

Gas-based detectors

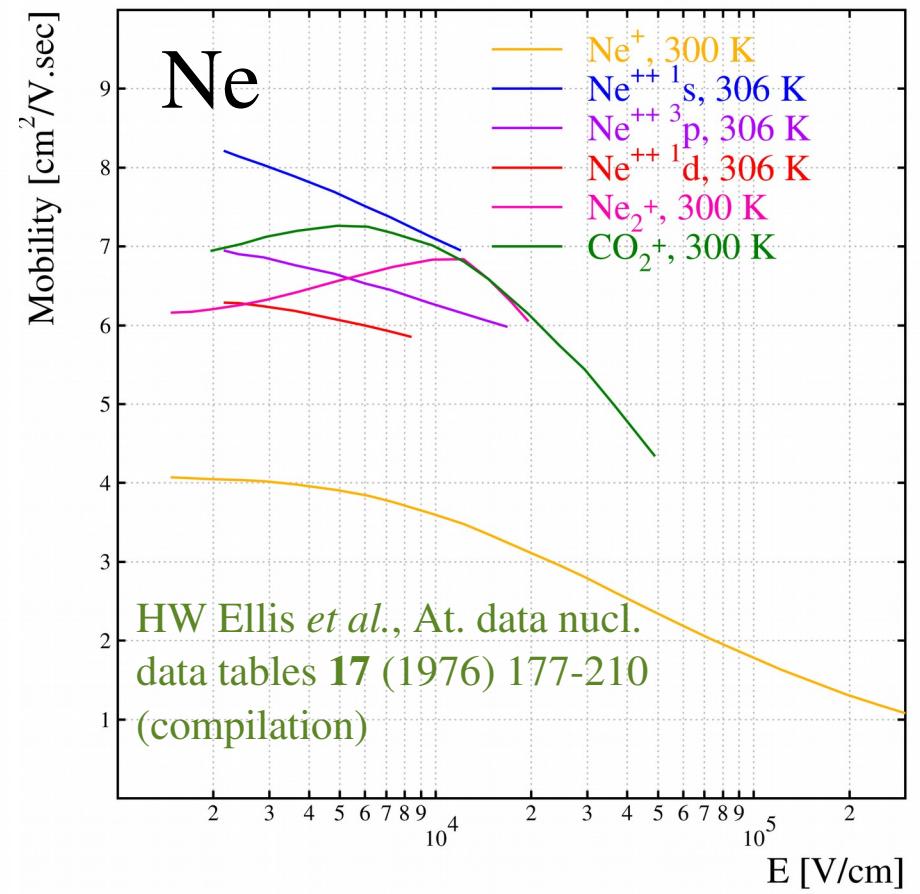
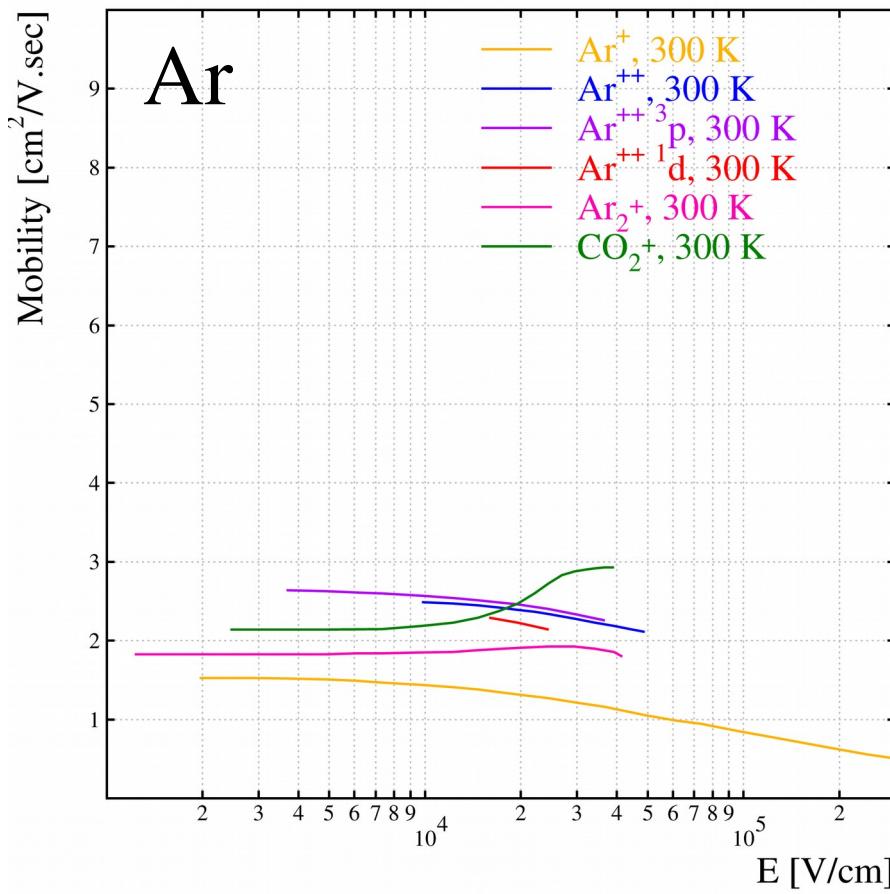
Ion transport

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* ?

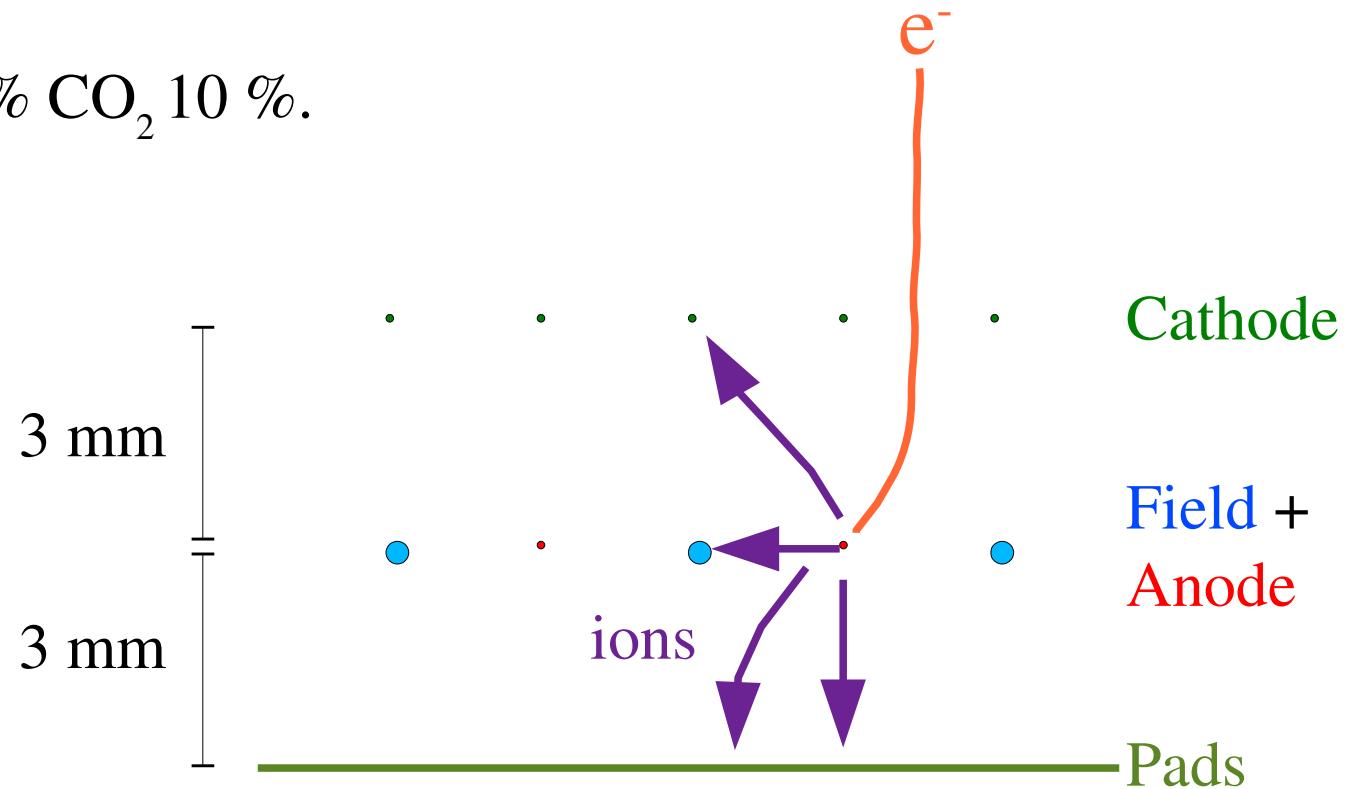
$$\text{Ar}^+ \text{ and Ne}^+ \text{ mobility} \equiv v_{\text{D}}(E) / E$$

► Noble gas ion mobilities are well known:



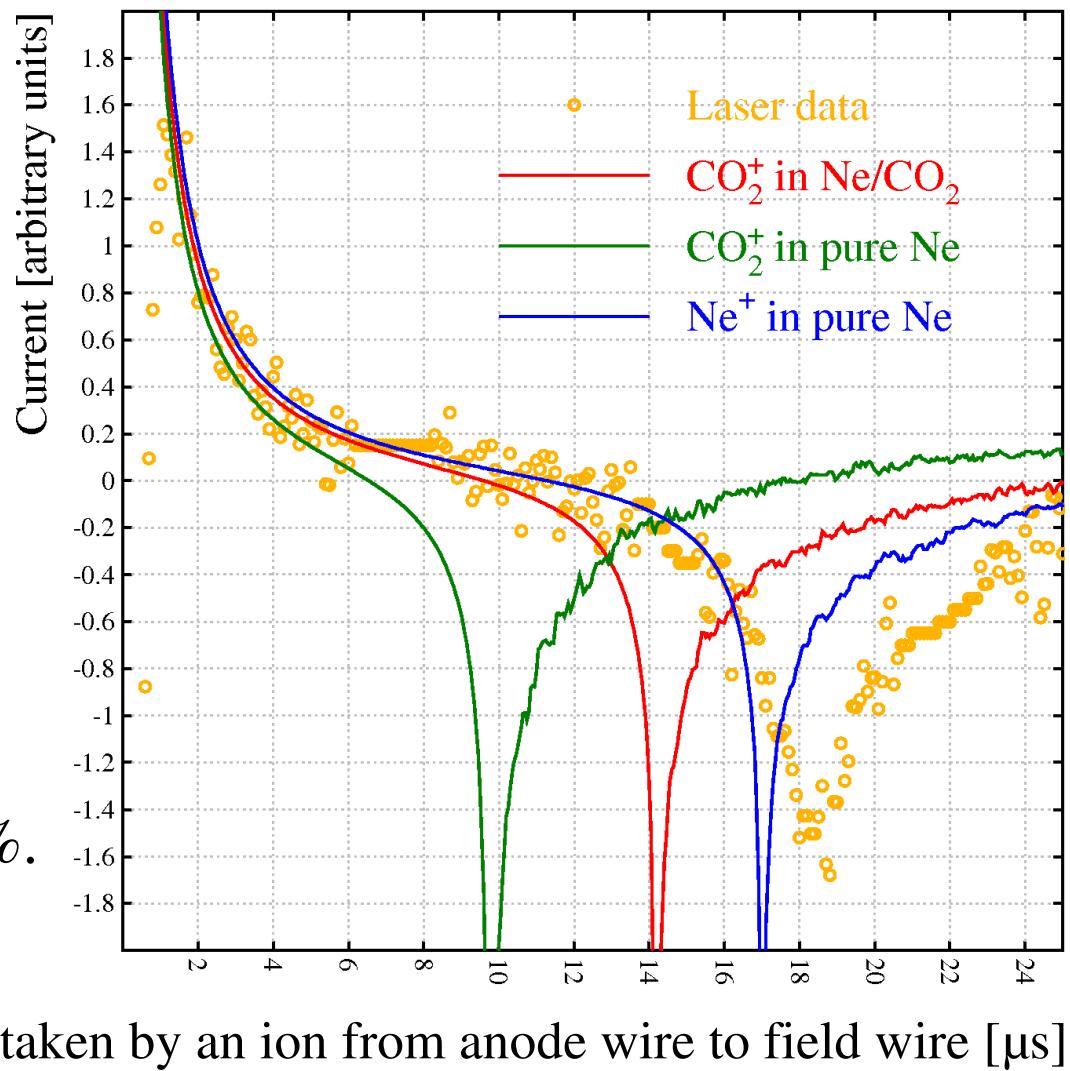
Ion induced signals

- ▶ 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 ?

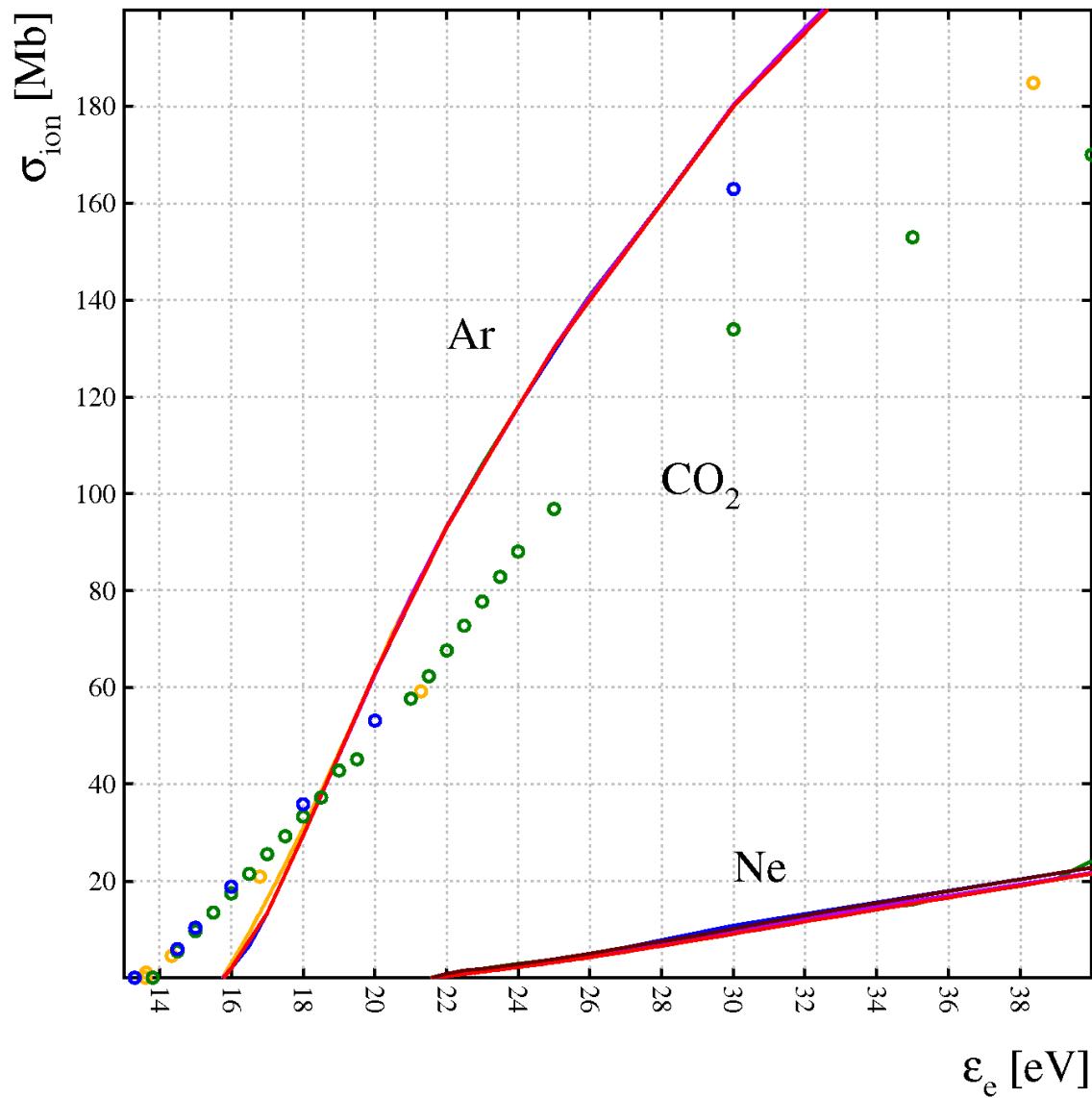
- ▶ Ne^+ ions in Ne come reasonably close to the measurements ...
- ▶ we've used it for years ...
- ▶ but does it make sense ?
- ▶ NA49 TPC: Ne 90 % CO_2 10 %.
[Data: Rainer Renfordt]



Electron-impact cross sections

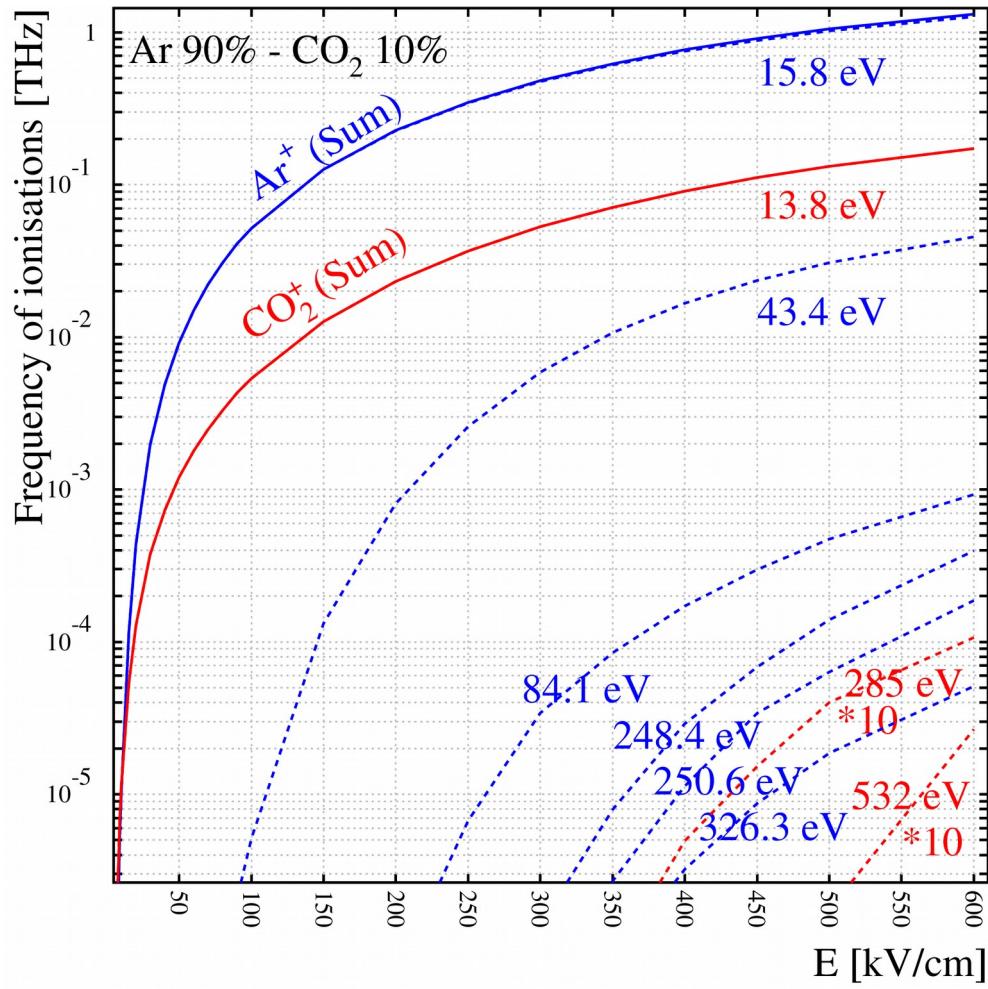
- ▶ CO_2^+ and Ar^+ compete.
- ▶ Ne^+ has higher threshold and is produced less.

[Pure gases, data from LXcat]

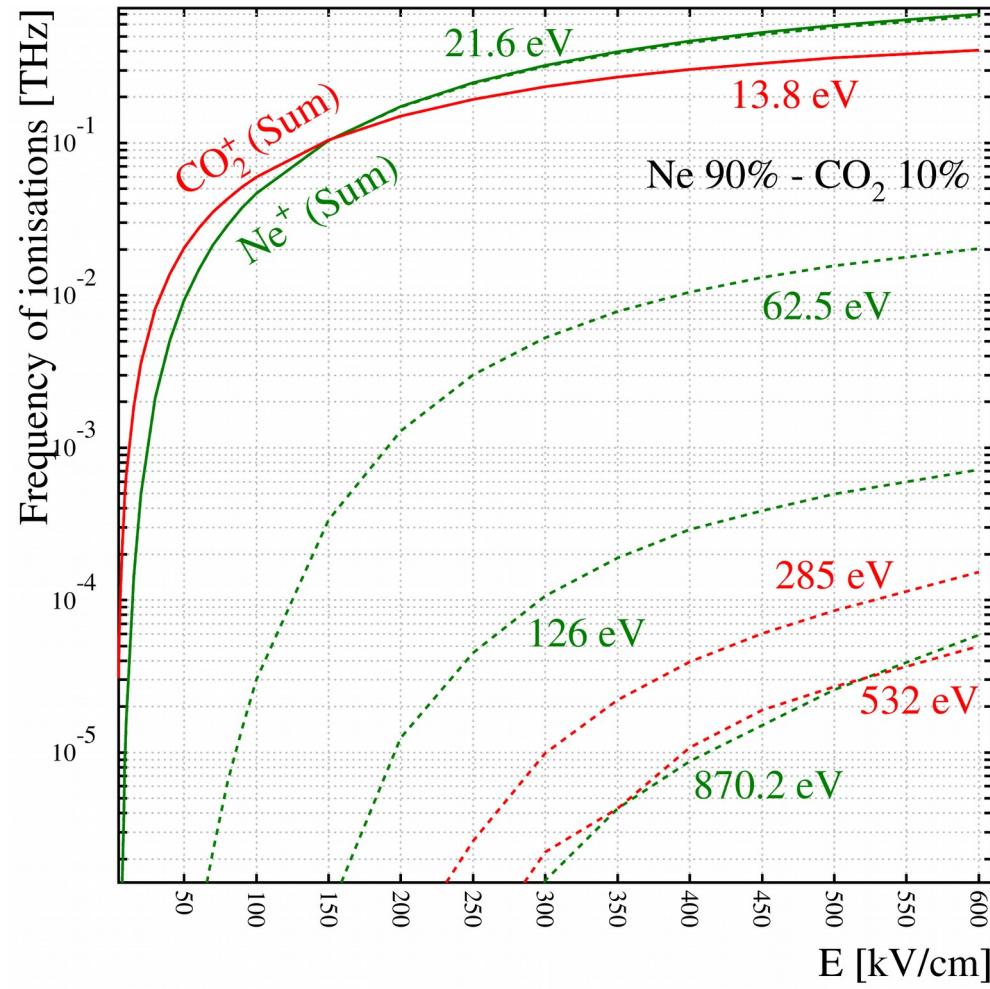


Avalanche products

► Ar⁺ dominates in Ar-CO₂,

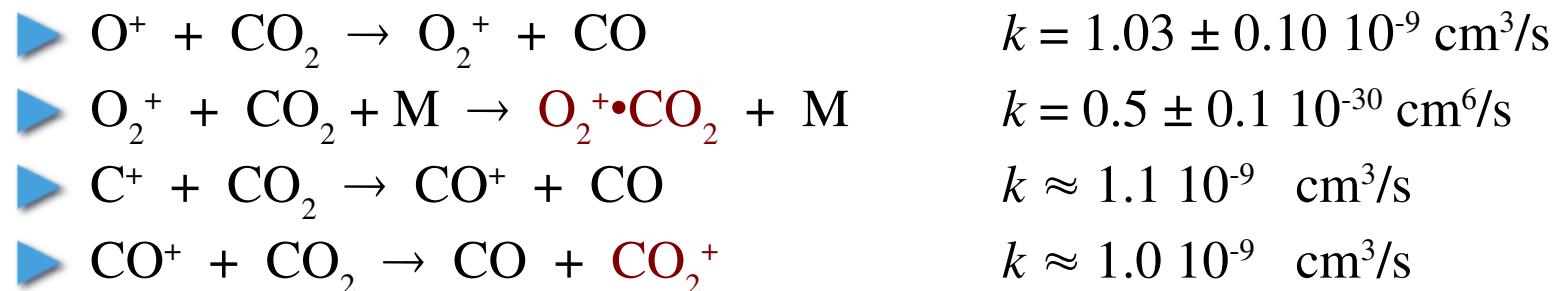


CO₂⁺ dominates in Ne-CO₂



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 O₂⁺.

[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, $N \approx 2.45 \cdot 10^{19}/\text{cm}^3$
 - ▶ 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 cm⁶/s.
- ▶ Example 1: Ar⁺ + Ar + Ar → Ar⁺•Ar + 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: CO₂⁺ + CO₂ + CO₂ → CO₂⁺•CO₂ + CO₂
 - ▶ $k = 2.4 \cdot 10^{-28} \text{ cm}^6/\text{s}$
 - ▶ rate = $k N^2 = 1.4 \cdot 10^{11}/\text{s}$, $\tau = 7 \text{ ps}$

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:

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

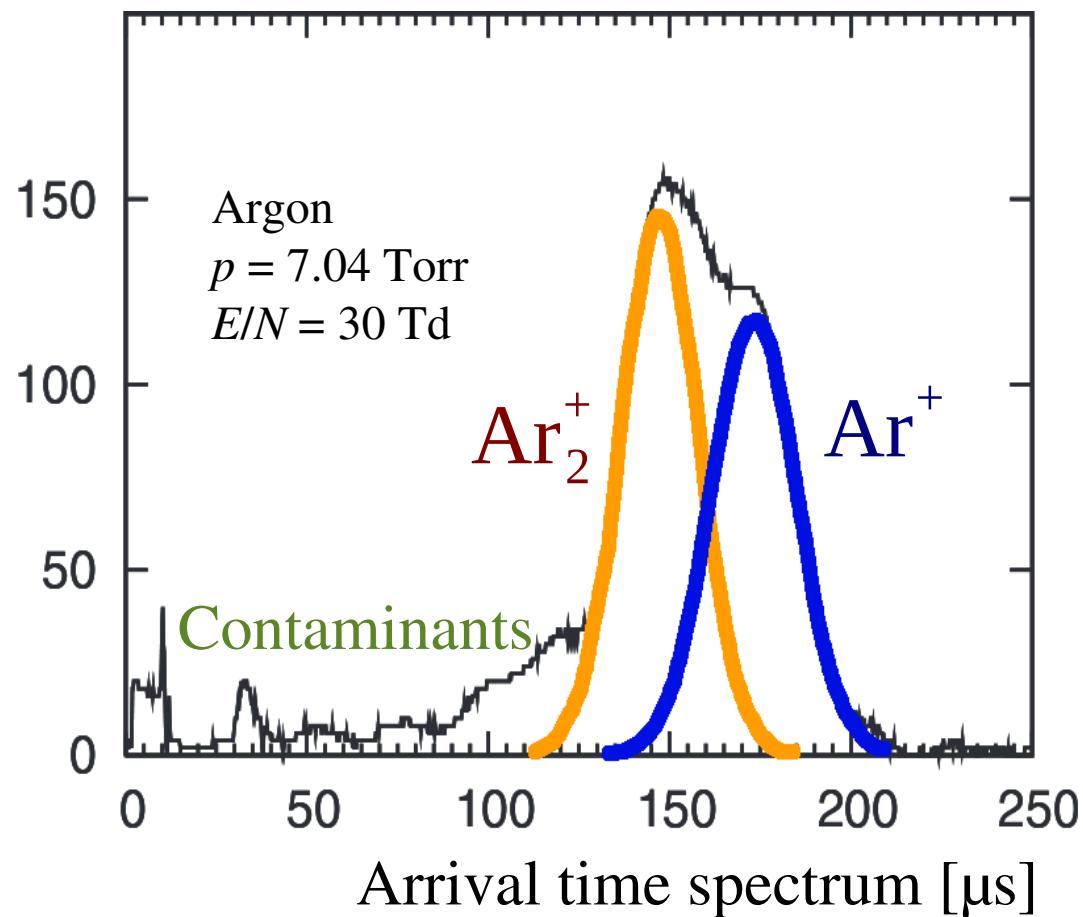
- ▶ Combine with the number density to get collision time:

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

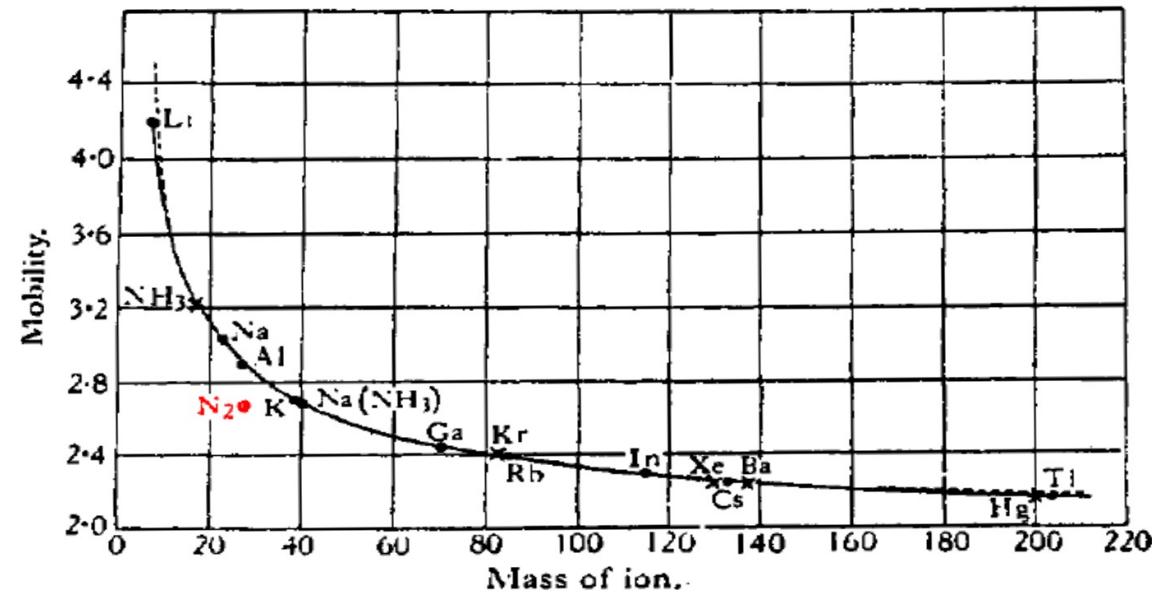
Ions drifting in pure Ar

- ▶ In pure argon, dimers are formed:
 - ▶ $\text{Ar}^+(\text{P}_{3/2}^o) + 2\text{Ar} \rightarrow \text{Ar}_2^+\bullet\text{Ar} + \text{Ar}$
($k = 2.3 \pm 0.1 \cdot 10^{-31} \text{ cm}^6/\text{s}$, 7 ns)
 - ▶ Note: dimers move *faster* than ions due to $\text{Ar} \leftrightarrow \text{Ar}^+$ resonant charge exchange

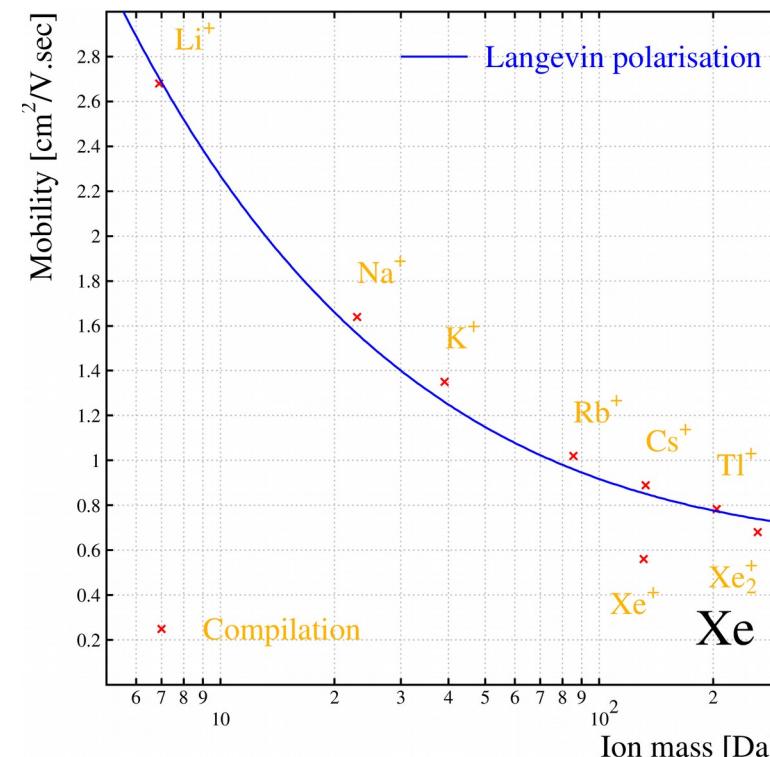
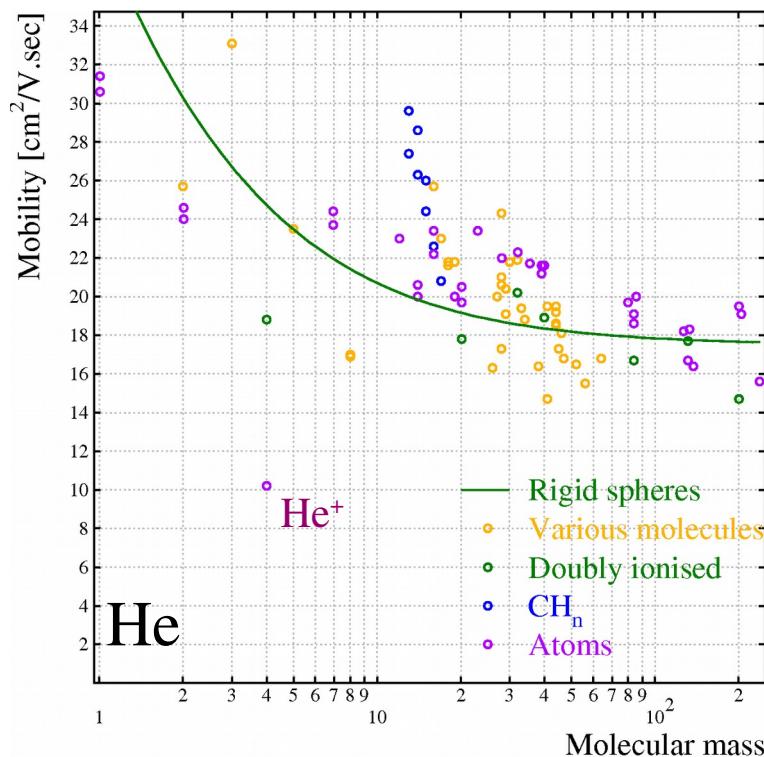
[P.N.B. Neves et al. 10.1063/1.3497651]



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
 - ▶ Ar⁺ + CO₂ → Ar + CO₂⁺
- ▶ Ne⁺: charge transfer in 2-steps, $\tau \approx 8$ ns
 - ▶ Ne⁺ + CO₂ → Ne + CO⁺ + O
 - ▶ CO⁺ + CO₂ → CO + CO₂⁺
- ▶ CO₂: 3-body association, 7-20 ps
 - ▶ CO₂⁺ + 2CO₂ → CO₂⁺•CO₂ + CO₂
- ▶ [For 10 % CO₂, atmospheric pressure, room temperature]

Ne⁺ in Ne ... did it make sense ?

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

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:

- CO₂⁺•CO₂: 0.60 eV (16.2 kcal/mol)
- CO₂⁺•2CO₂: 0.26 eV (6.0 kcal/mol)

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

- CO₂⁺•CO₂ 0.51 eV (11.8 ± 1.0 kcal/mol)
- (CO₂)₂⁺•CO₂ 0.14 eV (3.3 ± 1.4 kcal/mol)
- (CO₂)₃⁺•CO₂ 0.12 eV (2.8 ± 1.4 kcal/mol)

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

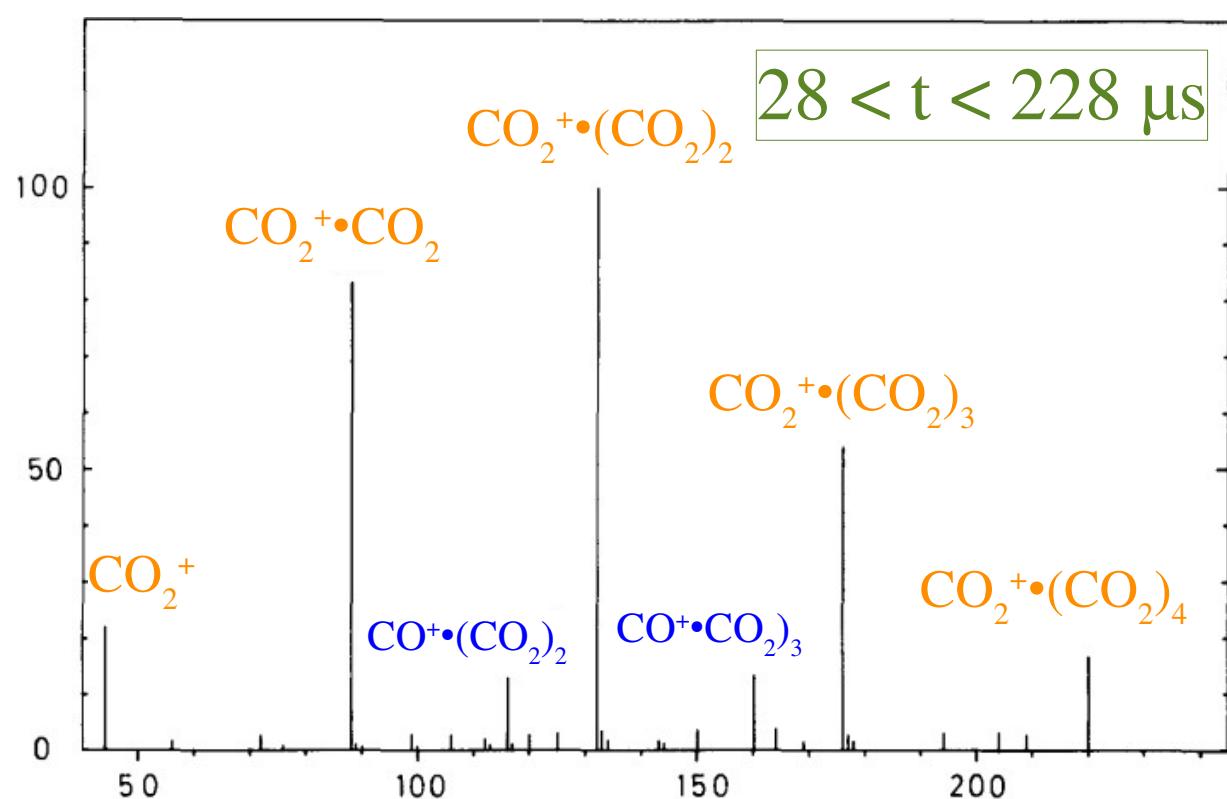
(Conversion: 1 kcal/mole = 0.043 eV, thermal: 0.03 eV.)

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 $\tau = 7\text{-}20 \text{ ps}$ 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.

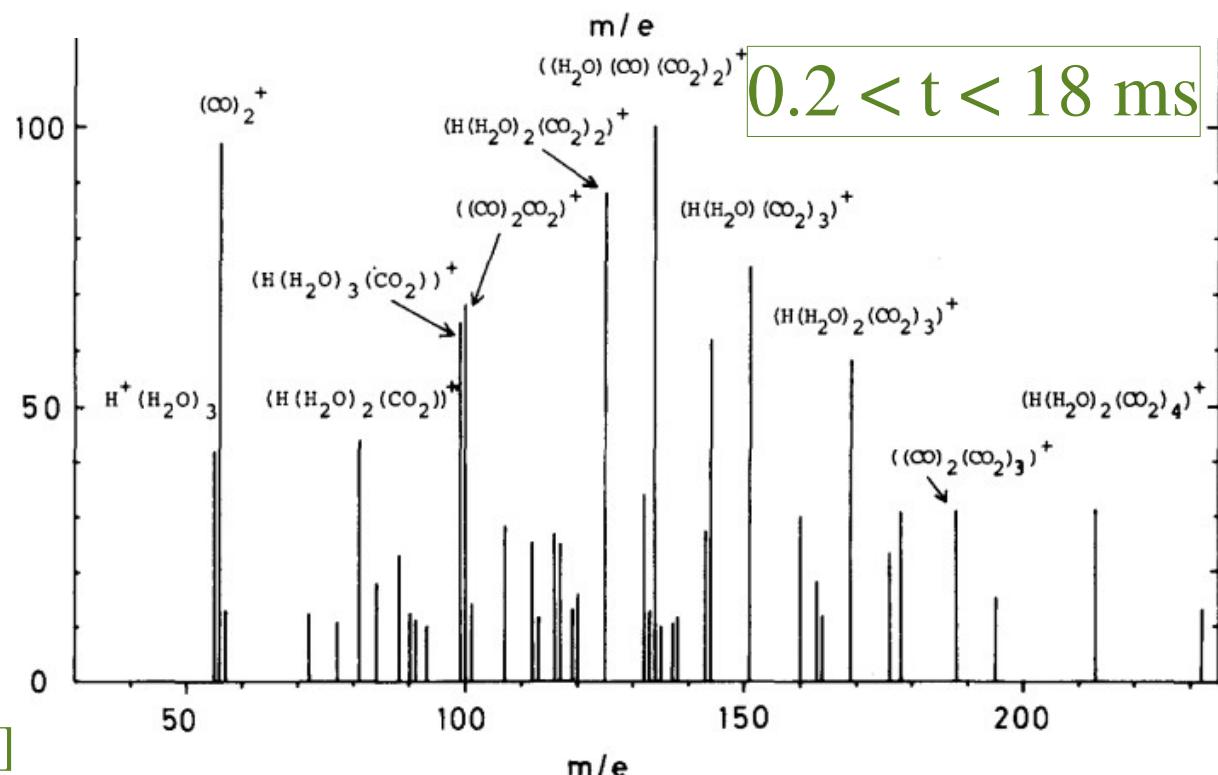
CO_2 at 1 bar

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



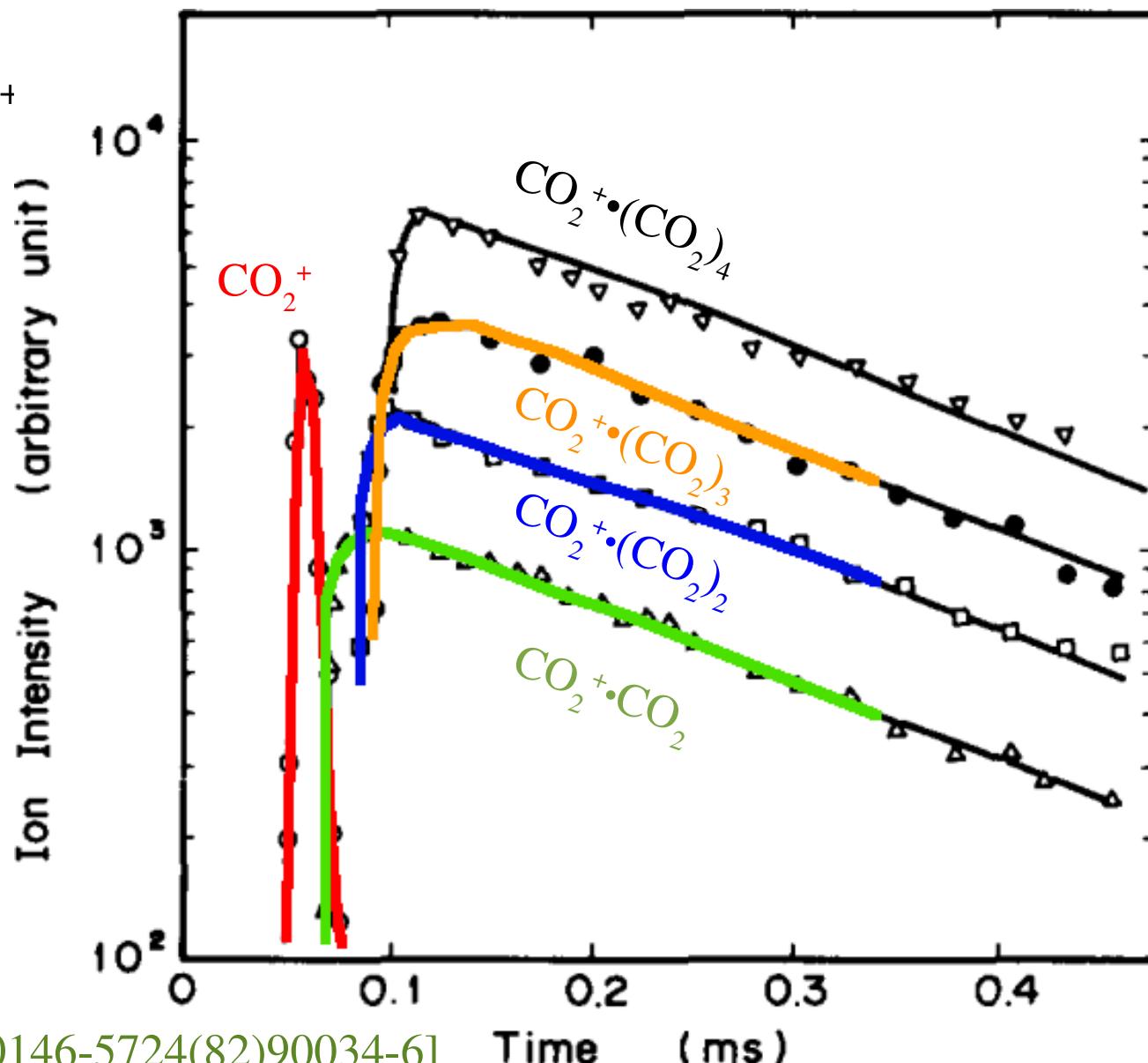
- ▶ Until $200 \mu\text{s}$:
 $\text{CO}_2^+\bullet(\text{CO}_2)_n$ and
 $\text{CO}^+\bullet(\text{CO}_2)_n$

- ▶ Later: *only* clusters from contaminants, e.g. H_2O , OH ...



CO_2 at 1 atm: cluster (dis)appearance

- ▶ Not clear why CO_2^+ forms at $t > 50 \mu\text{s}$.
- ▶ Clusters with CO_2^+ ion core form by $t = 100 \mu\text{s}$.
- ▶ React with contaminants $\tau \sim 190 \mu\text{s}$.



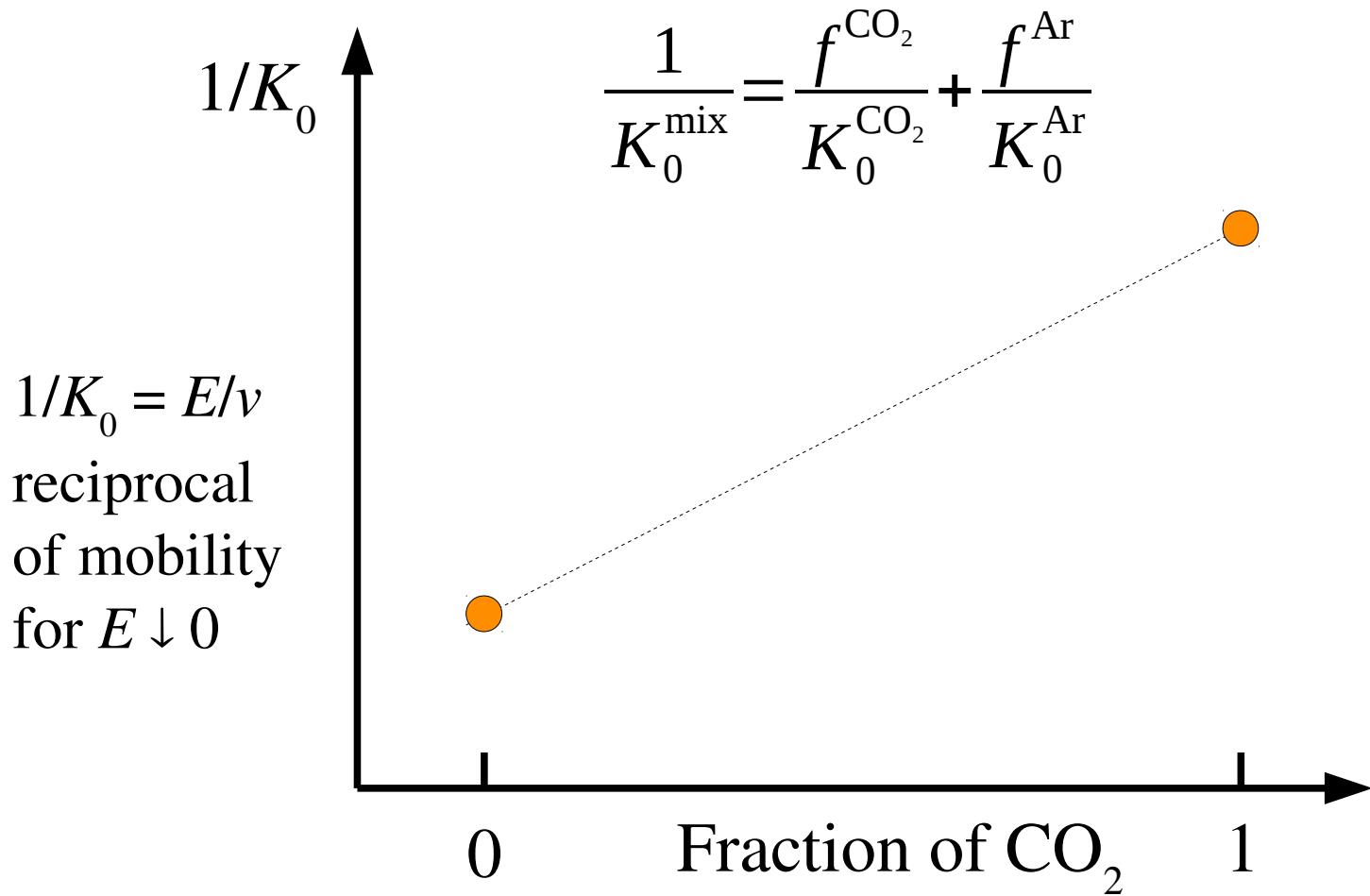
Experimental check

- ▶ 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.

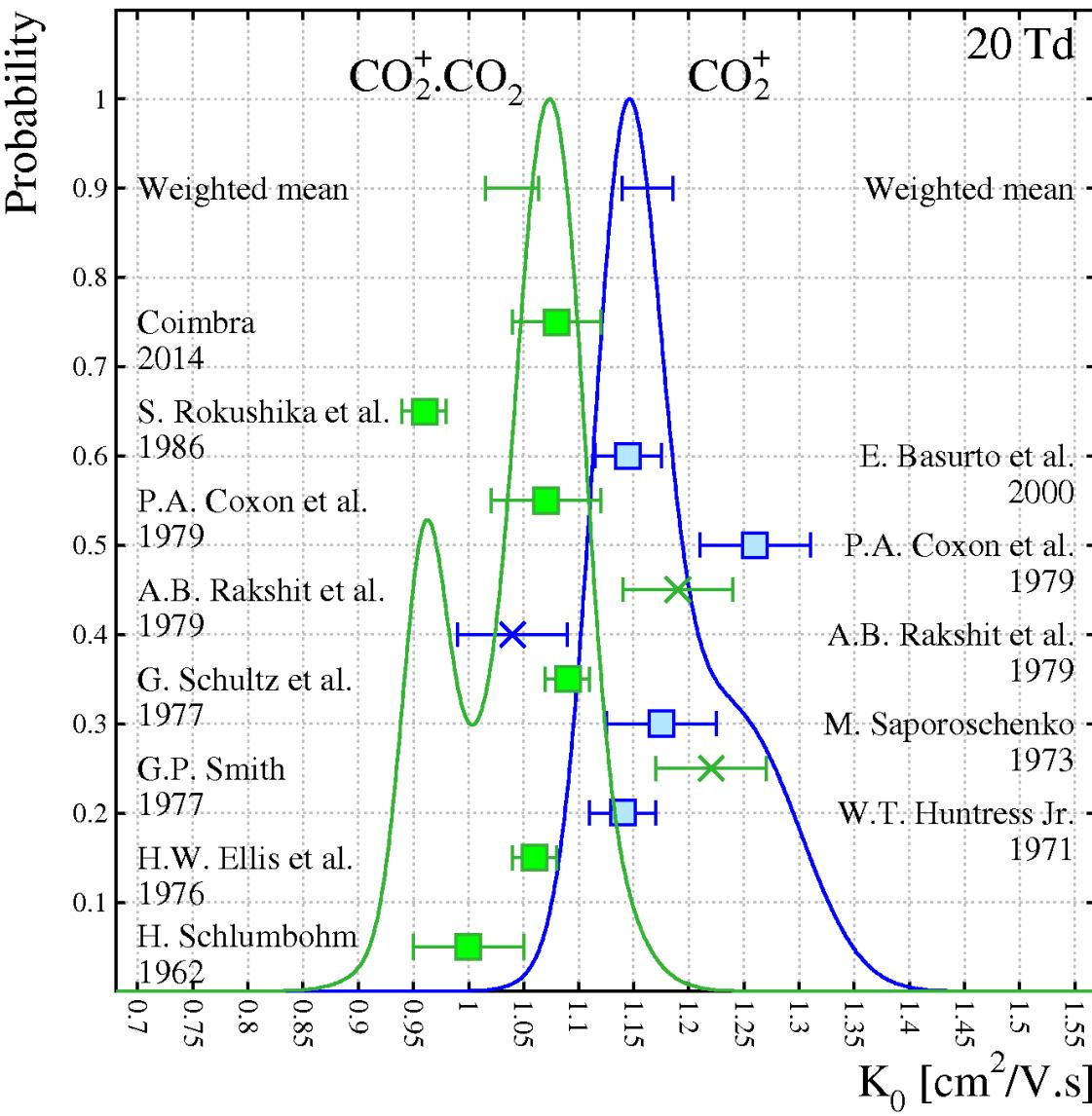
Blanc's mobility interpolation



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

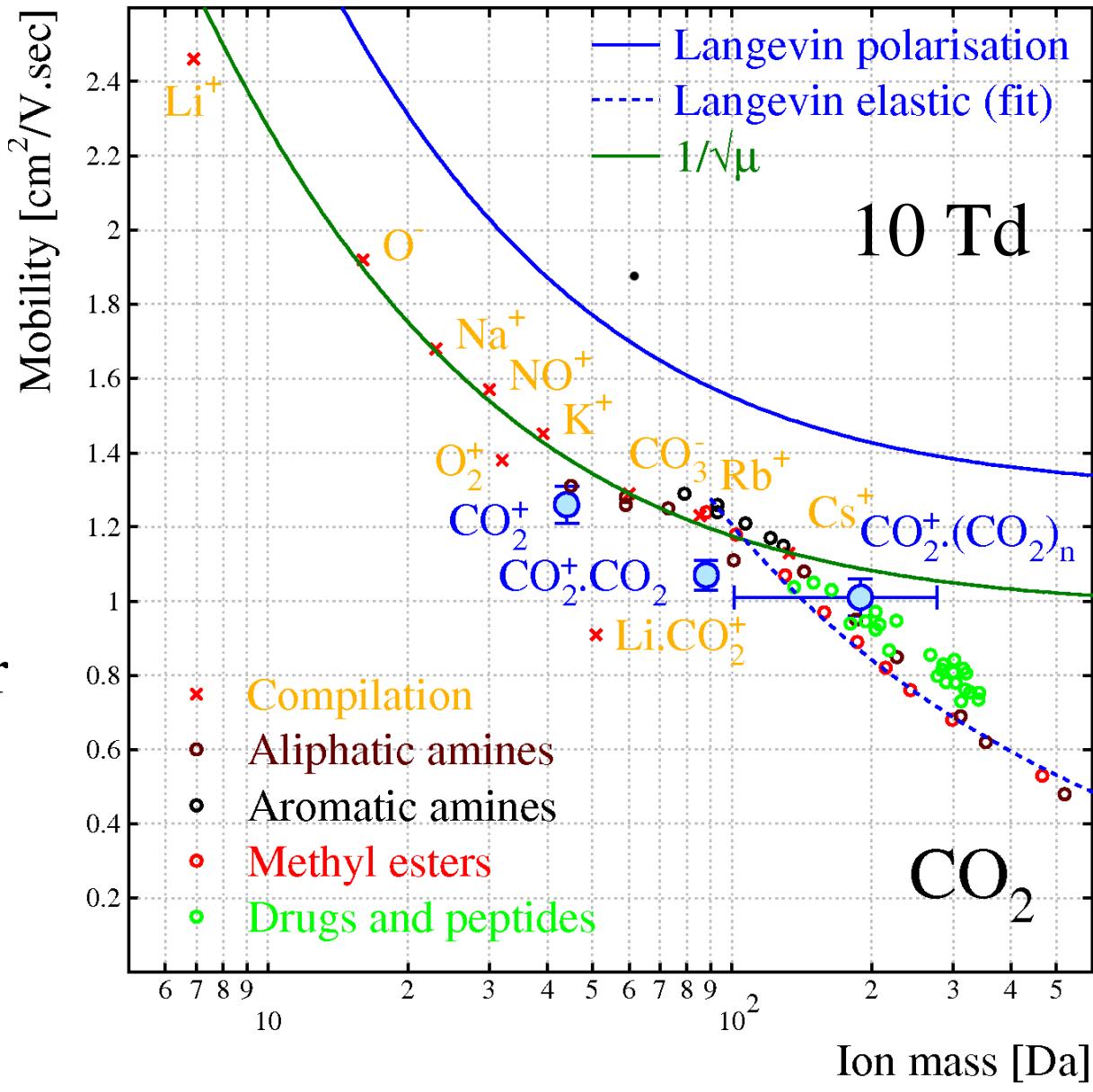
Mobility of CO_2^+ and $\text{CO}_2^{+\bullet}(\text{CO}_2)_n$ in CO_2

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

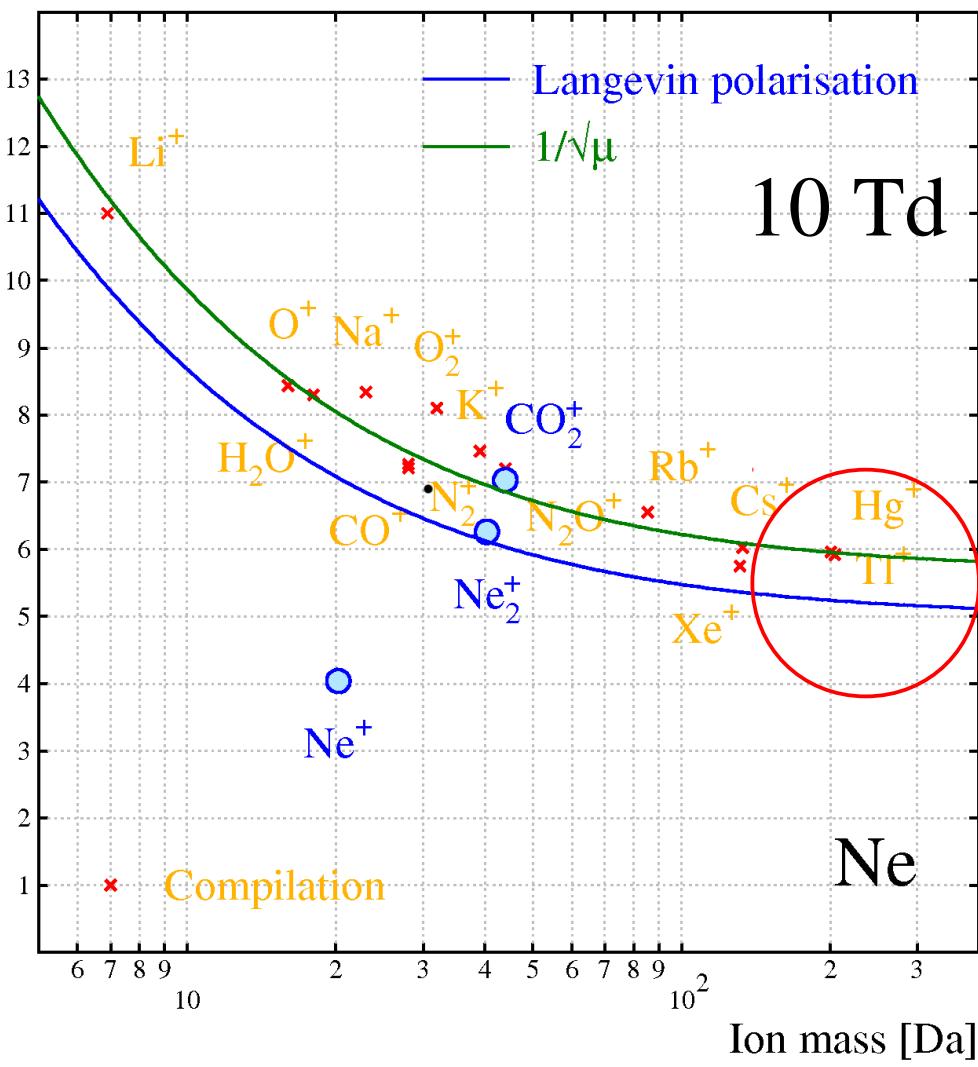
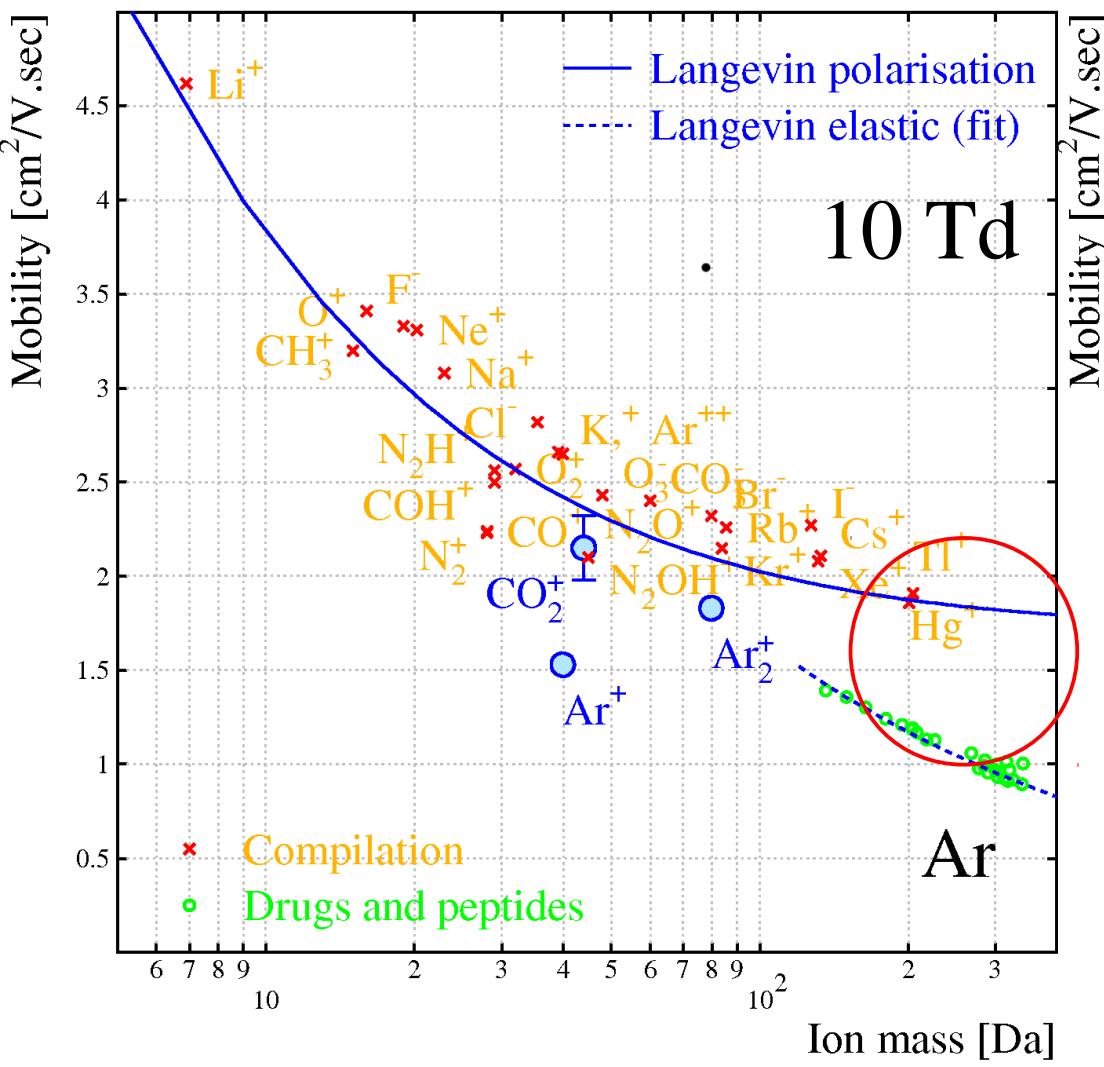


Mass-mobility in CO_2

- ▶ 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.

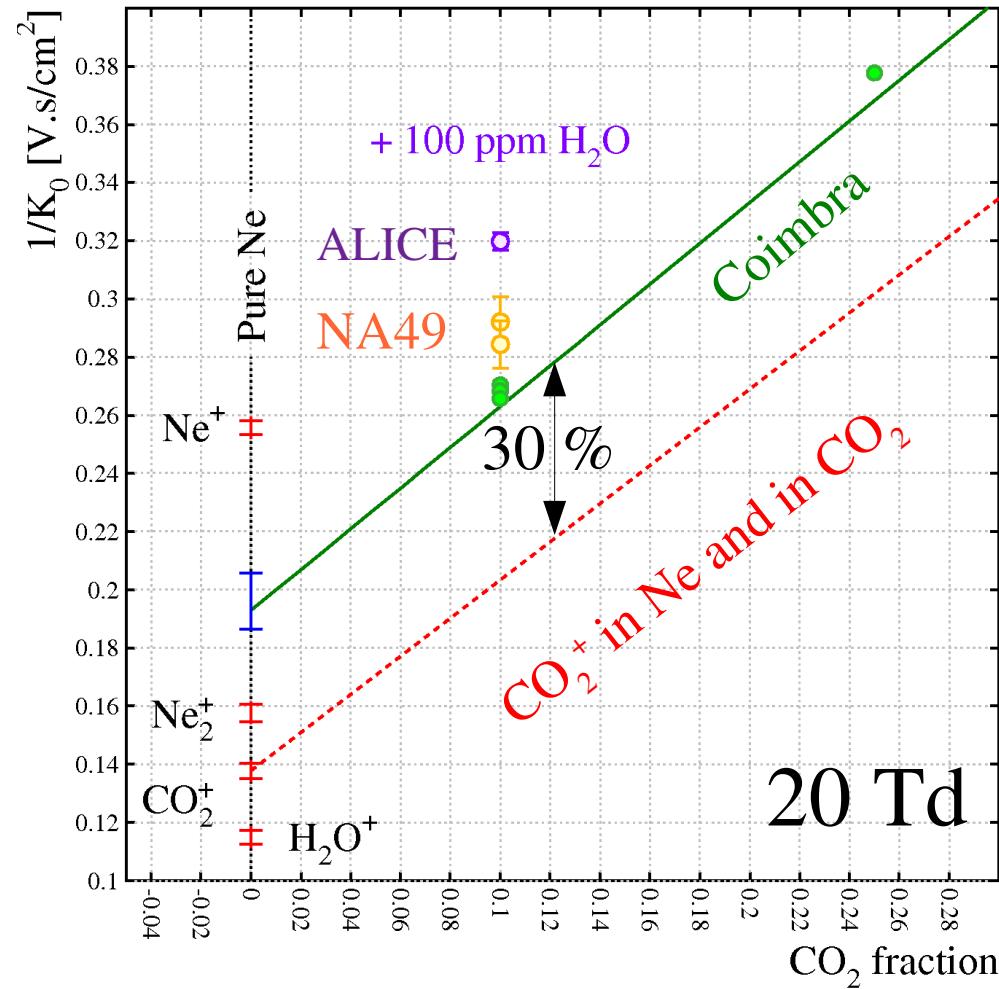
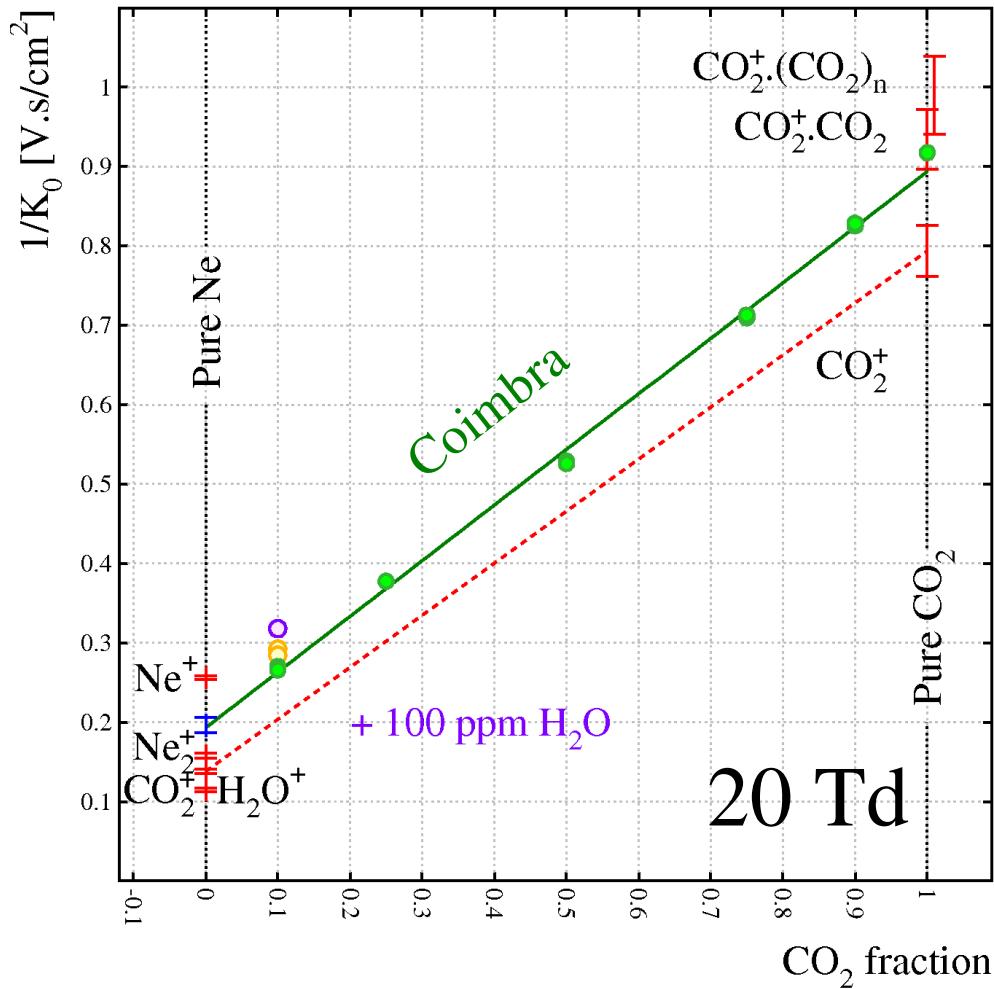


Mass-mobility in pure Ar and Ne



Blanc diagram for Ne-CO₂

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



Blanc diagram for Ar-CO₂

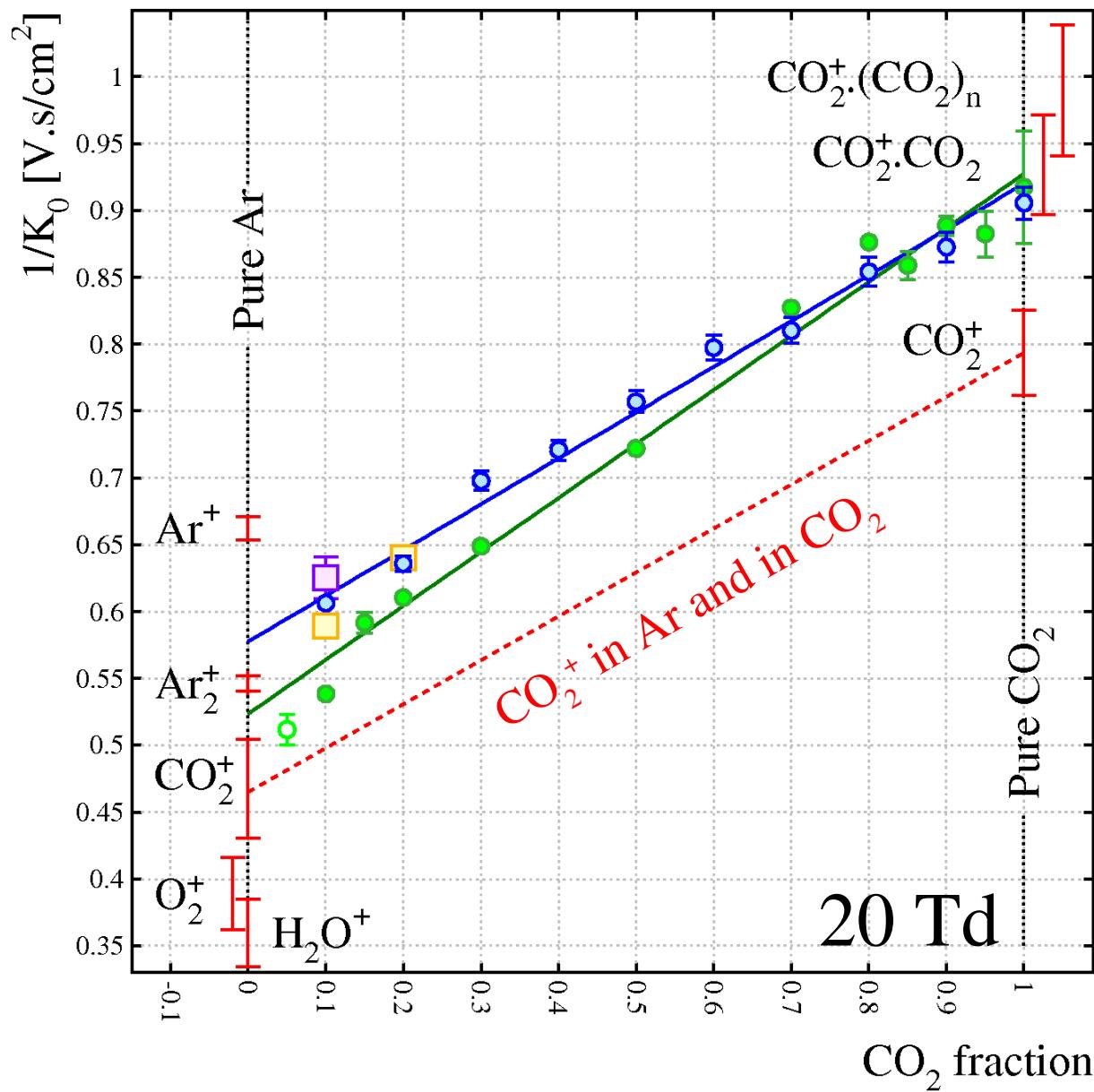
► Coxon: pure CO₂

► Schultz: 1 atm

► Coimbra: 0.01 atm,
smaller clusters ?

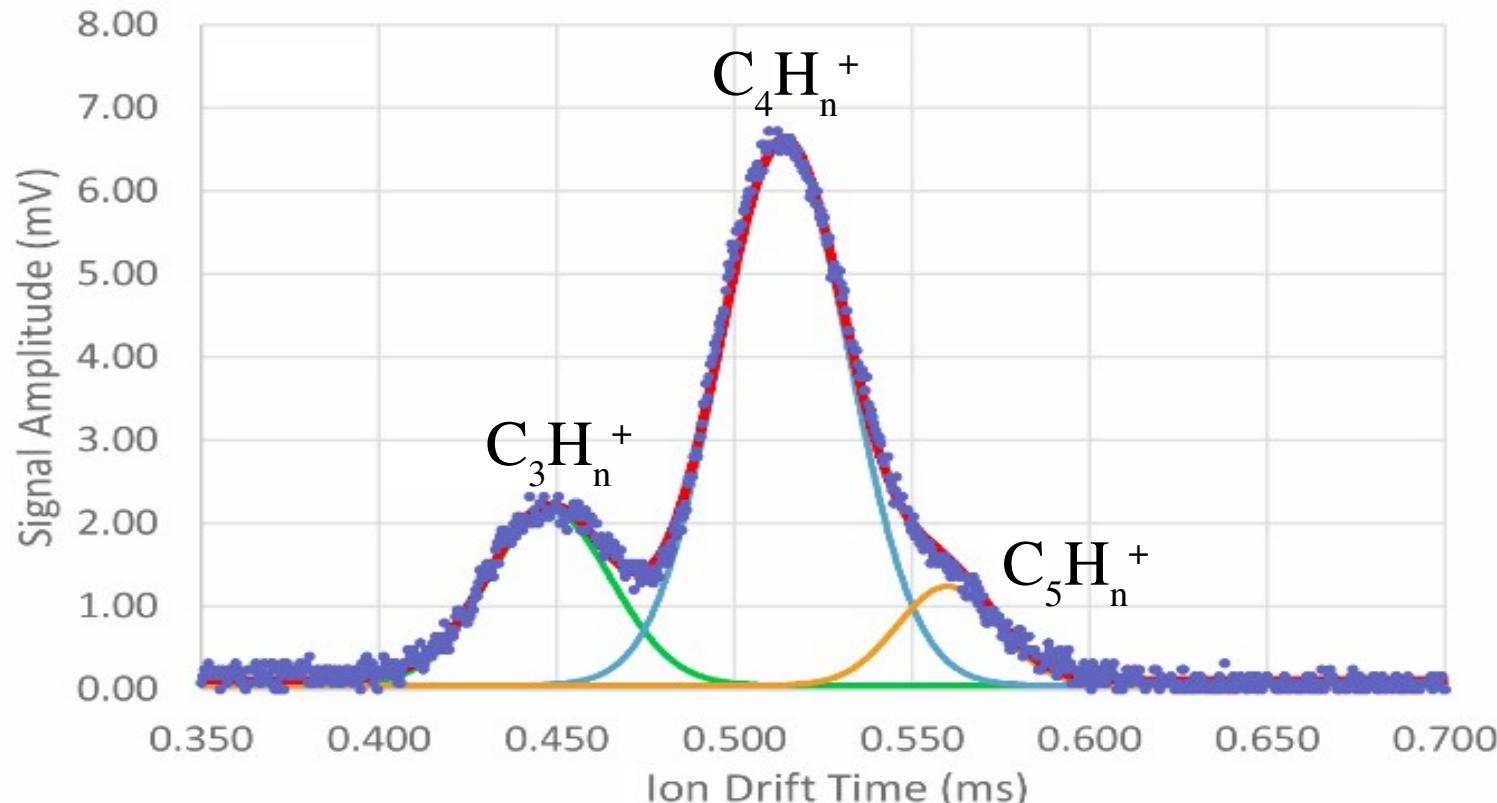
► NA49: 1 atm

► ALICE: 1 atm,
water clusters ?



How about alkanes ?

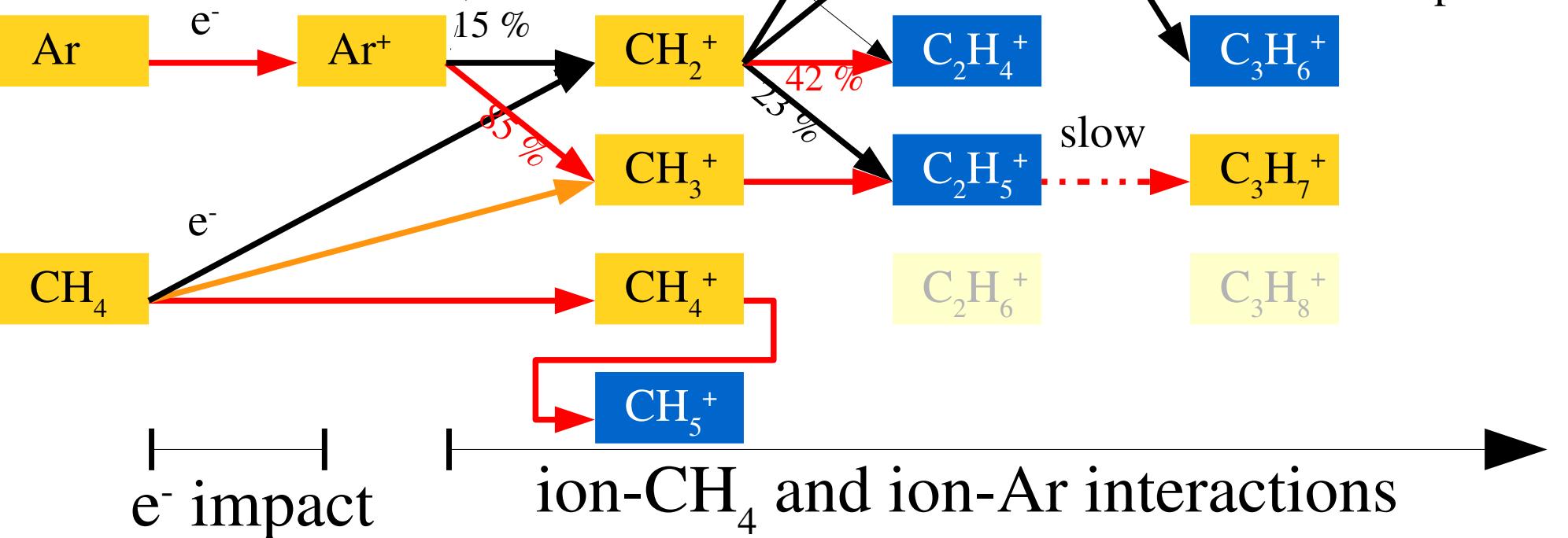
- ▶ Ar 90 % - C_2H_6 10 %, at low pressure.
- ▶ Expect Ar^+ or C_2H_6^+ but ... none are seen – why ?



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

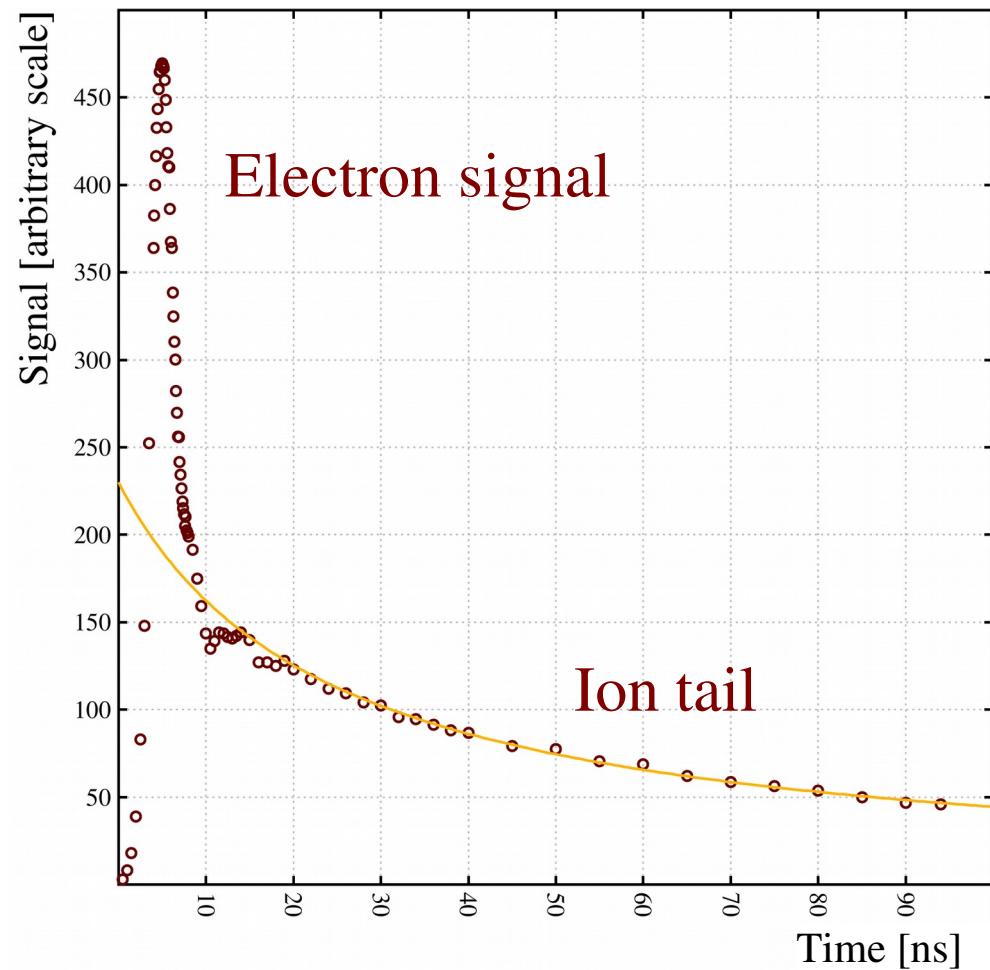
Ar-CH₄

Short lived
Long lived



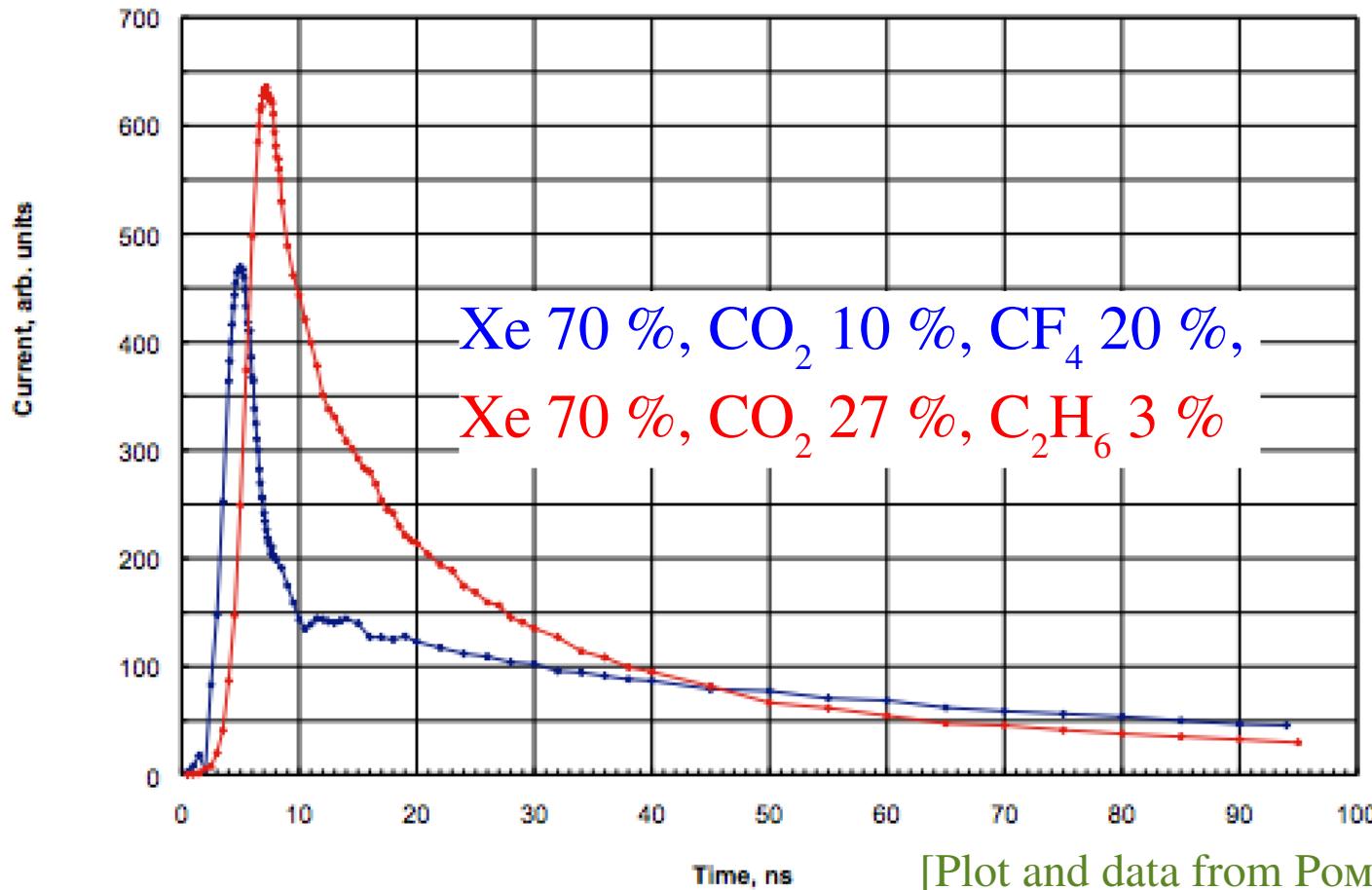
Atlas TRT signals

- ▶ Data:
 - ▶ Xe-CO₂-CF₄ 70/10/20
 - ▶ Straw tube
 - ▶ $V_w = 1530 \text{ V}$
 - ▶ $r_w = 15 \mu\text{m}, r_t = 2 \text{ mm}$
- ▶ 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]

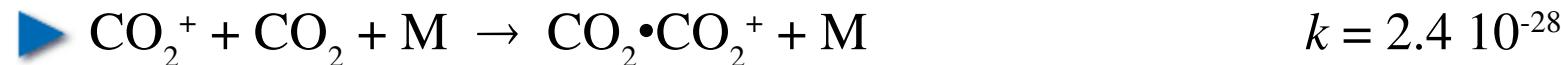
Ionisation potentials

- ▶ C₂H₆: 11.52 eV
- ▶ Xe⁺(²P_{3/2}): 12.129843 eV
- ▶ Xe⁺(²P_{1/2}): 13.44 eV
- ▶ CO₂: 13.776 eV
- ▶ CF₄: 15.70 eV for CF₃⁺ (main ionisation channel)
16.2 ± 0.1 eV for CF₄⁺

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]

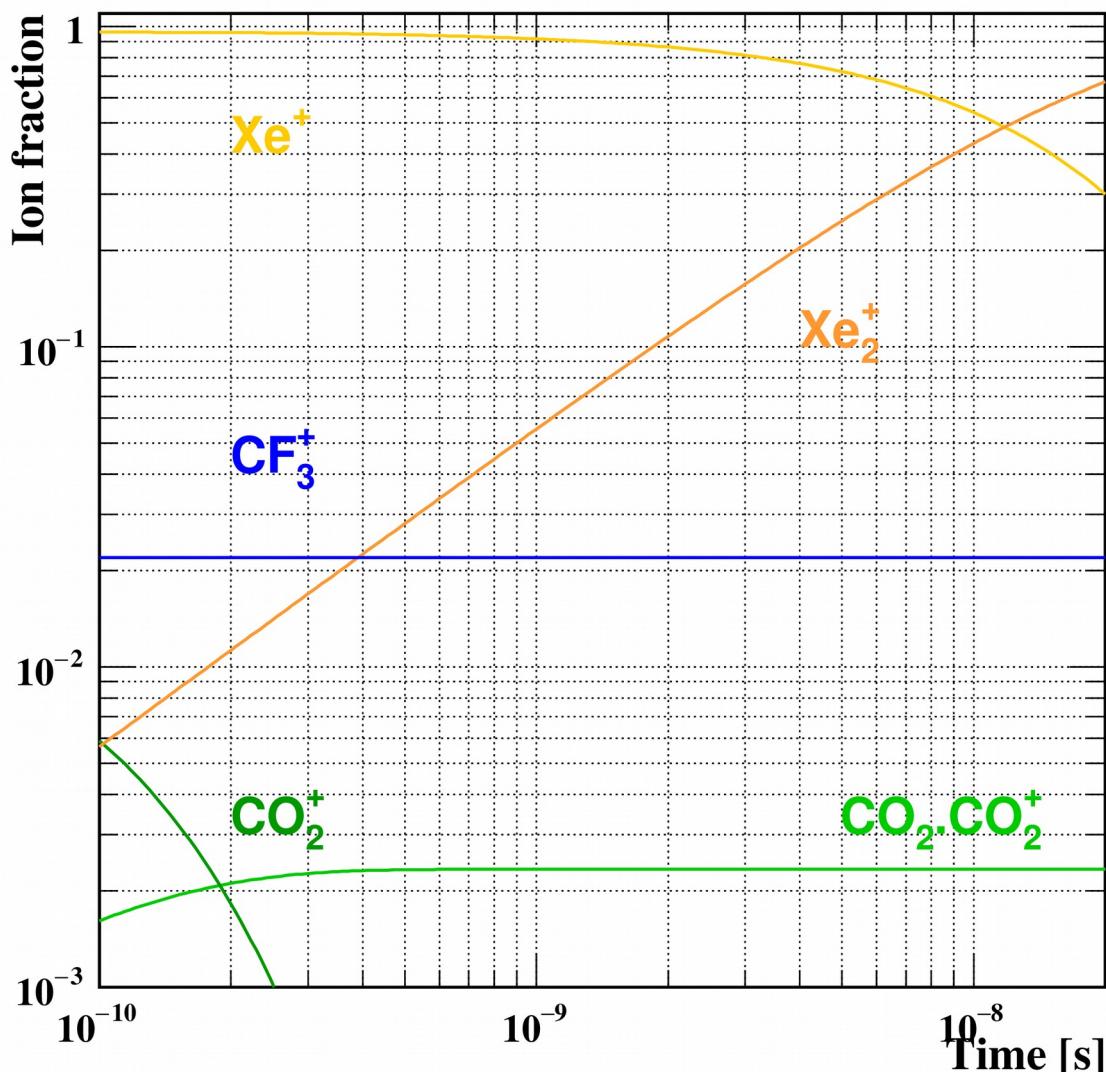


[V.G. Anicich and W.T. Huntress Jr., *Astrophys. J. Suppl.* **62** (1986) 553-672.]



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

| | | |
|---|--|------------------------------------|
| ► C ₂ H ₄ ⁺ + C ₂ H ₆ → C ₃ H ₆ ⁺ + CH ₄ | 7 % | $k = 5.3 \cdot 10^{-12} \pm 10\%$ |
| ► | → C ₃ H ₇ ⁺ + CH ₃ | 93 % |
| ► C ₂ H ₅ ⁺ + C ₂ H ₆ → C ₃ H ₇ ⁺ + CH ₄ | 14 % | $k = 3.8 \cdot 10^{-11} \pm 10\%$ |
| ► | → C ₄ H ₉ ⁺ + H ₂ | 86 % |
| ► C ₂ H ₆ ⁺ + C ₂ H ₆ → C ₃ H ₈ ⁺ + CH ₄ | 42 % | $k = 0.19 \cdot 10^{-10} \pm 10\%$ |
| ► | → C ₃ H ₉ ⁺ + CH ₃ | 58 % |

[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.]

| | | | |
|--|--|------|-----------------------------------|
| ► Xe ⁺ + C ₂ H ₆ | → Xe + C ₂ H ₄ ⁺ + H ₂ | 55 % | $k = 9.2 \cdot 10^{-10} \pm 20\%$ |
| ► | → Xe + C ₂ H ₅ ⁺ + H | 10 % | |
| ► | → Xe + C ₂ H ₆ ⁺ | 35 % | |
| ► Xe ₂ ⁺ + C ₂ H ₆ | → Xe C ₂ H ₆ ⁺ + Xe | | $k = 6.8 \cdot 10^{-10} \pm 20\%$ |

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

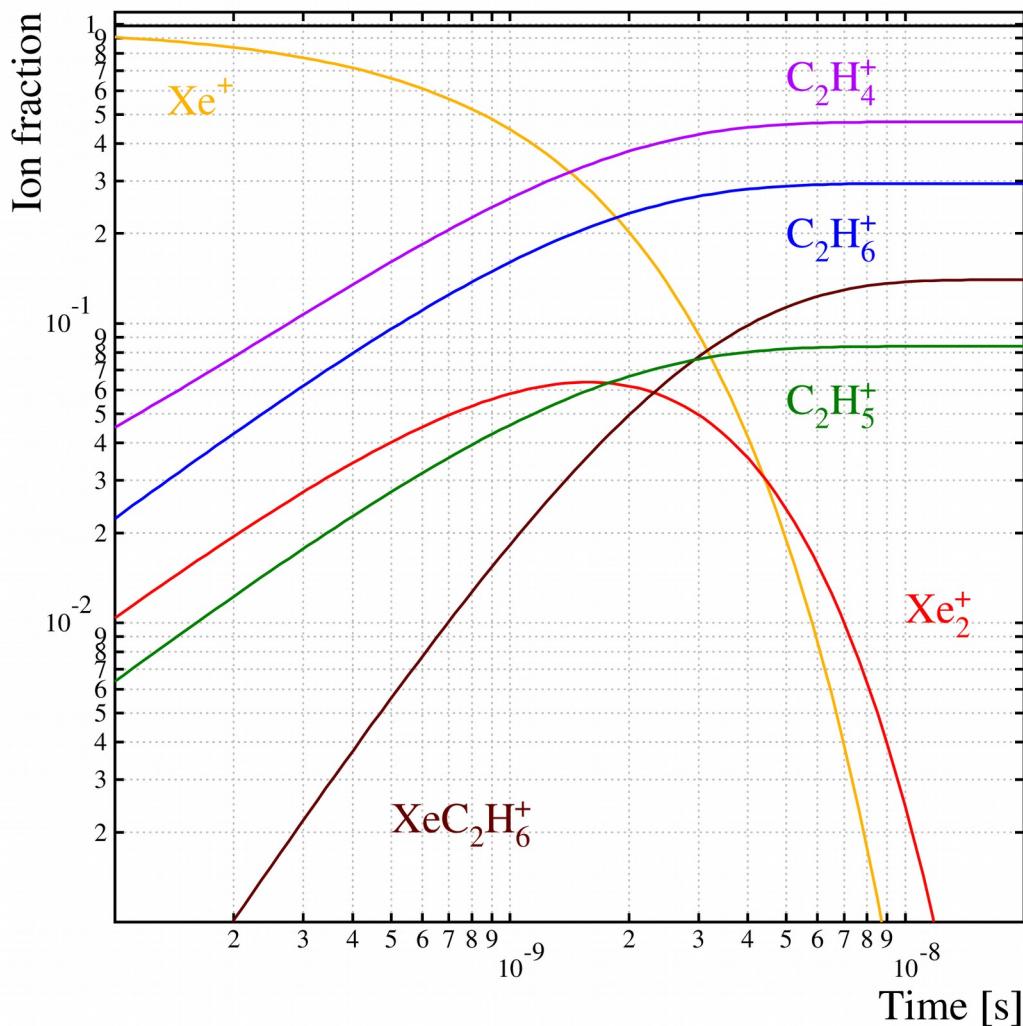
N.G. Adams et al., *J. Phys. B: At. Mol. Phys.* **13** (1980) 3235-3246.]

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

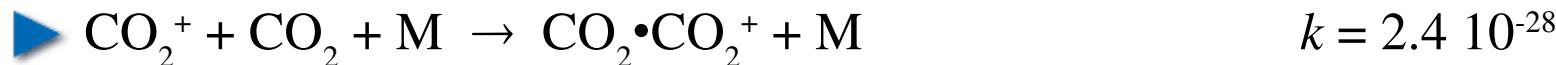


Reactions in Xe-CO₂-C₂H₆

► 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]



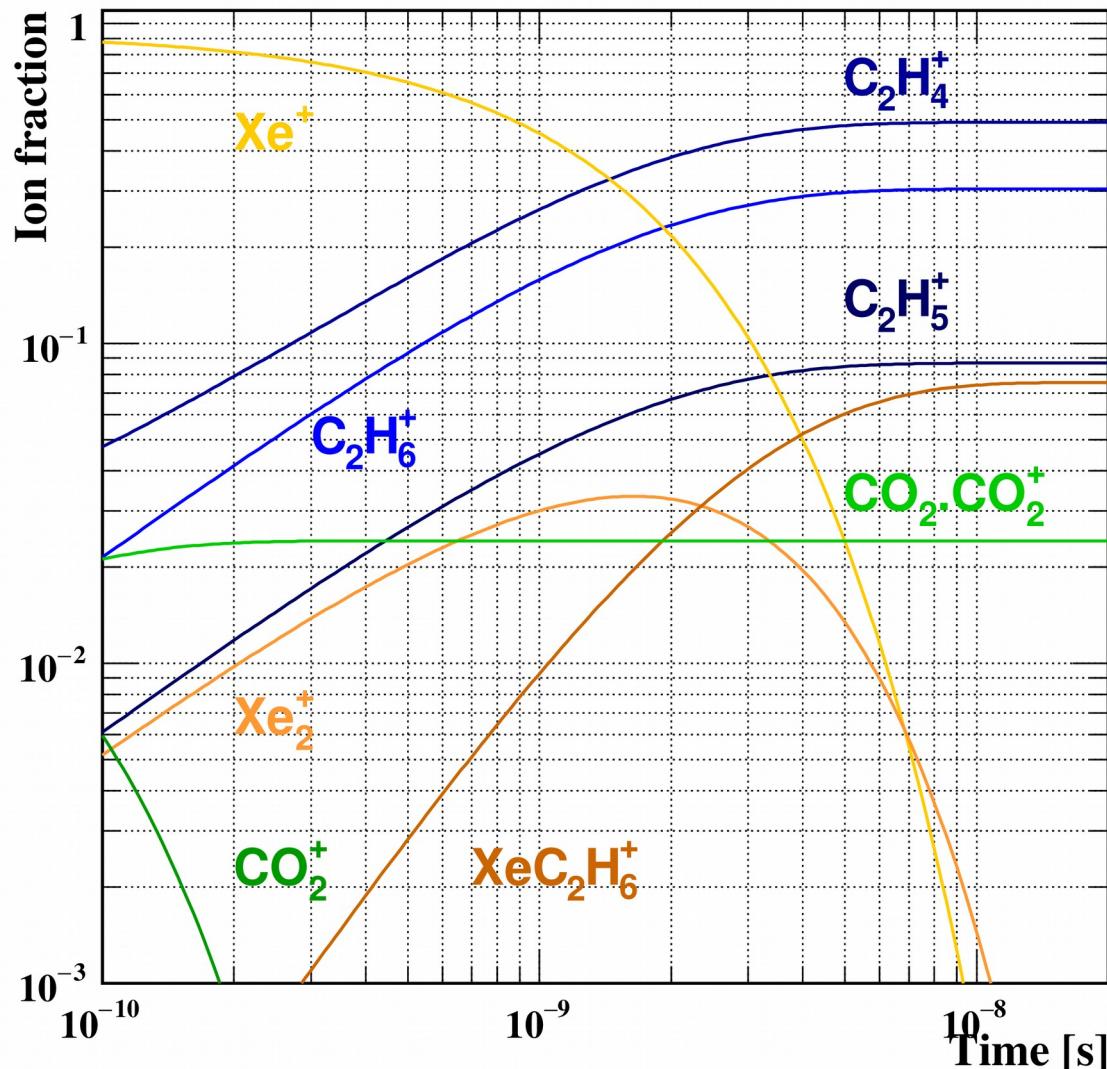
[V.G. Anicich and W.T. Huntress Jr., Astrophys. J. Suppl. **62** (1986) 553-672.]



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

Evolution of Xe-CO₂-C₂H₆ (70-27-3)

- ▶ Initial ion mix for 100 kV/cm;
- ▶ CO₂⁺ rapidly forms clusters due to the large CO₂ fraction;
- ▶ CO₂ does not affect the dominance of C_xH_y over Xe.
- ▶ Xe_n⁺ for $n > 2$ are not shown because rates are not known.



$\text{Xe}_2^+ - \text{Xe}_3^+$

- 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.

[H. Helm, 10.1103/PhysRevA.14.680]

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.

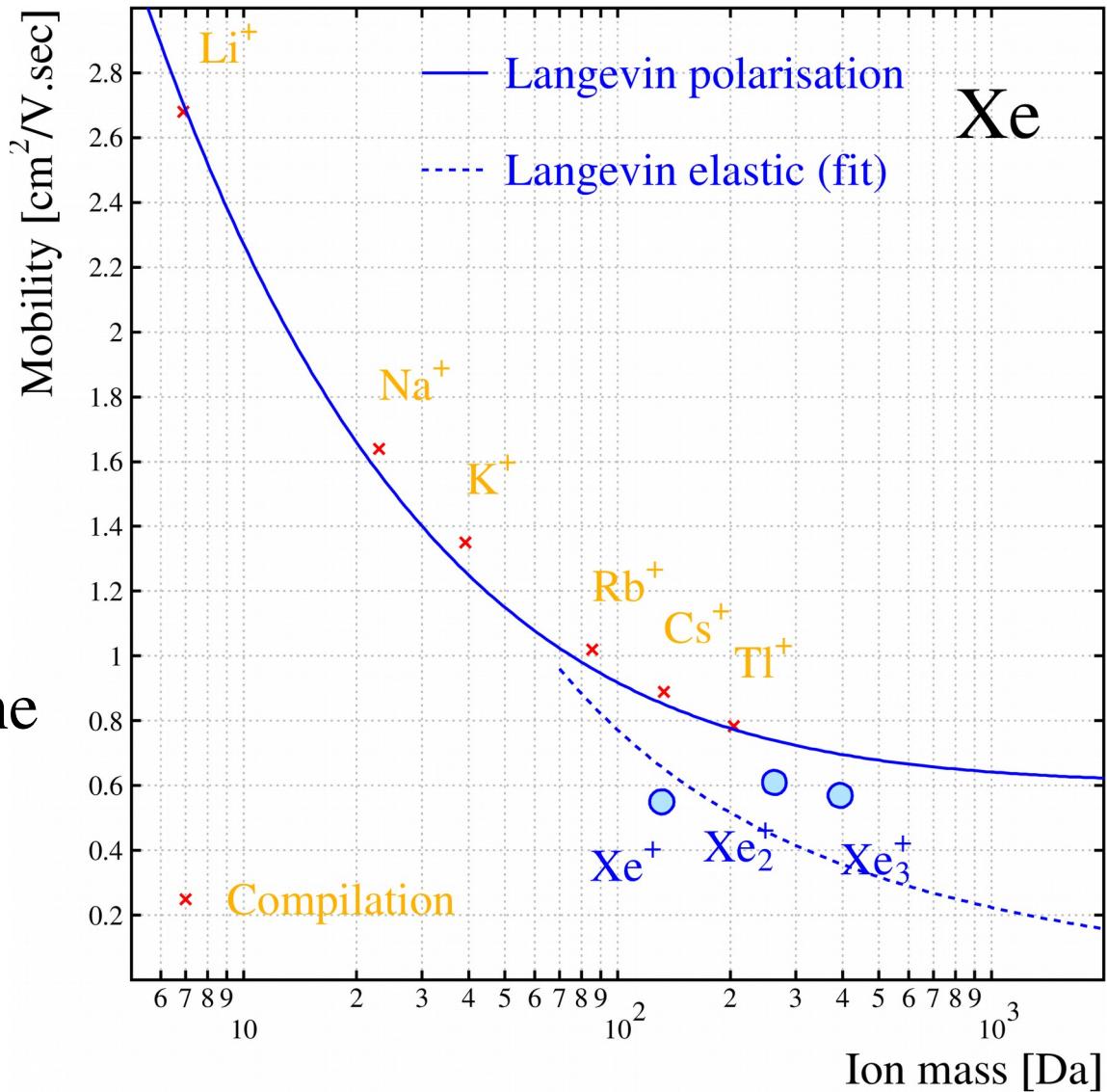
| Xe _n ⁺ | Mass | μ ($E = 0, T=300$ K) | ΔH $n-1 \rightarrow n$ | References |
|------------------------------|---------|---------------------------|--------------------------------|----------------------|
| | [Da] | [cm ² /V.s] | [eV] | |
| Xe ⁺ | 131.293 | 0.55 | - | Helm, Viehland-Mason |
| Xe ₂ ⁺ | 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 |

[Kenzo Hiraoka et al. 10.1063/1.457751, M. Amarouche et al. 10.1063/1.454267]

Mobility of ions in Xe

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