

$\text{Ar}^+\bullet\text{Ar}$, $\text{CO}_2^+\bullet\text{Ar}$ and $\text{CO}_2^+\bullet\text{CO}_2$ clusters

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RD51 collaboration and Uludağ university, Bursa, Turkey

Recall ...



Ion mobility in Neon-based mixtures

Dezső Varga
Wigner RCP, Budapest

- Experimental setup
- Preliminary results on Ne CO₂ and Ne CH₄ mixtures
- Consistency with earlier data and with Blanc-rule
- What migrates in CO₂? Existence of ion clusters
- Lessons from Ion Mobility Spectrometry, a well established technique

Binding energy of clusters

Time scale: rate constant

Which clusters are formed ?

Mobility of clusters

Comparison with data

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: 0.70 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)

Binding energy of Ar cluster ions

- ▶ Enthalpy of reaction (1 atm, 298.15 K):

- ▶ $\text{Ar}^+\bullet\text{Ar}$: 1.2 eV ($\sim 120 \text{ kJ/mol}$)
- ▶ $(\text{Ar}^+\bullet\text{Ar}) + \text{Ar}$ 0.2 eV
- ▶ $(\text{Ar}^+\bullet 2\text{Ar}) + \text{Ar}$ 0.2 eV
- ▶ $(\text{Ar}^+\bullet 3\text{Ar}) + \text{Ar}$ 0.07 eV

[NIST compilation, average by M. M. Meot-Ner (Mautner) and S. G. Lias]

- ▶ Higher Ar clusters seem to have a linear Ar_3^+ or Ar_4^+ ion core around which additional Ar atoms cluster.

[Hellmut Haberland et al., PRL **67** (1991) 3290, 10.1103/PhysRevLett.67.3290]

- ▶ Dissociation energy

- ▶ $\text{Ar}^+\bullet\text{Ar}$: 1.2 eV

[Robert D. Cloney et al., J. Chem. Phys. **36** (1962) 1103; 10.1063/1.1732665]

Binding energy Ar/CO₂ cluster ions

- ▶ Ar⁺•CO₂: 0.26 ± 0.04 eV
- ▶ Ar•CO₂⁺: 0.26 eV (6.0 kcal/mol)

Binding energy of clusters

Time scale: rate constant

Which clusters are formed ?

Mobility of clusters

Comparison with data

Thermal collision frequency

- Mean relative velocity (μ = reduced mass):

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

Example: Ar-Ar⁺ at 300 K and 1 atm, cross section is mobility $\Omega^{(1,1)}$.

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

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

- Combining with the number density gives the lifetime:

$$\tau = \frac{1}{N\sigma\bar{v}_{\text{rel}}} = \frac{k_{\text{B}}T}{p} \frac{1}{\sigma\bar{v}_{\text{rel}}} = \frac{1}{p\sigma} \sqrt{\frac{\pi\mu k_{\text{B}}T}{8}} \approx 46 \text{ ps}$$

Reaction time and Rate constant: 2-body

- ▶ A rate constant tells how fast a reaction goes.
- ▶ Consider a 2-body charge transfer reaction $A^+ B \rightarrow A B^+$:
 - ▶ rate \propto density of B molecules N_B [1/cm³];
 - ▶ rate varies with T , values quoted here are for ~ 300 K;
 - ▶ rate varies with v_{ion} , we assume $v_{\text{ion}} \approx v_{\text{thermal}}$.
- ▶ Hide reaction mechanism in a **rate constant k** :
 - ▶ rate = k [cm³/s] N_B [1/cm³];
 - ▶ 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, $\tau = 90$ ps.

3-body reactions

- ▶ Cluster formation requires the evacuation of excess energy & momentum of the bound state through internal degrees of freedom (rotation, vibration), or via a 3-body reaction. Cluster destruction is more likely a 2-body reaction.
- ▶ The rate constant in 3-body reactions has the unit of cm^6/s .
- ▶ Example 1: $\text{Ar}^+ + 2\text{Ar} \rightarrow \text{Ar}^+\bullet\text{Ar} + \text{Ar}$
 - ▶ $k = 2.2 \cdot 10^{-31} \text{ cm}^6/\text{s}$, 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: $\text{CO}_2^+ + 2\text{CO}_2 \rightarrow \text{CO}_2^+\bullet\text{CO}_2 + \text{CO}_2$
 - ▶ $k = 2.4 \cdot 10^{-28} \text{ cm}^6/\text{s}$
 - ▶ rate = $k N^2 = 1.4 \cdot 10^{11}/\text{s}$, $\tau = 7 \text{ ps}$

Binding energy of clusters

Time scale: rate constant

Which clusters are formed ?

Mobility of clusters

Comparison with data

Avalanche products & by-products

- ▶ $e^- + Ar/CO_2 \rightarrow Ar^+ \text{ and } CO_2^+$,
- ▶ along with traces of O^+ ,
 - ▶ $O^+ + CO_2 \rightarrow O_2^+ + CO \quad k \approx 1.0 \cdot 10^{-9} \text{ cm}^3/\text{s}$
 - ▶ $O_2^+ + CO_2 + M \rightarrow O_2^{+\bullet}CO_2 + M \quad k = ?$
 - ▶ $O_2^+ + CO_2 \quad \text{no 2-body reaction detected} \quad k < 10^{-11} \text{ cm}^3/\text{s}$
- ▶ of C^+ ,
 - ▶ $C^+ + CO_2 \rightarrow CO^+ + CO \quad k \approx 1.1 \cdot 10^{-9} \text{ cm}^3/\text{s}$
- ▶ and of CO^+
 - ▶ $CO^+ + CO_2 \rightarrow CO + CO_2^+ \quad k \approx 1.1 \cdot 10^{-9} \text{ cm}^3/\text{s}$
- ▶ O^+ , C^+ , and CO^+ are short-lived (40 ps at 1 bar) and are only observed below 2 μ bar.

Reactions of Ar⁺

- ▶ Resonant charge exchange:
 - ▶ Ar⁺ + Ar \leftrightarrow Ar + Ar⁺
 - ▶ $k = 4.6 \cdot 10^{-10} \text{ cm}^3/\text{s}$, $\tau \approx 90 \text{ ps}$ (for $N_{\text{Ar}} = 2.45 \cdot 10^{19}/\text{cm}^3$)
- ▶ Charge exchange:
 - ▶ Ar⁺ + CO₂ \rightarrow Ar + CO₂⁺
 - ▶ $k = 4.2 \cdot 10^{-10} \text{ cm}^3/\text{s}$, $\tau \approx 100 \text{ ps}$
Also reported as 2-step: Ar⁺ CO₂ \rightarrow Ar⁺•CO₂ \rightarrow Ar CO₂⁺ or Ar⁺ CO₂.
- ▶ Dimer formation:
 - ▶ Ar⁺(²P_{3/2}^o) + 2Ar \rightarrow Ar⁺•Ar + Ar
 - ▶ $k = 2.3 \pm 0.1 \cdot 10^{-31} \text{ cm}^6/\text{s}$, $\tau \approx 7 \text{ ns}$
Rate at 296 K; no reaction at room temperature for Ar⁺(²P_{1/2}^o).

Reactions of CO_2^+

► Association with Ar:

- $\text{CO}_2^+ + \text{Ar} + \text{M} \rightarrow \text{CO}_2^+\bullet\text{Ar} + \text{M}$
- $k = ?$ (believed to be fast)

► Thought to be followed by a ligand switch

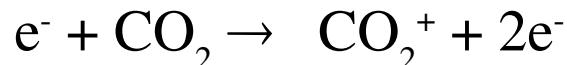
- $\text{CO}_2^+\bullet\text{Ar} + \text{CO}_2 \rightarrow \text{CO}_2^+\bullet\text{CO}_2 + \text{Ar}$
- $k = ?$ Energy gain: 0.435 eV

► Association with CO_2 :

- $\text{CO}_2^+ + 2\text{CO}_2 \rightarrow \text{CO}_2^+\bullet\text{CO}_2 + \text{CO}_2$
- $k = 2.4 \cdot 10^{-28} \text{ cm}^6/\text{s}, \tau = 7 \text{ ps}$

Forming bi-molecular clusters

► Avalanche process:



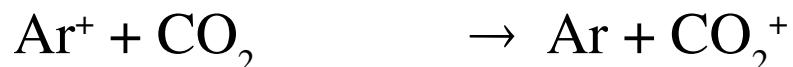
► Reaction products of Ar^+ :



$$k = 4.6 \cdot 10^{-10} \text{ cm}^3/\text{s}$$

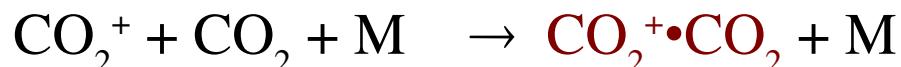


$$k = 2.2 \cdot 10^{-31} \text{ cm}^6/\text{s}$$



$$k = 4.2 \cdot 10^{-10} \text{ cm}^3/\text{s}$$

► Reaction products of CO_2^+ :



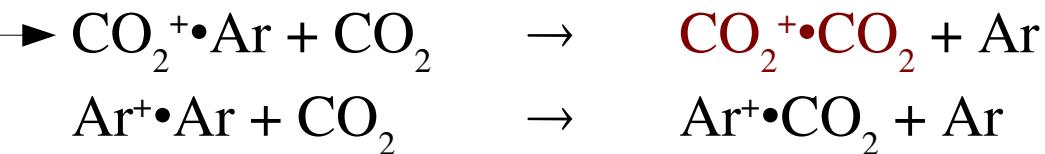
$$k = 2.4 \cdot 10^{-28} \text{ cm}^6/\text{s}$$



$$k = ?$$

Cluster rearrangements

► Ligand switching:



► Charge exchange:



- Rate constants not known, but the reactions are thought to be fast. They are energetically favourable.
- Initial clustering probably produces mainly $\text{CO}_2^+ \bullet \text{CO}_2$

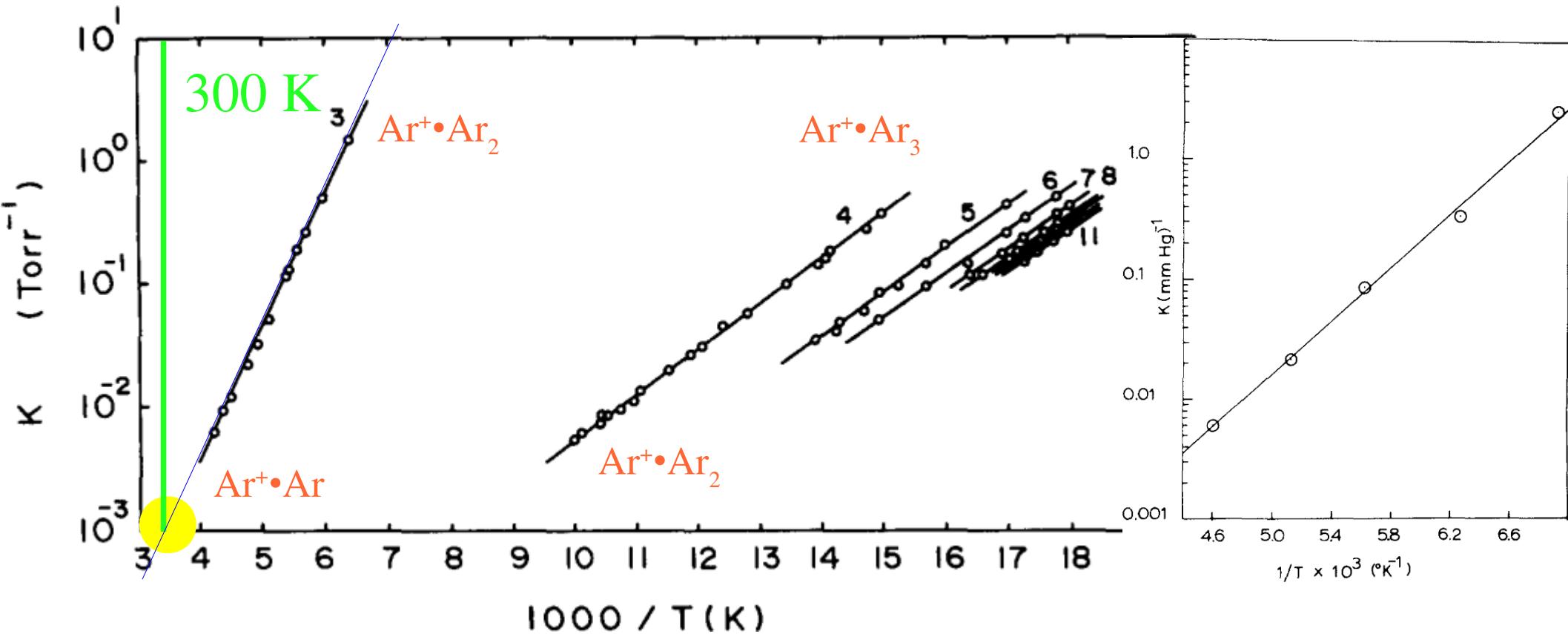
Further clustering ?

- ▶ The equilibrium between size $n-1$ and size n clusters shifts towards larger clusters at lower temperature.
- ▶ This trend can be read from the van 't Hoff graphs:

$$\frac{[A^+ \cdot B_n]}{[A^+ \cdot B_{n-1}] p} \text{ vs } \frac{1}{T}$$

where [...] represents the abundance of the clusters when equilibrium has been reached and p the partial pressure of the B molecules.

van 't Hoff plots low- p Ar clustering



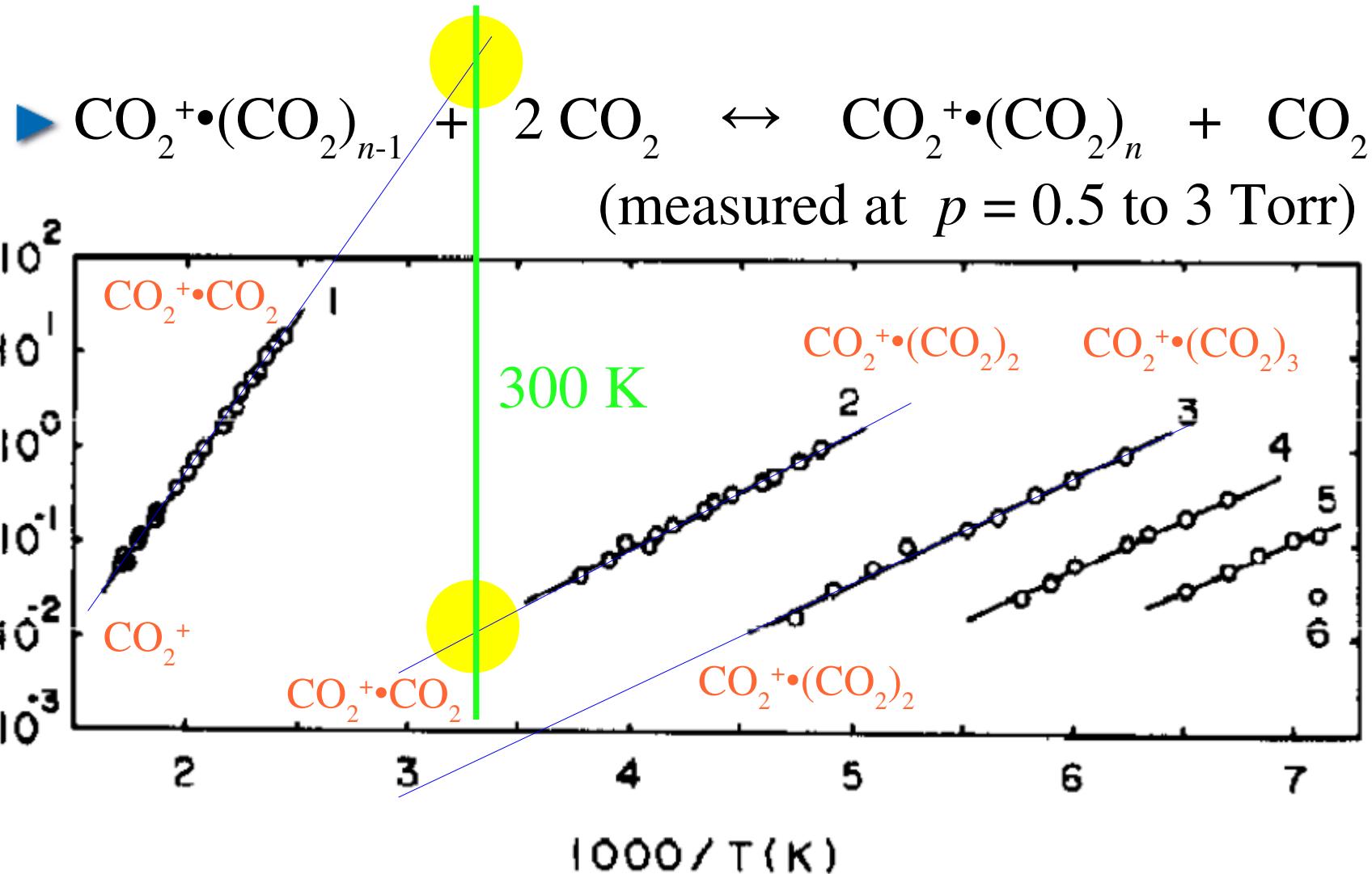
[D.L. Turner and D.C. Conway, J. Chem. Phys. **71** (1979) 1899

10.1063/1.438544

K. Hiraoka and T. Mori, J. Chem. Phys. **90** (1989) 7143

10.1063/1.456245]

van 't Hoff plot low- p CO₂ clustering



[Kenzo Hiraoka et al. Chem. Phys. Lett. **146** (1988) 535-538,
10.1016/0009-2614(88)87495-5]

Cluster composition at low pressure

- ▶ van 't Hoff plots show that clusters larger than $\text{CO}_2^+ \bullet \text{CO}_2$ and $\text{Ar}^+ \bullet \text{Ar}$ are not formed at 300 K and 600 μbar - 4 mbar.
- ▶ Larger clusters are formed at lower temperatures and higher pressure.

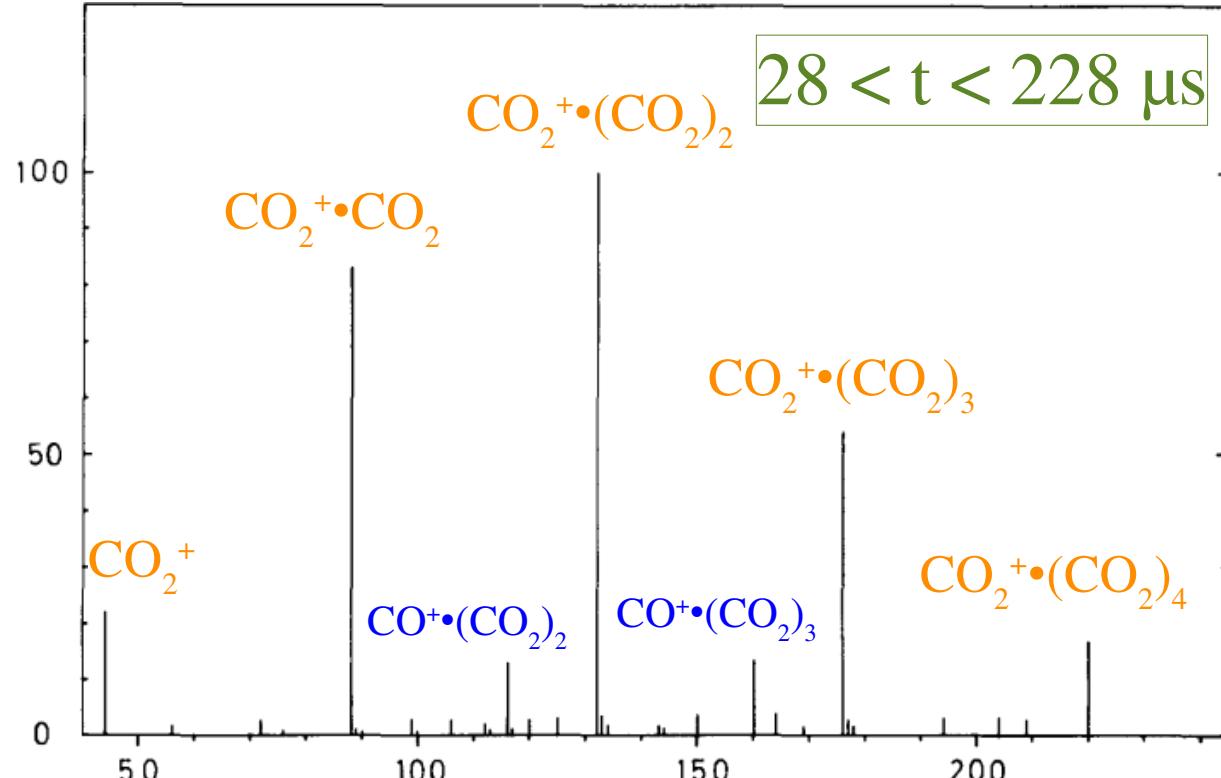
CO_2 clustering at 1 bar

- ▶ 1 bar and 25°C: “the positive ion spectrum exhibited a single family of ions, whose masses were 117, 161, 205, 249, 293, 337, and 381 amu.”
[H. W. Ellis et al. J. Chem. Phys. **64** (1976) 3935, 10.1063/1.432024]
- ▶ The H must be a contamination. The spectrum hints at an HCO^+ or C_2H_5^+ core surrounded by $(\text{CO}_2)_n$ with $n = 2 \dots$
- ▶ The time-evolution of the cluster mix has been measured (but mobility is not reported by this experiment).

[Y. Ikezoe et al., Ions in carbon dioxide at an atmospheric pressure, Rad. Phys. Chem. **20** (1982) 253–257, 10.1016/0146-5724(82)90034-6.]

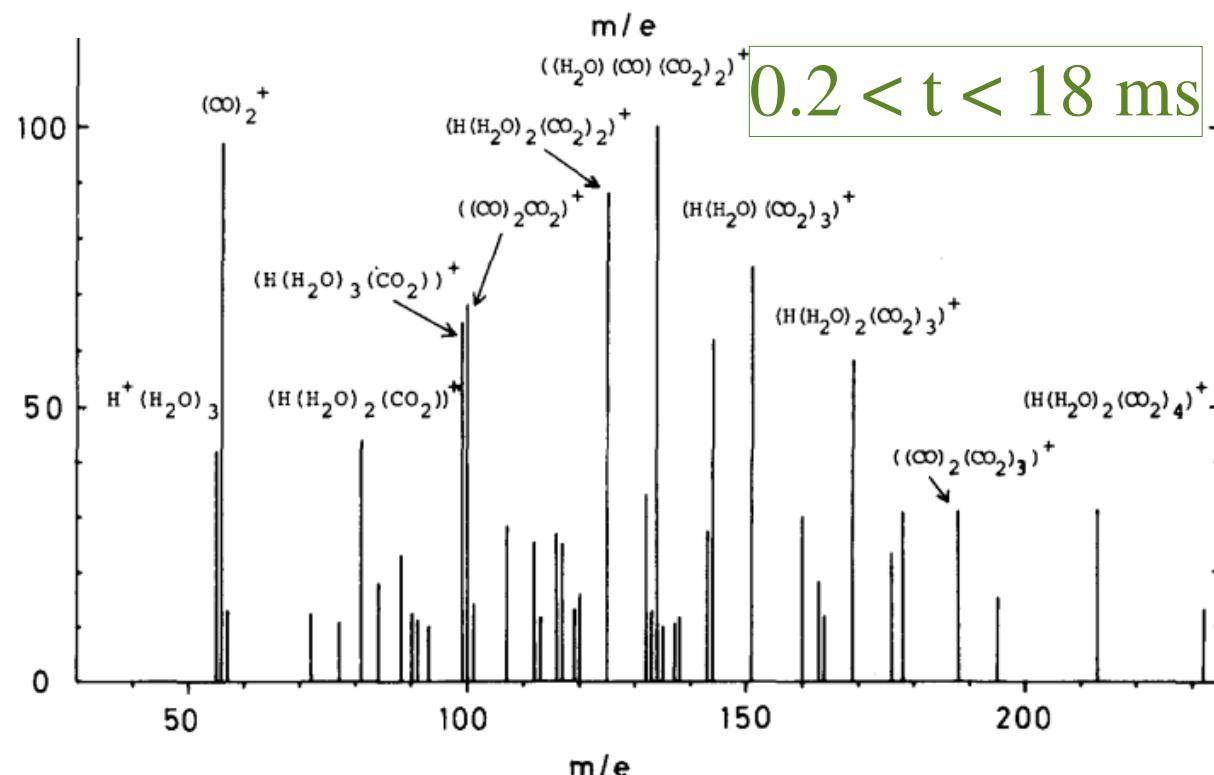
CO_2 at 1 bar

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



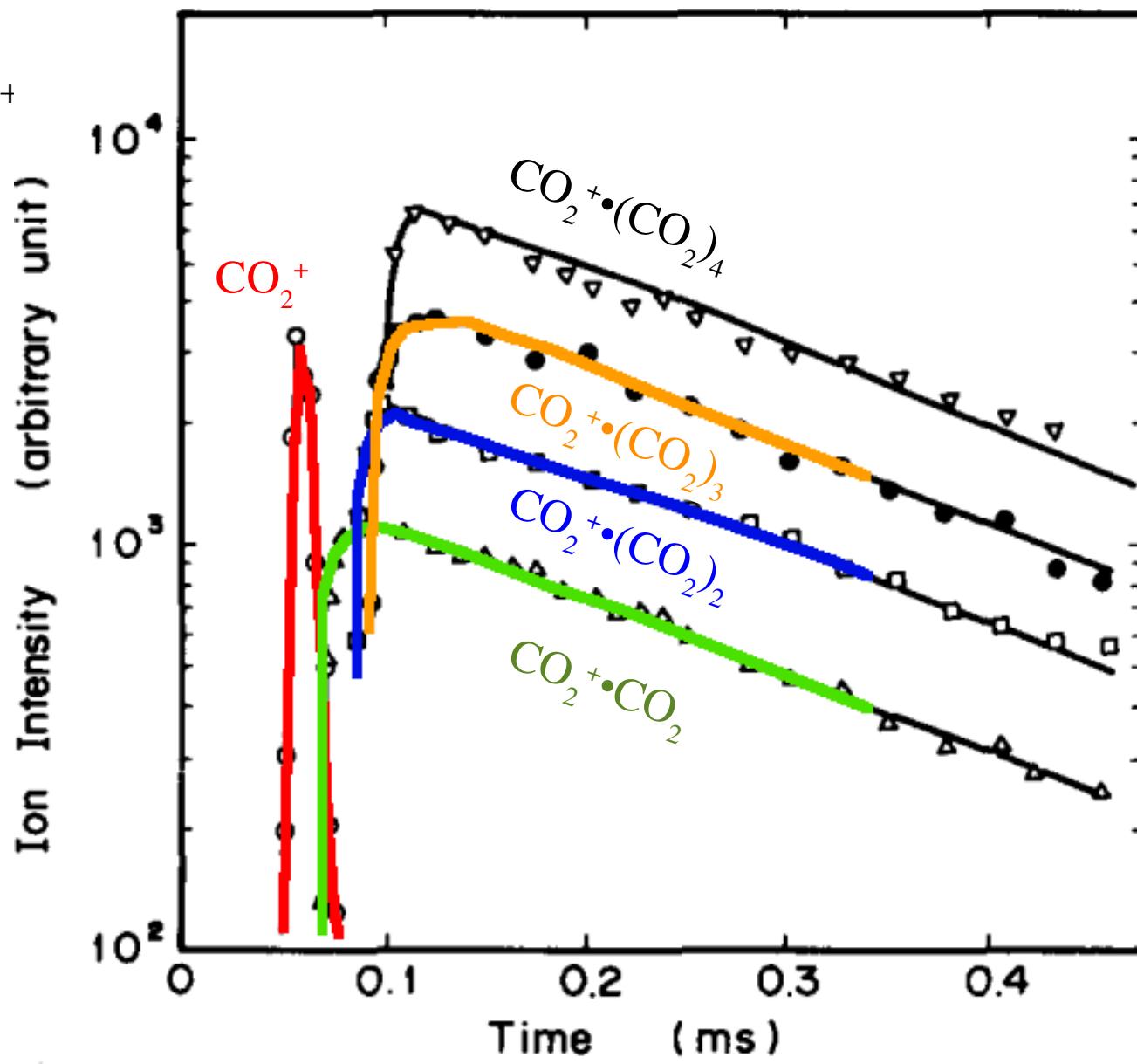
- ▶ Until $200 \mu\text{s}$:
 $\text{CO}_2^+\bullet(\text{CO}_2)_n$ and
 $\text{CO}^+\bullet(\text{CO}_2)_n$

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



CO_2 at 1 atm: cluster disappearance

- ▶ Not clear why CO_2^+ forms at $t > 50 \mu\text{s}$.
- ▶ Clusters with CO_2^+ ion core form by $t = 100 \mu\text{s}$.
- ▶ They react with contaminants to disappear with a time constant of $\tau \sim 190 \mu\text{s}$.



Binding energy of clusters

Time scale: rate constant

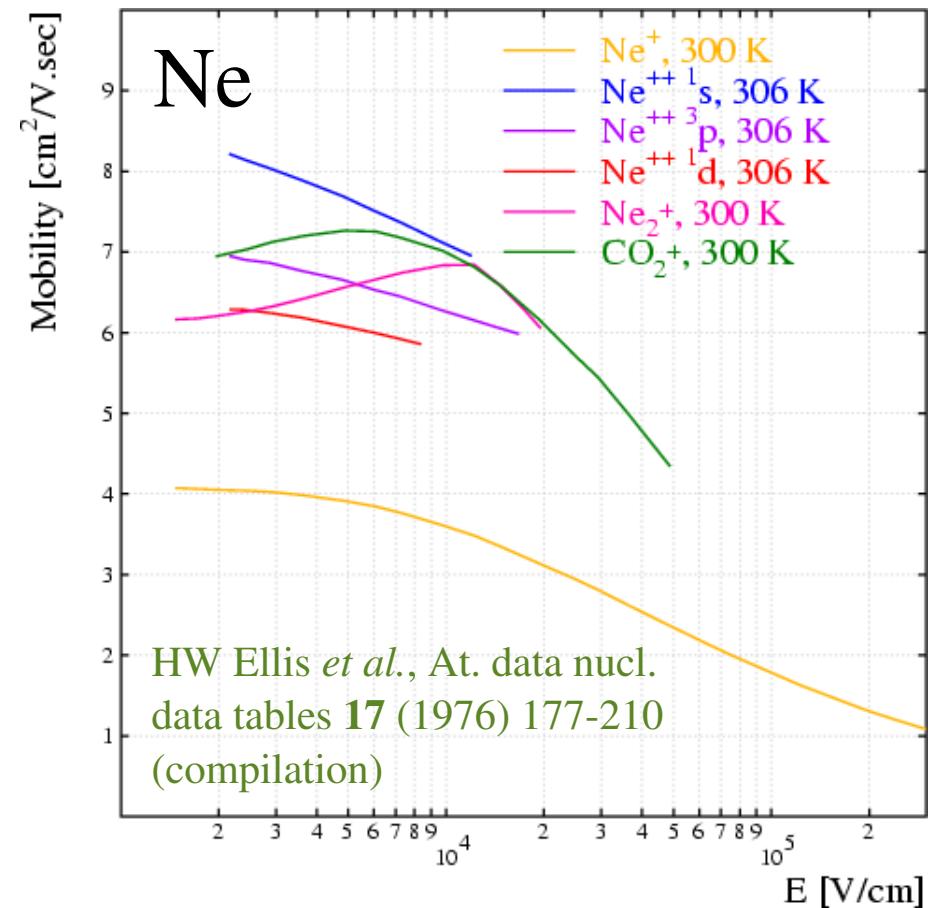
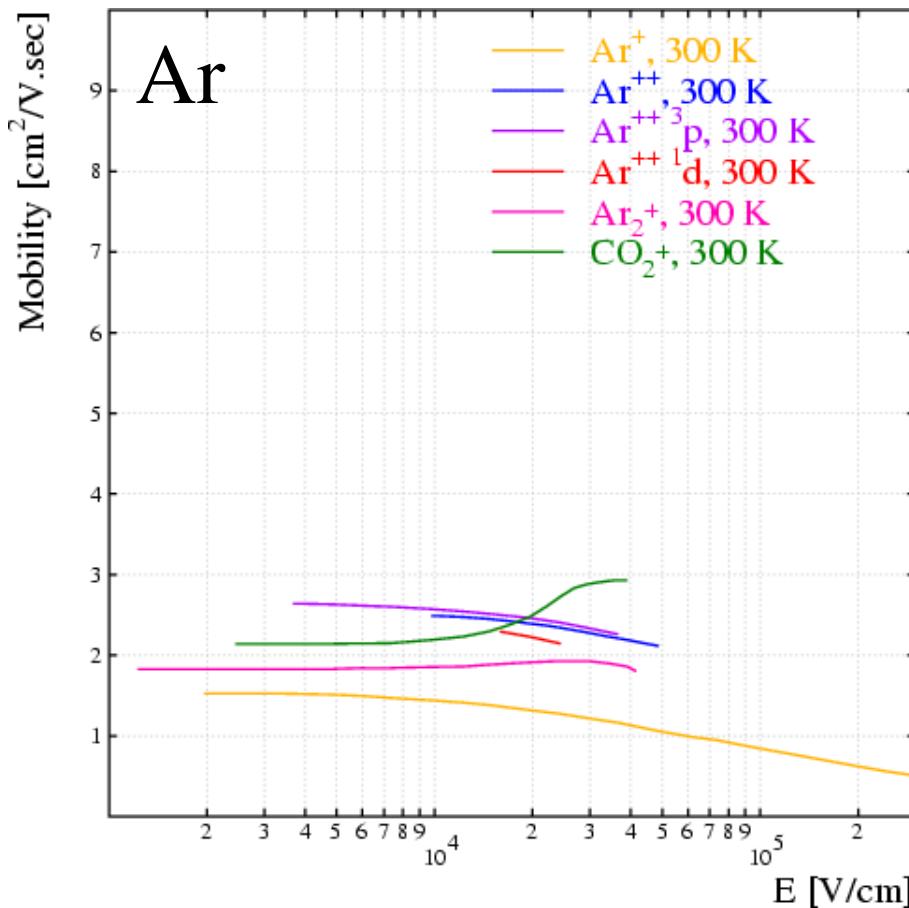
Which clusters are formed ?

Mobility of clusters

Comparison with data

Mobility of Ar^+ and $\text{Ar}^+\bullet\text{Ar}$ in Ar

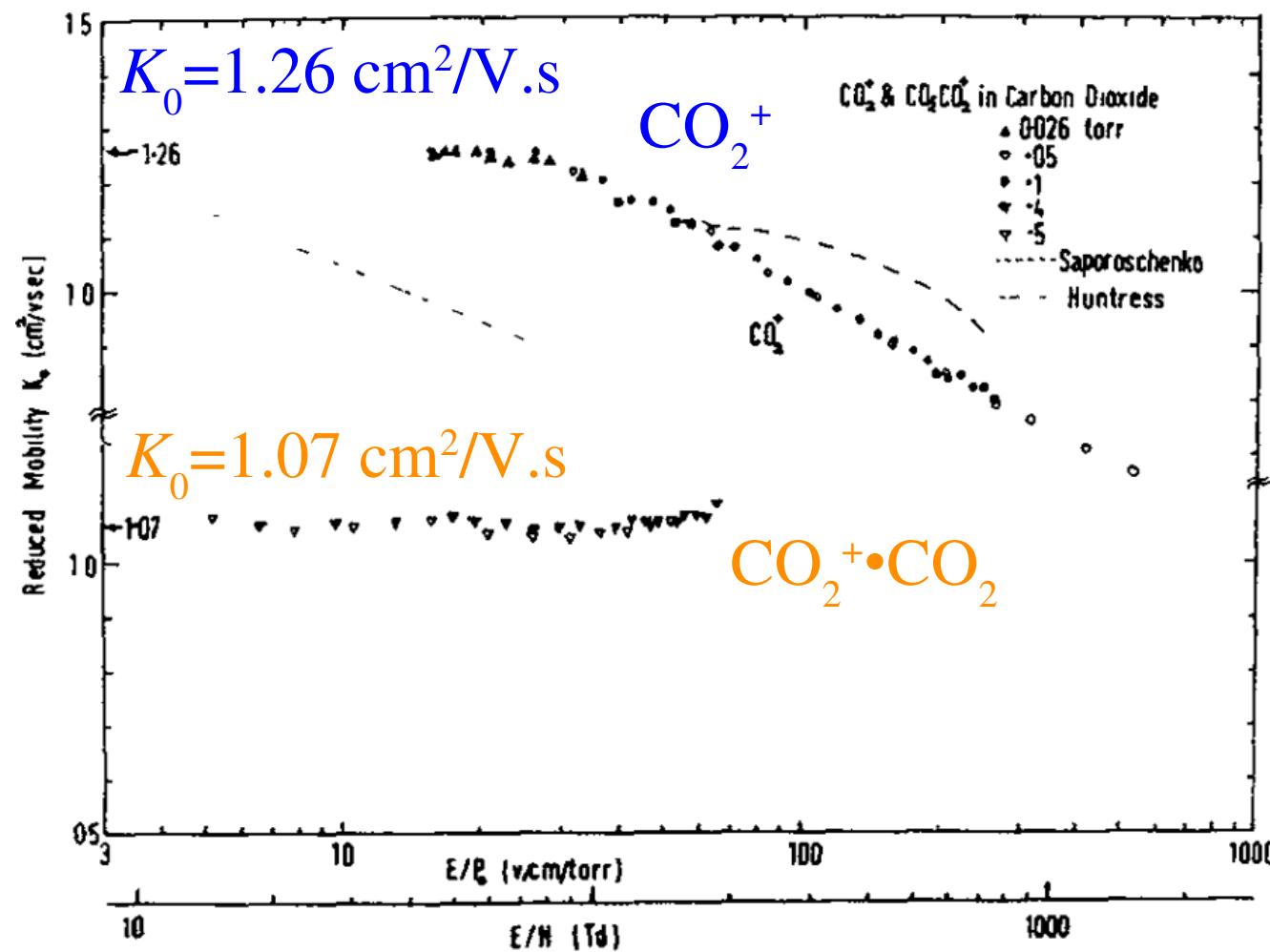
- The mobility of noble gas ions and molecular ions has been measured in various pure gases:



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

- ▶ CO_2^+ , $\text{CO}_2^+\bullet\text{CO}_2$, and $\text{CO}_2^+\bullet(\text{CO}_2)_2$ were observed, but no other clusters (i.e. the gas was clean).

- ▶ Adopted in the Ellis et al. compilation.



[P.A. Coxon and J.L. Moruzzi, J. Phys. Coll. **40** (1979) C7-117 – C7-118, 10.1051/jphyscol:1979758.]

CO_2^+ • CO_2 & CO_2^+ mobility – sources

- ▶ R.A. Beyer and J.A. Vanderhoff:
 - ▶ concerns primarily photo-dissociation
 - ▶ J. Chem. Phys. **65** (1976) 2313 10.1063/1.433342
- ▶ G. Schultz et al.:
 - ▶ no mass spectroscopy no attempt to identify ions;
 - ▶ finds a mobility of $1.09 \text{ cm}^2/\text{V.s}$ of “ CO_2^+ “ in CO_2 .
 - ▶ Rev. Phys. Appl. **12** (1977) 67-70, 10.1051/rphysap:0197700120106700
- ▶ M. Saporoschenko:
 - ▶ finds $K_0 = 1.13 \text{ cm}/\text{V.s}$ for CO_2^+ ;
 - ▶ mass spectroscopy performed;
 - ▶ no clusters observed, abundant O_2 (contamination ?).
 - ▶ Phys. Rev. A **8** (1973) 1044, 10.1103/PhysRevA.8.1044

$\text{CO}_2^+ \cdot (\text{CO}_2)_n$ mobility vs cluster size n

► Souji Rokushika et al.:

- Single peak: all clusters have same mobility
- $K_0 = 0.96 \pm 0.02 \text{ cm}^2/\text{V.s}$ (25 °C, atmospheric pressure);

[Anal. Chem 58 (1986) 361-365]

► H.W. Ellis et al.:

- Identifies numerous clusters, all containing contaminants;
- common $K_0 = 1.06 \pm 0.02 \text{ cm}^2/\text{V.s}$

[J. Chem. Phys. 64 (1976) 3935, 10.1063/1.432024]

► Both find that, at atmospheric pressure, the mobility is independent of the core ion and the cluster size n .

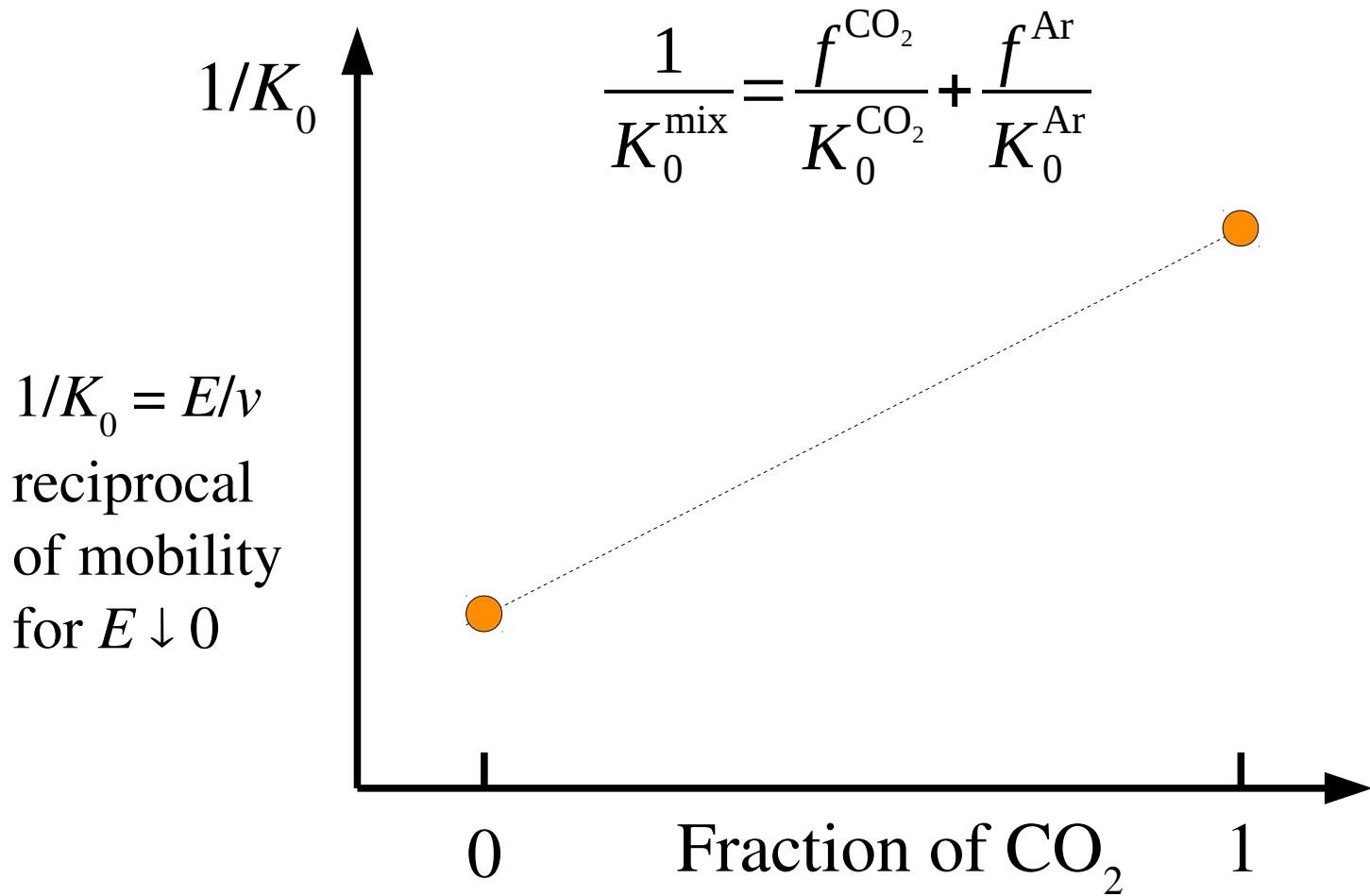
Life cycle of $\text{CO}_2^{+\bullet}(\text{CO}_2)_n$

- ▶ $\text{CO}_2^{+\bullet}\text{CO}_2$ 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 $\tau = 70$ 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.

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]

Blanc's law: example

- ▶ CO_2^+ in Ar- CO_2 mixtures (values for zero-field limit)
 - ▶ mobility of CO_2^+ in pure Ar = $2.14 \text{ cm}^2/\text{V.s}$
 - ▶ mobility of CO_2^+ in 10 % CO_2 = $2.00 \text{ cm}^2/\text{V.s}$
 - ▶ mobility of CO_2^+ in pure CO_2 = $1.26 \text{ cm}^2/\text{V.s}$
- ▶ One can't use this for Ar^+ in CO_2 . Why ?

Binding energy of clusters

Time scale: rate constant

Which clusters are formed ?

Mobility of clusters

Comparison with data

Experimental information

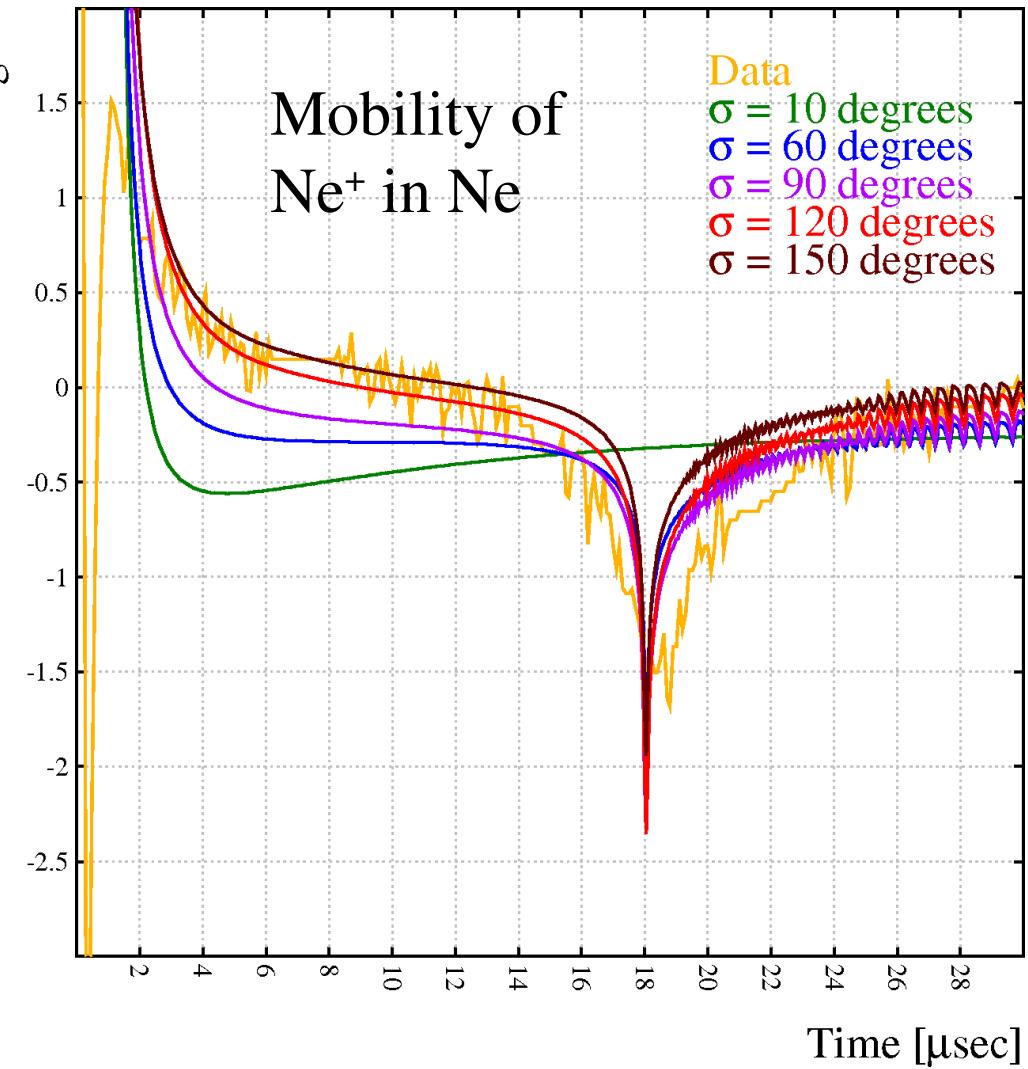
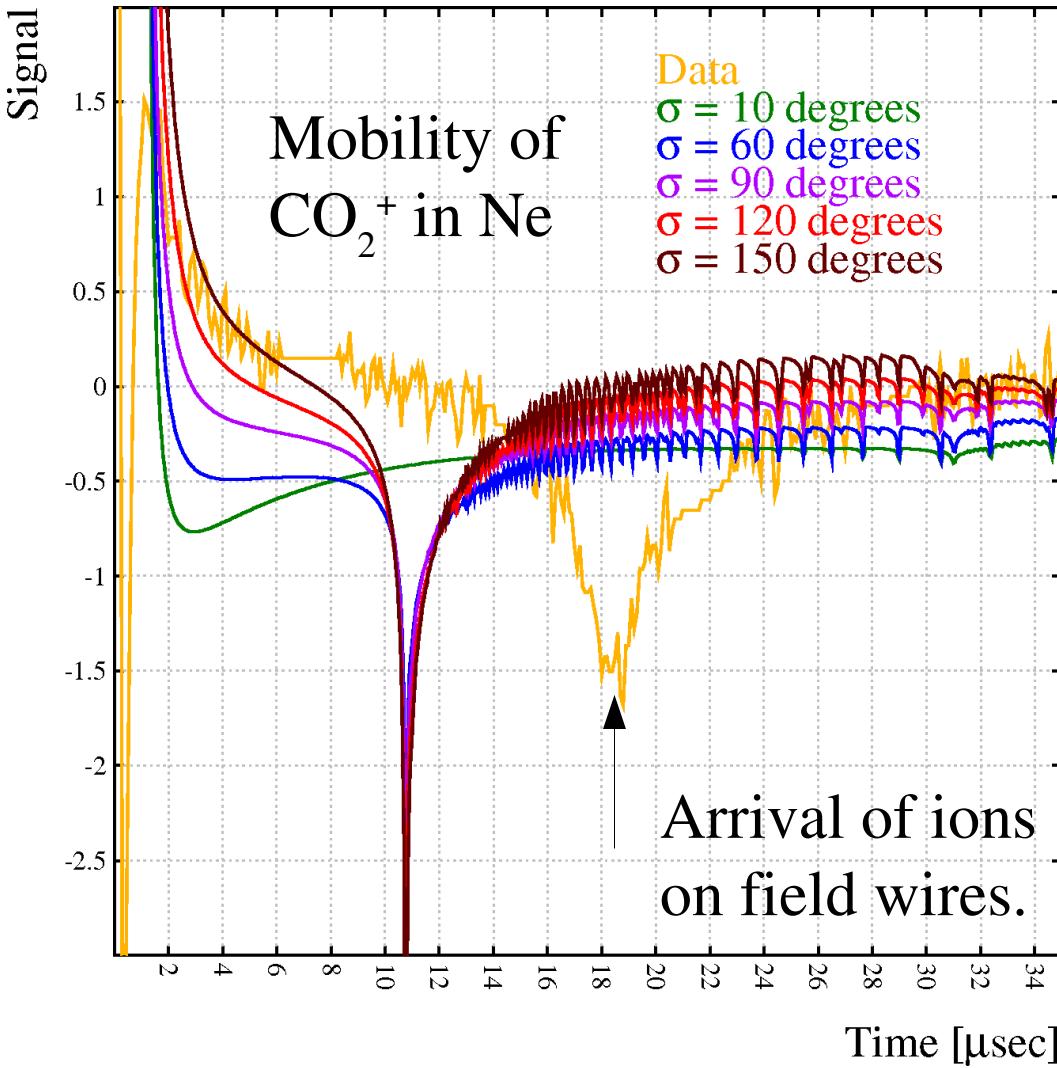
- ▶ Ne-CO₂:
 - ▶ NA49;
 - ▶ Alice – Mesut;
 - ▶ Alice – Stefan (Ne-CO₂-N₂);
 - ▶ hopefully, Coimbra will measure these mixtures.

- ▶ Ar-CO₂:
 - ▶ Coimbra;
 - ▶ G. Schultz et al..

Ne-CO₂

- ▶ Charge transfer is a (slower) 2-step process:
 - ▶ $\text{Ne}^+ + \text{CO}_2 \rightarrow \text{Ne} + \text{CO}^+ + \text{O}$ $k = 5.0 \cdot 10^{-11} \text{ cm}^3/\text{s}$
 - ▶ $\text{CO}^+ + \text{CO}_2 \rightarrow \text{CO} + \text{CO}_2^+$ $k = 1.0 \cdot 10^{-9} \text{ cm}^3/\text{s}$
 - ▶ $\tau = 0.8 \text{ ns}$ (pure gas)
- ▶ Usual clustering reactions:
 - ▶ $\text{Ne}^+ + 2\text{Ne} \rightarrow \text{Ne}^+\bullet\text{Ne} + \text{Ne}$ $k = 0.6 \cdot 10^{-31} \text{ cm}^6/\text{s}$
 - ▶ $\text{CO}_2^+ + 2\text{CO}_2 \rightarrow \text{CO}_2^+\bullet\text{CO}_2 + \text{CO}_2$ $k = 2.4 \cdot 10^{-28} \text{ cm}^6/\text{s}$
 - ▶ $\tau = 7 \text{ ps}$ (pure gas)
 - ▶ $\text{CO}^+ + 2\text{CO}_2 \rightarrow \text{CO}^+\bullet\text{CO}_2 + \text{CO}_2$ $k = ?$
 - ▶ $\tau = ? \text{ ps}$ (pure gas)

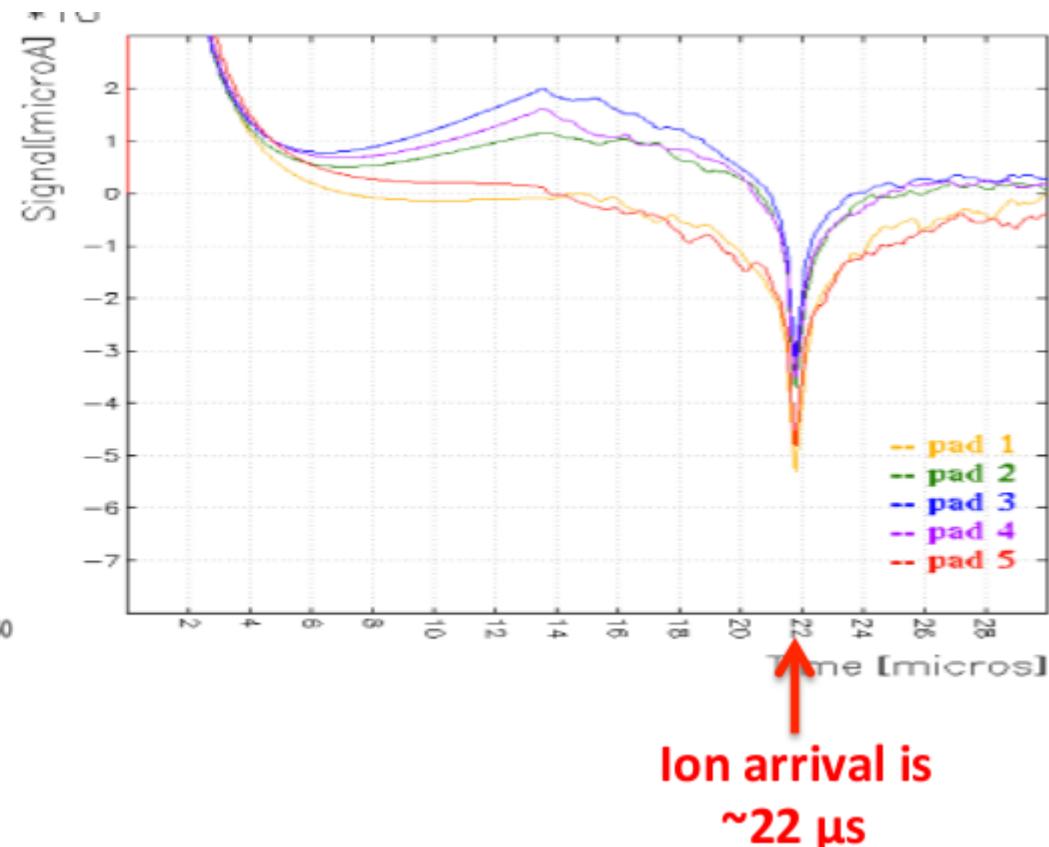
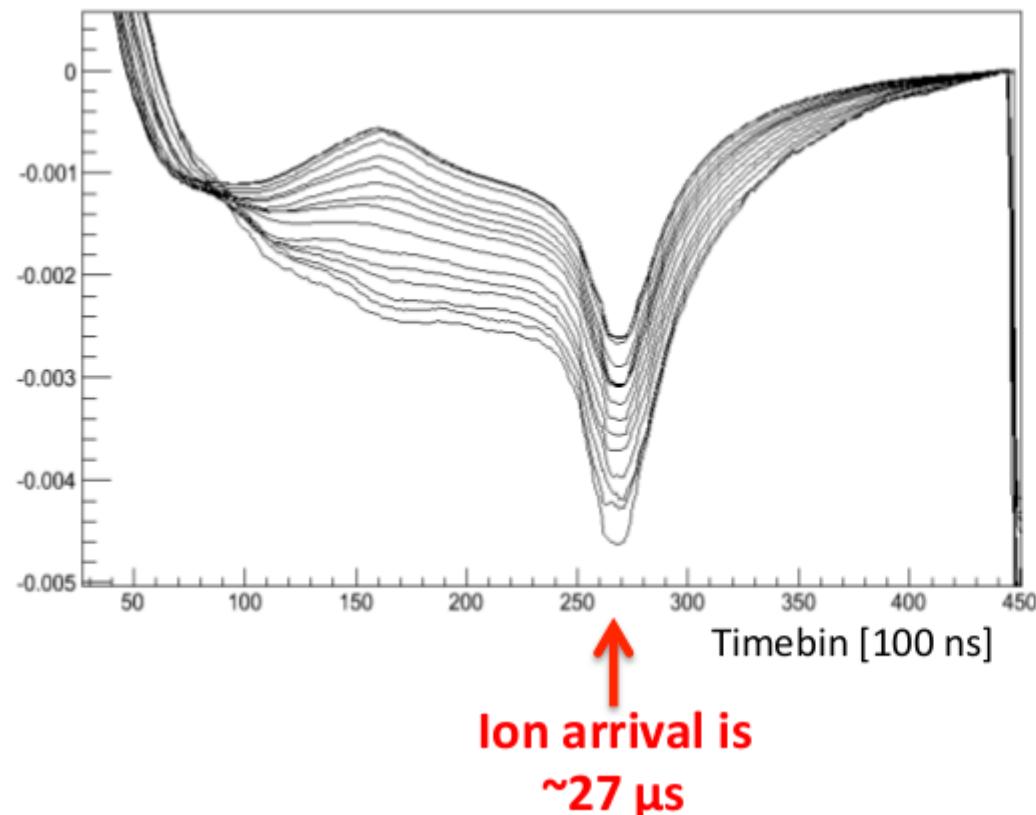
NA49 TPC



- ▶ Gas: Ne 90 % + CO_2 10 %
- ▶ Calculation of the ion-induced signal on the pads for various avalanche spreads around the anode wire.

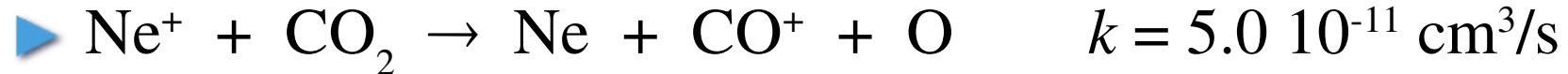
Alice TPC – Mesut

- ▶ Gas: 90 % Ne + 10 % CO₂;
- ▶ calculations use mobility of Ne⁺ in pure Ne.



Ne-CO₂-N₂

► Charge transfer still produces CO₂⁺:



► Clustering is expected to produce mainly CO₂⁺•(CO₂)_n:

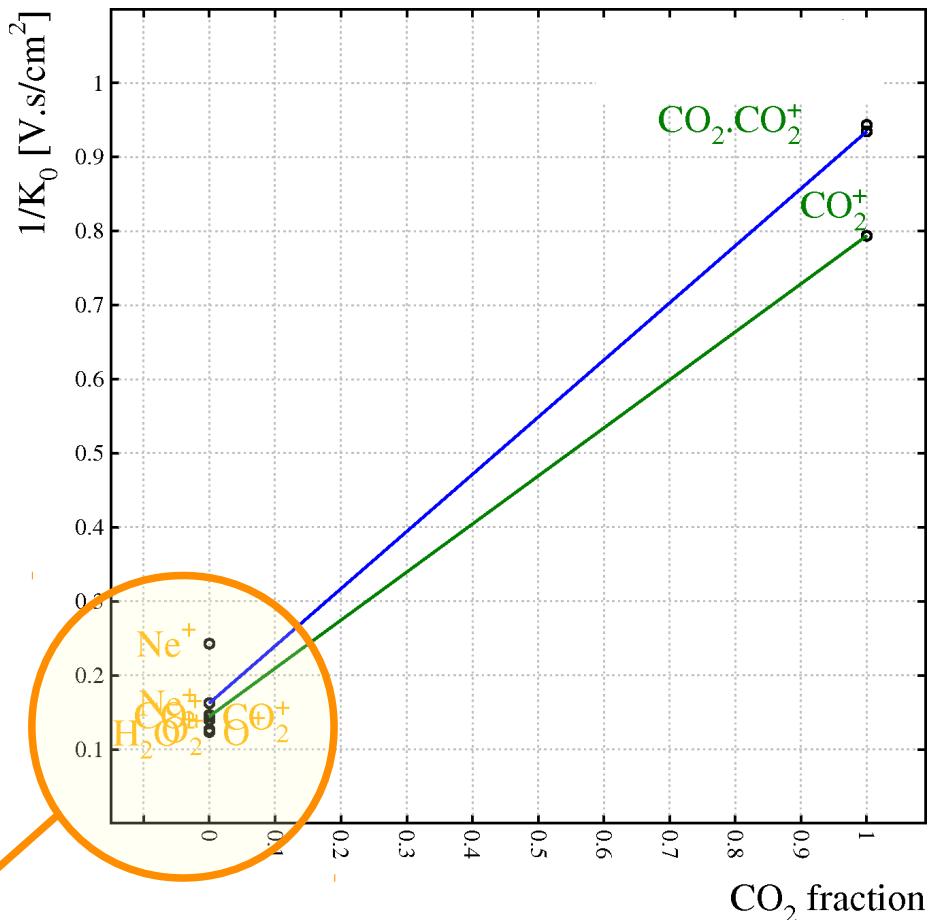
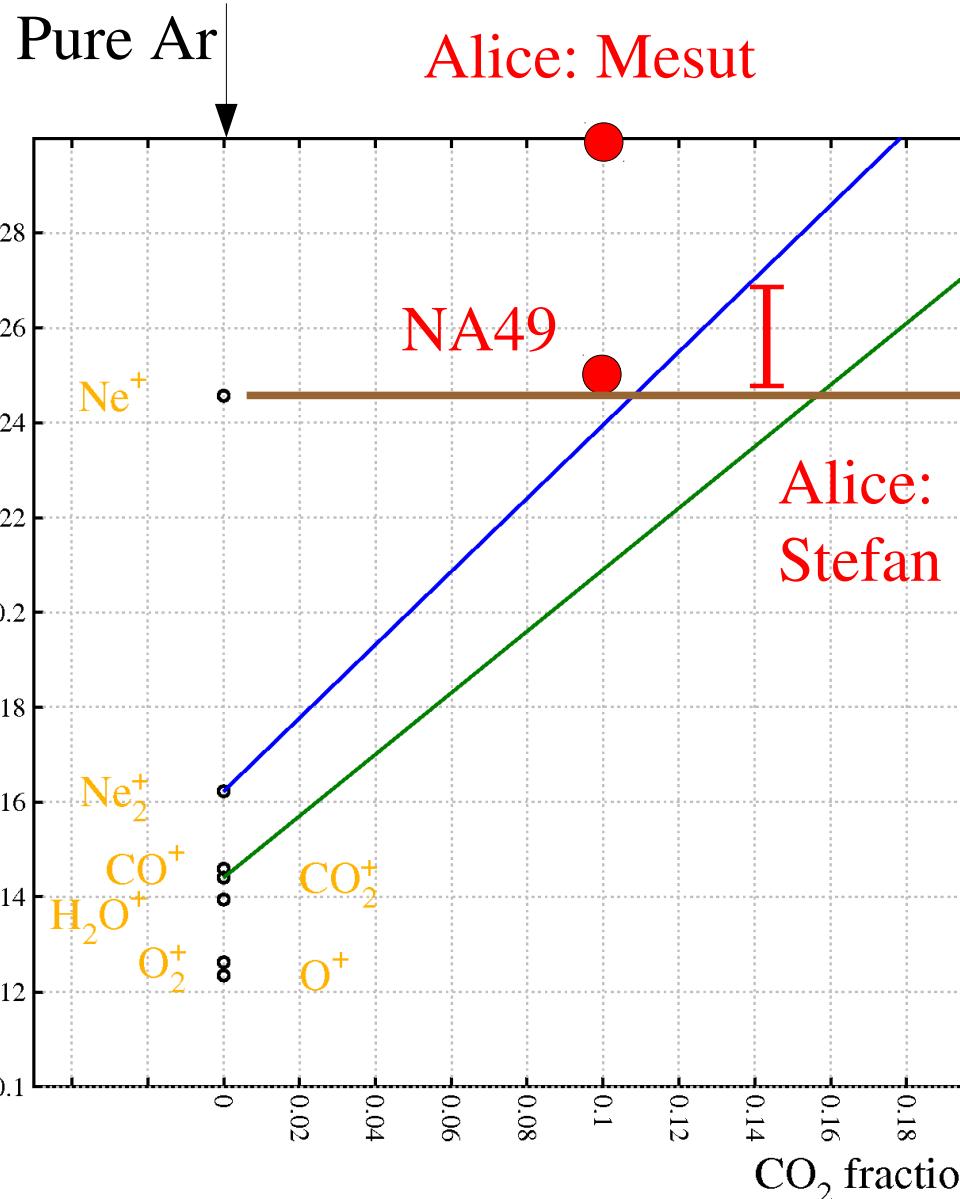


Alice TPC – Stefan

- ▶ Gas: Ne 85.7 %, CO₂ 9.5 %, N₂ 4.8 %
- ▶ Offset between a calculation assuming Ne⁺ in Ne:
 - ▶ assumed mobility systematically higher than data;
 - ▶ difference 10 % at low gain, smaller at high gain.

[S. Rossegger and W. Riegler 10.1016/j.nima.2010.07.061]

Blanc plot Ne/CO₂



- ▶ Blue: assume $\text{CO}_2^+ \cdot \text{CO}_2$ for pure CO_2 and $\text{Ne}^+ \cdot \text{Ne}$ for pure Ne.
- ▶ Green: assume CO_2^+ both in CO_2 and in Ne.
- ▶ Brown: assume Ne^+ in Ne also for CO_2 (i.e. neglect charge transfer).

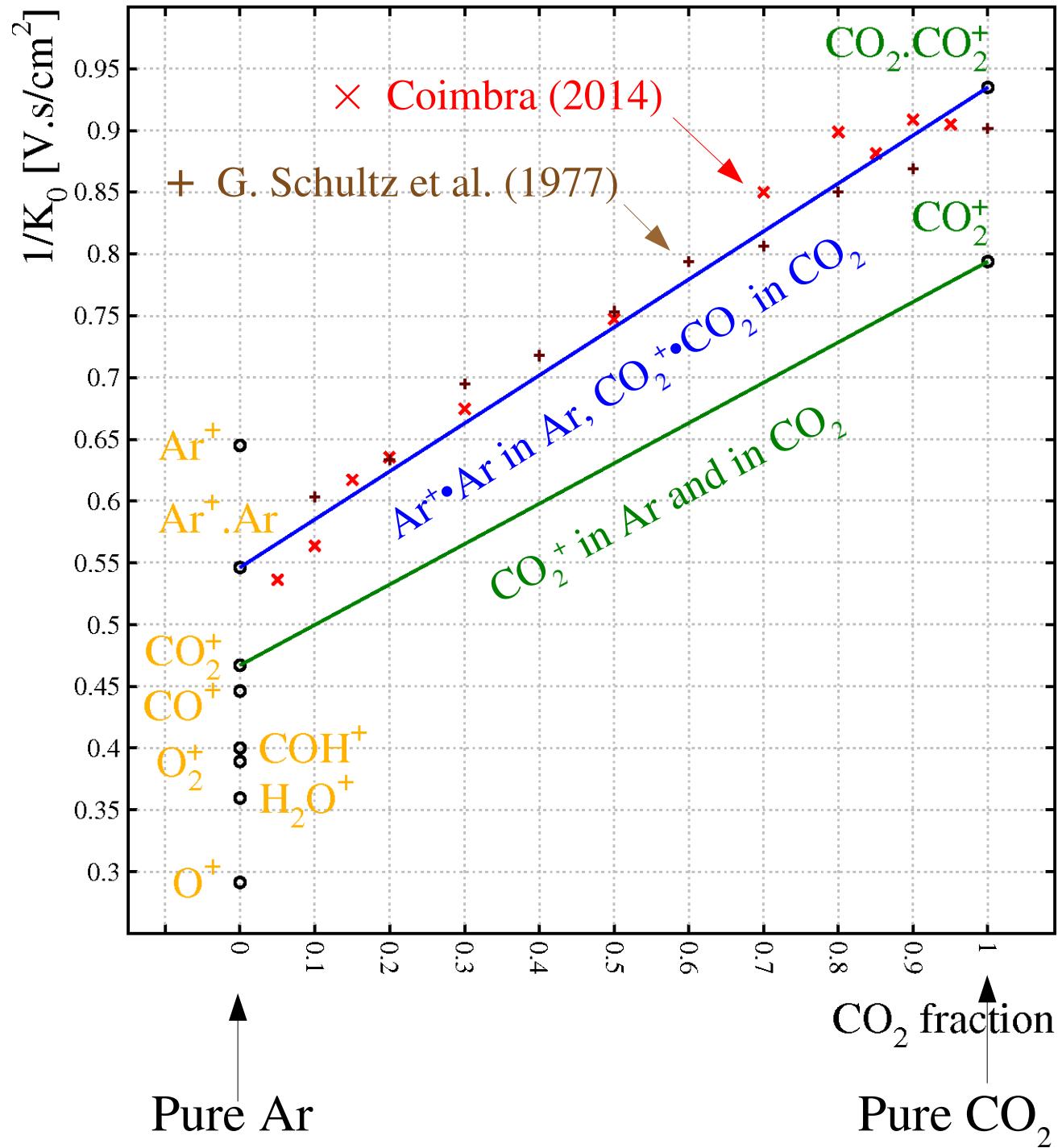
Ne-CO₂ comparison

- ▶ NA49:
 - ▶ mobility CO₂⁺ in Ne is nearly a factor 2 higher than data;
 - ▶ mobility Ne⁺ in Ne is just 2-3 % higher than data.
- ▶ Alice – Mesut:
 - ▶ mobility Ne⁺ in Ne is ~25 % higher than data.
- ▶ Alice – Stefan:
 - ▶ Ne/CO₂/N₂ mixture;
 - ▶ mobility Ne⁺ in Ne is higher than data, 10 % at the lowest gain and less at higher gain.

Ar-CO₂

- ▶ CO₂⁺•CO₂ is expected and is confirmed on the CO₂ side.
- ▶ Mobility of the cluster ion in Ar yet to be found.
- ▶ Pending this, the low-Ar area is uncertain.

Blanc's law for Ar/CO₂



Conclusion

- ▶ Ion signals in wire-TPCs operated with Ar-CO₂ and Ne-CO₂ are due to CO₂⁺•(CO₂)_n cluster ions – not CO₂⁺.
 - ▶ Cluster ions have a mobility in CO₂ of ~1.07 cm²/V.s while CO₂⁺ has a mobility in CO₂ of ~1.26 cm²/V.s.
 - ▶ Some experiments without mass-spectrometer have miss-identified the 1.07 cm²/V.s ion as CO₂⁺.
- ▶ Both the G. Schultz et al. and the Coimbra data agree with the CO₂⁺•(CO₂)_n and Ar⁺•Ar model.
- ▶ The near-agreement of the Ne⁺ hypothesis with the Ne-CO₂ data of the NA49 TPC may well be fortuitous.
- ▶ Mobility of CO₂⁺•(CO₂)_n in Ar and Ne yet to be found.

Not used

Mixed clusters

- ▶ Although avalanches produce abundant Ar⁺ ions, these transfer their charge to CO₂:
 - ▶ Ar⁺ + CO₂ → Ar⁺•CO₂ → Ar + CO₂⁺ Charge transfer
 - ▶ $k = 4.2 \cdot 10^{-10} \text{ cm}^3/\text{s}$, $\tau \approx 100 \text{ ps}$
- ▶ The CO₂⁺ ions react further, forming CO₂ clusters:
 - ▶ CO₂⁺ + Ar + M → CO₂⁺•Ar + M Association
 - ▶ CO₂⁺•Ar + CO₂ → CO₂⁺•CO₂ + Ar Ligand switch
 - ▶ CO₂⁺ + CO₂ + M → CO₂⁺•CO₂ + M Association

[Andreas J. Illies et al., “Photoinduced Intramolecular Charge Transfer: Photodissociation of CO₂⁺•Ar Cluster Ions,” J. Am. Chem. Soc. **107** (1985) 2842-2849, 10.1021/ja00296a003]

Making CO₂ and Ne/Ar ion clusters

► Cluster ion formation requires the evacuation of excess energy of the bound state through internal degrees of freedom (rotation, vibration), or via a 3-body reaction:



At 296 K; no reaction at room temperature for Ar⁺(²P_{1/2}^o).

[B.M. Smirnov, “Cluster Ions and Van Der Waals Molecules,” CRC press;
Wei-cheng F. Liu and D.C. Conway, J. Chem. Phys. **62** (1975) 3070]

Charge transfer

- ▶ Rarely available when the IP of the ion is larger than the IP of the carrier gas due to charge transfer:
- ▶ Transfer times at stp:
 - ▶ $10^{-10} \text{ cm}^3/\text{s}$: 370 ps
 - ▶ $10^{-12} \text{ cm}^3/\text{s}$: 37 ns
 - ▶ $10^{-15} \text{ cm}^3/\text{s}$: 37 μs
- ▶ AFV Cortez *et al.* take data at 7 Torr with typical transit times of 200-800 μs . This is equivalent at stp to
 - ▶ 2-8 μs

Charge exchange rate constants [cm³/s]

	He	Ne	Ar	Kr	Xe
He ⁺	$5.0 \cdot 10^{-10}$ ± 10 %	$1.2 \cdot 10^{-15}$ ± 30 %	< $1.0 \cdot 10^{-13}$	< $1.0 \cdot 10^{-11}$	$7.0 \cdot 10^{-12}$ ± 20 %
Ne ⁺		-	$6.0 \cdot 10^{-15}$ ± 50 %	< $1.0 \cdot 10^{-14}$	-
Ar ⁺			$4.6 \cdot 10^{-10}$	< $1.0 \cdot 10^{-14}$	-
Kr ⁺		Forbidden		$8.3 \cdot 10^{-10}$ ± 20 %	-
Xe ⁺					-

At $T = 300$ K. Ar⁺Ar Peter M. Martin, Handbook of Deposition Technologies for Films and Coatings

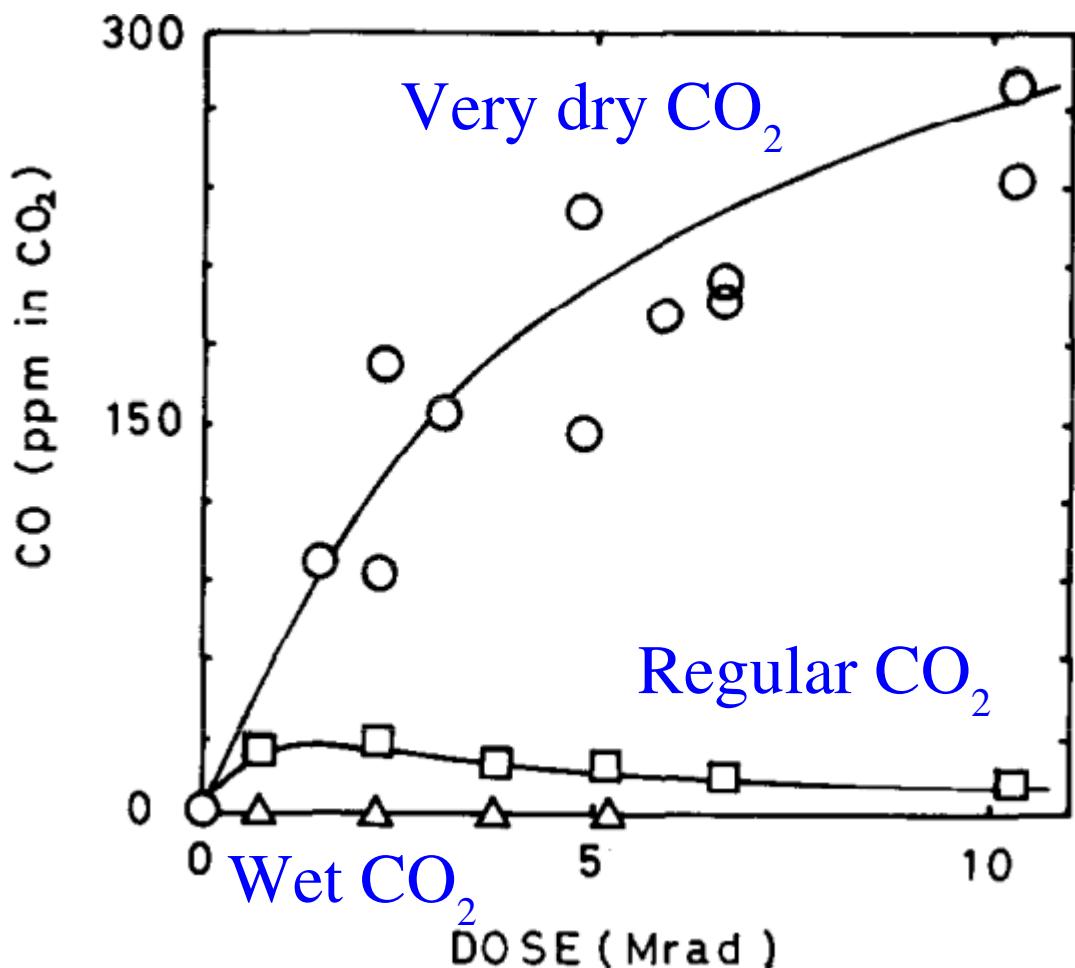
Contaminants 2 μ bar to 1 mbar

- ▶ > 2 μ bar:
 - ▶ O_2^+ emerges – and soon becomes dominant;
 - ▶ *Origin of this ion not clear – perhaps a contaminant;*
- ▶ 80 μ bar:
 - ▶ $C_2O_2^+$, $C_2O_3^+$, $C_2O_4^+$, CO^+ , CO_4^+ ... appear in addition;
 - ▶ perhaps clusters: $CO^+\bullet CO$, $CO^+\bullet CO_2$, $CO_2^+\bullet CO_2$, $O_2^+\bullet CO_2$
- ▶ 0.5 mbar:
 - ▶ O_2^+ represents 75 % of the ions,
 - ▶ $O_2^+\bullet CO_2$ clusters follow;
- ▶ 1 mbar:
 - ▶ $O_2^+\bullet(CO_2)_2$ clusters appear;
 - ▶ *No mention of $CO_2^+\bullet CO_2$ clusters.*

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

Contaminants

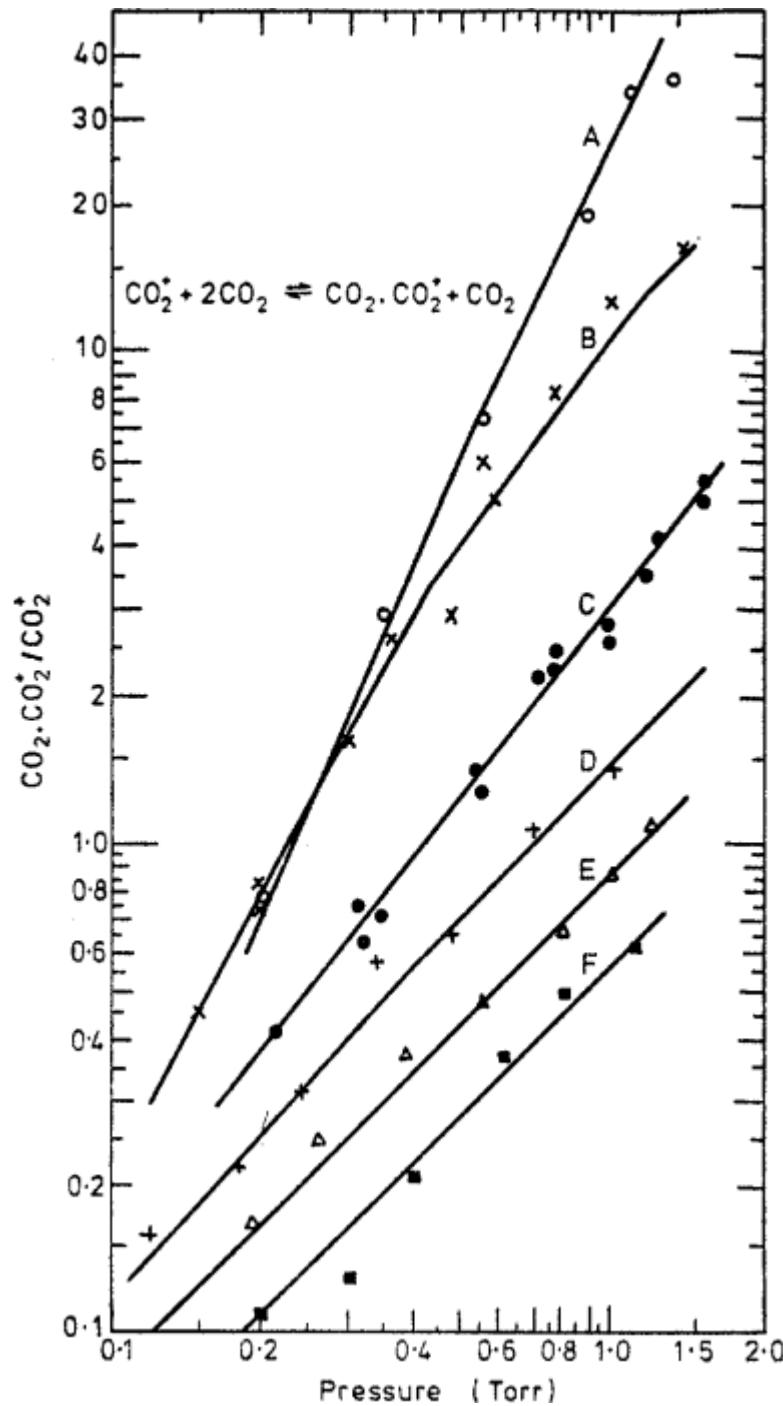
- ▶ H_2O :
 - ▶ from the surroundings.
- ▶ O_2 and CO:
 - ▶ O_2 from environment;
 - ▶ radiolysis of CO_2 ;
known in discharges,
presumably in
avalanches;
 - ▶ CO is rapidly oxidised in
the presence of H_2O !



[Y. Ikezoe, Rad. Phys. Chem 17 (1981) 69–70,
10.1016/0146-5724(81)90002-9]

Clustering at ~ 1 mbar

- ▶ $p = 0.13\text{-}2.6$ mbar, T unknown:
 - ▶ With clean CO_2 , only CO_2^+ and $(\text{CO}_2 \cdot \text{CO}_2)^+$ are seen.
 - ▶ “Despite a careful search for larger cluster ions, no evidence of any ion with a mass above $(\text{CO}_2 \cdot \text{CO}_2)^+$ was observed”
 - ▶ With increasing p , $(\text{CO}_2 \cdot \text{CO}_2)^+$ dominates.



[P Coxon and J L Moruzzi, J. Phys. D: Appl. Phys. **10** (1977) 969-977, 10.1088/0022-3727/10/7/003.]