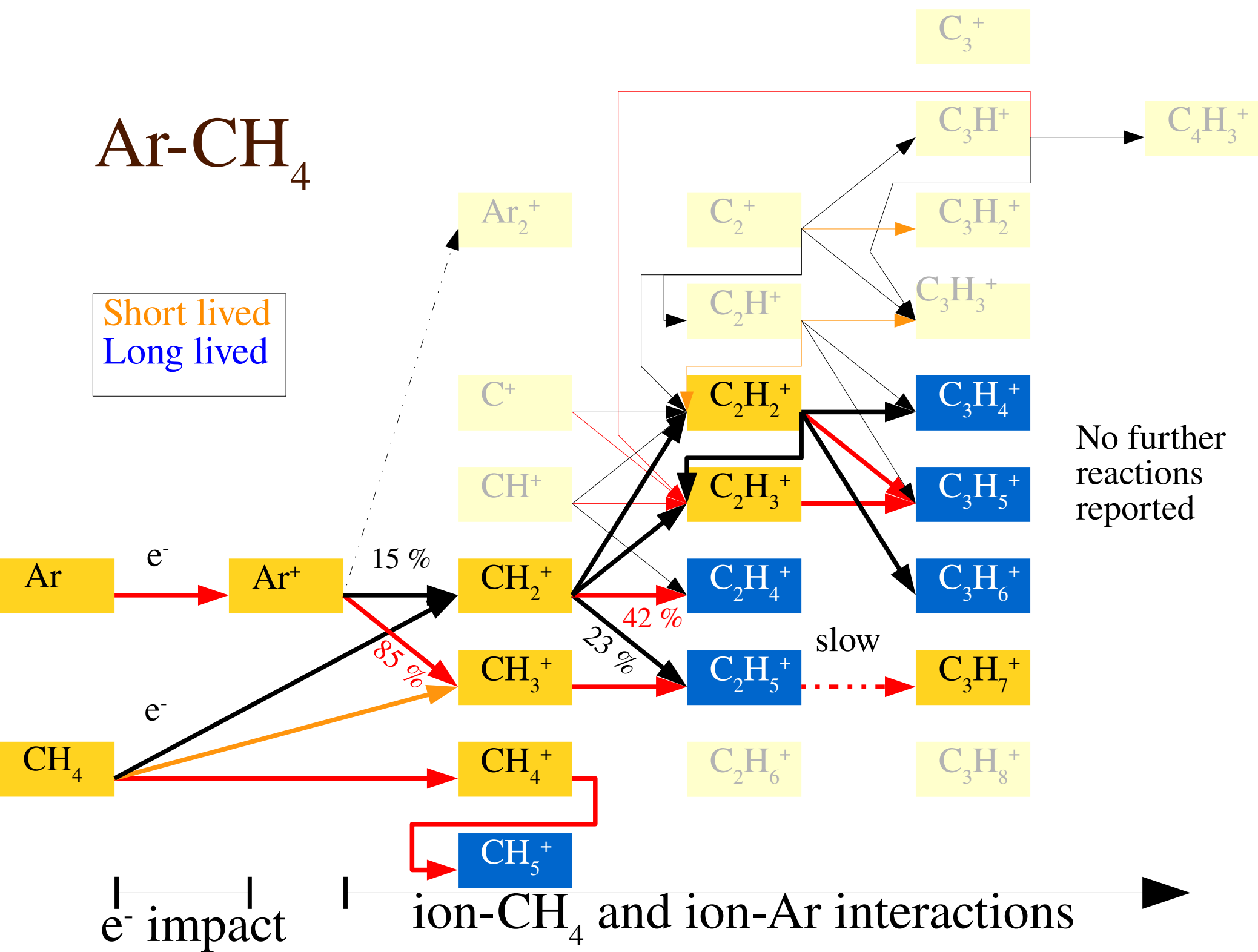
# How about alkanes ?

- ▶ Ar 90 % - C<sub>2</sub>H<sub>6</sub> 10 %, at low pressure.
- ▶ Expect Ar<sup>+</sup> or C<sub>2</sub>H<sub>6</sub><sup>+</sup> but ... none are seen – why ?





Short lived  
Long lived



# Avalanche ions in Ar-CO<sub>2</sub>-CH<sub>4</sub> (90-7-3)

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

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

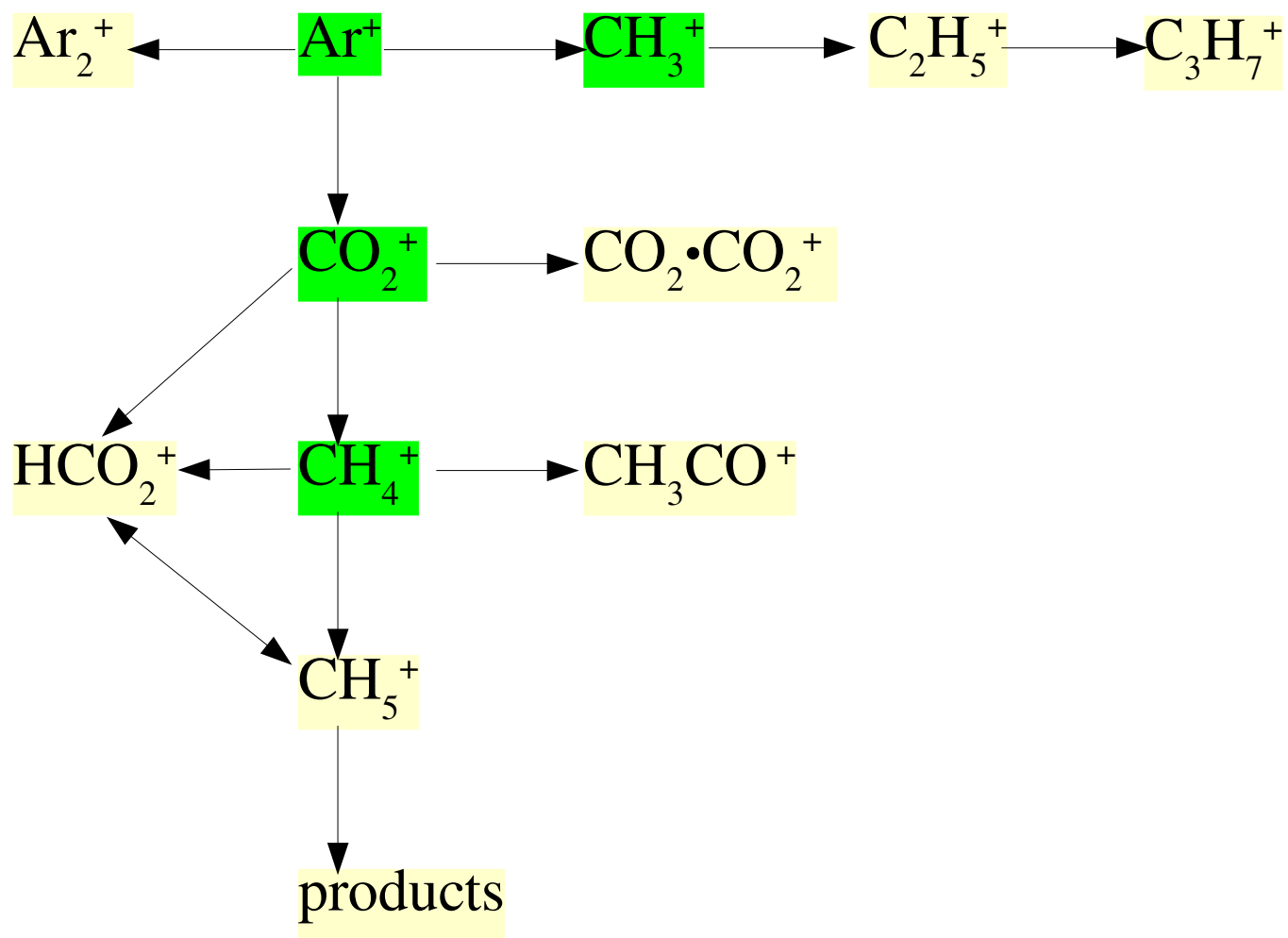
# Reactions in Ar-CO<sub>2</sub>-CH<sub>4</sub>

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

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

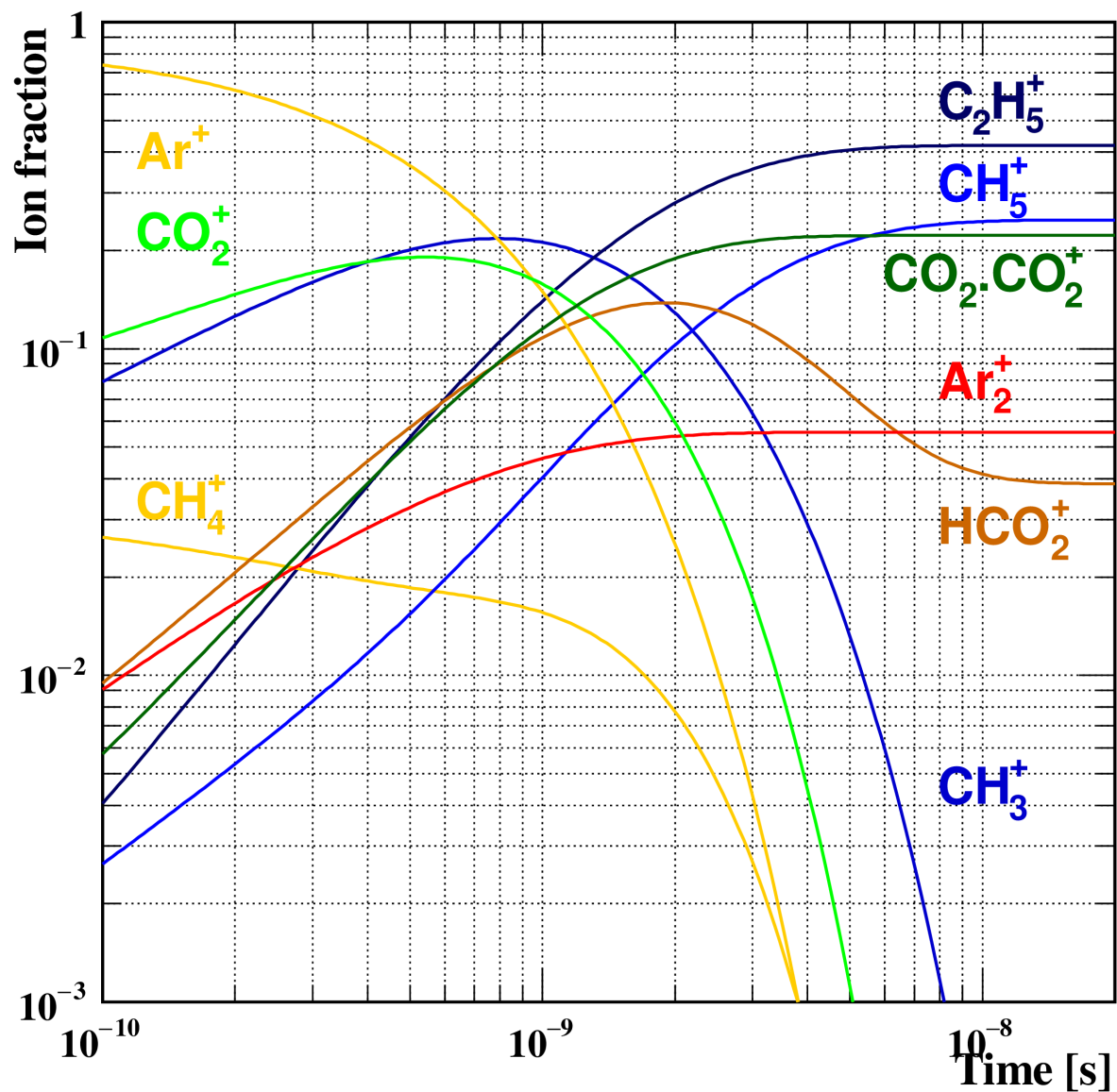
[V.G. Anicich and W.T. Huntress Jr., Astrophys. J. Suppl. **62** (1986) 553-672.]

# Reaction chains



# Evolution in Ar-CO<sub>2</sub>-CH<sub>4</sub> (90-7-3)

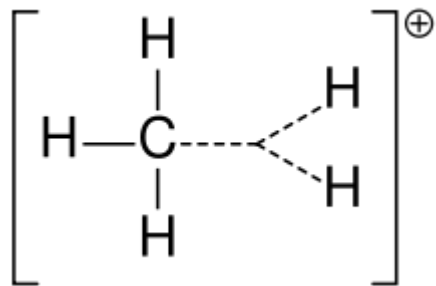
- Initial ions:
- ▶ Ar<sup>+</sup> →
  - ▶ CO<sub>2</sub><sup>+</sup>,
  - ▶ CH<sub>3</sub><sup>+</sup>,
  - ▶ Ar<sub>2</sub><sup>+</sup>
  - ▶ CO<sub>2</sub><sup>+</sup> →
  - ▶ CH<sub>4</sub><sup>+</sup>
  - ▶ CO<sub>2</sub><sup>+</sup>·CO<sub>2</sub>
  - ▶ HCO<sub>2</sub><sup>+</sup>
  - ▶ CH<sub>4</sub><sup>+</sup> →
  - ▶ CH<sub>5</sub><sup>+</sup>,
  - ▶ HCO<sub>2</sub><sup>+</sup>
  - ▶ CH<sub>3</sub>CO<sup>+</sup>
  - ▶ CH<sub>3</sub><sup>+</sup> →
  - ▶ C<sub>2</sub>H<sub>5</sub><sup>+</sup>



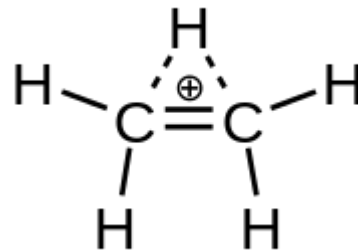


# Products after 10 ns

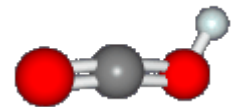
- ▶  $\text{C}_2\text{H}_5^+ \rightarrow \text{C}_3\text{H}_7^+$  slow reaction,  $k = 1 \cdot 10^{-14}$   
[Hiraoka & Kebarle <https://doi.org/10.1063/1.431116>]
- ▶  $\text{CH}_5^+ \rightarrow$  “products” slow reaction,  $k = 3 \cdot 10^{-11}$
- ▶  $\text{CO}_2 \cdot \text{CO}_2^+ \rightarrow$  grows to  $n = 3-4$ , reacts with  $\text{CH}_4$  to  $\text{HCO}_2^+$  ?  
[Y. Kalkan et al. 2015 JINST 10 P07004]
- ▶  $\text{Ar}^+ \rightarrow \text{Ar}_2^+$  drifts faster than  $\text{Ar}^+$
- ▶  $\text{HCO}_2^+ \rightarrow \text{CH}_5^+$   $\text{HCO}_2^+$  decays at  $k = 6 \cdot 10^{-10}$



methanium



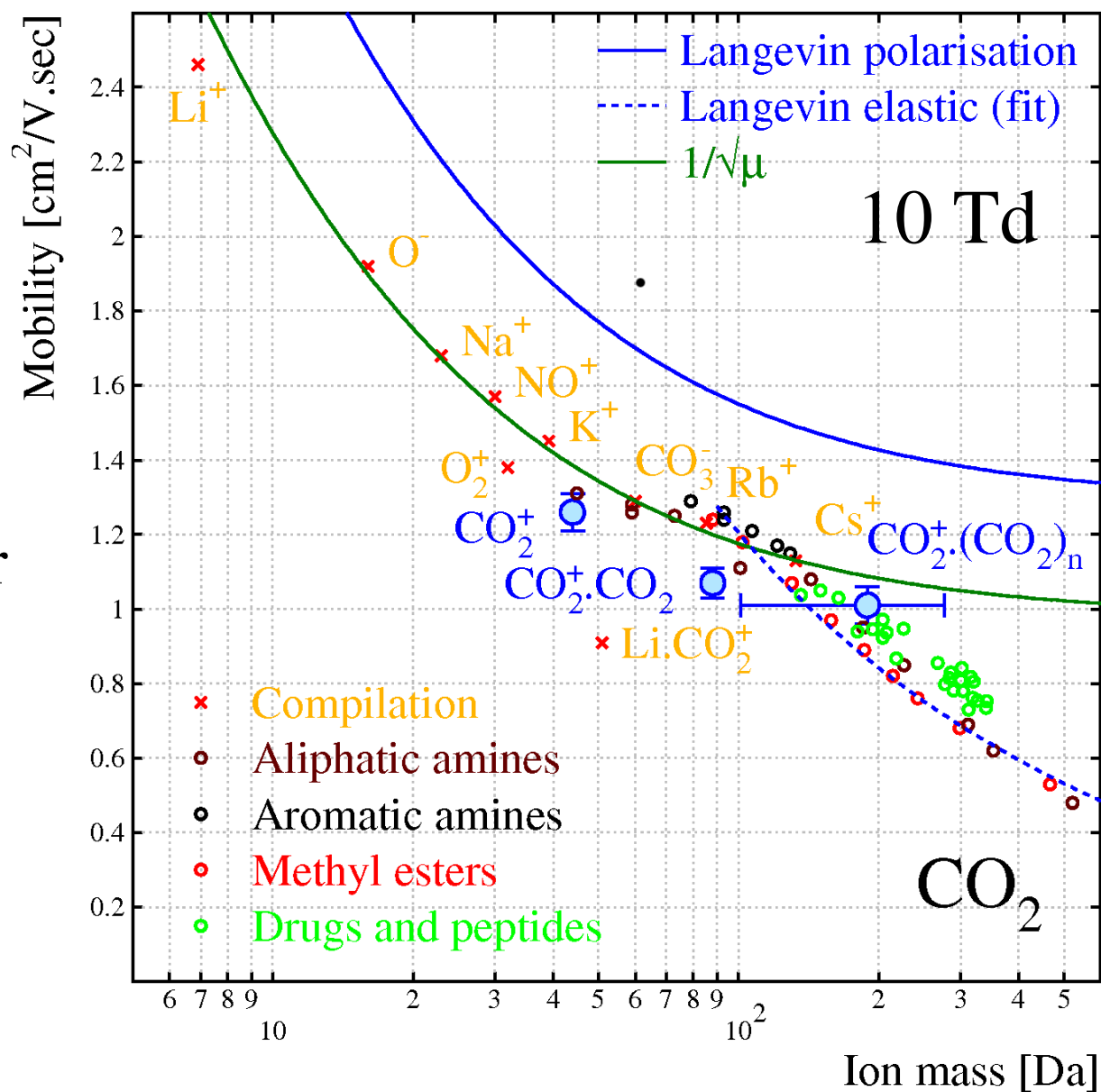
ethenium



protonated  
carbon dioxide

# Mass-mobility in CO<sub>2</sub>

- ▶ 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.



# Summary ions

- ▶ Avalanches ionise the constituent gases, and the initial ions undergo a staggering sequence of reactions.
  - ▶ In Ar-CO<sub>2</sub> and Ne-CO<sub>2</sub> mixtures, the signal ions are CO<sub>2</sub><sup>+</sup>•(CO<sub>2</sub>)<sub>n</sub> clusters;
  - ▶ water forms larger clusters, further reducing the mobility;
  - ▶ pure noble gases form dimers, Ar<sub>2</sub><sup>+</sup>, Ne<sub>2</sub><sup>+</sup> which are faster than Ar<sup>+</sup> and Ne<sup>+</sup> due to resonant charge exchange;
  - ▶ Xe forms dimers, trimers and probably bigger objects;
  - ▶ alkanes combine to form heavier molecules;
  - ▶ CH<sub>4</sub> leads to exotic molecules.
- ▶ There is room for these in this field.

# Overview

- ▶ Xe-CH<sub>4</sub>
  - ▶ CH<sub>5</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>7</sub><sup>+</sup>, Xe<sub>2</sub><sup>+</sup>
- ▶ Xe-C<sub>2</sub>H<sub>6</sub>
  - ▶ C<sub>3</sub>H<sub>n</sub><sup>+</sup>, C<sub>4</sub>H<sub>n</sub><sup>+</sup>, Xe<sub>2</sub><sup>+</sup>
- ▶ Xe-CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub>
  - ▶ C<sub>2</sub>H<sub>4</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, C<sub>2</sub>H<sub>6</sub><sup>+</sup>, XeC<sub>2</sub>H<sub>6</sub><sup>+</sup>, CO<sub>2</sub>•CO<sub>2</sub><sup>+</sup>
- ▶ Xe-CF<sub>4</sub>
  - ▶ CF<sub>3</sub><sup>+</sup>, Xe<sub>2</sub><sup>+</sup>
- ▶ Xe-CF<sub>4</sub>-CO<sub>2</sub>
  - ▶ Xe<sup>+</sup>, Xe<sub>2</sub><sup>+</sup>, CF<sub>3</sub><sup>+</sup>, CO<sub>2</sub>•CO<sub>2</sub><sup>+</sup>
- ▶ Ar-CH<sub>4</sub>
  - ▶ CH<sub>5</sub><sup>+</sup>, C<sub>2</sub>H<sub>4</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>4</sub><sup>+</sup>, C<sub>3</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>6</sub><sup>+</sup>, C<sub>3</sub>H<sub>7</sub><sup>+</sup>, Ar<sub>2</sub><sup>+</sup>
- ▶ Ar-C<sub>2</sub>H<sub>6</sub>
  - ▶ C<sub>3</sub>H<sub>n</sub><sup>+</sup>, C<sub>4</sub>H<sub>n</sub><sup>+</sup>, Ar<sub>2</sub><sup>+</sup>
- ▶ Ar-iC<sub>4</sub>H<sub>10</sub>
  - ▶ C<sub>4</sub>H<sub>10</sub><sup>+</sup>, C<sub>8</sub>H<sub>n</sub><sup>+</sup>, C<sub>12</sub>H<sub>m</sub><sup>+</sup>
- ▶ Ar-CF<sub>4</sub>
  - ▶ CF<sub>3</sub><sup>+</sup>
- ▶ Ar-CO<sub>2</sub>
  - ▶ CO<sub>2</sub>•CO<sub>2</sub><sup>+</sup>, Ar<sub>2</sub><sup>+</sup>
- ▶ Ar-CO<sub>2</sub>-CH<sub>4</sub>
  - ▶ C<sub>2</sub>H<sub>5</sub><sup>+</sup>, CH<sub>5</sub><sup>+</sup>, CO<sub>2</sub>•CO<sub>2</sub><sup>+</sup>, Ar<sub>2</sub><sup>+</sup>, HCO<sub>2</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>
- ▶ Ne-CF<sub>4</sub>
  - ▶ CF<sub>3</sub><sup>+</sup>
- ▶ Ne-CO<sub>2</sub>
  - ▶ CO<sub>2</sub>•CO<sub>2</sub><sup>+</sup>, Ne<sub>2</sub><sup>+</sup>
- ▶ N<sub>2</sub>
  - ▶ N<sub>2</sub>•N<sub>2</sub><sup>+</sup>
- ▶ C<sub>2</sub>H<sub>6</sub>
  - ▶ C<sub>2</sub>H<sub>4</sub><sup>+</sup>, C<sub>3</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>7</sub><sup>+</sup>, C<sub>3</sub>H<sub>8</sub><sup>+</sup>, C<sub>3</sub>H<sub>9</sub><sup>+</sup>, C<sub>4</sub>H<sub>9</sub><sup>+</sup>, C<sub>4</sub>H<sub>10</sub><sup>+</sup>, C<sub>4</sub>H<sub>12</sub><sup>+</sup>
- ▶ Xe-N<sub>2</sub>
  - ▶ Xe<sup>+</sup>, Xe<sub>2</sub><sup>+</sup>
- ▶ iC<sub>4</sub>H<sub>10</sub>
  - ▶ C<sub>8</sub>H<sub>n</sub><sup>+</sup>, C<sub>12</sub>H<sub>m</sub><sup>+</sup>

Not used

# Ionisation potentials

▶ Xe:	12.129843 eV
▶ Ar:	15.759 eV
▶ Ne:	21.56454 eV
▶ CO <sub>2</sub> :	13.777 eV
▶ CH <sub>4</sub> :	12.61 eV
▶ C <sub>2</sub> H <sub>6</sub> :	11.52 eV
▶ C <sub>3</sub> H <sub>8</sub> :	10.94 eV
▶ <i>i</i> C <sub>4</sub> H <sub>10</sub> :	10.68 eV
▶ <i>n</i> C <sub>4</sub> H <sub>10</sub> :	10.53 eV
▶ C <sub>2</sub> H <sub>5</sub> :	8.4 eV
▶ CH <sub>5</sub> :	8.3 eV ?
▶ HCO <sub>2</sub> :	8.3 eV ?
▶ C <sub>3</sub> H <sub>7</sub> :	7.5 eV

# Cluster mobility in Ar-CO<sub>2</sub> & Ne-CO<sub>2</sub>

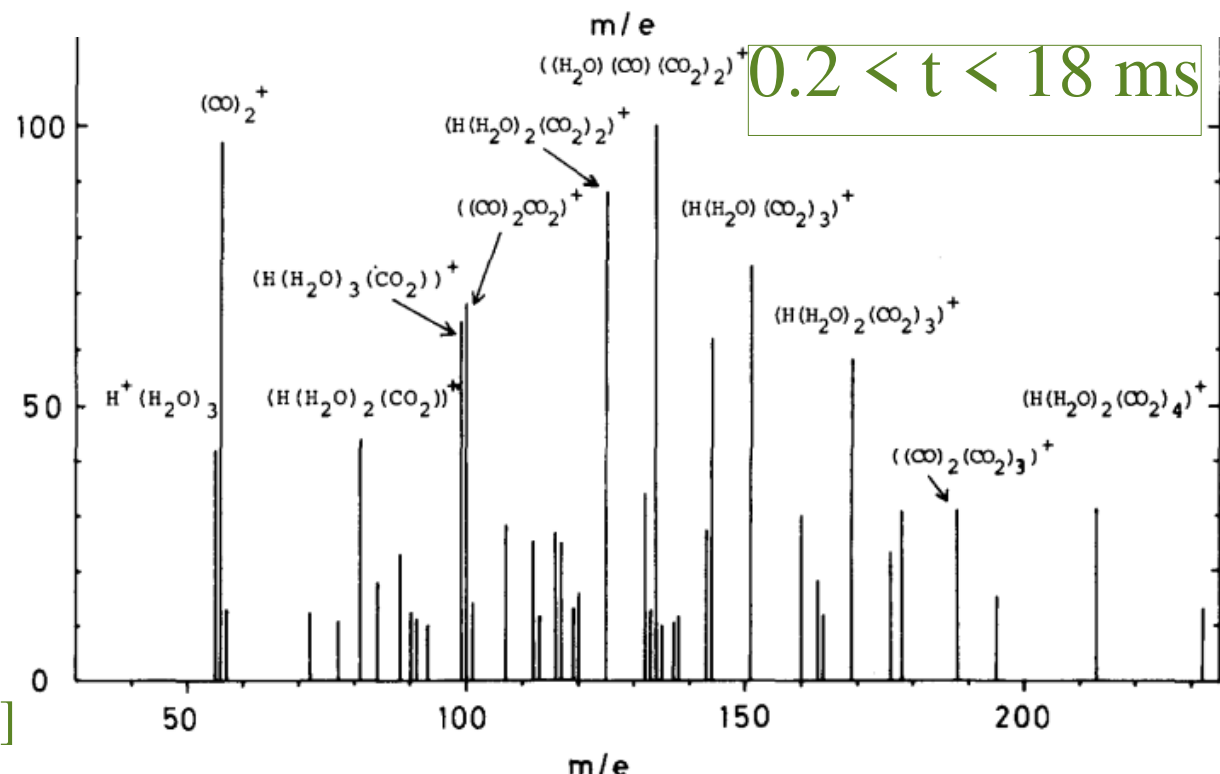
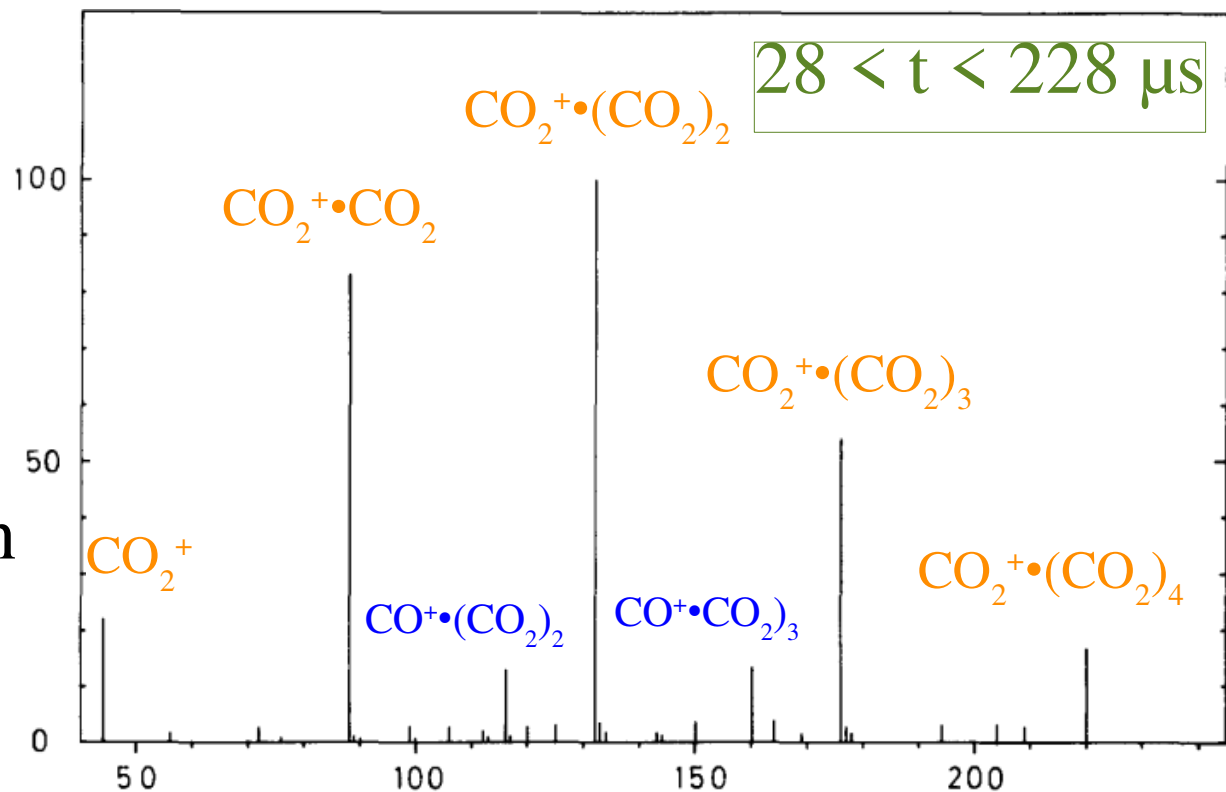
- ▶ One needs as ingredients:
  - ▶ the Blanc interpolation formula;
  - ▶ the mobility of the ions in the pure gases.
- ▶ There are measurements of:
  - ▶ Ar<sup>+</sup> in Ar, Ne<sup>+</sup> in Ne,
  - ▶ CO<sub>2</sub><sup>+</sup> in Ar and in Ne;
  - ▶ CO<sub>2</sub><sup>+</sup>, CO<sub>2</sub><sup>+</sup>•CO<sub>2</sub> and CO<sub>2</sub><sup>+</sup>•(CO<sub>2</sub>)<sub>n</sub> in CO<sub>2</sub>.
- ▶ But we have not found measurements of:
  - ▶ mobility of CO<sub>2</sub><sup>+</sup>•(CO<sub>2</sub>)<sub>n</sub> neither in Ar nor in Ne;
  - ▶ we can get an idea from the mass-mobility relation.

# CO<sub>2</sub> 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. H<sub>2</sub>O, OH ...



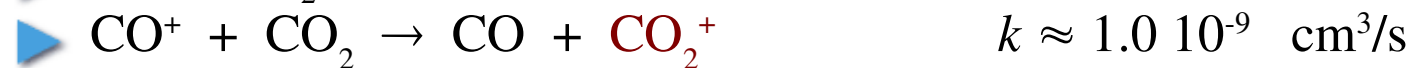


# Experimental check

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

# Avalanche products & by-products

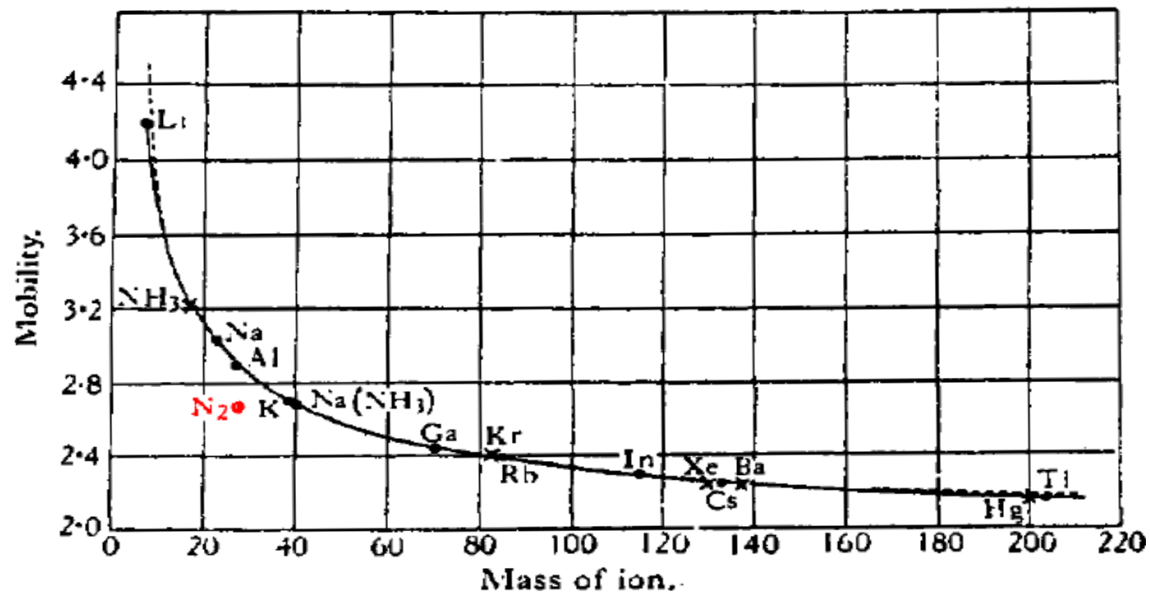
▶ At very low pressure, there are traces of  $O^+$ ,  $C^+$  and  $CO^+$ :



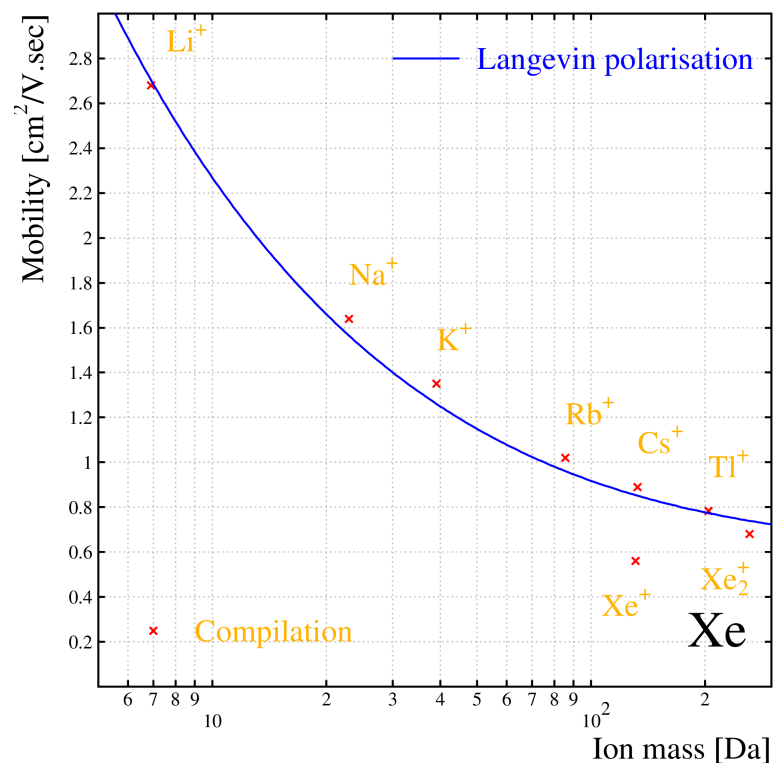
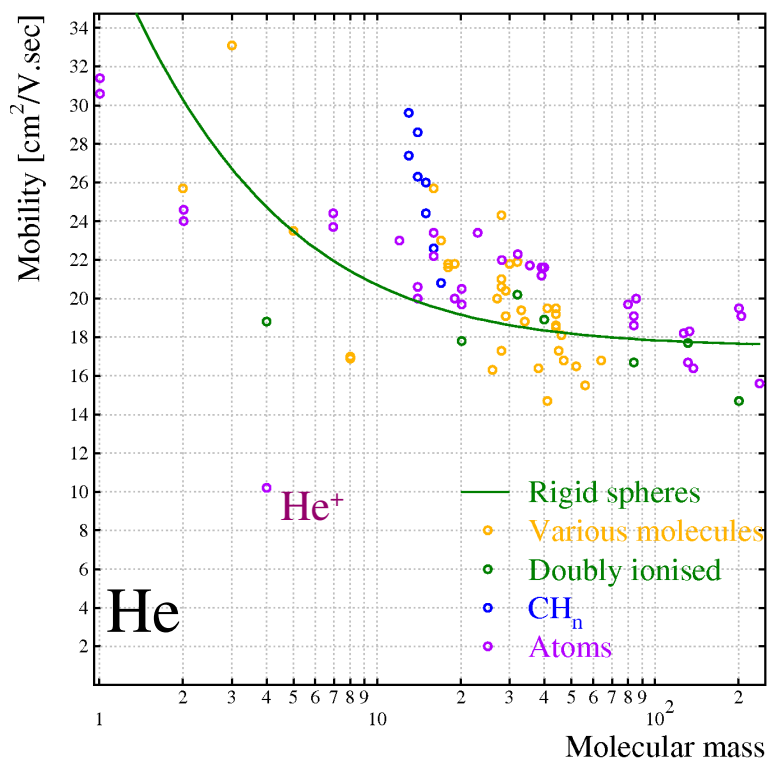
▶ These traces probably also exist at higher pressure, but they disappear rapidly, except the cluster and  $O_2^+$ .

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

# He, Xe, N<sub>2</sub>



[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.]

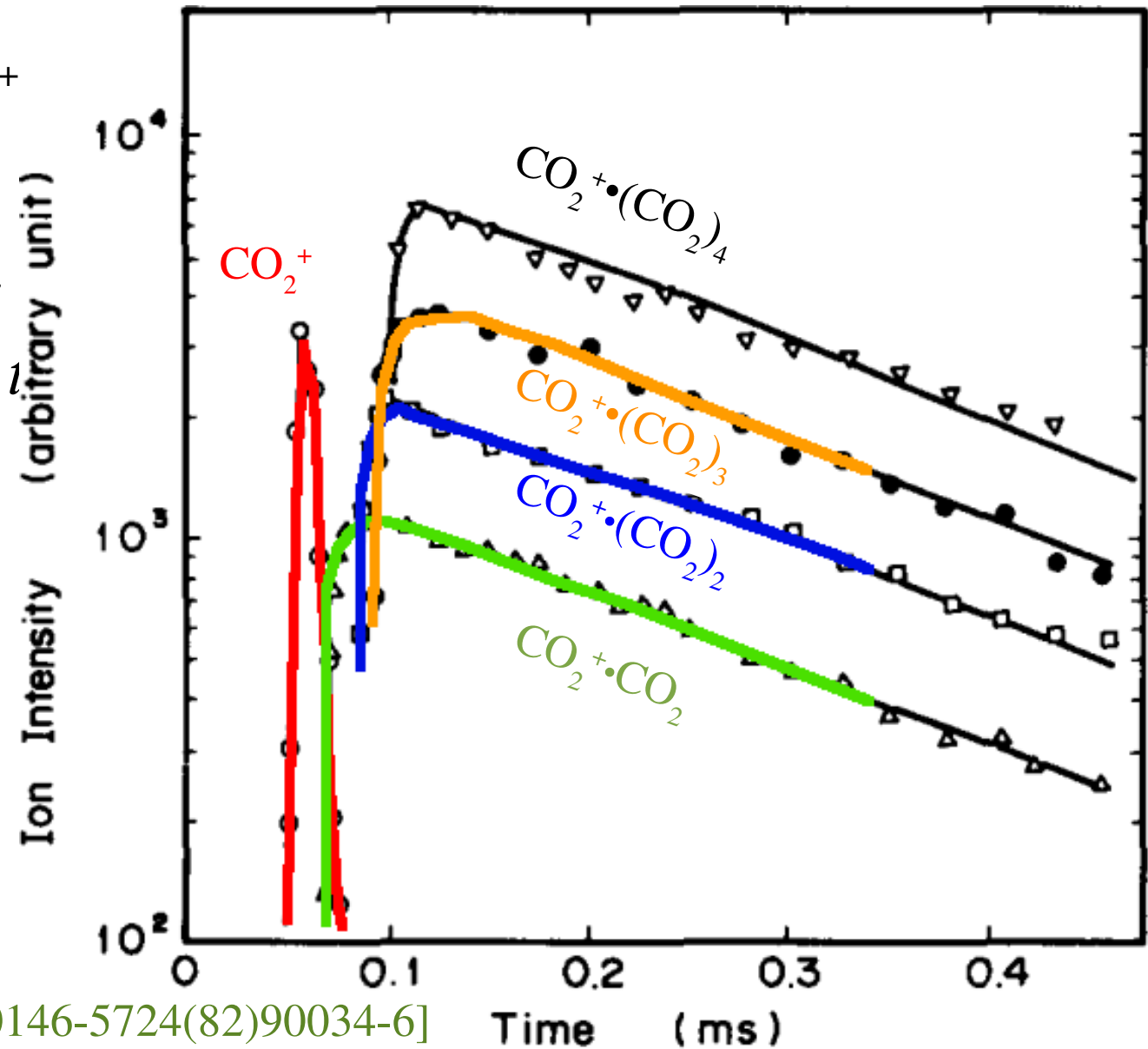


# Ne<sup>+</sup> in Ne ... did it make sense ?

- ▶ The avalanche produced little Ne<sup>+</sup> to begin with;
- ▶  $IP_{\text{Ne}^+} > IP_{\text{CO}_2^+}$  : Ne<sup>+</sup> took 8 ns to generate a CO<sub>2</sub><sup>+</sup>;
- ▶ in nearly pure Ne, there could be some Ne<sub>2</sub><sup>+</sup>.
- ▶ Instead, we obtained  $\text{CO}_2^+ \bullet \text{CO}_2$ .

# CO<sub>2</sub> at 1 atm: cluster (dis)appearance

- ▶ Not clear why CO<sub>2</sub><sup>+</sup> forms at  $t > 50 \mu\text{s}$ .
- ▶ Clusters with CO<sub>2</sub><sup>+</sup> ion core form by  $\approx 100 \mu\text{s}$ .
- ▶ React with contaminants  $\tau \sim 190 \mu\text{s}$ .

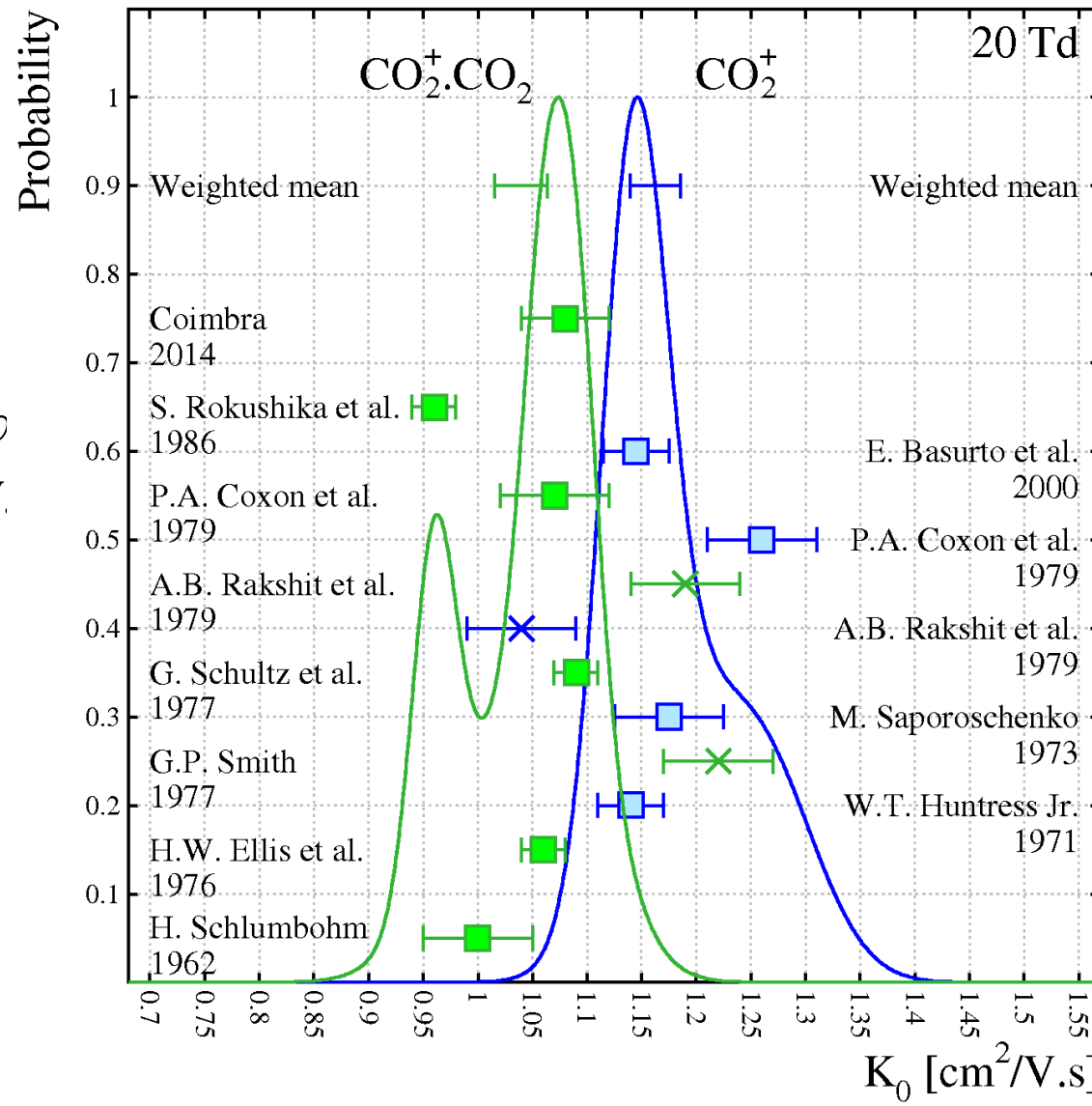


# Life cycle of $\text{CO}_2^+\bullet(\text{CO}_2)_n$

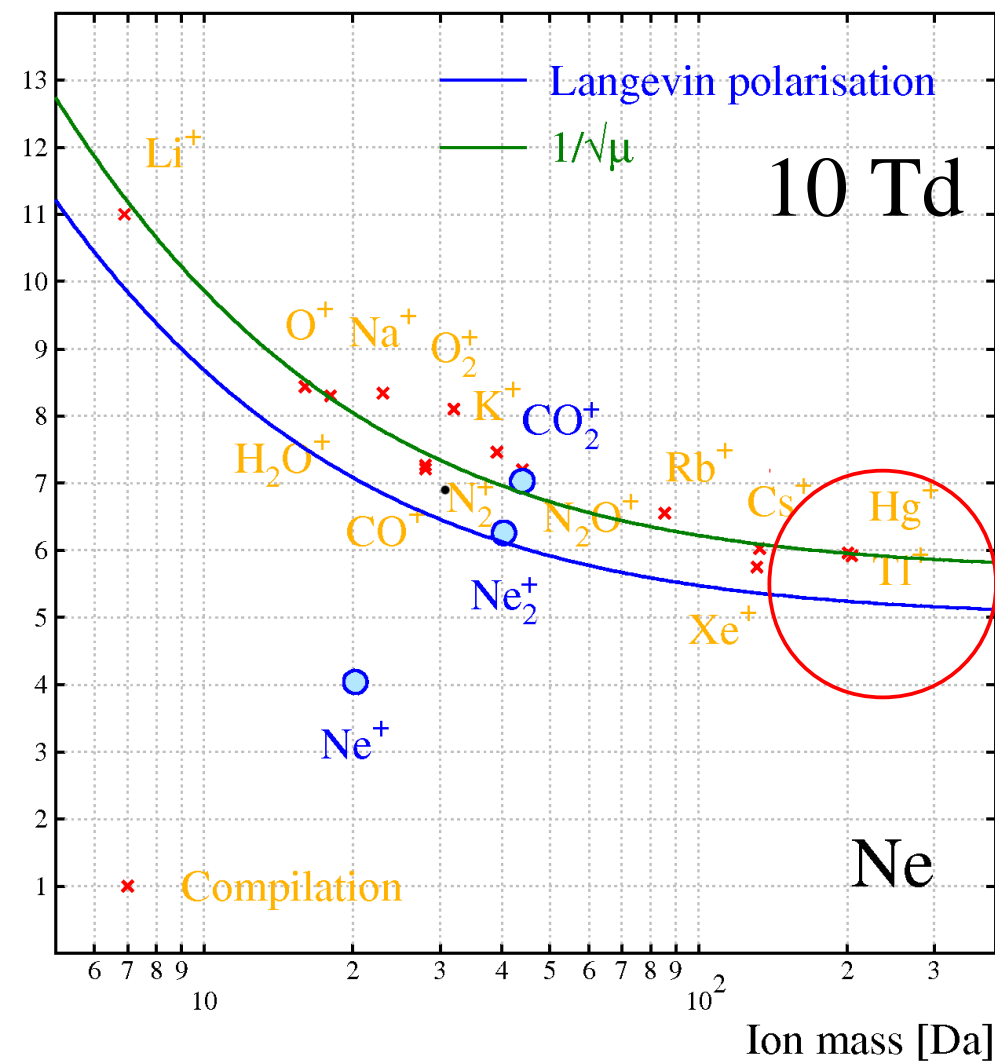
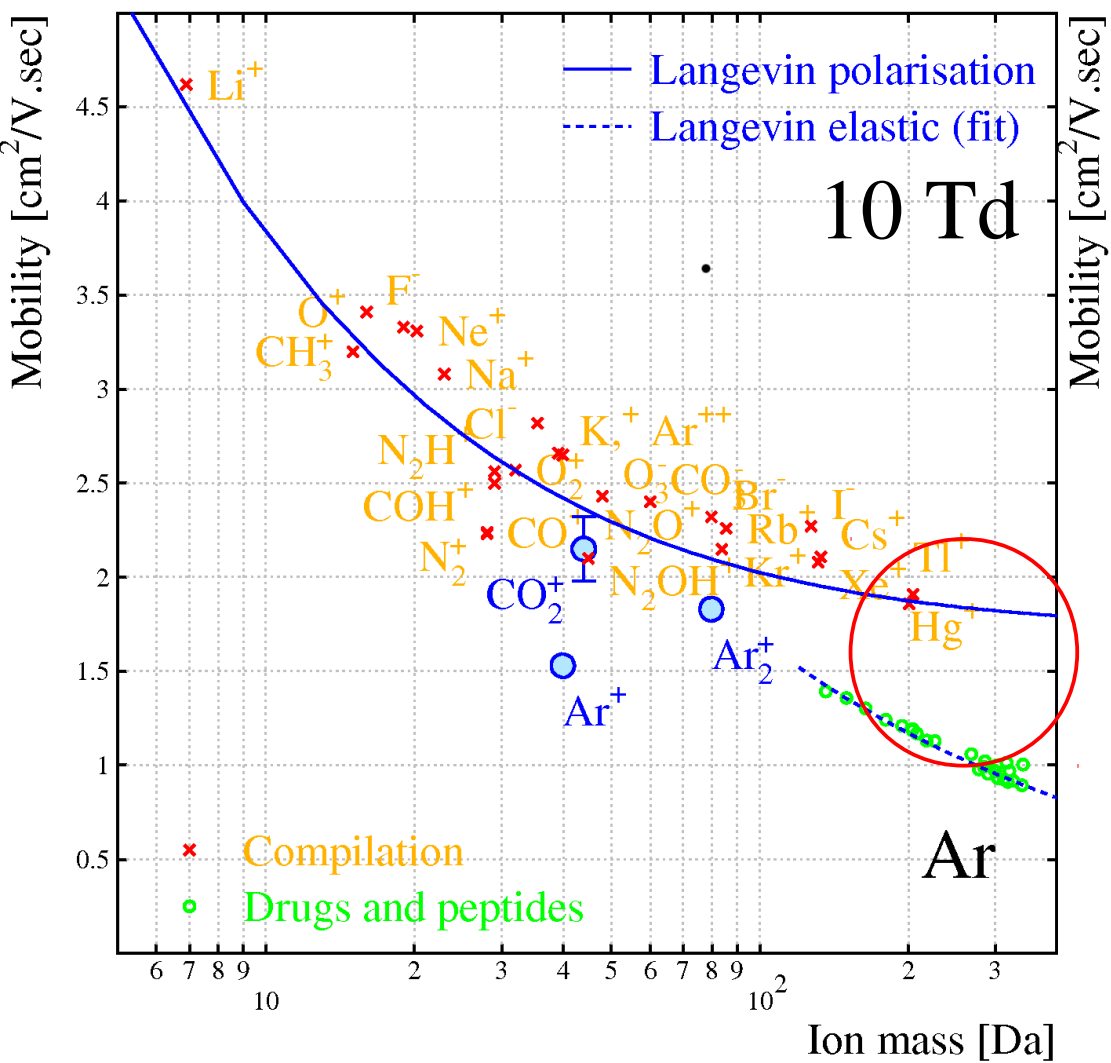
- ▶  $\text{CO}_2^+\bullet\text{CO}_2$  has a dissociation energy of 0.6 eV far above thermal energies at 1 bar. It is a so-called long-lived cluster:
  - ▶ calculated lifetime = 5 ns
  - [B.M. Smirnov, “Cluster Ions and Van Der Waals Molecules,” CRC press]
- ▶ much longer than the formation time  $\tau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

- ▶ 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 pure Ar and Ne





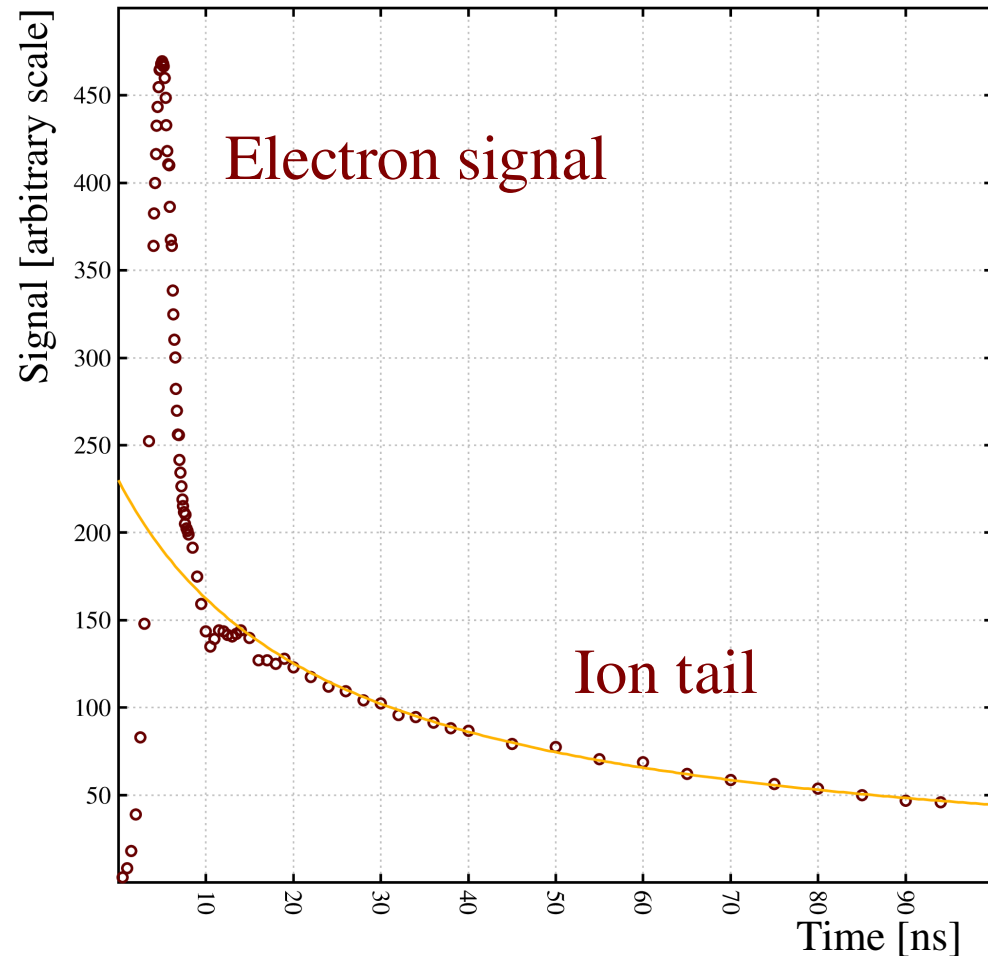
# Atlas TRT signals

## ► Data:

- Xe-CO<sub>2</sub>-CF<sub>4</sub> 70/10/20
- Straw tube
- $V_w = 1530$  V
- $r_w = 15$   $\mu\text{m}$ ,  $r_t = 2$  mm

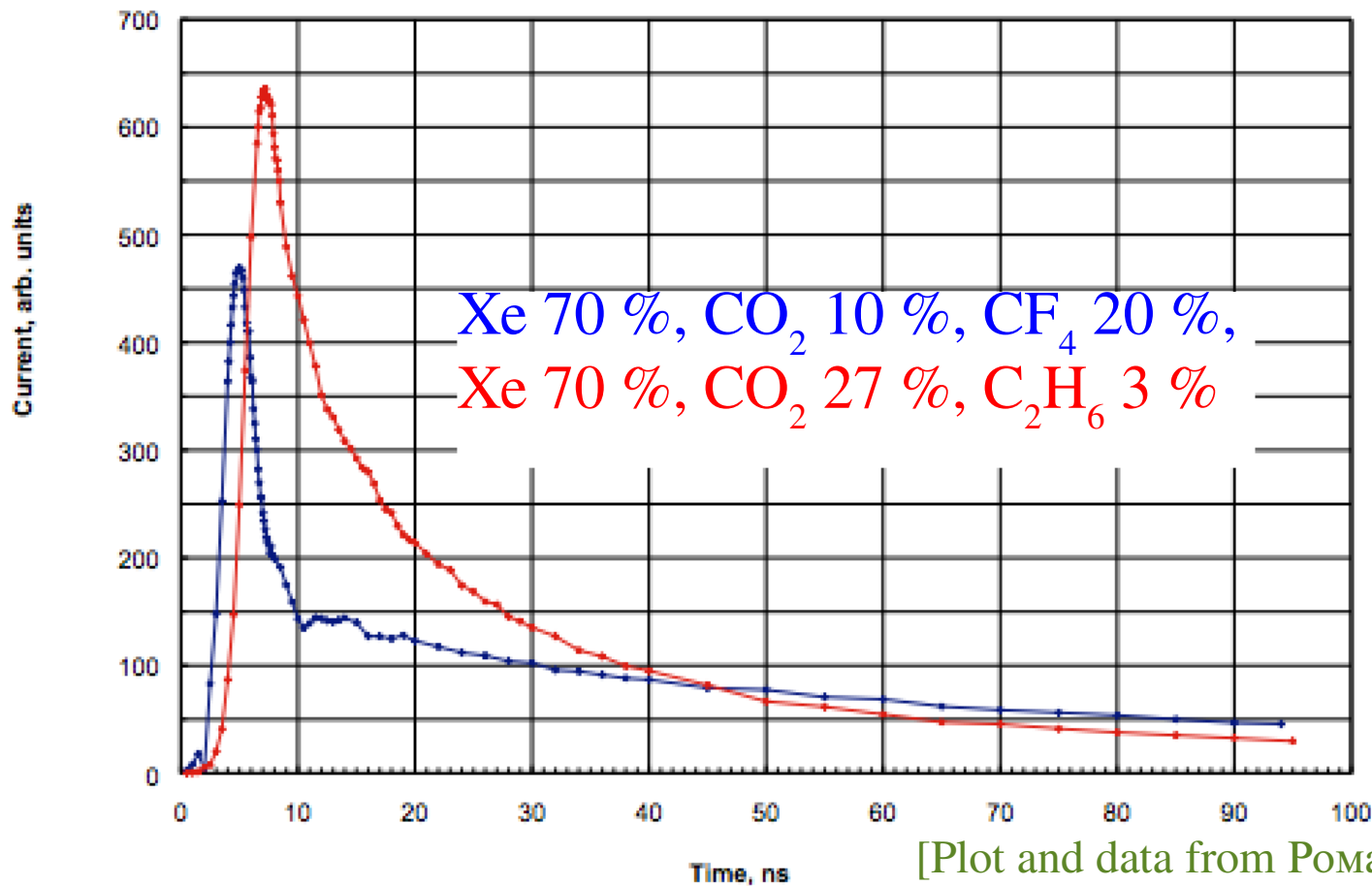
## ► Fit:

- $1/(t+t_0)$



# Adding $C_2H_6$

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



# Ionisation potentials

- ▶  $\text{C}_2\text{H}_6$ : 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
- ▶  $\text{CO}_2$ : 13.776 eV
- ▶  $\text{CF}_4$ : 15.70 eV for  $\text{CF}_3^+$  (main ionisation channel)  
16.2 ± 0.1 eV for  $\text{CF}_4^+$

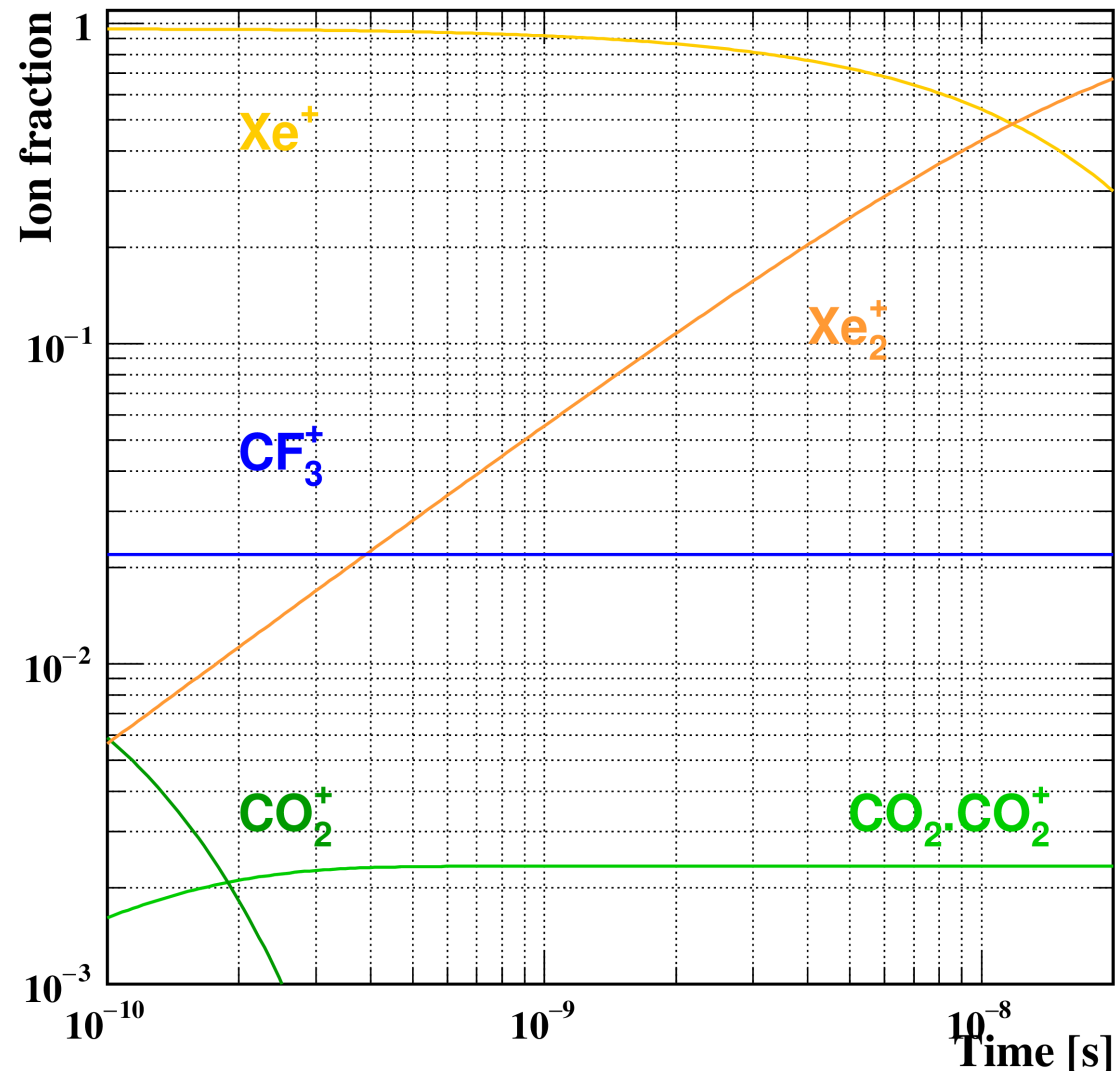
# Reactions in Xe-CO<sub>2</sub>-CF<sub>4</sub>



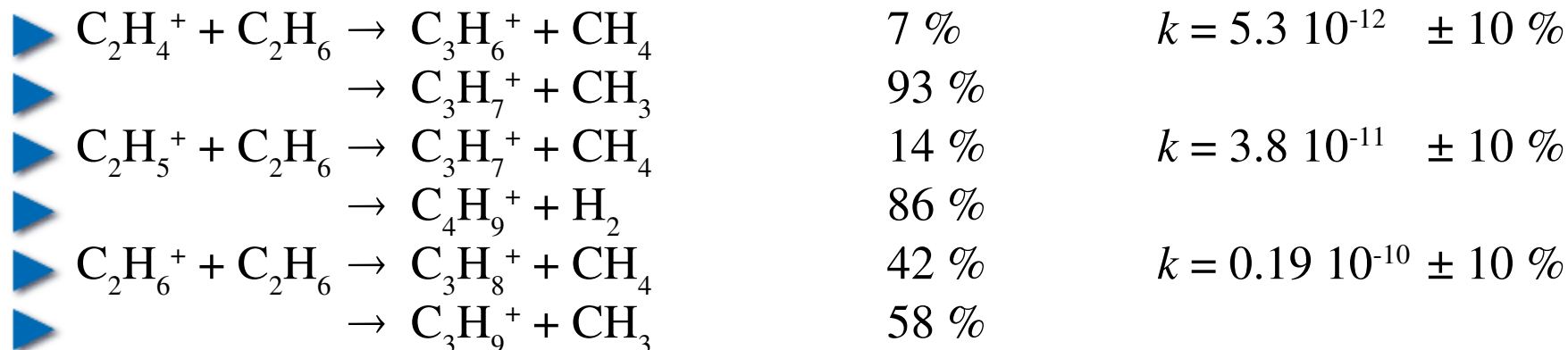
▶ Note: CF<sub>4</sub><sup>+</sup> is not produced, (only CF<sub>3</sub><sup>+</sup>)

# Evolution of Xe-CO<sub>2</sub>-CF<sub>4</sub> (70-10-20)

- ▶ Initial ion mix for 100 kV/cm;
- ▶ Xe<sup>+</sup> and Xe<sub>2</sub><sup>+</sup> dominate from 10 ns on, Xe<sub>n</sub><sup>+</sup> for  $n > 2$  are not shown: rates are not known.
- ▶ CF<sub>3</sub><sup>+</sup> is an avalanche product; with its low IP, it does not react;
- ▶ CF<sub>4</sub><sup>+</sup> is not produced, CF<sub>4</sub> has a high IP, is not attacked by ions.
- ▶ CO<sub>2</sub><sup>+</sup> transfers to Xe<sup>+</sup> and rapidly forms clusters.



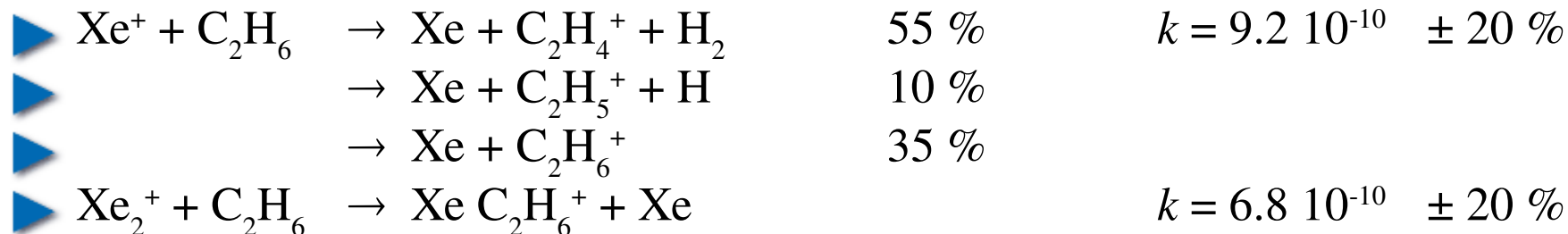
# Reactions in Xe-C<sub>2</sub>H<sub>6</sub>



[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]]]

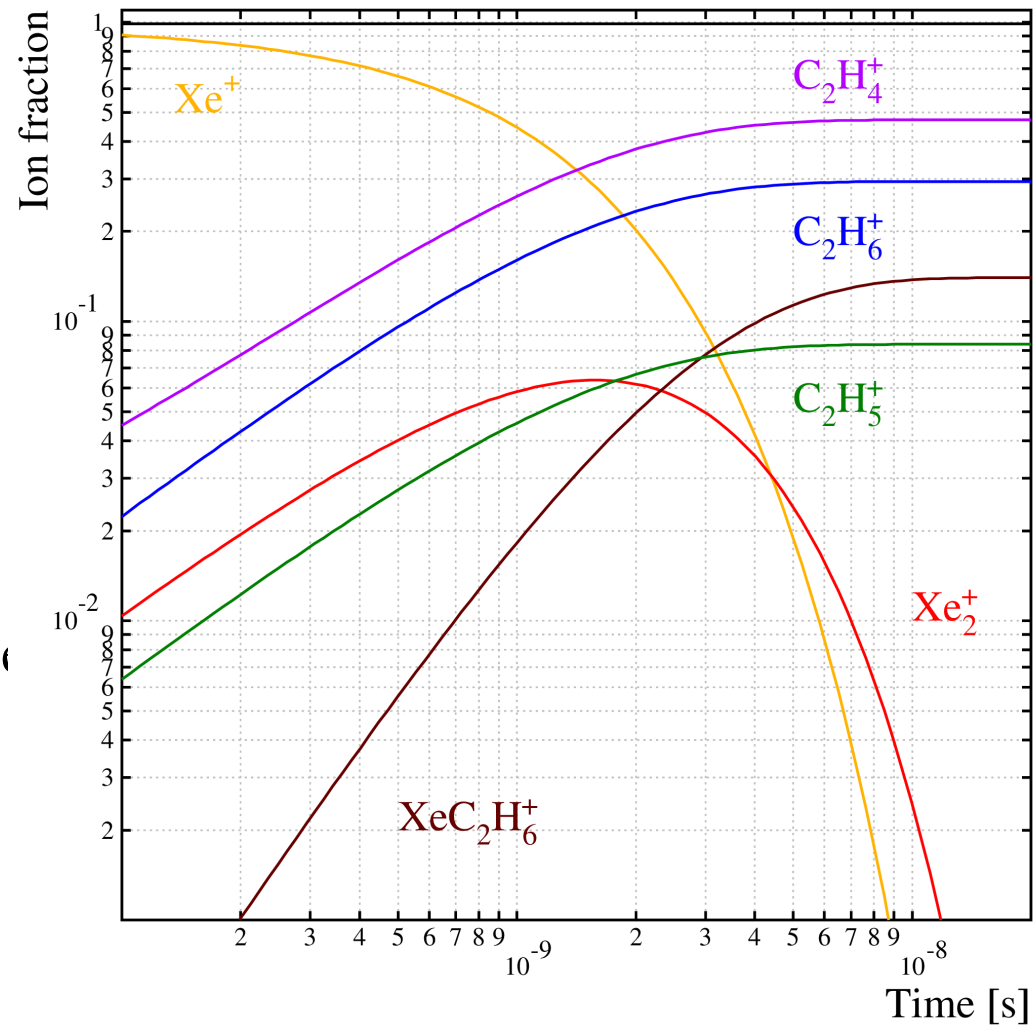
```

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 Xe-C<sub>2</sub>H<sub>6</sub> (97-3)

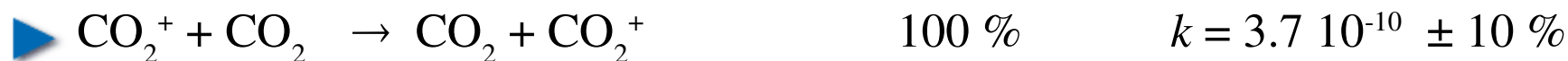
- ▶ Initial ion mix for 100 kV/cm;
- ▶ after 10 ns, the only Xe-related ion that remains is XeC<sub>2</sub>H<sub>6</sub><sup>+</sup> which is made from Xe<sub>2</sub><sup>+</sup>;
- ▶ the diagram does not show the C<sub>3</sub>H<sub>x</sub><sup>+</sup> and C<sub>4</sub>H<sub>x</sub><sup>+</sup> ions subsequently generated by C<sub>2</sub>H<sub>4</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup>;
- ▶ Xe<sub>n</sub><sup>+</sup> for  $n > 2$  are not shown because the rates are not known.



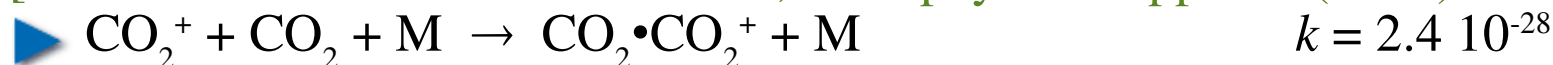


# Reactions in Xe-CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub>

▶ All reactions from Xe-C<sub>2</sub>H<sub>6</sub> and in addition:



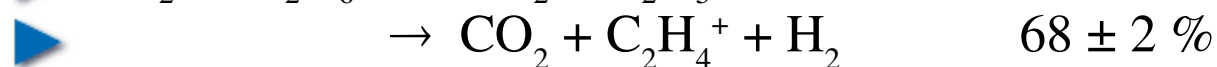
[V.G. Anicich and W.T. Huntress Jr., *Astrophys. J. Suppl.* **62** (1986) 553-672.]



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



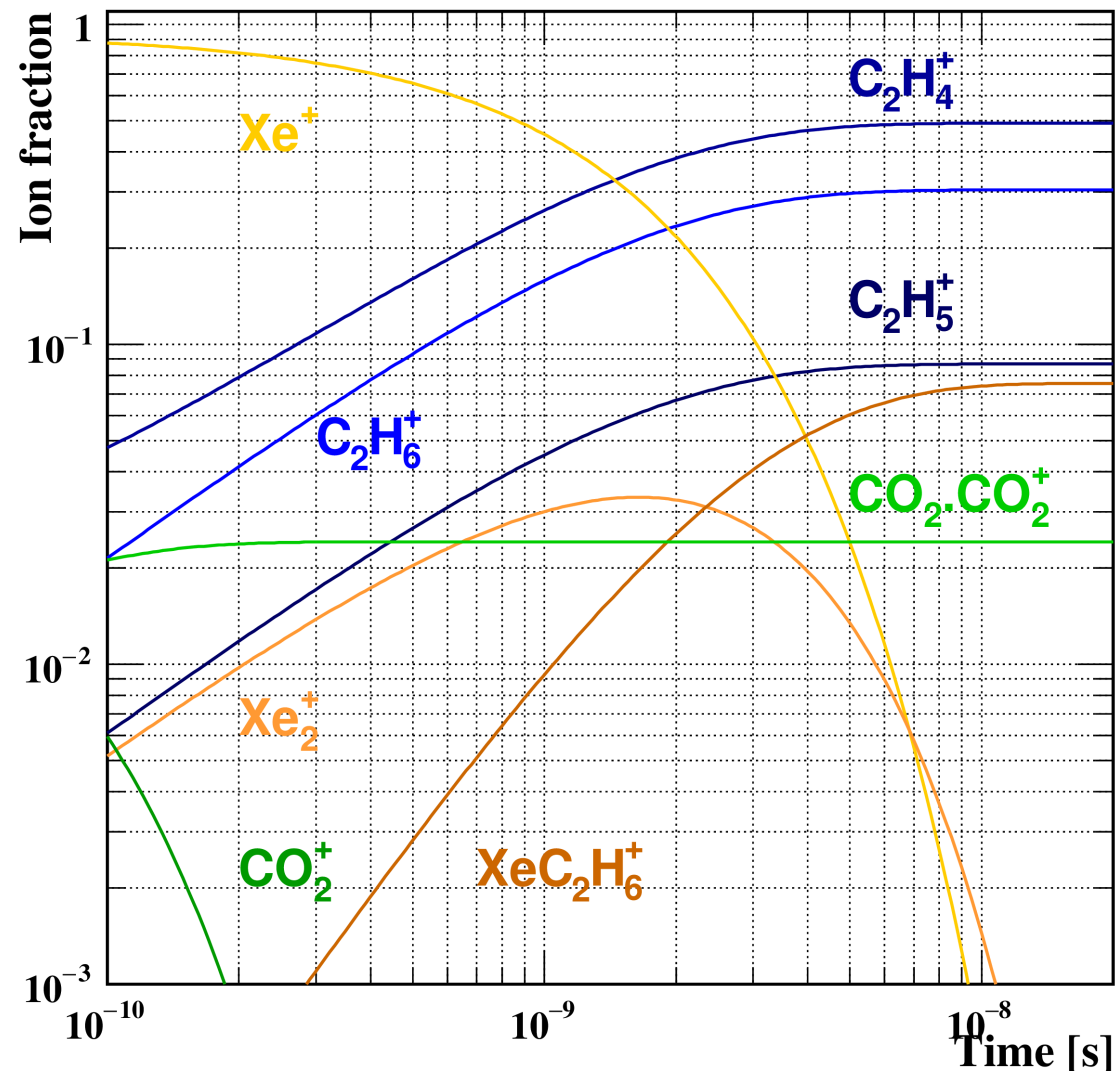
[V.G. Anicich and W.T. Huntress Jr., *Astrophys. J. Suppl.* **62** (1986) 553-672.]

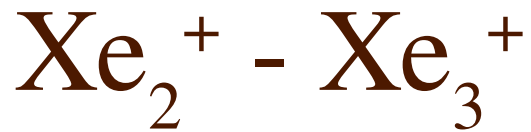


[Masaharu Tsuji, [10.1016/0168-1176\(94\)03996-8](https://doi.org/10.1016/0168-1176(94)03996-8)]

# Evolution of Xe-CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub> (70-27-3)

- ▶ Initial ion mix for 100 kV/cm;
- ▶ CO<sub>2</sub><sup>+</sup> rapidly forms clusters due to the large CO<sub>2</sub> fraction;
- ▶ CO<sub>2</sub> does not affect the dominance of C<sub>x</sub>H<sub>y</sub> over Xe.
- ▶ Xe<sub>n</sub><sup>+</sup> for  $n > 2$  are not shown because rates are not known.





- ▶ We have not found the rate constant for  $\text{Xe}_3^+$  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  $\text{Xe}_2^+$  to  $\text{Xe}_3^+$ , and  $k_r$  the rate for the reverse reaction.
- ▶ Given that  $[\text{Xe}_3^+] / [\text{Xe}_2^+] = 3.6 \pm 0.6 \cdot 10^{-19} \text{ N}$ , the ratio of concentrations is  $9.7 \pm 1.6$  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 $\text{Xe}_n^+$

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

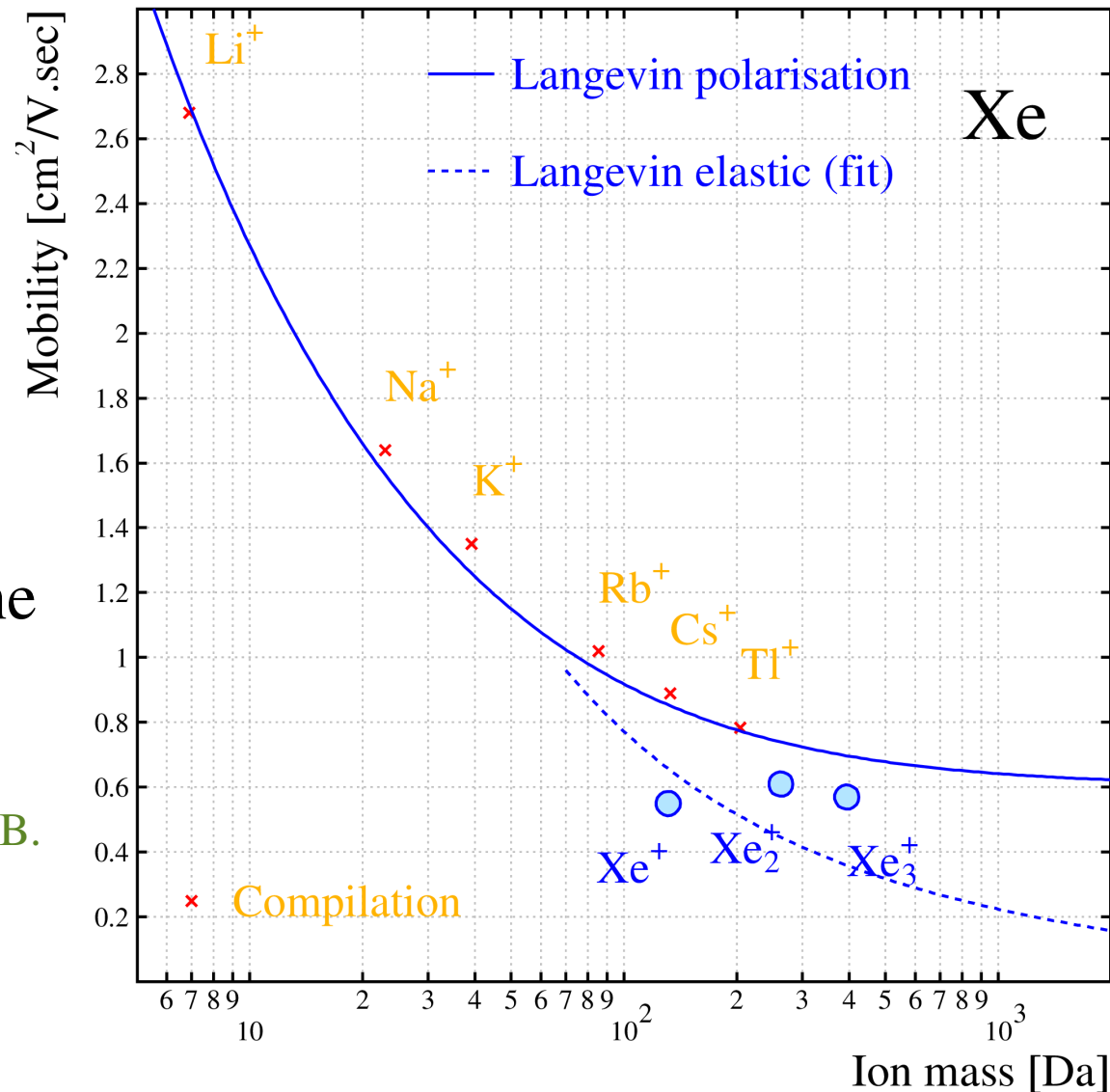
$\text{Xe}_n^+$	Mass	$\mu$ ( $E = 0, T = 300$ K)	$\Delta H$ $n-1 \rightarrow n$	References
	[Da]	[ $\text{cm}^2/\text{V.s}$ ]	[eV]	
$\text{Xe}^+$	131.293	0.55	-	Helm, Viehland-Mason
$\text{Xe}_2^+$	262.586	0.61	1.05 (5 %)	NIST, Helm 1976
$\text{Xe}_3^+$	393.879	0.57	0.29 (5 %)	NIST, Helm 1976
$\text{Xe}_4^+$	525.172	?	0.26 (3 %)	NIST, Hiraoka
$\text{Xe}_5^+$	656.465	?	0.11 (5 %)	NIST, Hiraoka

[Ker]

# Mobility of ions in Xe

- ▶  $E/N = 10$  Td, extrapolated from higher  $E/N$  where needed ( $\text{Xe}^+$ ).
- ▶ Polarisation limit assuming  $\alpha_{\text{Xe}} = 4.01$  D.
- ▶  $\text{Xe}_2^+$  and  $\text{Xe}_3^+$  are below the polarisation limit.

[From the H.W. Ellis et al. compilations except  $\text{Xe}^+$  and  $\text{Xe}_2^+$ , which are from P.N.B. Neves, 10.1063/1.3497651]



# Large $\text{Xe}_n$ 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-CO<sub>2</sub>-CH<sub>4</sub> (93-4-3)

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

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



# Evolution in Ar-CO<sub>2</sub>-CH<sub>4</sub> (93-4-3)

- ▶ Initial ions:
- ▶ Ar<sup>+</sup> →
- ▶ CO<sub>2</sub><sup>+</sup>,
- ▶ CH<sub>3</sub><sup>+</sup>,
- ▶ Ar<sub>2</sub><sup>+</sup>
- ▶ CO<sub>2</sub><sup>+</sup> →
- ▶ CH<sub>4</sub><sup>+</sup>
- ▶ CO<sub>2</sub><sup>+</sup>·CO<sub>2</sub>
- ▶ HCO<sub>2</sub><sup>+</sup>
- ▶ CH<sub>4</sub><sup>+</sup> →
- ▶ CH<sub>5</sub><sup>+</sup>,
- ▶ HCO<sub>2</sub><sup>+</sup>
- ▶ CH<sub>3</sub>CO<sup>+</sup>
- ▶ CH<sub>3</sub><sup>+</sup> →
- ▶ C<sub>2</sub>H<sub>5</sub><sup>+</sup>

