

Gas-based detectors

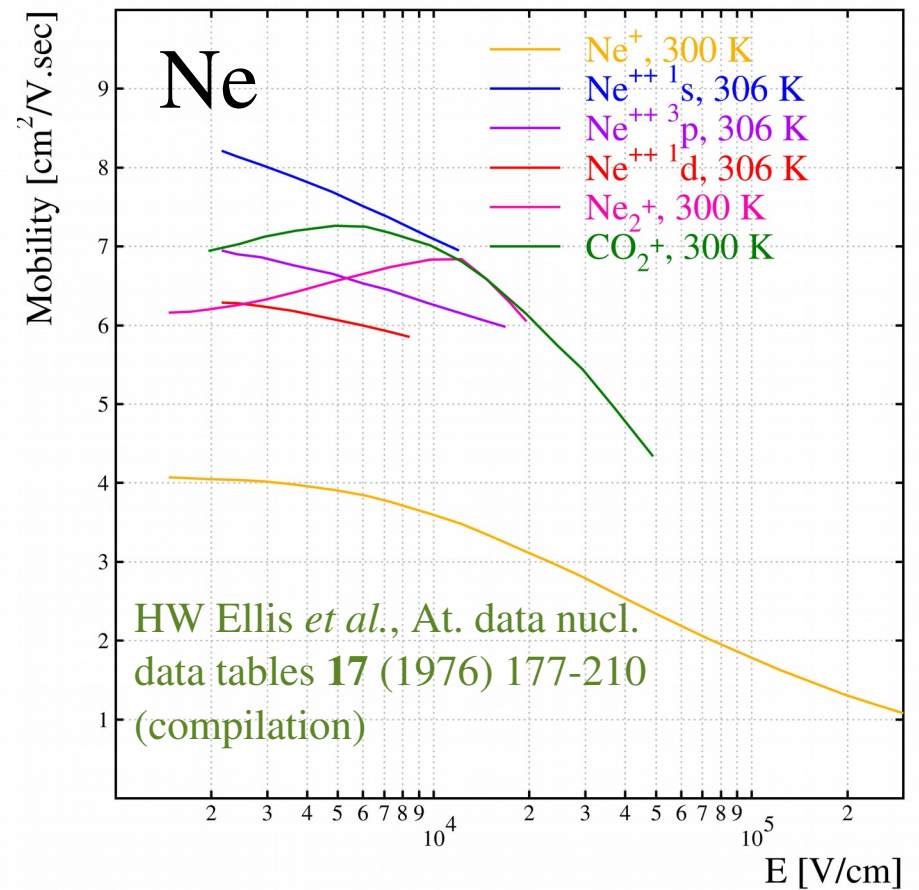
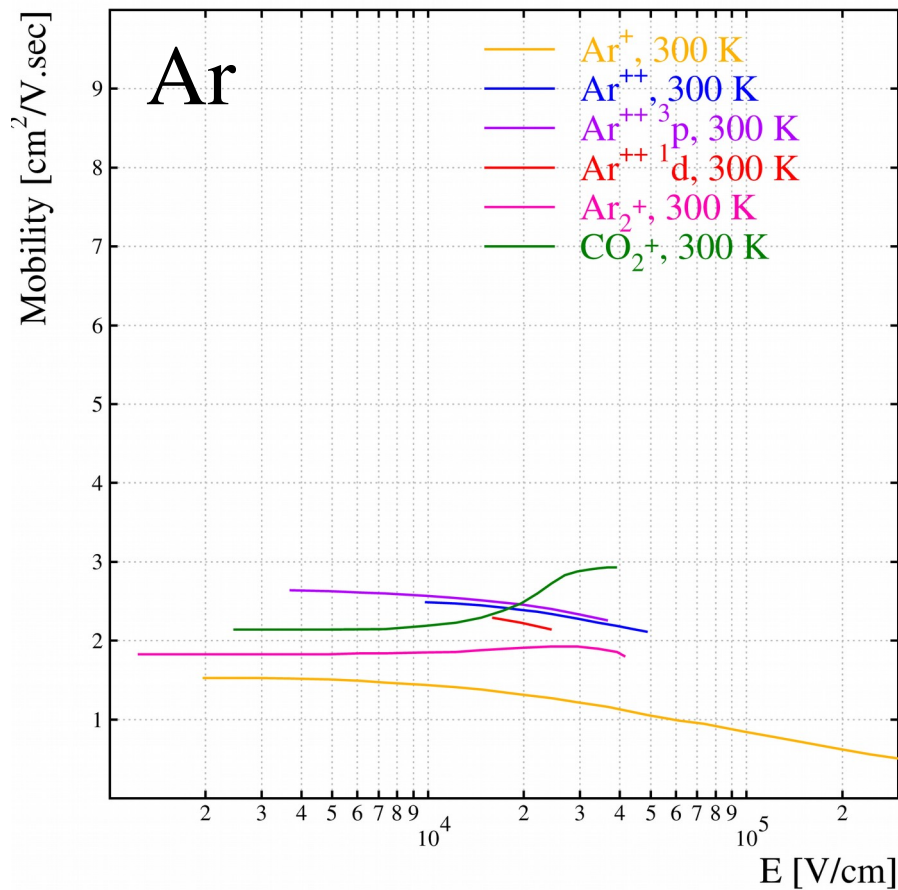
Ion transport

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 (→ **Signals**).
- ▶ Hence we better know the basics of ions:
 - ▶ *which ions* are moving ?
 - ▶ *how fast* do the ions move ?
 - ▶ are they subject to *diffusion* ?

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

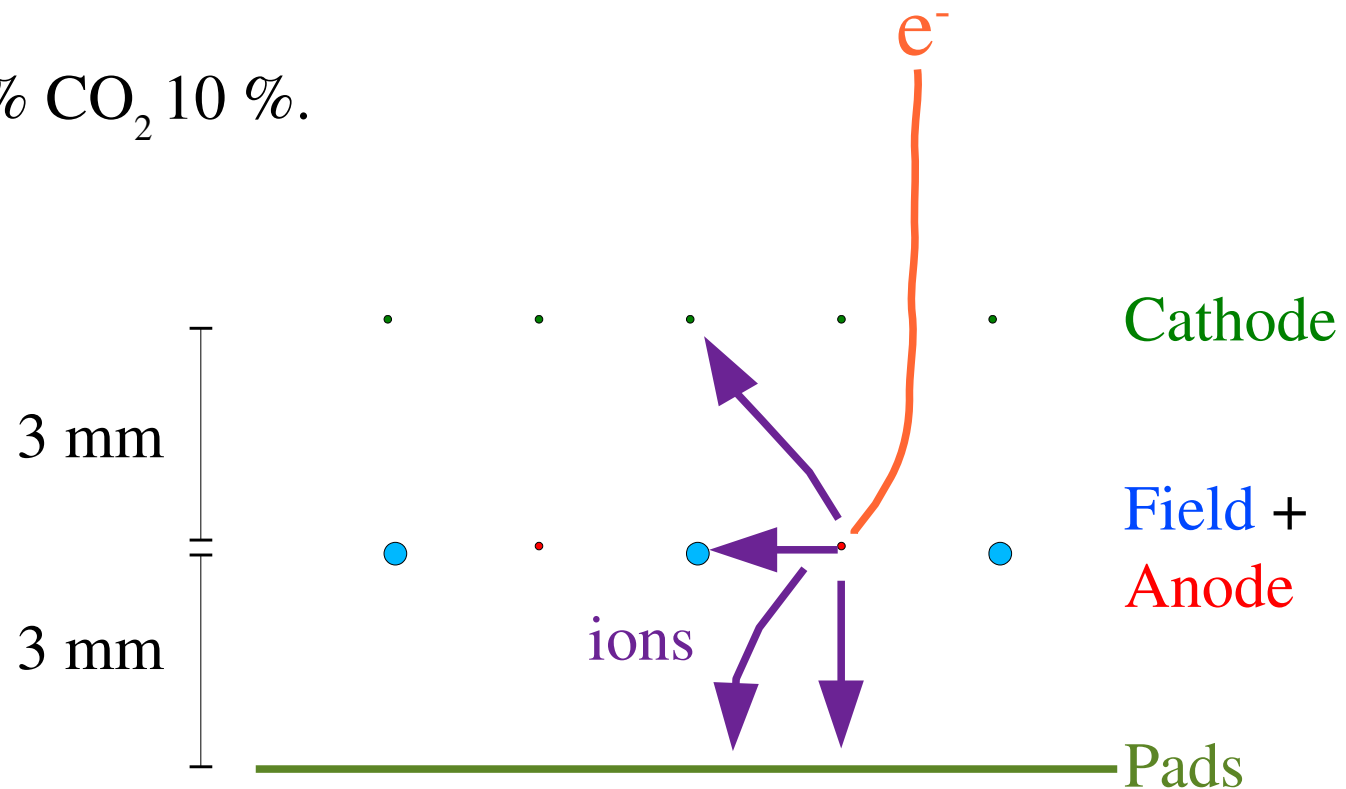
► Noble gas ion mobilities are well known:



Ion induced signals

► After the break, we will calculate the current induced on the pads of a TPC by ions moving from the anode wires to the field wires:

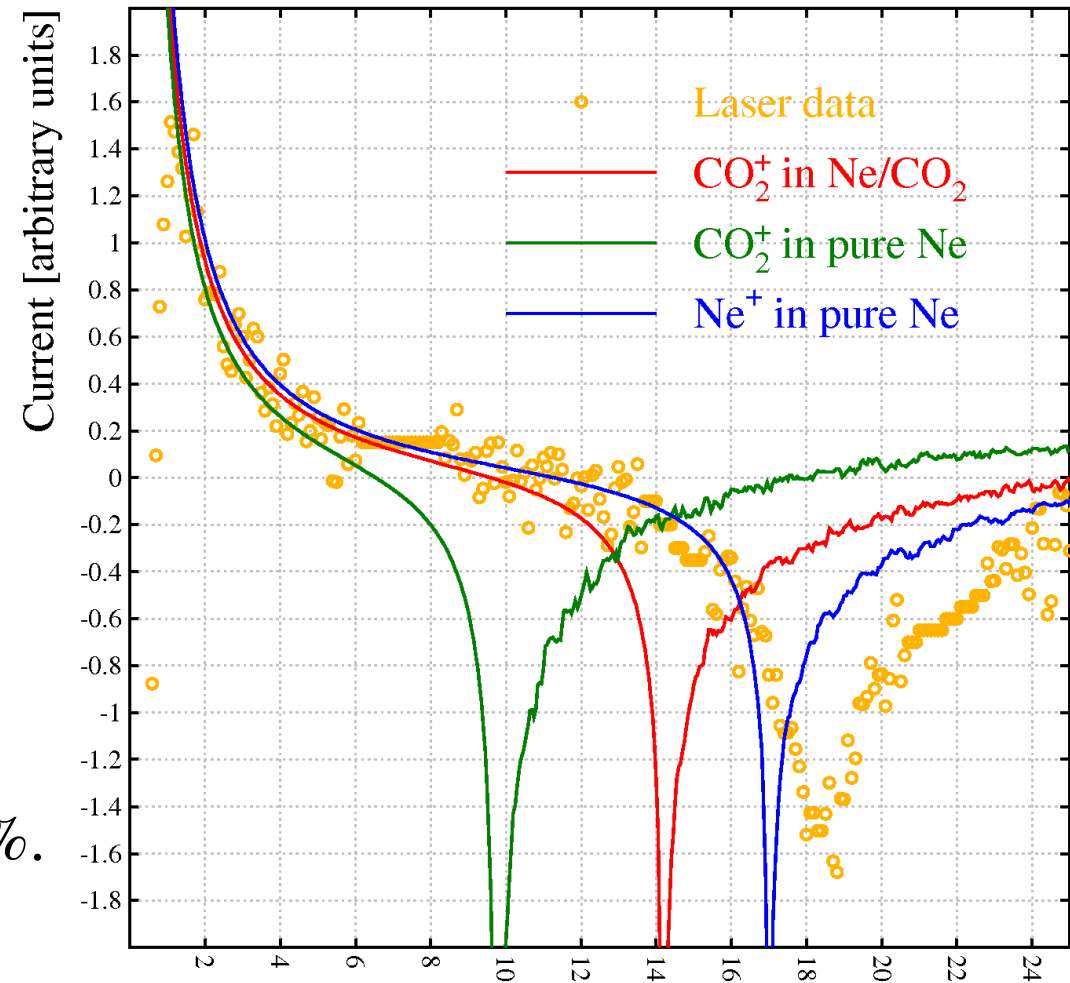
► NA49 TPC: Ne 90 % CO₂ 10 %.



How about Ne⁺ in Ne ?

- ▶ Ne⁺ ions in Ne come reasonably close to the measurements ...
- ▶ we've used it for years ...
- ▶ but does it make sense ?
- ▶ NA49 TPC: Ne 90 % CO₂ 10 %.

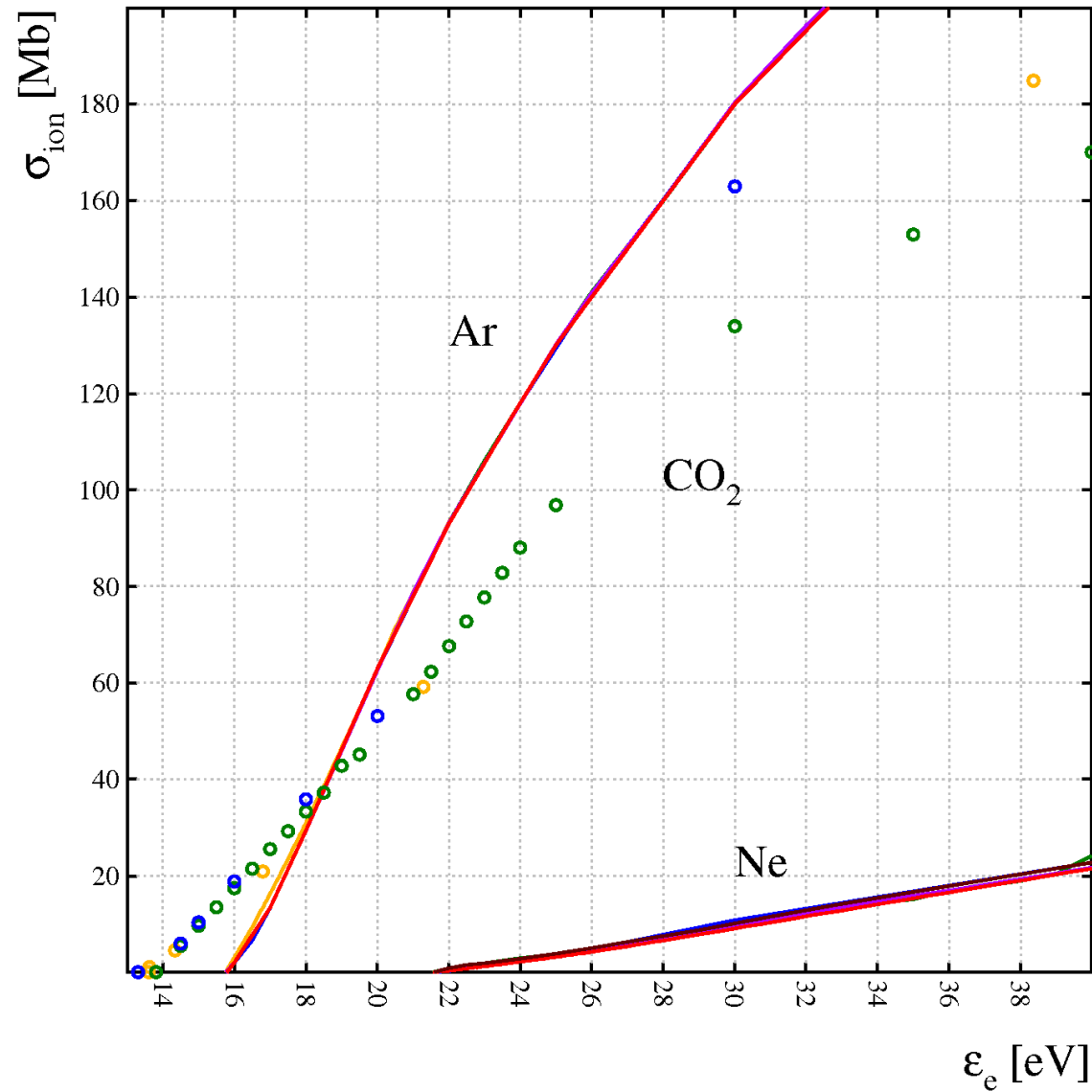
[Data: Rainer Renfordt]



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

Electron-impact cross sections

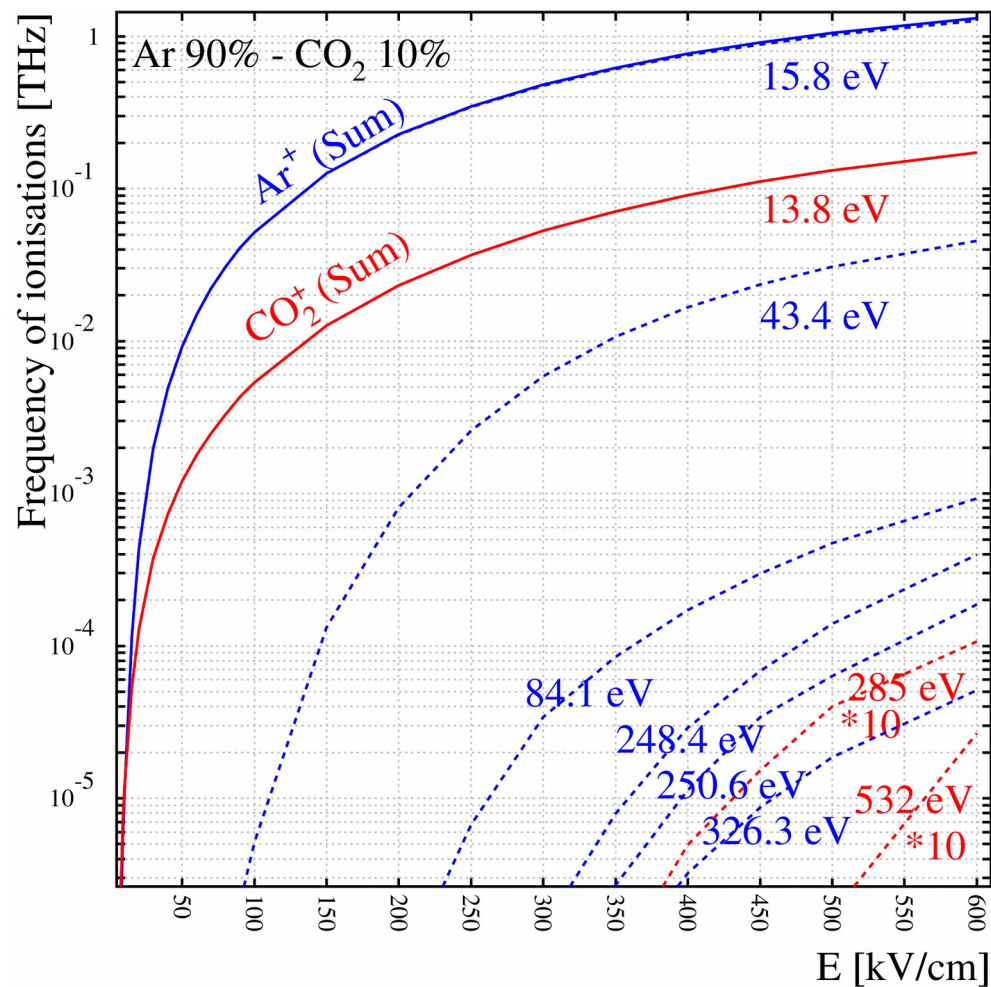
- ▶ CO_2^+ and Ar^+ compete.
- ▶ Ne^+ has higher threshold and is produced less.



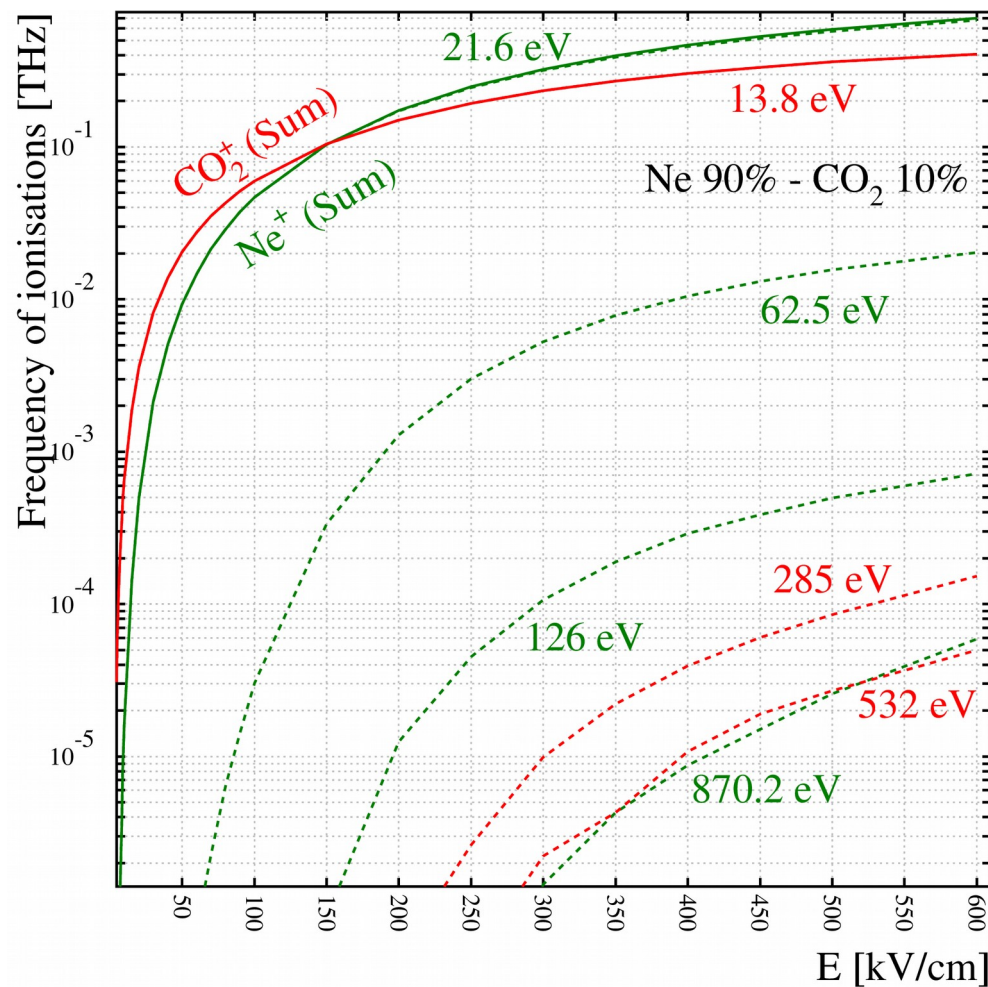
[Pure gases, data from LXcat]

Avalanche products

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



CO_2^+ dominates in $\text{Ne}-\text{CO}_2$



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]

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/cm³];
- ▶ The proportionality factor is called **rate constant k** :
 - ▶ rate = k [cm³/s] N_B [1/cm³].
 - ▶ The reaction time τ is the reciprocal of the rate.
- ▶ Example: Ar⁺ in Ar (resonant charge exchange)
 - ▶ $k = 4.6 \cdot 10^{-10}$ cm³/s, $N \approx 2.45 \cdot 10^{19}$ /cm³
 - ▶ rate = $1.1 \cdot 10^{10}$ /s, $\tau = 100$ ps.

3-body reactions

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

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:

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

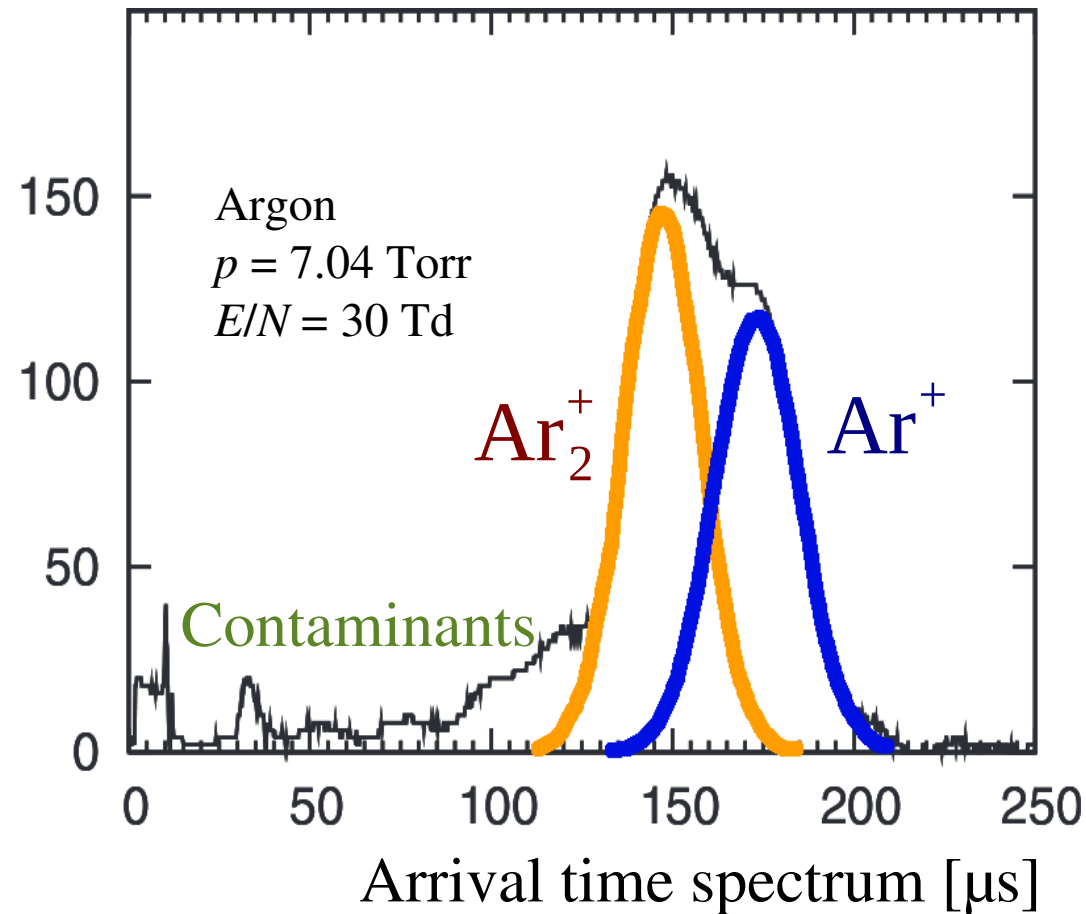
- ▶ Combine with the number density to get collision time:

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

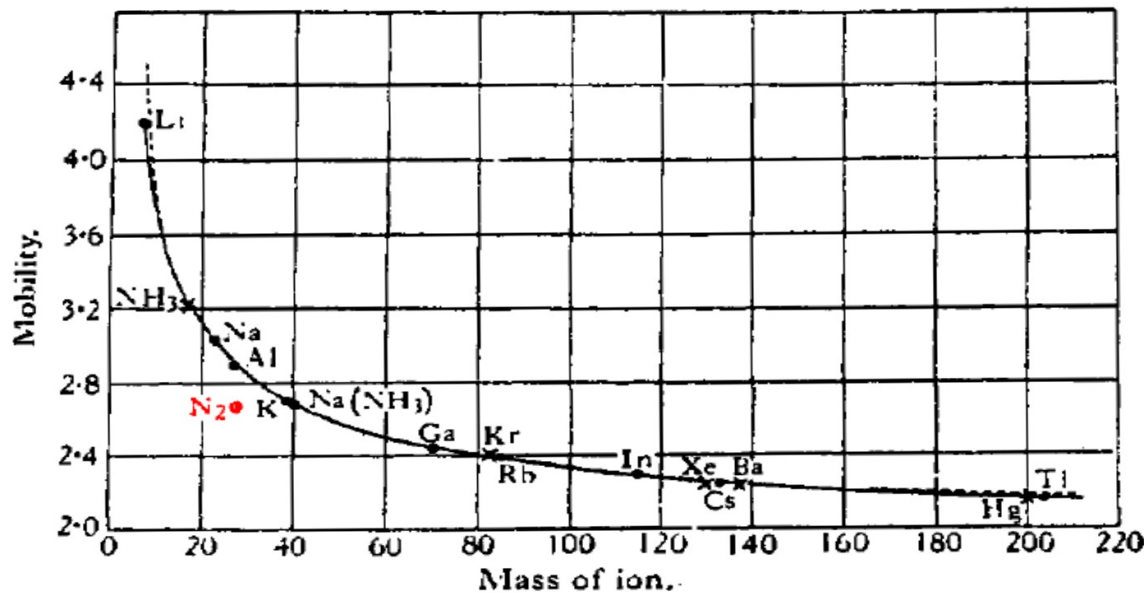
Ions drifting in pure Ar

- ▶ In pure argon, dimers are formed:
 - ▶ $\text{Ar}^+(^2\text{P}^0_{3/2}) + 2\text{Ar} \rightarrow \text{Ar}^+\cdot\text{Ar} + \text{Ar}$
($k = 2.3 \pm 0.1 \cdot 10^{-31} \text{ cm}^6/\text{s}$, 7 ns)
 - ▶ Note: dimers move *faster* than ions due to $\text{Ar} \leftrightarrow \text{Ar}^+$ resonant charge exchange

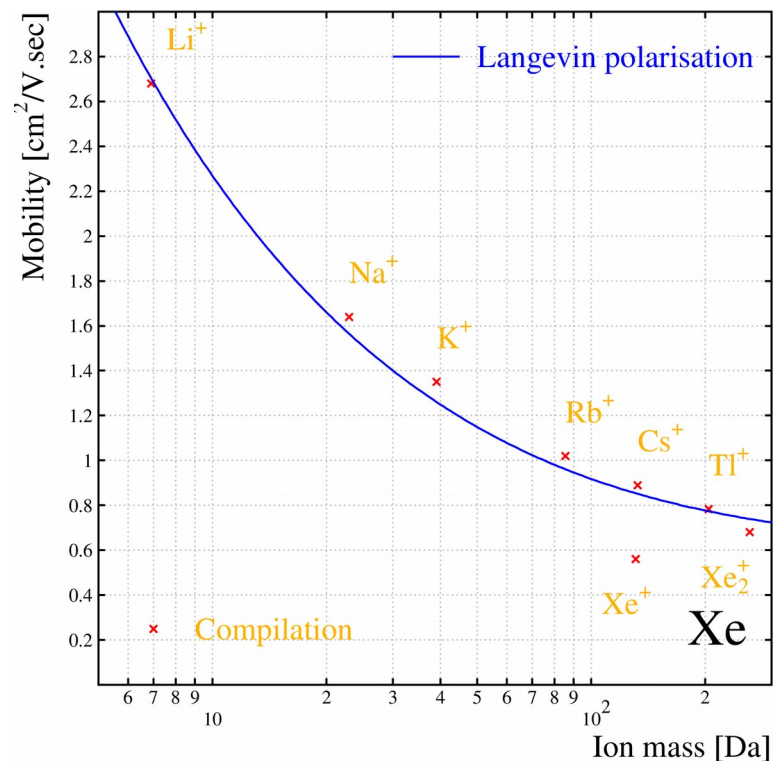
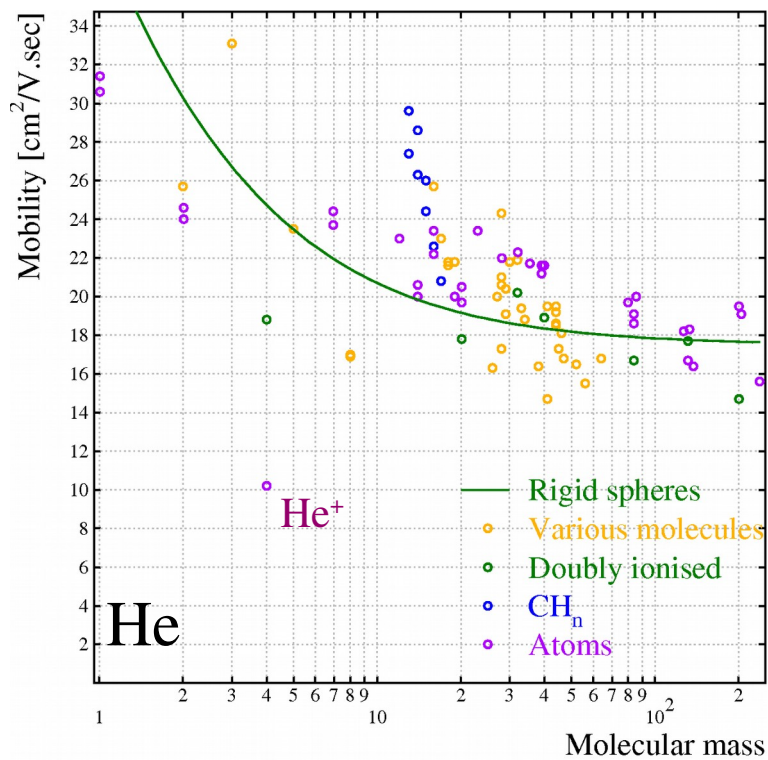
[P.N.B. Neves et al. 10.1063/1.3497651]



He, Xe, N₂

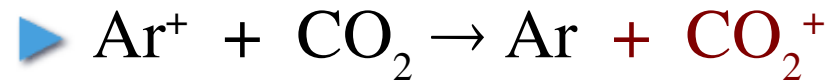


[J. A. Hornbeck, *J. Phys. Chem.* **56** (1952) 829–831 10.1021/j150499a003, copied from J.H. Mitchell and K.E.W. Ridler, *Proc. Roy. Soc (London) A* **146** (1934) 911.]

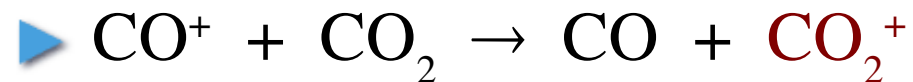
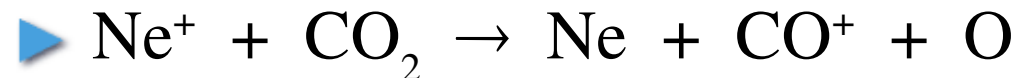


Principal reactions involving CO₂

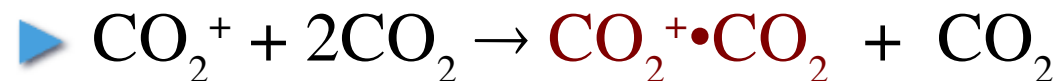
▶ Ar⁺: charge exchange, $\tau \approx 0.85$ ns



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



▶ CO₂⁺: 3-body association, 7-20 ps



▶ [For 10 % CO₂, atmospheric pressure, room temperature]

Ne⁺ in Ne ... did it make sense ?

- ▶ The avalanche produced little Ne⁺ to begin with;
- ▶ $IP_{\text{Ne}^+} > IP_{\text{CO}_2^+}$: Ne⁺ took 8 ns to generate a CO₂⁺;
- ▶ in nearly pure Ne, there could be some Ne₂⁺.
- ▶ Instead, we obtained $\text{CO}_2^+ \cdot \text{CO}_2$.

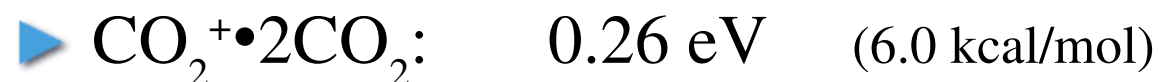
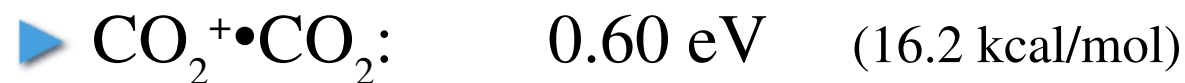
Situating cluster ions

- ▶ 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

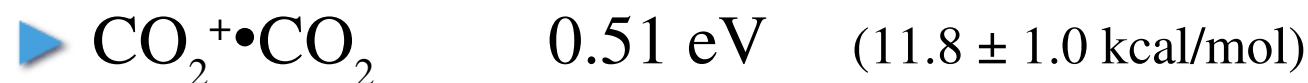
[B.M. Smirnov, "Cluster Ions and Van Der Waals Molecules," CRC press]

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, thermal: 0.03 eV.)

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

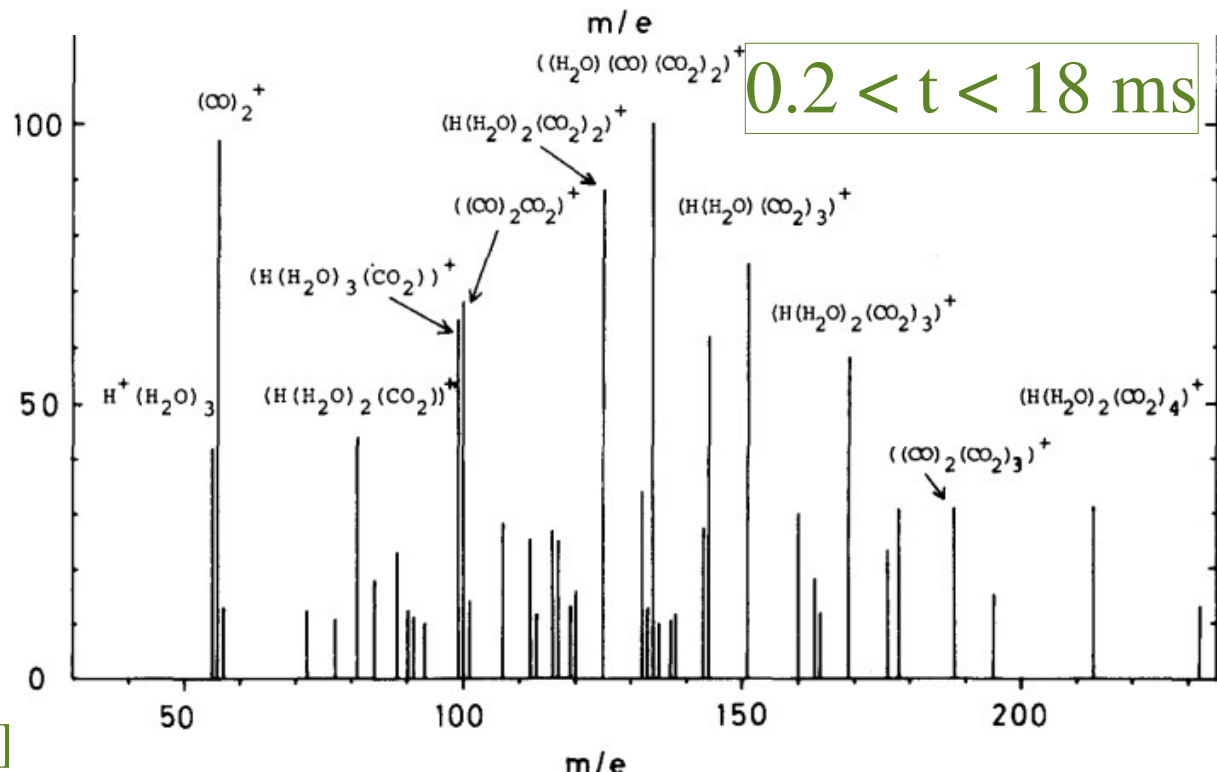
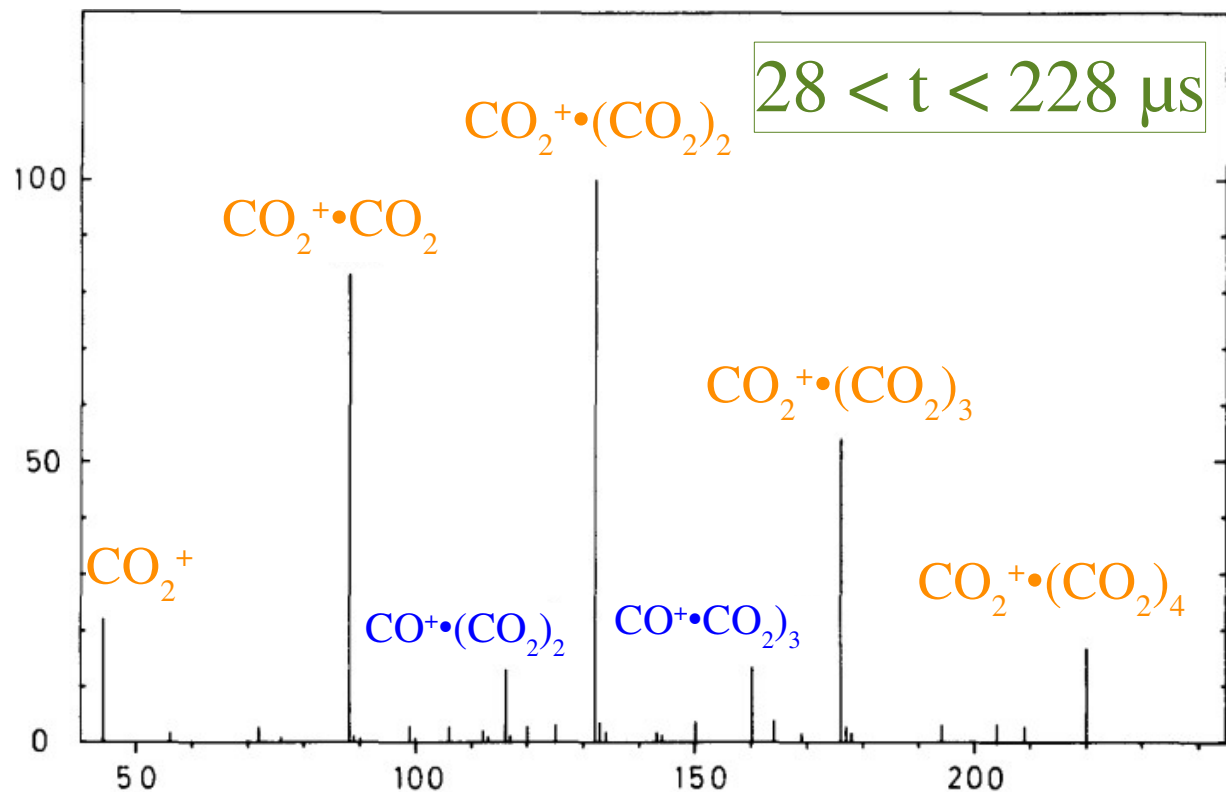
- ▶ $\text{CO}_2^+\bullet\text{CO}_2$ has a dissociation energy of 0.6 eV far above thermal energies at 1 bar. It is a so-called long-lived cluster:
 - ▶ calculated lifetime = 5 ns
 - [B.M. Smirnov, “Cluster Ions and Van Der Waals Molecules,” CRC press]
- ▶ much longer than the formation time $\tau = 7\text{-}20$ 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.

CO₂ at 1 bar

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

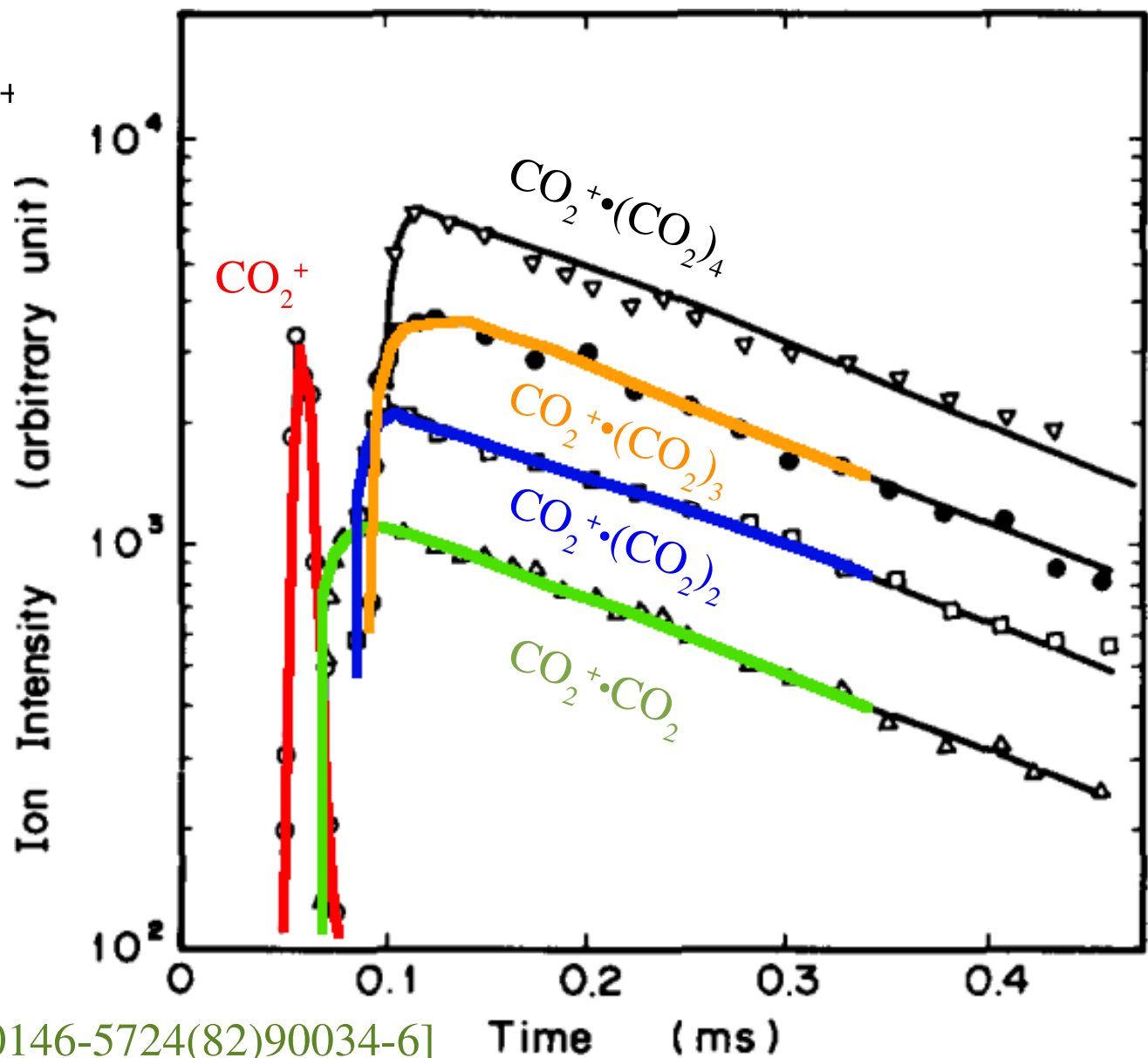
▶ Until 200 μs:
 $\text{CO}_2^+ \cdot (\text{CO}_2)_n$ and
 $\text{CO}^+ \cdot (\text{CO}_2)_n$

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



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 $\tau \sim 190 \mu\text{s}$.



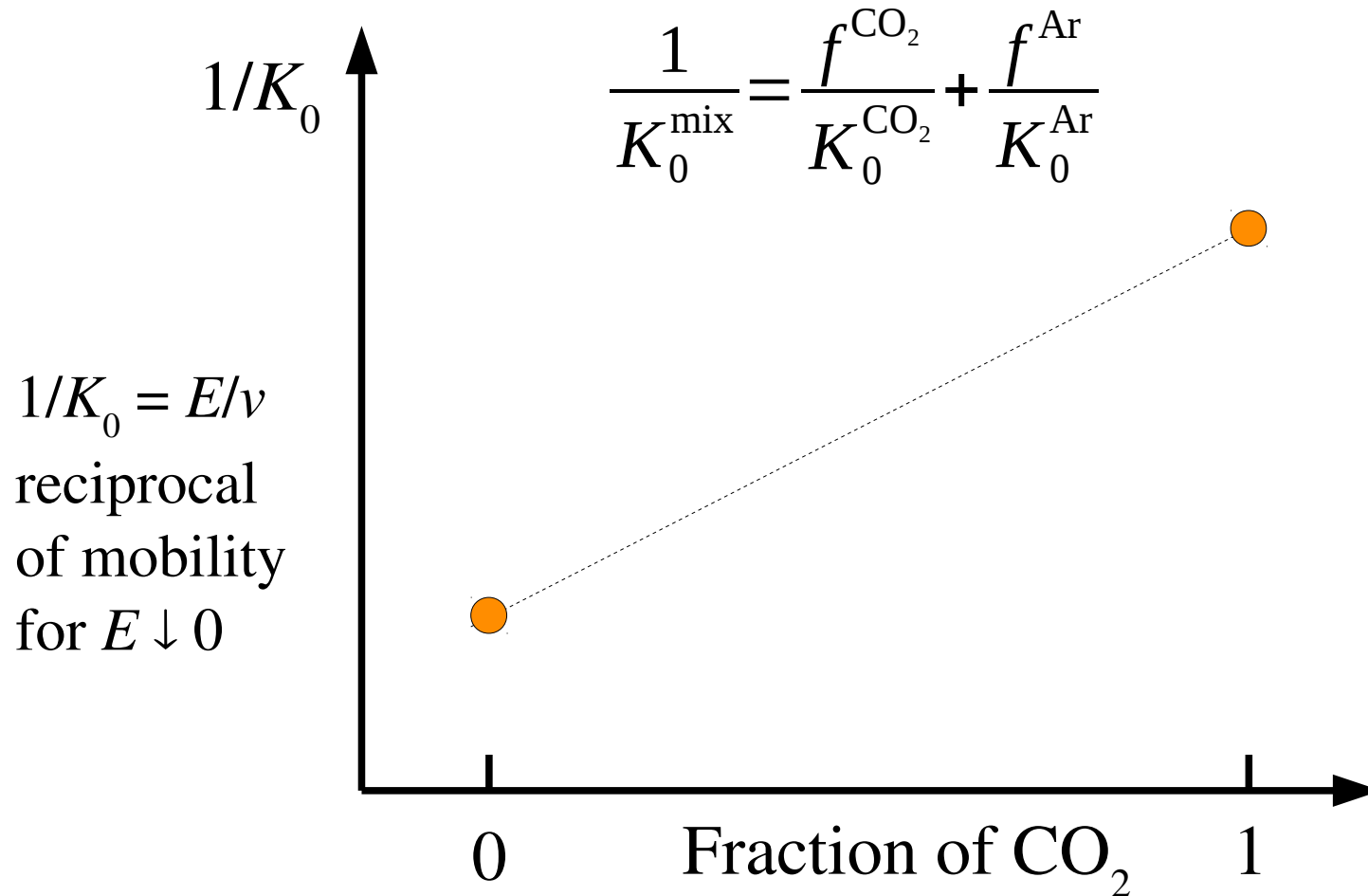
Experimental check

- ▶ 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^+ , CO_2^+ clusters, Ar^+ and Ne^+ from literature.

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.

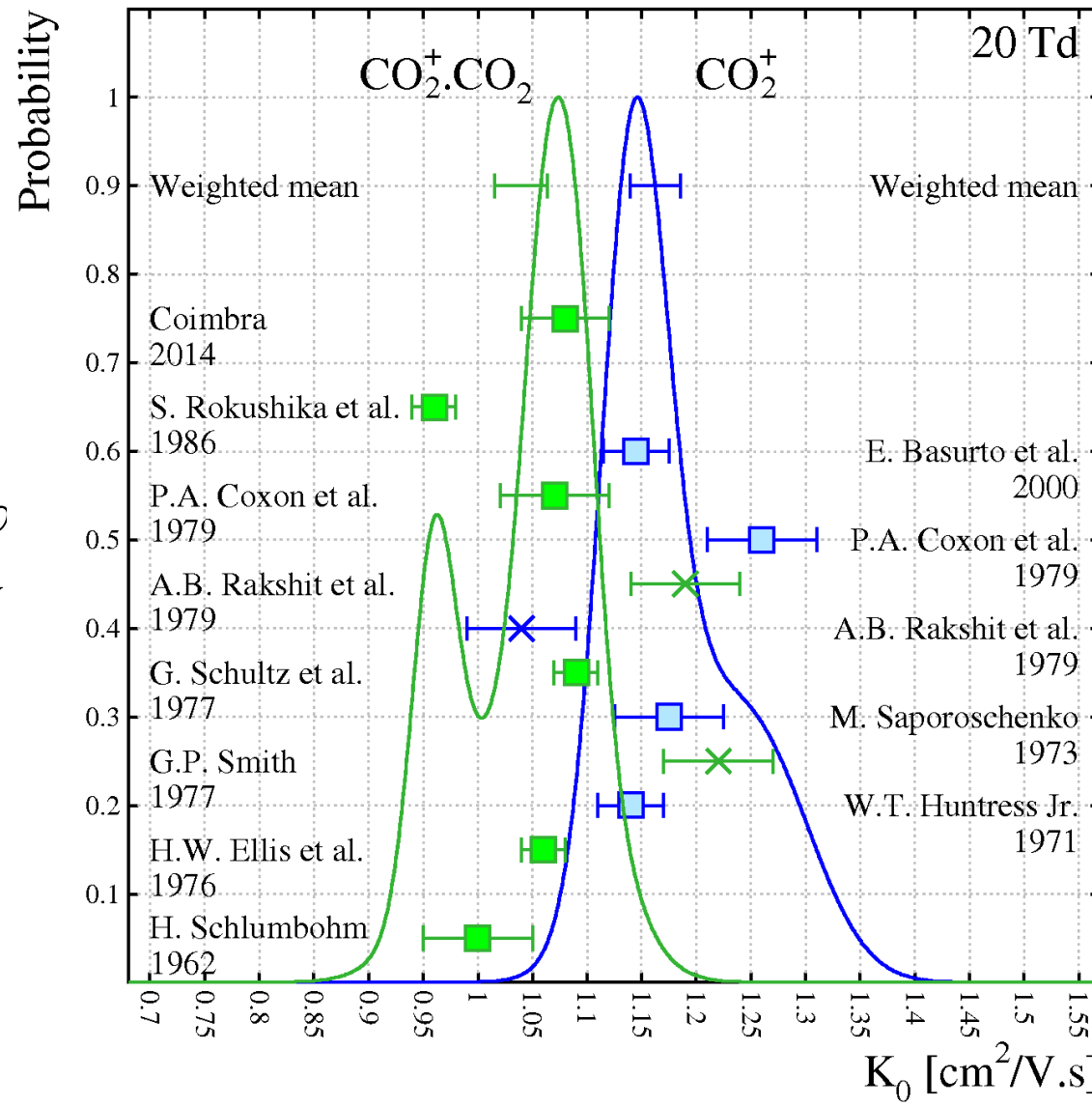
Blanc's mobility interpolation



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

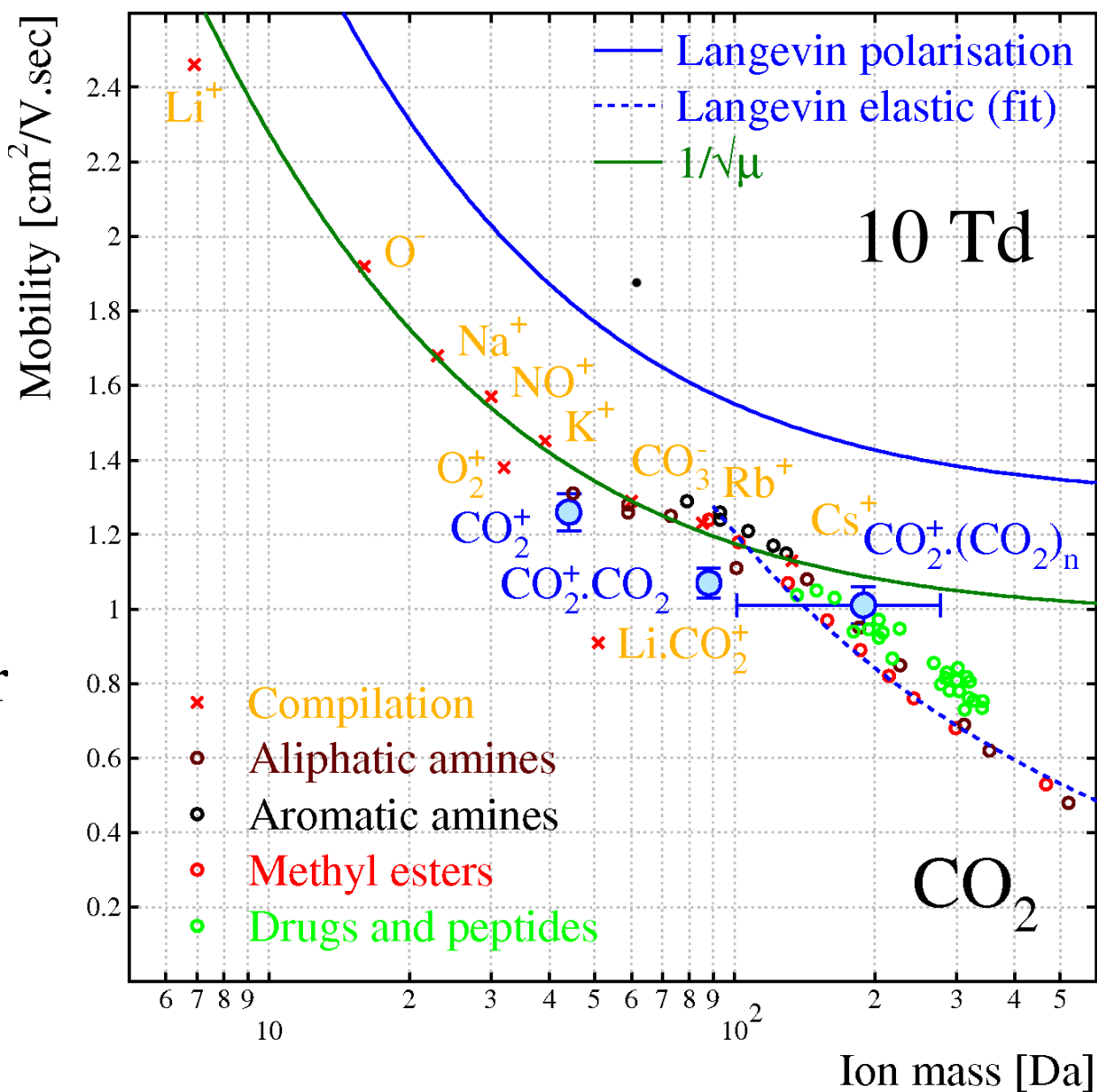
Mobility of CO_2^+ and $\text{CO}_2^+\cdot(\text{CO}_2)_n$ in CO_2

- ▶ 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 .

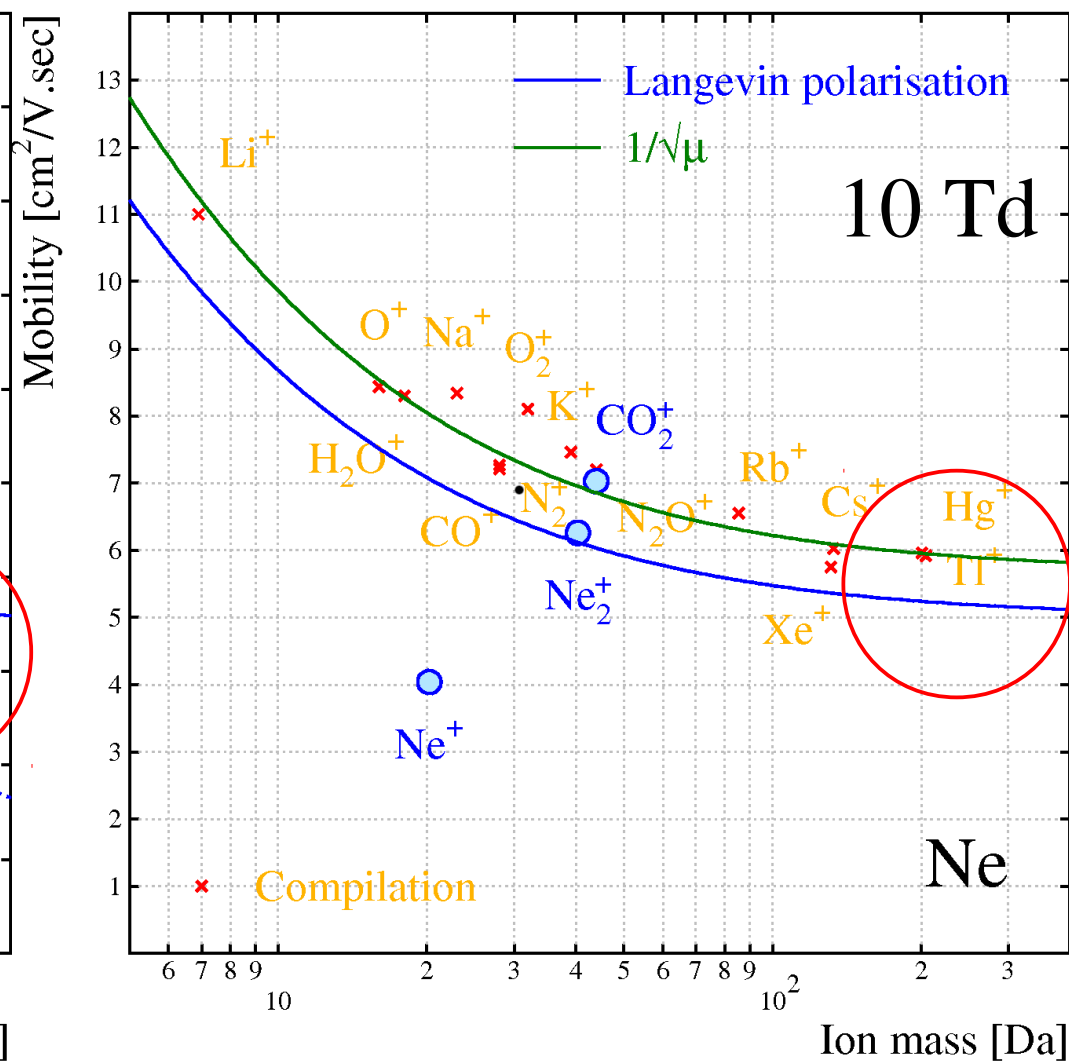
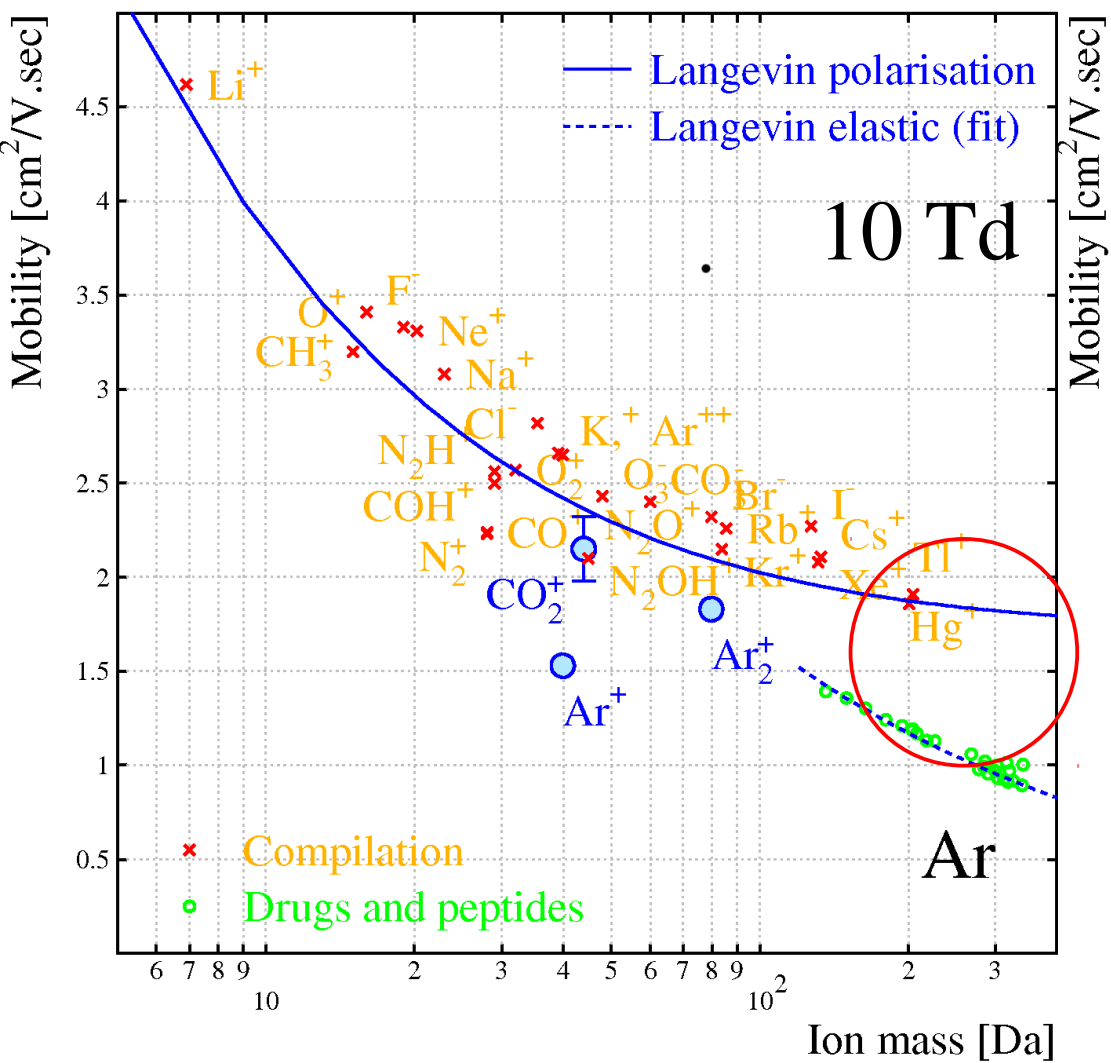


Mass-mobility in CO₂

- ▶ 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.

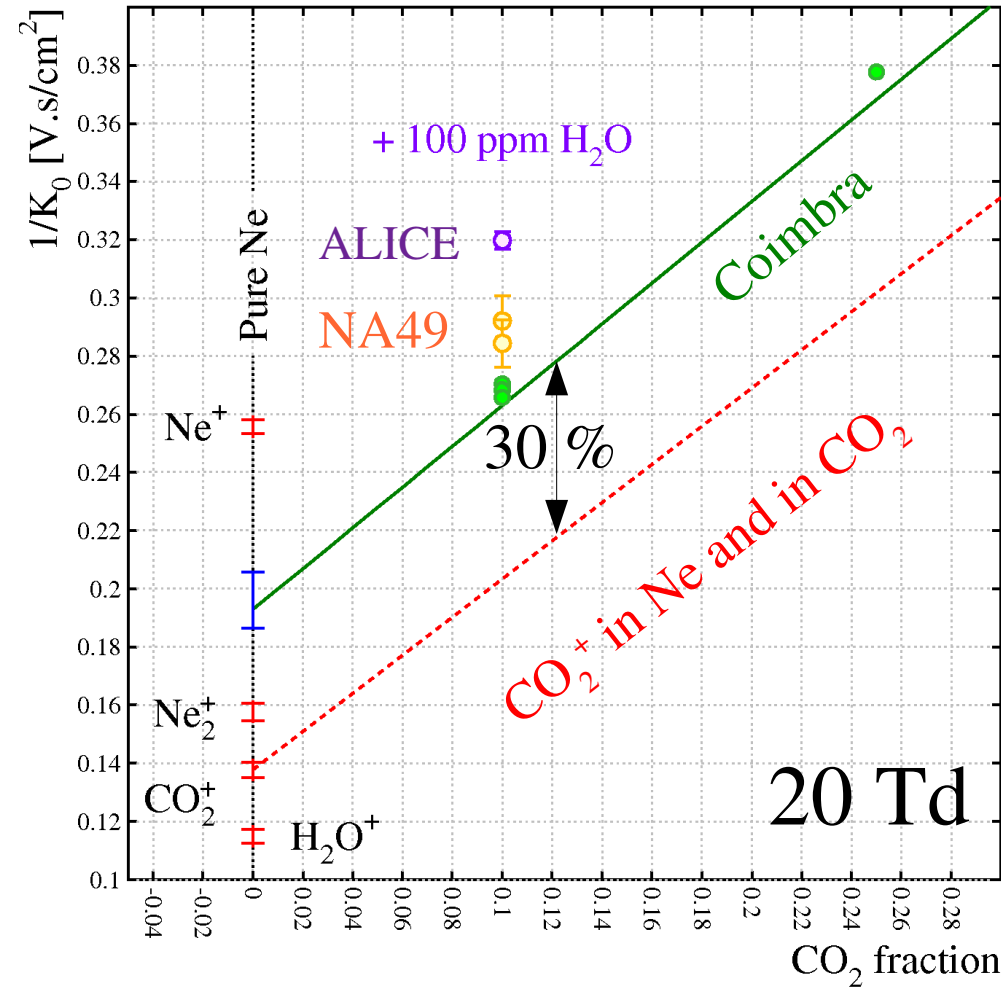
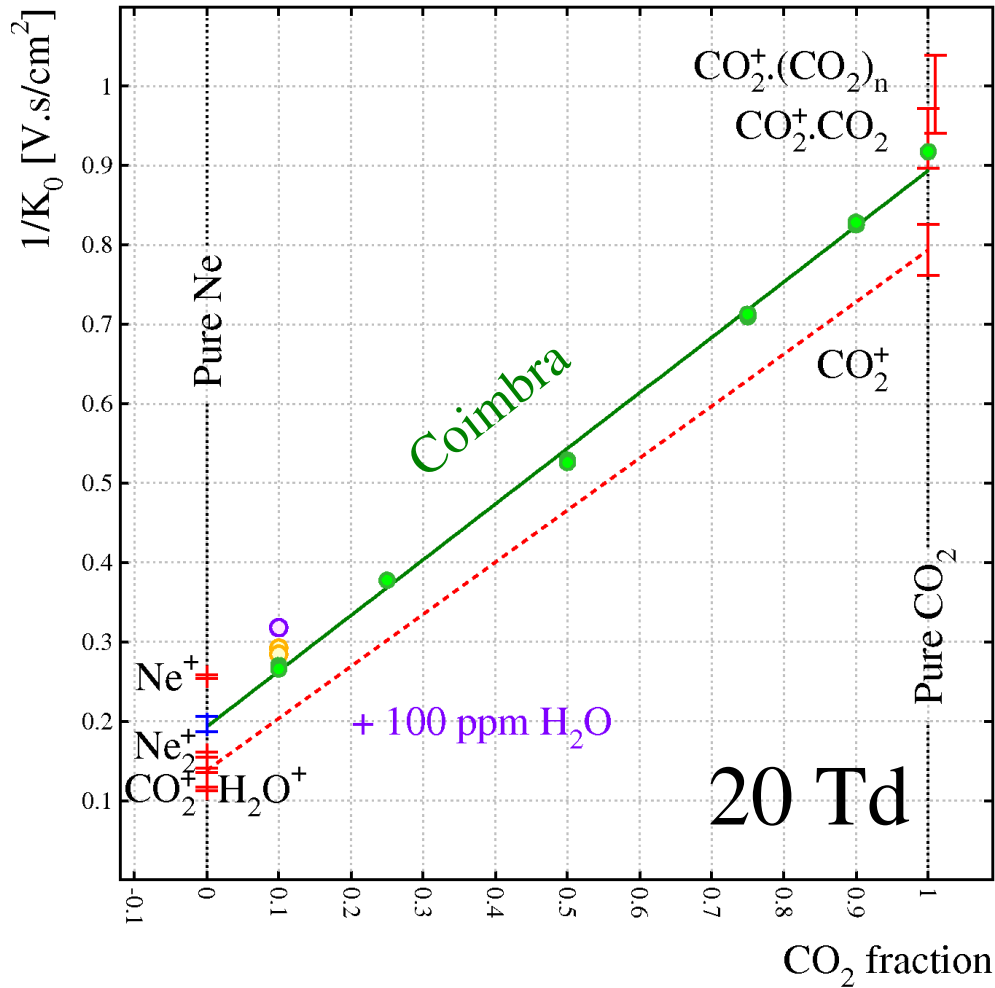


Mass-mobility in pure Ar and Ne



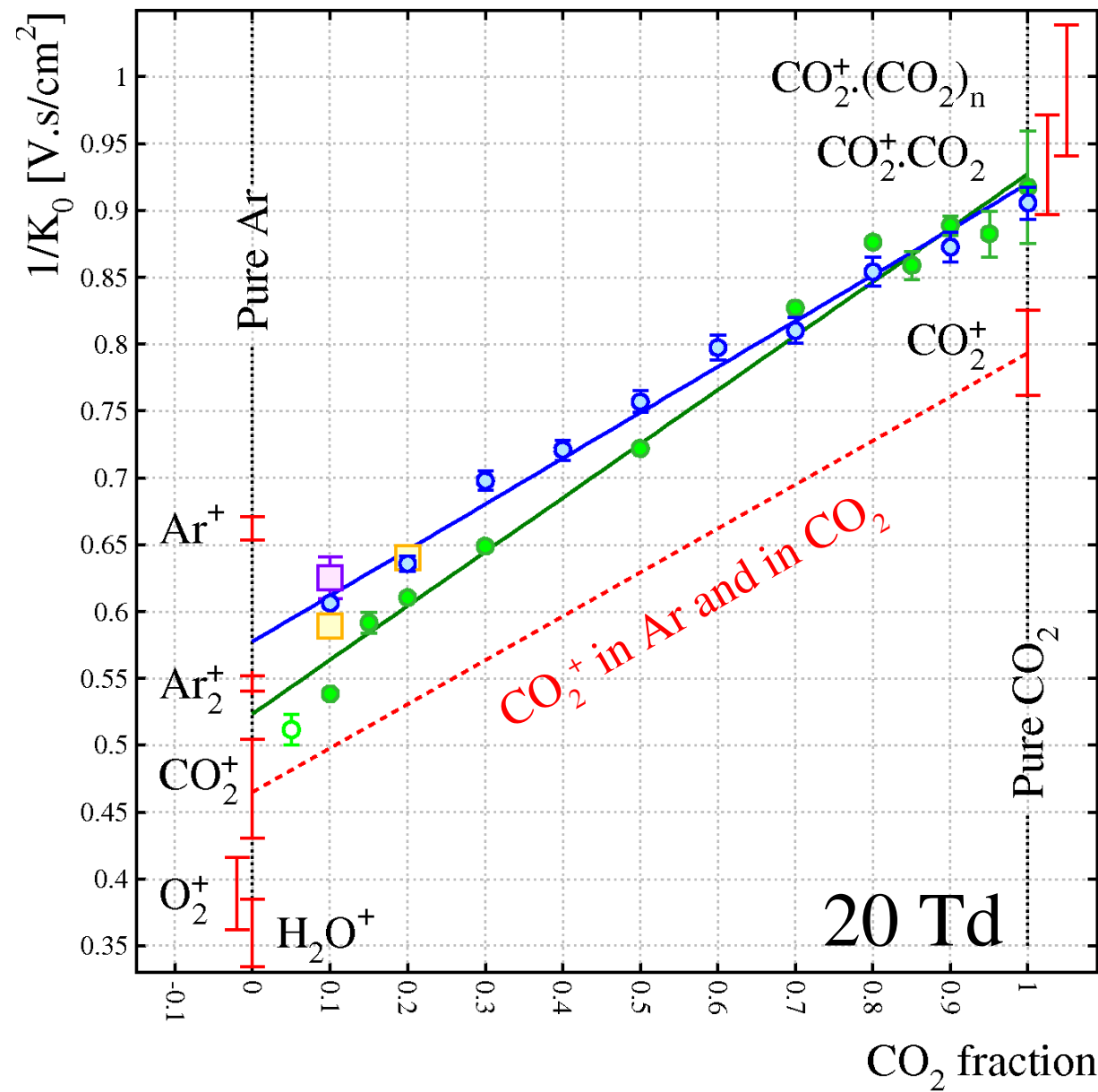
Blanc diagram for Ne-CO₂

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



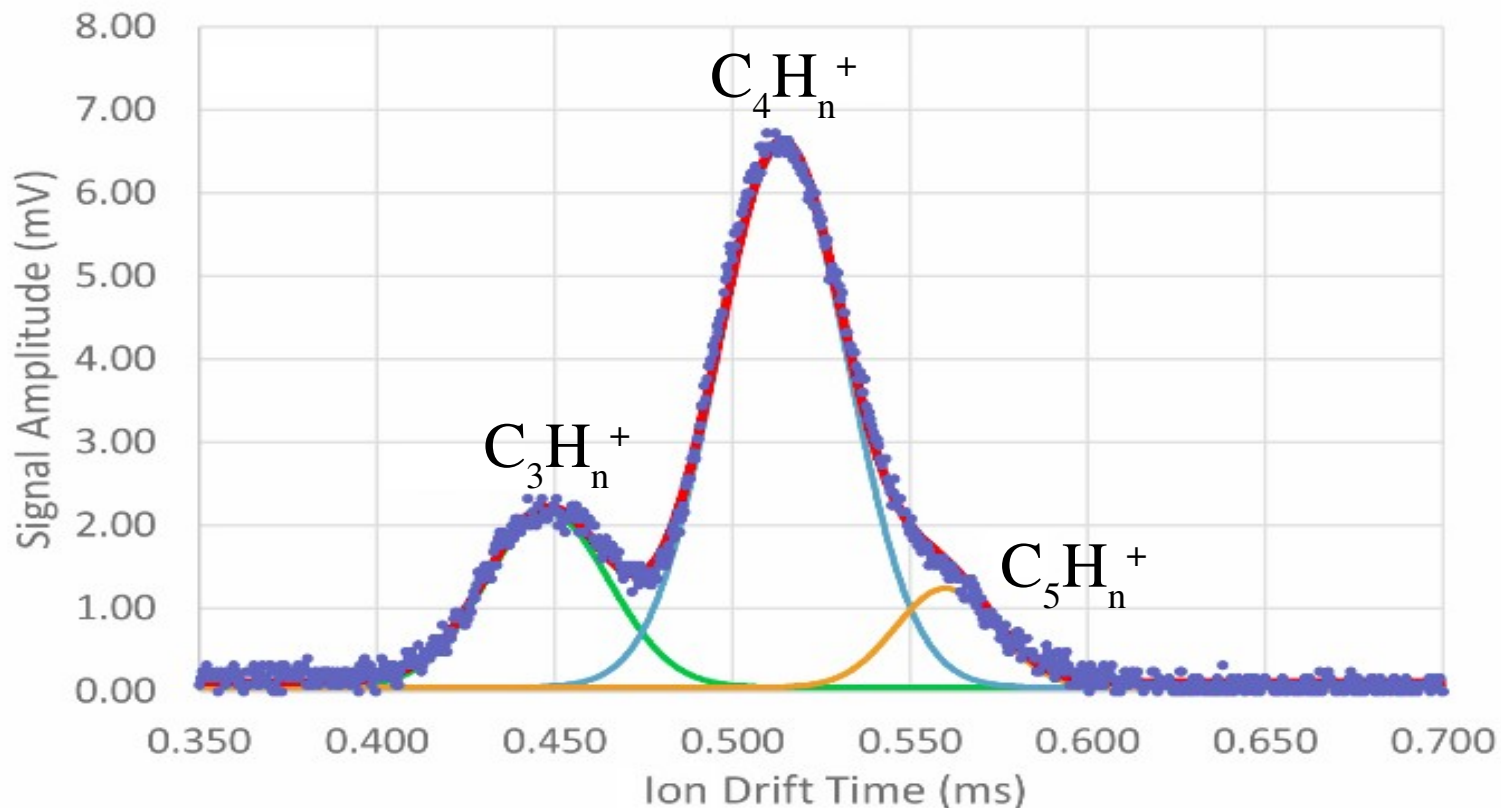
Blanc diagram for Ar-CO₂

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



How about alkanes ?

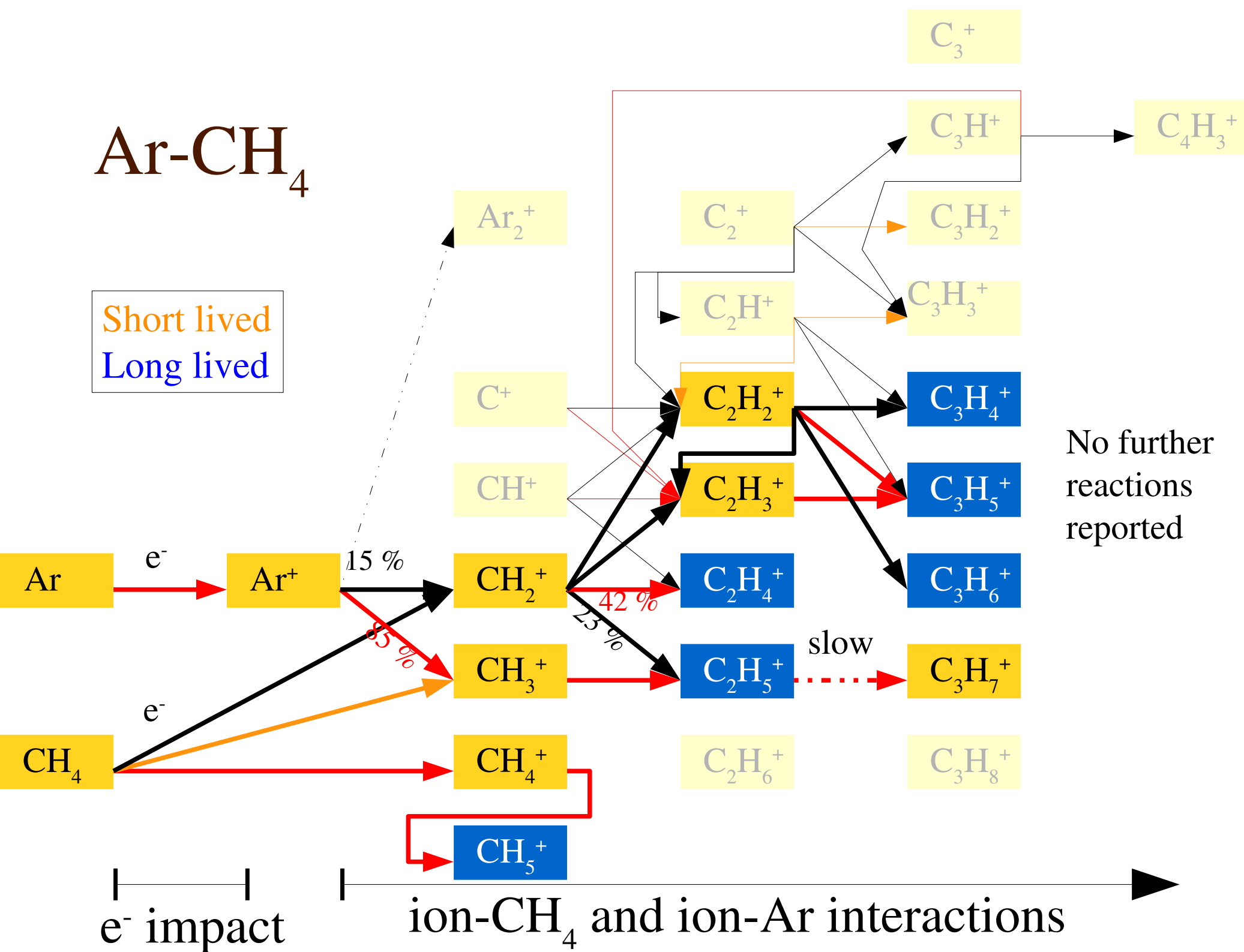
- ▶ Ar 90 % - C₂H₆ 10 %, at low pressure.
- ▶ Expect Ar⁺ or C₂H₆⁺ but ... none are seen – why ?



[André Cortez et al. 10.1088/1748-0221/8/12/P12012]

Ar-CH₄

Short lived
Long lived



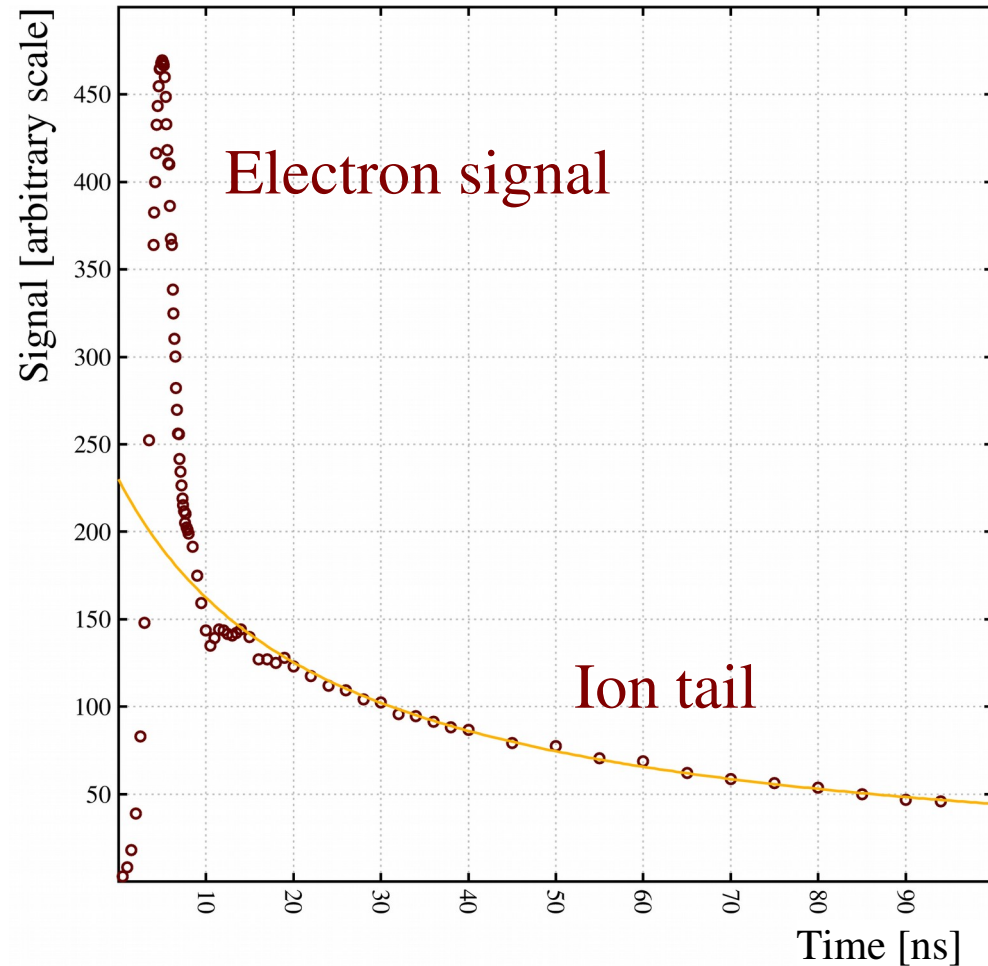
Atlas TRT signals

► Data:

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

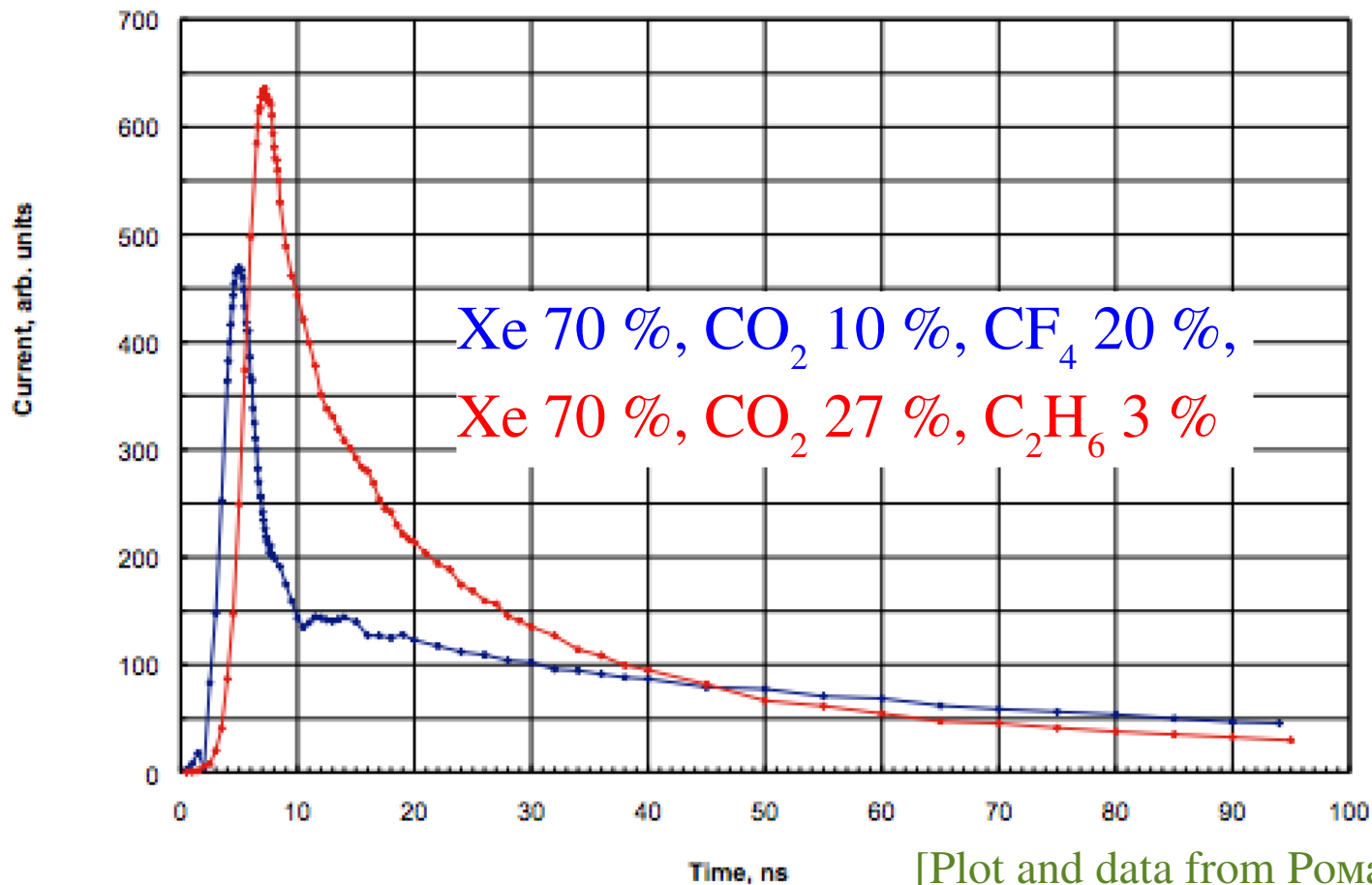
► Fit:

- $1/(t+t_0)$



Adding C_2H_6

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



[Plot and data from Романюк Анатолий Самсонович]

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

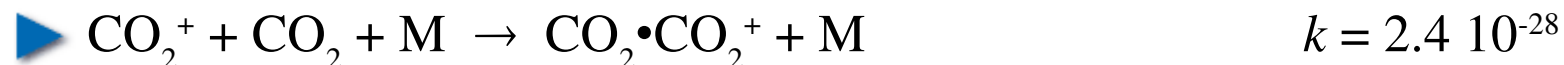
▶ CO_2 : 13.776 eV

▶ CF_4 : 15.70 eV for CF_3^+ (main ionisation channel)
16.2 ± 0.1 eV for CF_4^+

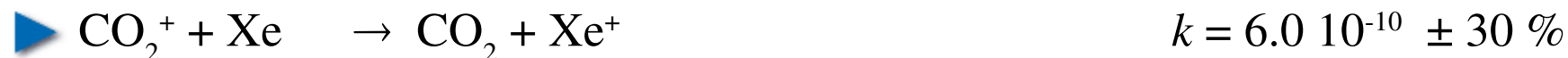
Reactions in Xe-CO₂-CF₄



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



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

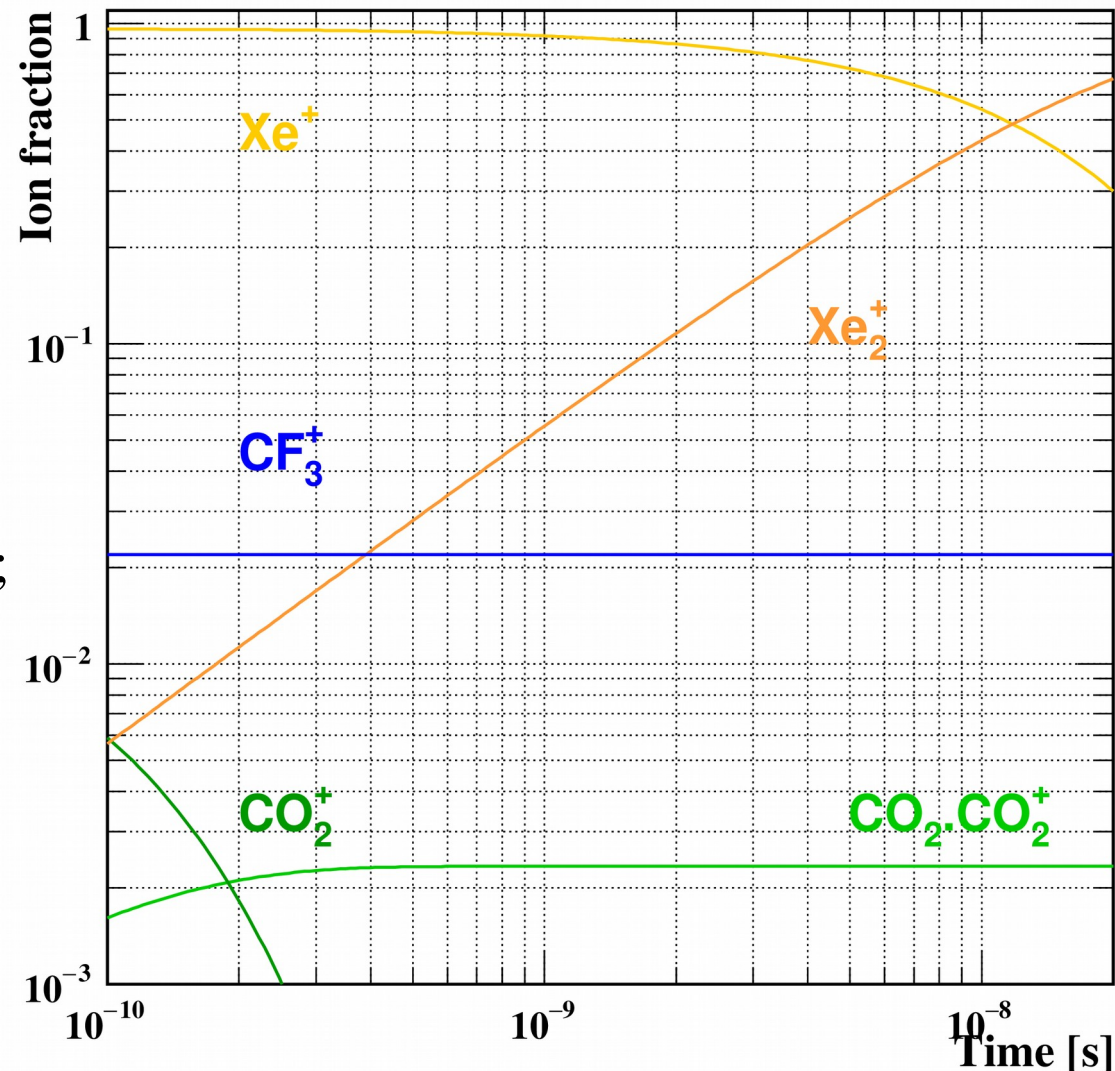


[V.G. Anicich and W.T. Huntress Jr., Astrophys. J. Suppl. **62** (1986) 553-672.]

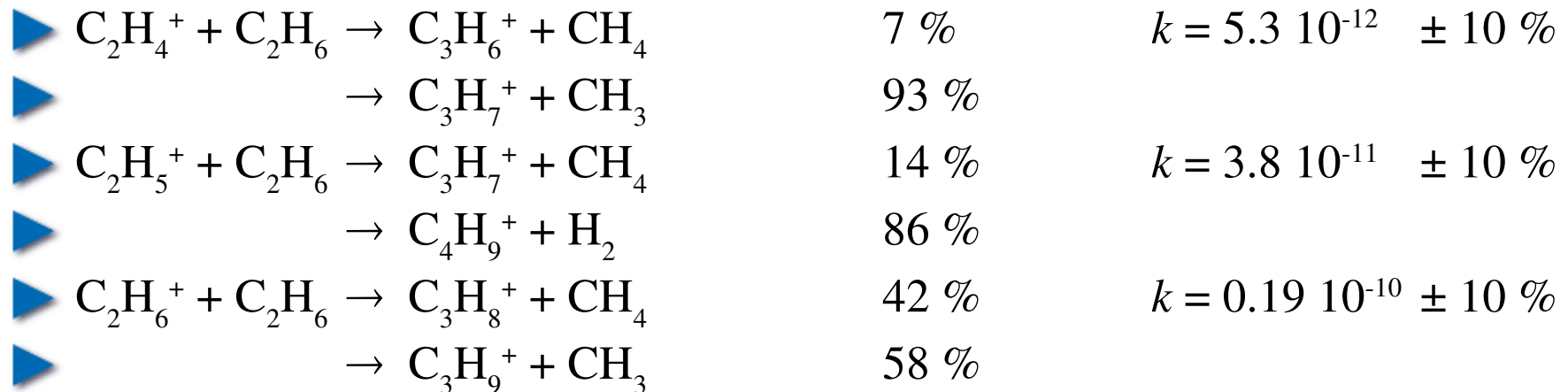


Evolution of Xe-CO₂-CF₄ (70-10-20)

- ▶ Initial ion mix for 100 kV/cm;
- ▶ Xe⁺ and Xe₂⁺ dominate, 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.



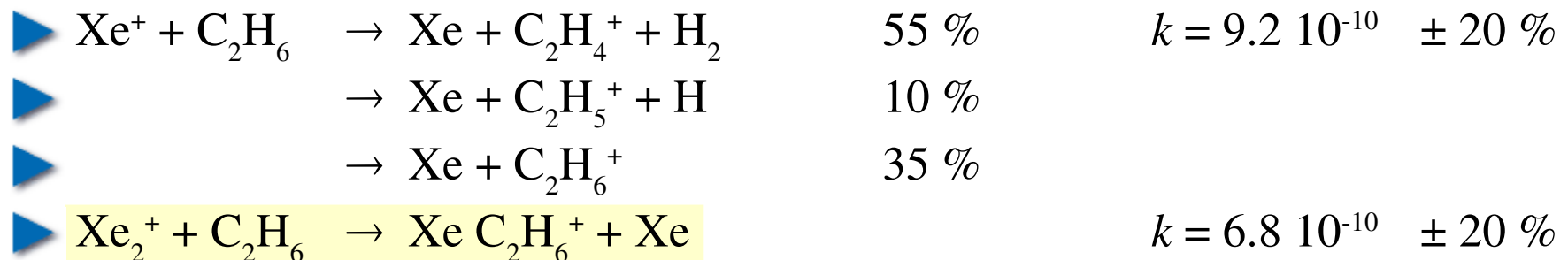
Reactions in Xe-C₂H₆



[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

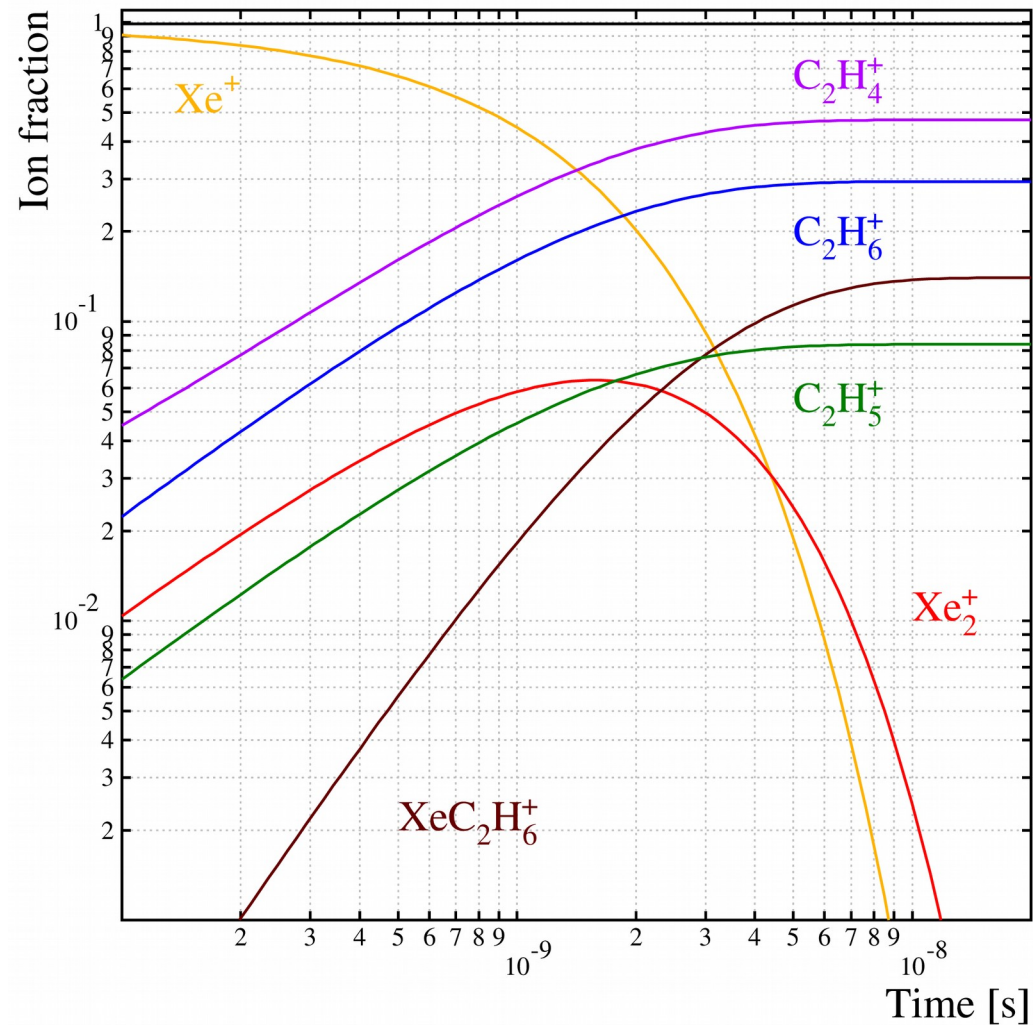
```
Clear[nXe, nXe2, nXeC2H6, nC2H4, nC2H5, nC2H6]
evol = Assuming[{rXeXe2 > 0, rXe2XeC2H6 > 0, rXeC2H4 > 0, rXeC2H5 > 0,
  rXeC2H6 > 0, n0Xe > 0, n0C2H4 > 0, x > 0},
Simplify[DSolve[
  {nXe'[x] == -(rXeXe2 + rXeC2H4 + rXeC2H5 + rXeC2H6) nXe[x],
  nXe[0] == n0Xe,
  nXe2'[x] == rXeXe2 nXe[x] - rXe2XeC2H6 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 Xe-C₂H₆ (97-3)

- ▶ Initial ion mix for 100 kV/cm;
- ▶ after 10 ns, the only Xe-related ion that remains is XeC₂H₆⁺ which is made from Xe₂⁺;
- ▶ the diagram does not show the C₃H_x⁺ and C₄H_x⁺ ions subsequently generated by C₂H₄⁺ and C₂H₅⁺;
- ▶ Xe_n⁺ for $n > 2$ are not shown because the rates are not known.

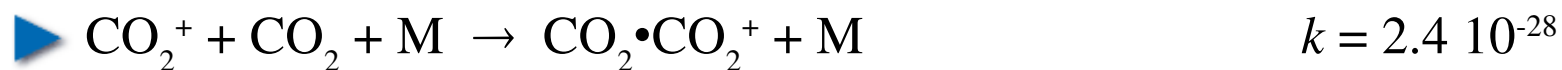


Reactions in Xe-CO₂-C₂H₆

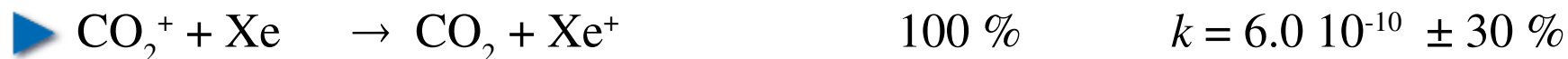
▶ All reactions from Xe-C₂H₆ and in addition:



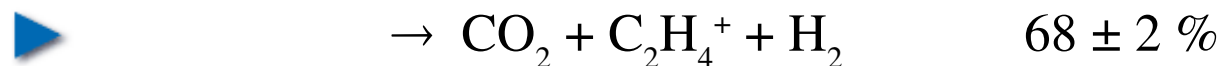
[V.G. Anicich and W.T. Huntress Jr., *Astrophys. J. Suppl.* **62** (1986) 553-672.]



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



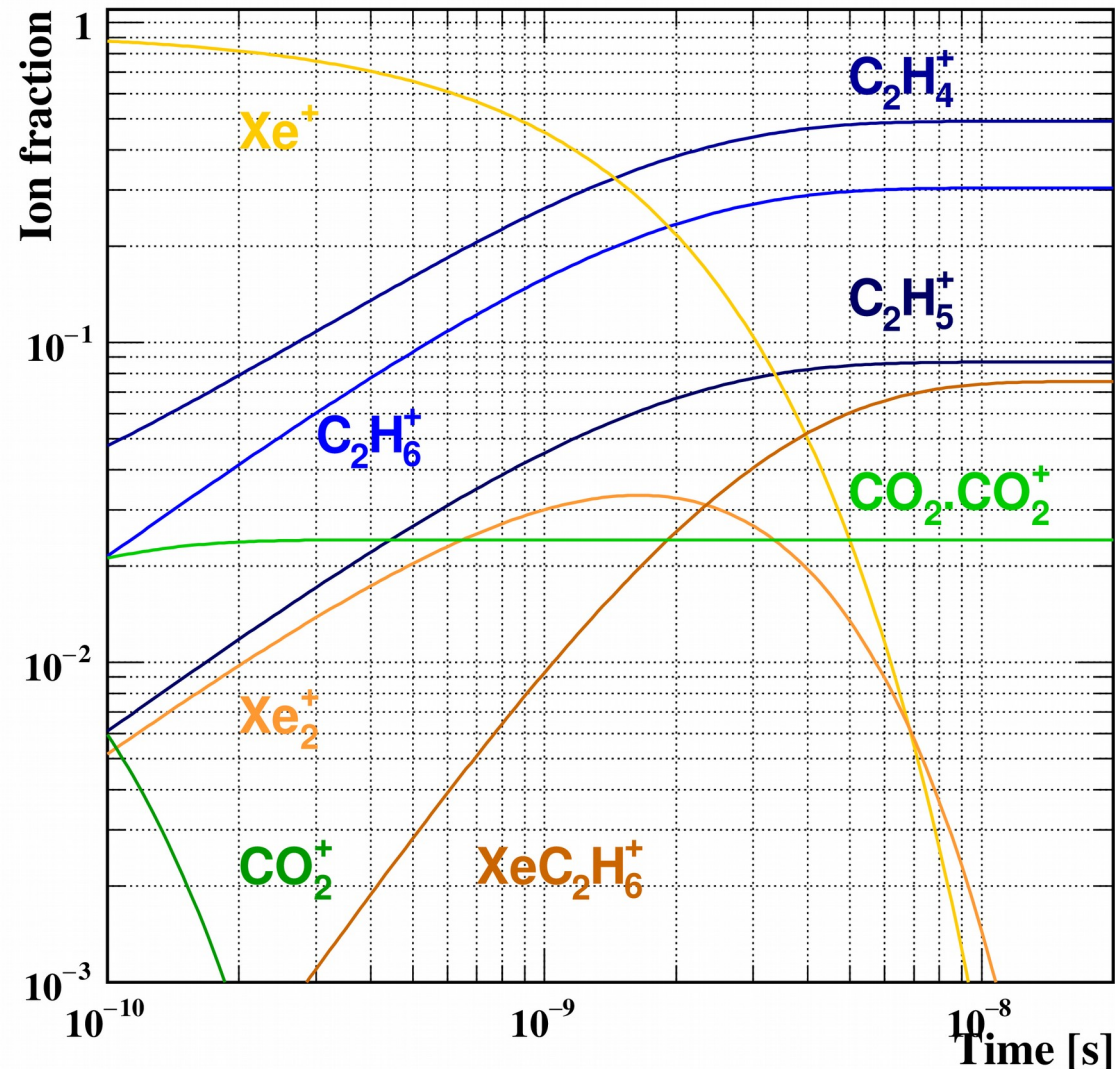
[V.G. Anicich and W.T. Huntress Jr., *Astrophys. J. Suppl.* **62** (1986) 553-672.]

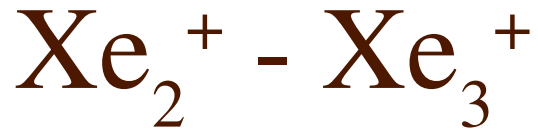


[Masaharu Tsuji, 10.1016/0168-1176(94)03996-8]

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.





- ▶ 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^+

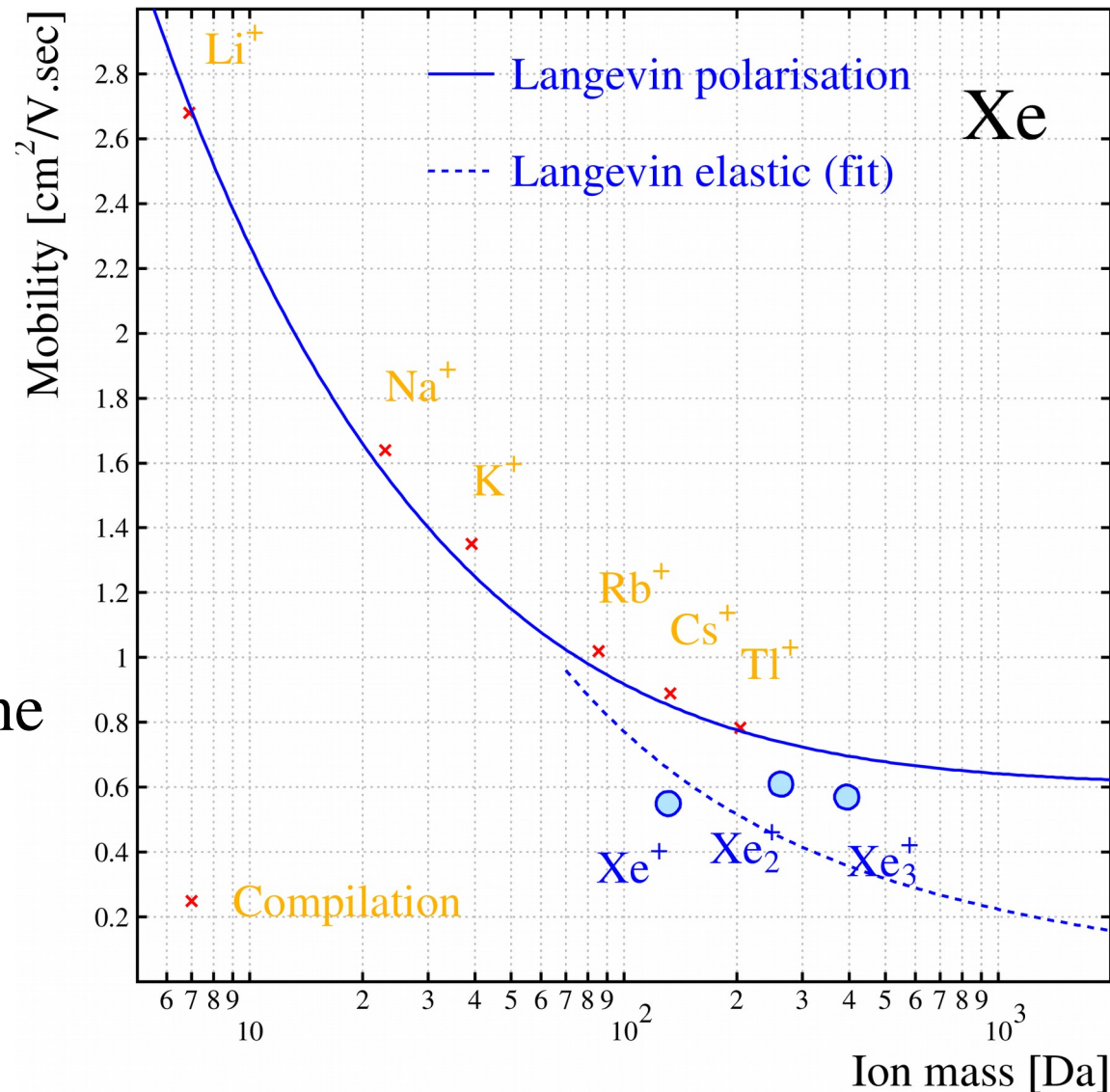
- ▶ Mobilities are known for the smallest Xe clusters;
- ▶ these are remarkably stable;
- ▶ ΔH for $n \geq 5$ clusters is nearly constant at ~ 0.1 eV.

Xe_n^+	Mass	μ ($E = 0, T = 300$ K)	ΔH $n-1 \rightarrow n$	References
	[Da]	[$\text{cm}^2/\text{V}\cdot\text{s}$]	[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

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]



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.”

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, which are slower than CO₂⁺;
 - ▶ 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.
- ▶ There is room for theses in this field.