

Ion transport

Yalçın Kalkan

Uludağ university, Bursa, Turkey

Pedro Encarnação

André Cortez

LIP Coimbra, Portugal

Overview

- ▶ Goal: provide simulation of ion motion in a gas, similar to what Magboltz does for electrons.
- ▶ Operating point:
 - ▶ pressure: ~atmospheric; (*as opposed to* \ll mbar);
 - ▶ room temperature;
 - ▶ mixtures of gases.
- ▶ We need to know for the ions:
 - ▶ identity: reactions of ions and carrier gas;
 - ▶ mobility K ;
 - ▶ longitudinal diffusion σ_{\parallel} and transverse diffusion σ_{\perp} .

Clustering reactions involving CO₂

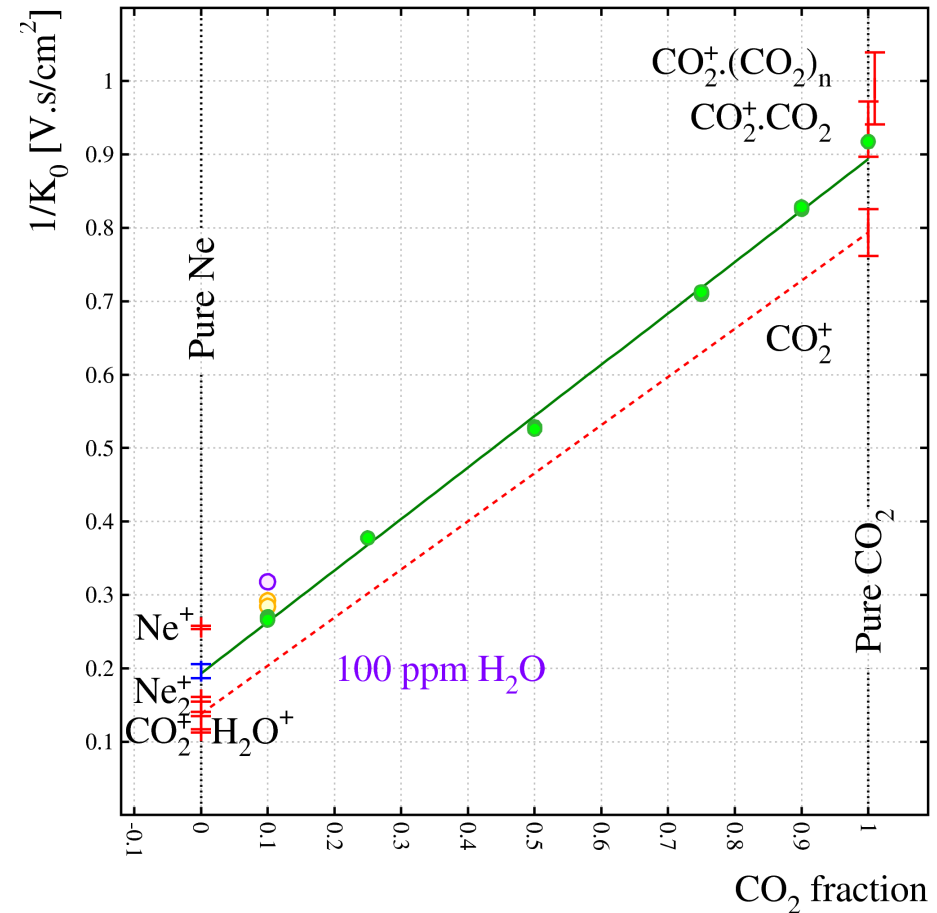
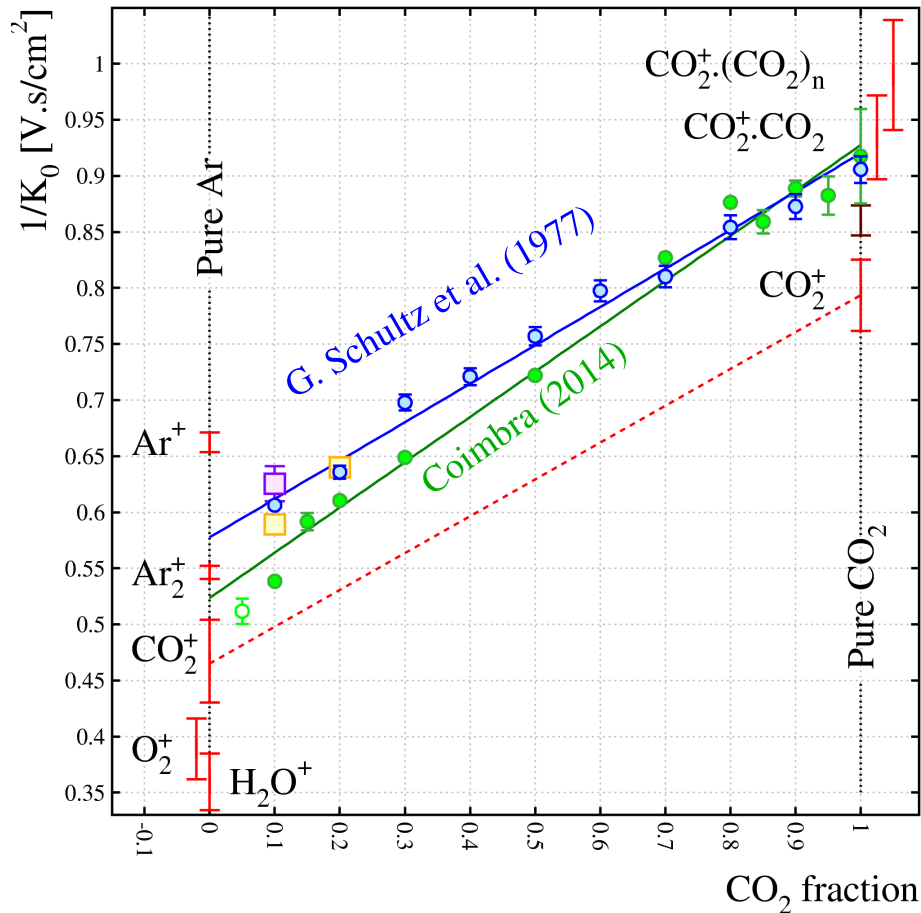
- ▶ Ar⁺: charge exchange, $\tau \approx 0.85$ ns
 - ▶ $\text{Ar}^+ + \text{CO}_2 \rightarrow \text{Ar} + \text{CO}_2^+$
- ▶ Ne⁺: charge transfer in 2-steps, $\tau \approx 8$ ns
 - ▶ $\text{Ne}^+ + \text{CO}_2 \rightarrow \text{Ne} + \text{CO}^+ + \text{O}$
 - ▶ $\text{CO}^+ + \text{CO}_2 \rightarrow \text{CO} + \text{CO}_2^+$
- ▶ CO₂: 3-body association, $\tau = 0.7\text{-}2.0$ ns (faster if Ar helps)
 - ▶ $\text{CO}_2^+ + 2\text{CO}_2 \rightarrow \text{CO}_2^+ \cdot \text{CO}_2 + \text{CO}_2$
- ▶ [For 10 % CO₂, atmospheric pressure, room temperature]

Induced dipole moments

- ▶ Induced dipole moments are quantified in the form of the polarisability α : $\mu = \alpha E$
- ▶ A polarisable atom or molecule acquires a dipole moment when approached by an ion or a dipole, and also in an external field.
- ▶ Induced dipoles are small in external fields: e.g. for water $\alpha = 1.5 \text{ \AA}^3$. If $E = 10 \text{ kV/cm}$ then $\mu_{\text{ind}} = 5 \cdot 10^{-5} \text{ D}$. But the effect can be significant in the ion-field.
- ▶ Charge-induced dipole forces are always attractive.

Ions drifting in Ar-CO₂ and Ne-CO₂

▶ Little Ar⁺, Ne⁺, CO₂⁺ but CO₂⁺•(CO₂)_n



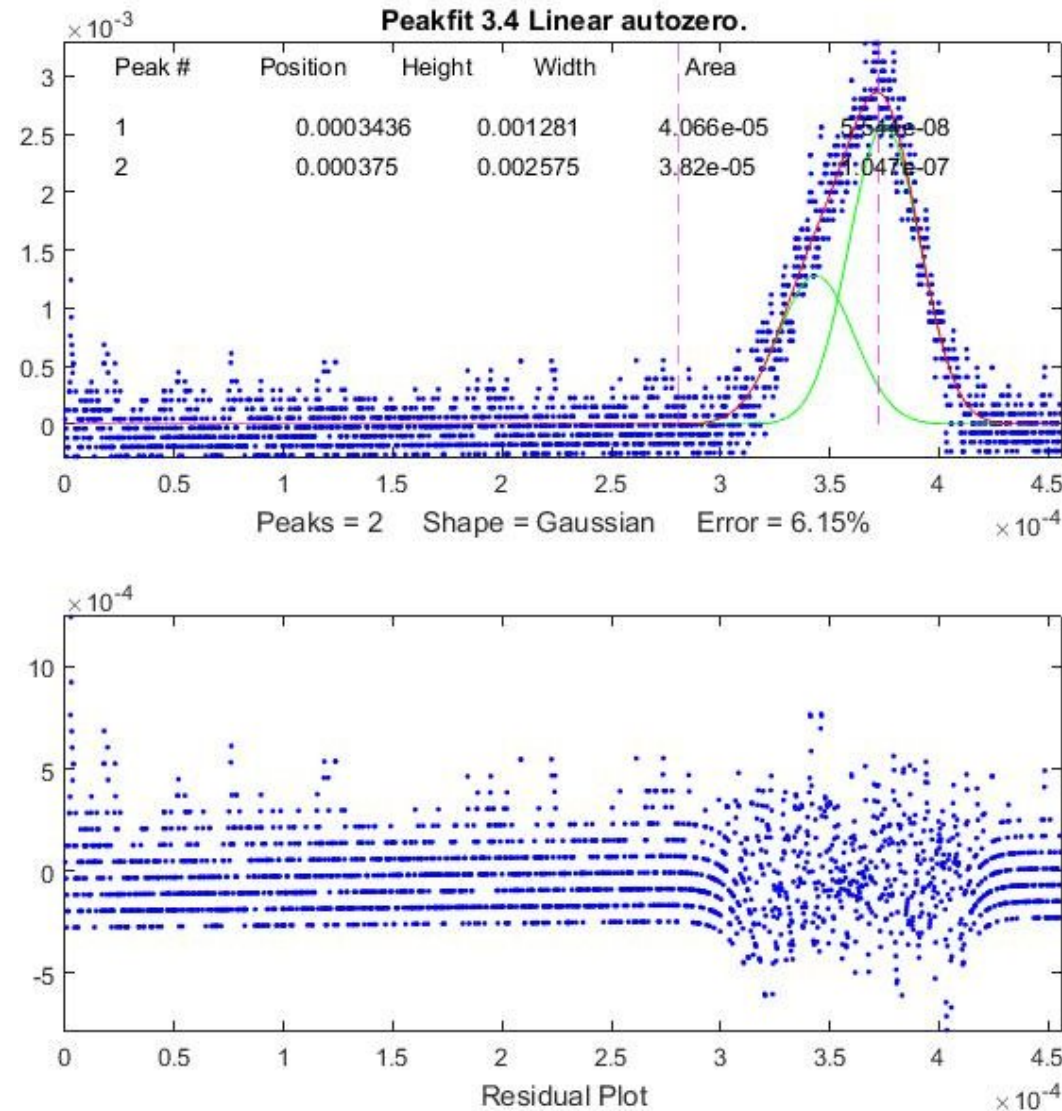
N_2 - CO_2 time spectra: N_2 -rich mixtures

- ▶ 97 % N_2 + 3 % CO_2 :
 - ▶ pressure: 8 Torr
 - ▶ minor peak: 344 μs
 - ▶ major peak: 375 μs
 - ▶ offset: 27.8 μs
 - ▶ drift gap: 4.273 cm
 - ▶ E field: 20 Td

▶ Mobility

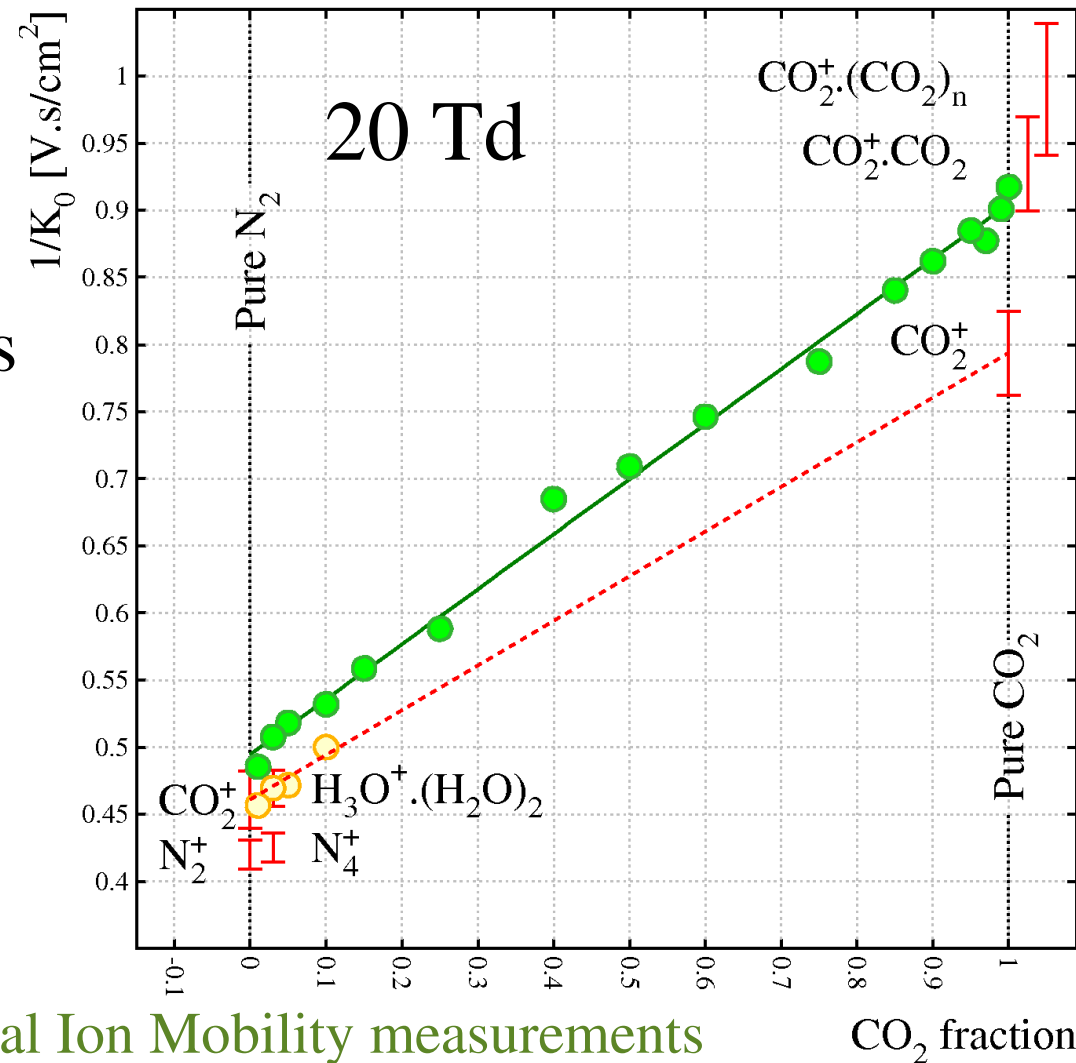
- ▶ $K_{\text{minor}} = 2.14 \text{ cm}^2/\text{V.s}$
- ▶ $K_{\text{major}} = 1.97 \text{ cm}^2/\text{V.s}$

- ▶ Identity of minor (faster) peak yet to be established.

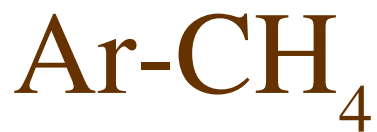


Ions drifting in $\text{CO}_2\text{-N}_2$: $E/N = 20 \text{ Td}$

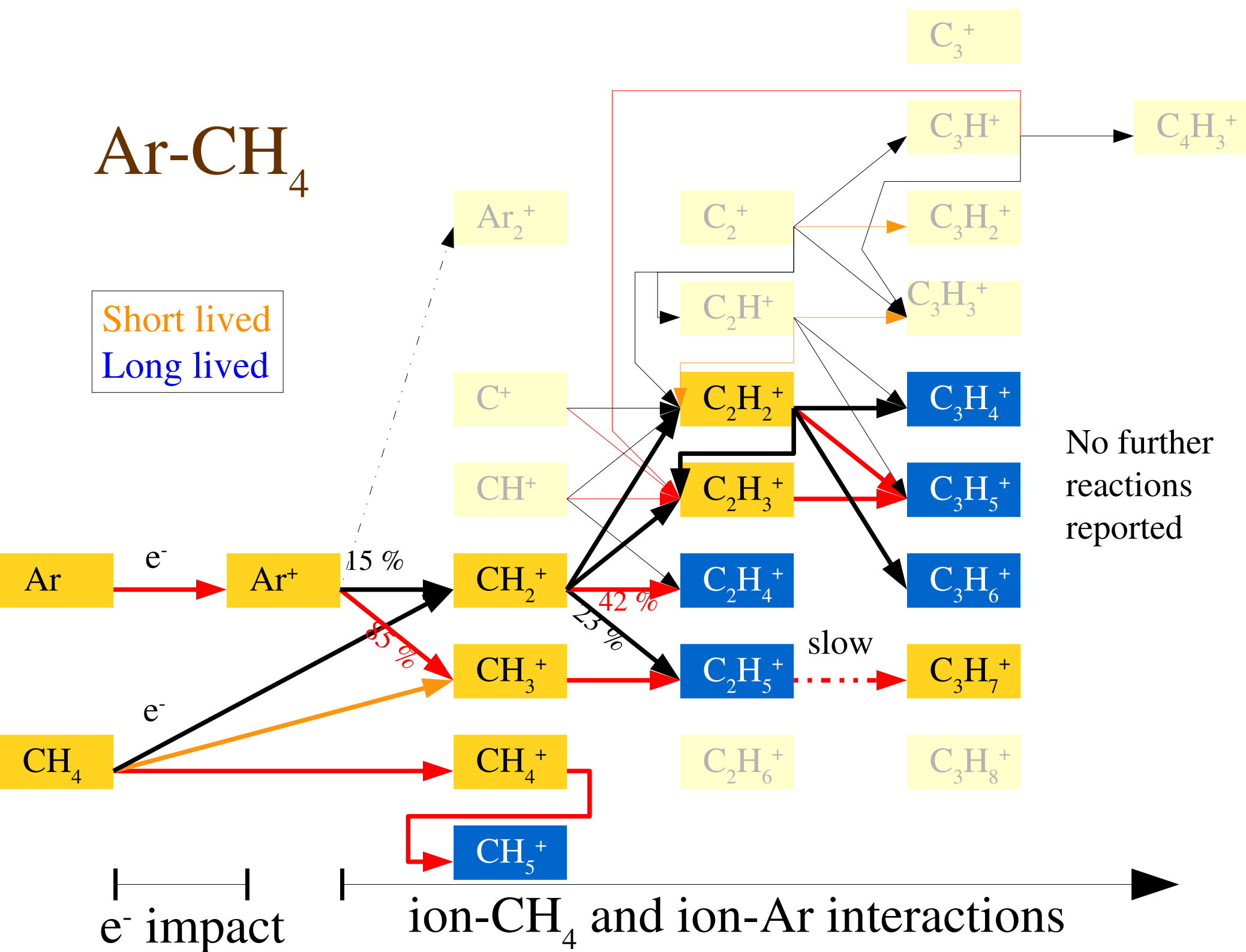
- ▶ Most ions in $\text{N}_2\text{-CO}_2$ are slower than CO_2^+ ;
- ▶ $\text{CO}_2^+\cdot\text{CO}_2$ is a candidate, as in Ar-CO_2 and Ne-CO_2 ;
- ▶ There is evidence for an additional, faster ion in nearly pure N_2 .



[A.F.V. Cortez *et al.*, "Experimental Ion Mobility measurements in Ne-CO_2 and $\text{CO}_2\text{-N}_2$ mixtures", submitted to JINST]



Short lived
Long lived



How to obtain pure-gas mobilities ?

▶ Experimental data exists for many, but not all, ion-gas pairs.

▶ Cases where a simple calculation helps:

▶ stationary gas (“ $T = 0$ K”):

$$K \propto \frac{1}{\sqrt{E}}$$

▶ thermal motion \gg effect of electric field:

K constant

▶ Using the relation between mass and mobility.

Mobility at $T = 0$ K

- ▶ Simplest model:
 - ▶ gas atoms are stationary;
 - ▶ head-on collisions only;
 - ▶ equal mass of gas and ions;
 - ▶ on colliding with gas, an ion loses all its energy.

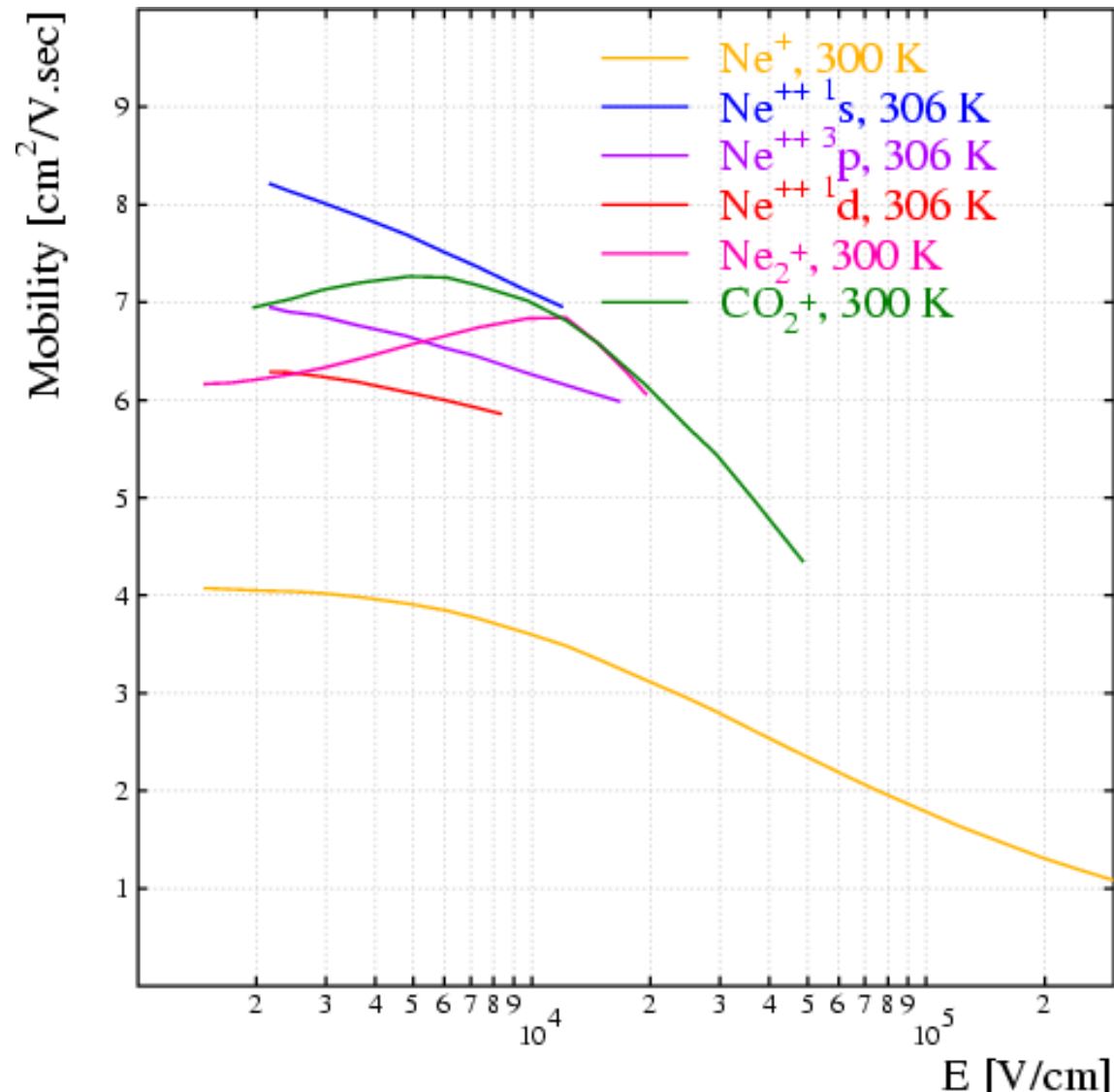
- ▶ Mobility:

$$K = \sqrt{\frac{\pi}{8}} \sqrt{\frac{q}{m N \sigma} \frac{1}{E}}$$

- ▶ Holds for larger fields. Density dependence is wrong.

Comparison with Ne data

- ▶ Mobility of Ne^+ in Ne, is constant for weak fields, becoming $1/\sqrt{E}$ at higher fields.
- ▶ Mobilities of CO_2^+ and noble gas molecular ions in their parent gas rise with E .



Weak field mobility

- ▶ Weak E field: the energy picked up by the ions from E is *much smaller* than their thermal energy: $v_{\text{ion}} = v_{\text{thermal}}$;
- ▶ A free path x has probability $e^{-x/\lambda}/\lambda$ (λ : mean free path). The ion covers the distance x in a time x/v_{thermal} during which it is moved along the E field. Average displacement:

$$d_E = \int_0^{\infty} dx \underbrace{\frac{1}{2} \frac{qE}{m}}_{\text{Acceleration}} \underbrace{\left(\frac{x}{v_{\text{thermal}}}\right)^2}_{\text{Duration}} \underbrace{\frac{e^{-x/\lambda}}{\lambda}}_{\text{Weight}} = \frac{qE\lambda^2}{m v_{\text{thermal}}^2}$$

- ▶ Mean time between collisions is $\lambda/v_{\text{thermal}}$

$$K = d_E \frac{v_{\text{thermal}}}{\lambda} \frac{1}{E} = \frac{q}{m v_{\text{thermal}} N \sigma} \dots \text{not a function of } E$$

[P. Langevin, *Annales de chimie et de physique* **28** (1903) p 334-336.

Note: there are 2 papers by P. Langevin in this volume.]

Kinetic theory

► Chapman-Enskog kinetic theory:

$$K = \frac{3\sqrt{2\pi}}{16} \frac{1}{\sqrt{k_B T}} \frac{z}{N \Omega} \sqrt{\frac{1}{m_{\text{ion}}} + \frac{1}{m_{\text{gas}}}}$$

Ion charge: force exercised by the electric field E

Temperature

Number density

Ion-gas cross section

Ion-gas reduced mass

► No dependence on the electric field !

Hard sphere approximation for Ω

- ▶ The simplest approximation consists in assuming hard sphere scattering: $\Omega = \pi (r_{\text{ion}} + r_{\text{gas}})^2$.
- ▶ For a covalent radius $r_{\text{Ar}} = r_{\text{Ar}^+} = 106$ pm, the estimated mobility is $K = 12$ cm²/V·s, to be compared with the experimental value of $K = 1.5$ cm²/V·s ...
- ▶ The effective cross section for He is nearly compatible with the van der Waals radii. The effective cross sections for Ne and Ar are up to 2.5 times larger.

[Covalent radius from Webelements]

Mass-mobility relation: Ar

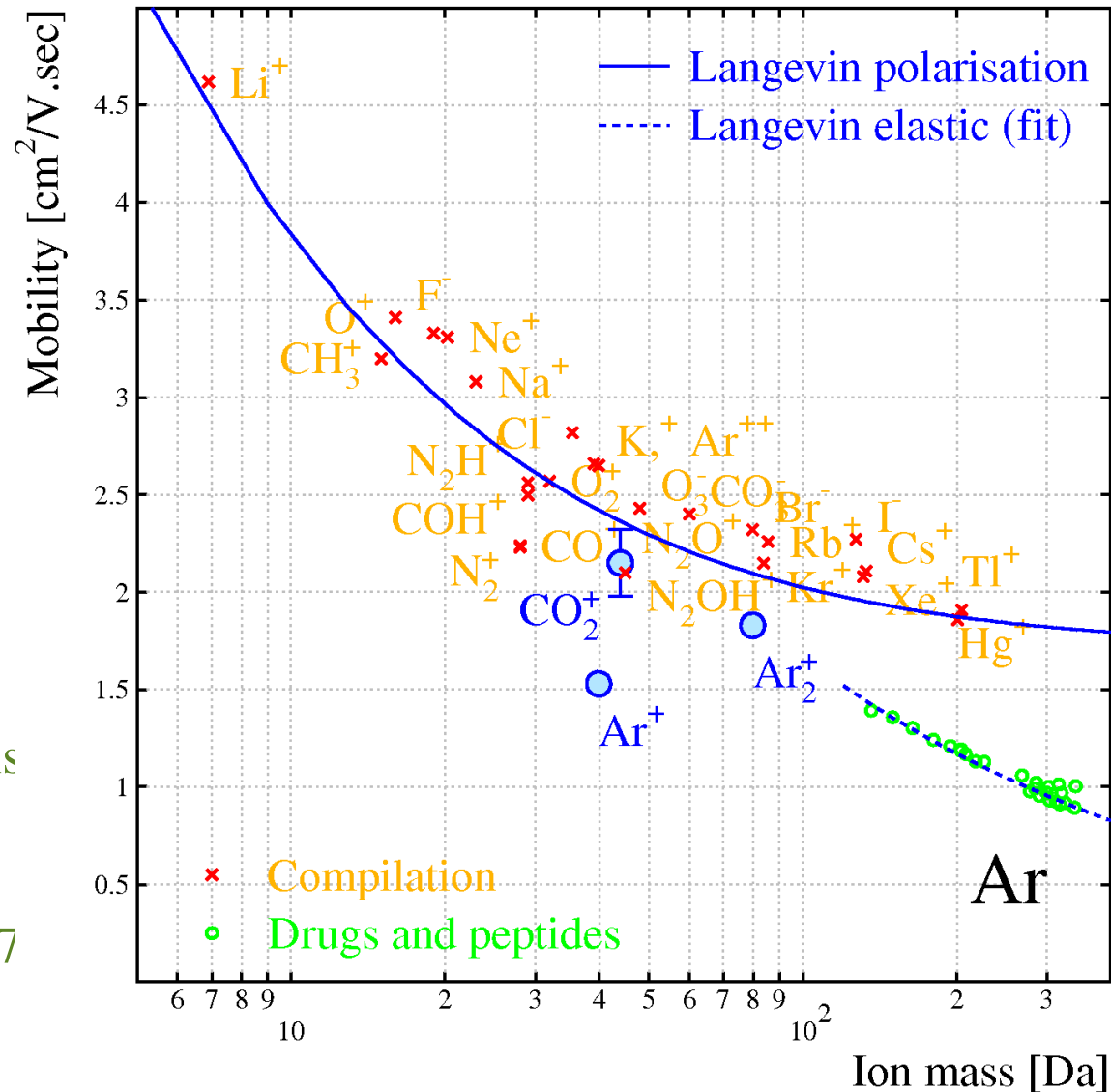
- ▶ Langevin:
 - ▶ all ions: $K \propto 1/\sqrt{\mu}$
 - ▶ polarisable: $K \propto 1/\sqrt{\alpha}$
 - ▶ large: $K \propto 1/d^2$
- ▶ Exception:
 - ▶ Noble gas ions in their parent gas: resonant charge exchange.

["Transport properties of gaseous ions over a wide energy range"]

At. Data and Nucl. Data Tables

17 (1976) 177-210, 22 (1978) 179-217

31 (1984) 113-151, 60 (1995) 37-95.]



Mobility in mixtures: Blanc's law

- ▶ Assume that the gases can be “decoupled” and drift the ion through successive layers of thickness d_i containing the various components of the mixture:

$$t_{\text{mix}} = t_1 + t_2 + \dots = \frac{d_1}{E K_1} + \frac{d_2}{E K_2} \dots = \frac{d_{\text{mix}}}{E K_{\text{mix}}}$$

- ▶ which yields Blanc's law:

$$\frac{d_{\text{mix}}}{K_{\text{mix}}} = \frac{d_1}{K_1} + \frac{d_2}{K_2} \dots$$

Blanc's law for diffusion

- ▶ J.H. Wheaton and E.A. Mason have shown that the diffusion law at low fields is similar to the mobility law:

$$\frac{d_{\text{mix}}}{D_{\text{mix}}} = \sum_i \frac{d_i}{D_i}$$

- ▶ This should not come as a surprise: at low fields, the mobility and diffusion coefficients are proportional (Einstein relation.)

How to obtain the diffusion ?

- ▶ Only few diffusion coefficients relevant for us have been measured.
- ▶ Using the relation between mass and diffusion.
- ▶ At low field, the Einstein relation between diffusion and mobility can be used:

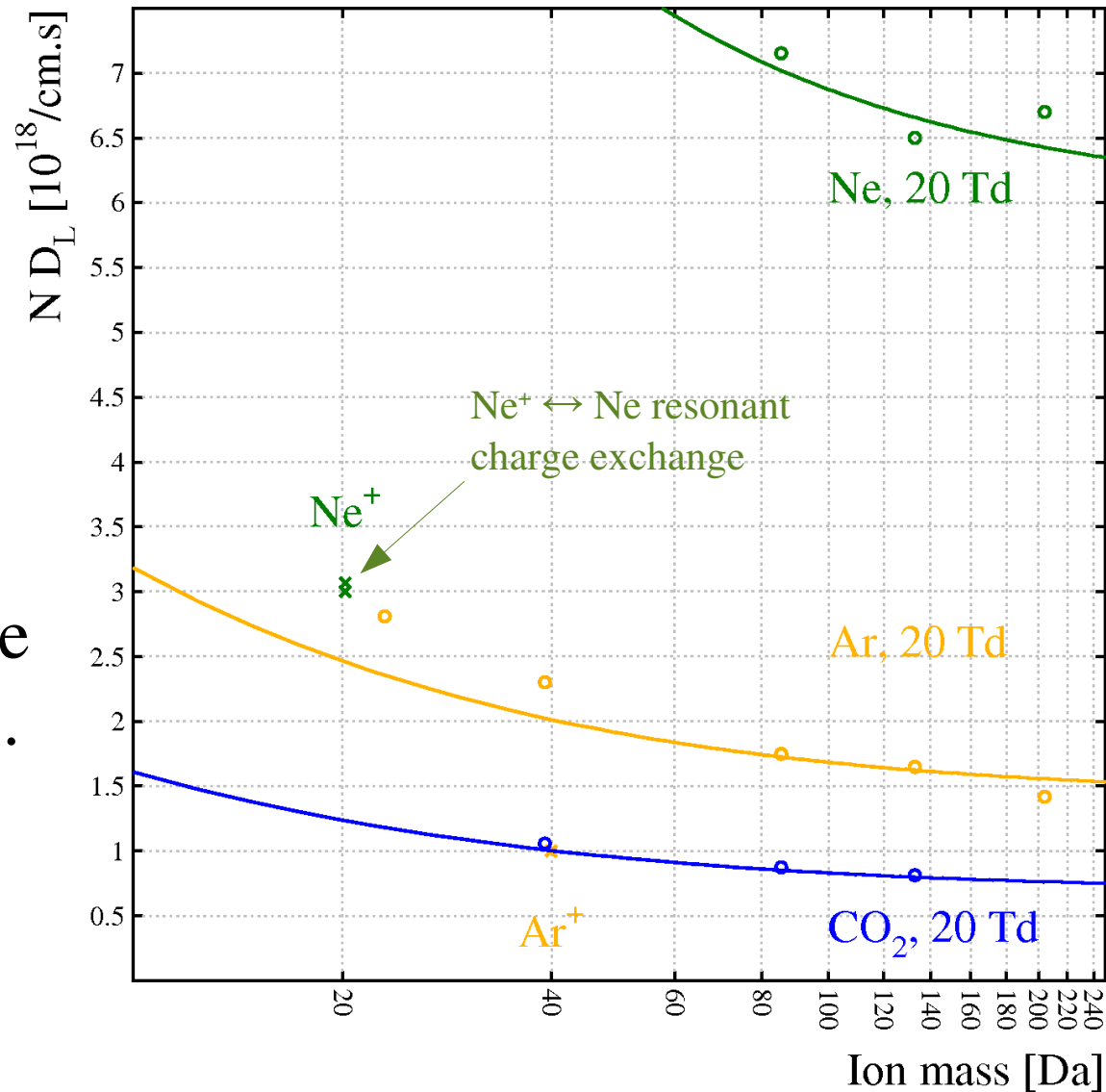
$$D \propto K \propto \frac{1}{\sqrt{E}}$$

- ▶ A generalised version extends the precision and the range of applicability.

Mass-diffusion relation

- ▶ Data: alkali metals.
- ▶ Mass dependence of diffusion coefficients is reminiscent of mass-mobility relation.
- ▶ Effect of resonant charge exchange in noble gases.

["Transport properties of gaseous ions over a wide energy range"
At. Data and Nucl. Data Tables
17 (1976) 177-210, **22** (1978) 179-217,
31 (1984) 113-151, **60** (1995) 37-95.]



E : electric field
 k_B : Boltzmann constant
 T : temperature
 D : diffusion coefficient
 σ : spatial diffusion
 K : mobility of the ion
 q : charge of the ion

Thermal diffusion

- ▶ Einstein equation [1905]. The equation is also named after Walther Nernst [1888], John Sealy Townsend [1900], William Sutherland [1905], Marian Smoluchowski [1906] and probably others. Earlier workers noted the proportionality of D and K in liquids.

$$K = \frac{qD}{k_B T}$$

- ▶ Only for E -fields so low that the ions are thermal.
- ▶ Diffusion in terms of σ is the same for all gases !

$$\sigma_{\text{diff}} = \sqrt{\frac{2D}{v_D}} = \sqrt{\frac{2D}{KE}} = \sqrt{\frac{2k_B T}{qE}}$$

Generalised Einstein equations

- ▶ Start from Gregory Wannier's (1953) proposal:

$$D_{\parallel} = \frac{d v_D}{d a} \overline{(v - v_D)^2}, \quad a = \frac{q E}{m}, \quad v_D = K E$$

- ▶ evaluate the derivative of v_D to E :

$$\frac{d v_D}{d a} = \frac{m}{q} \frac{d K E}{d E} = \frac{m}{q} \left(E \frac{d K}{d E} + K \right) = \frac{m K}{q} \left(\frac{E}{K} \frac{d K}{d E} + 1 \right)$$

- ▶ and recall the definition of longitudinal temperature:

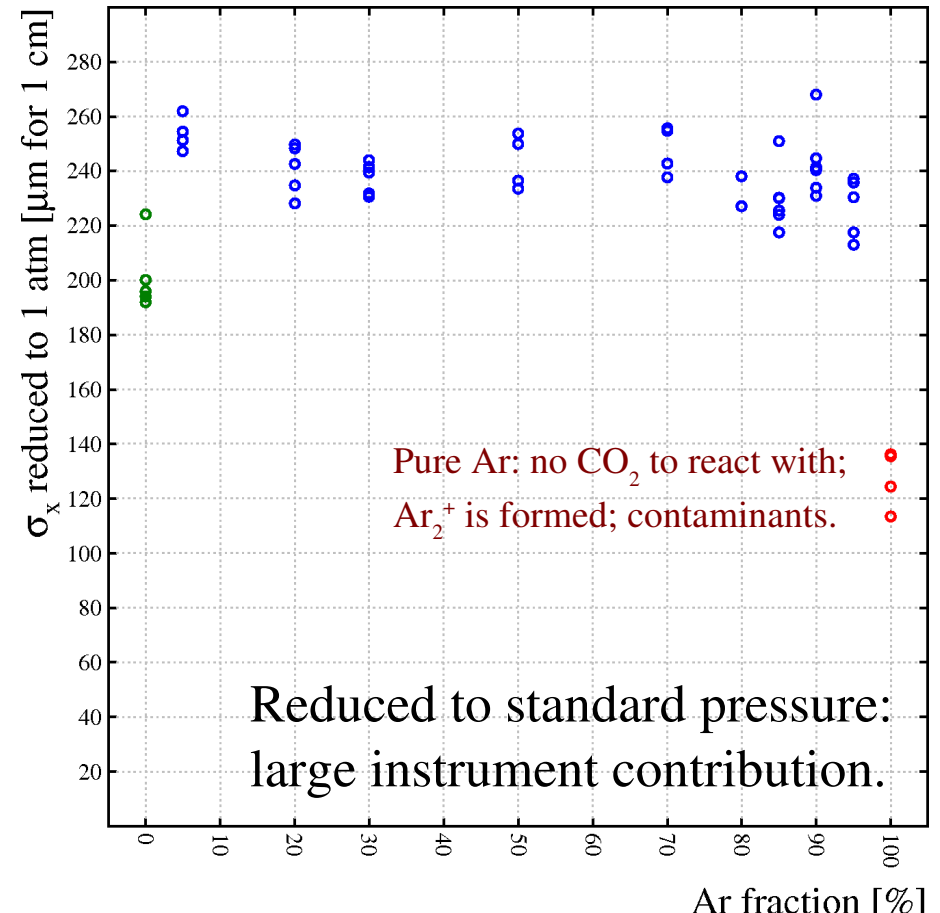
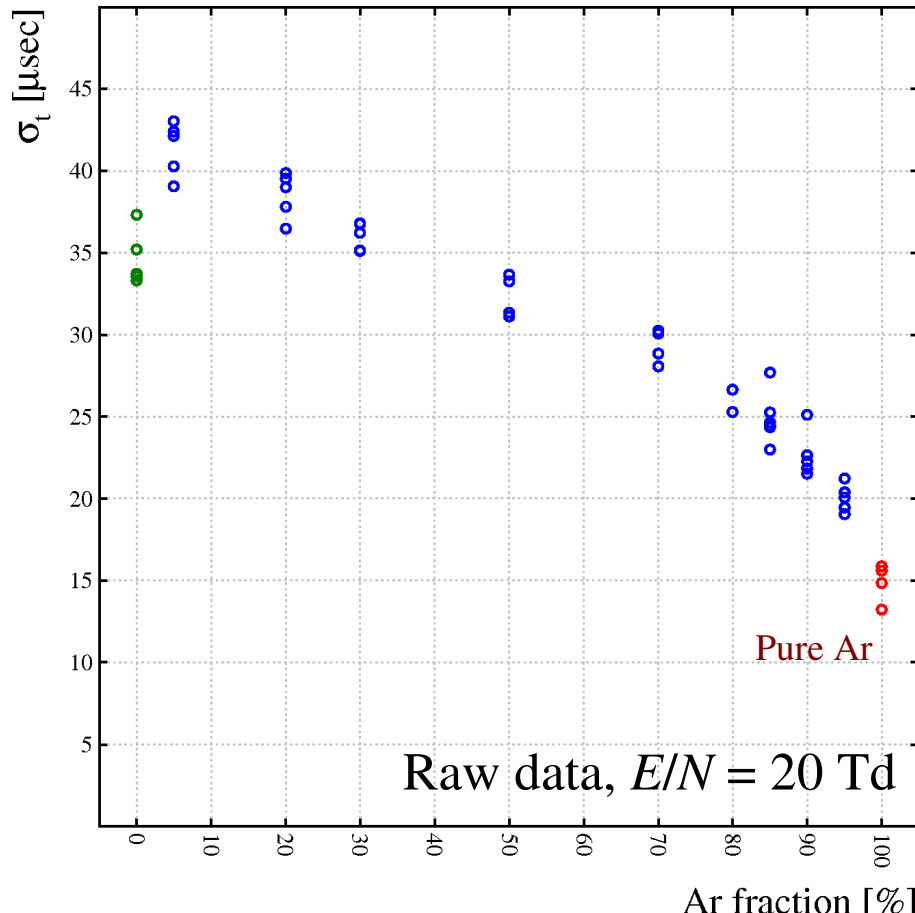
$$\frac{1}{2} k_B T_{\parallel} = \frac{1}{2} m \overline{(v - v_D)^2}$$

- ▶ to obtain the expression for the diffusion:

$$D_{\parallel} = \frac{m K}{q} \left(\frac{E}{K} \frac{d K}{d E} + 1 \right) \frac{k_B T_{\parallel}}{m}, \quad \frac{D_{\parallel}}{K} = \frac{k_B T_{\parallel}}{q} \left(1 + \frac{d \log K}{d \log E} \right)$$

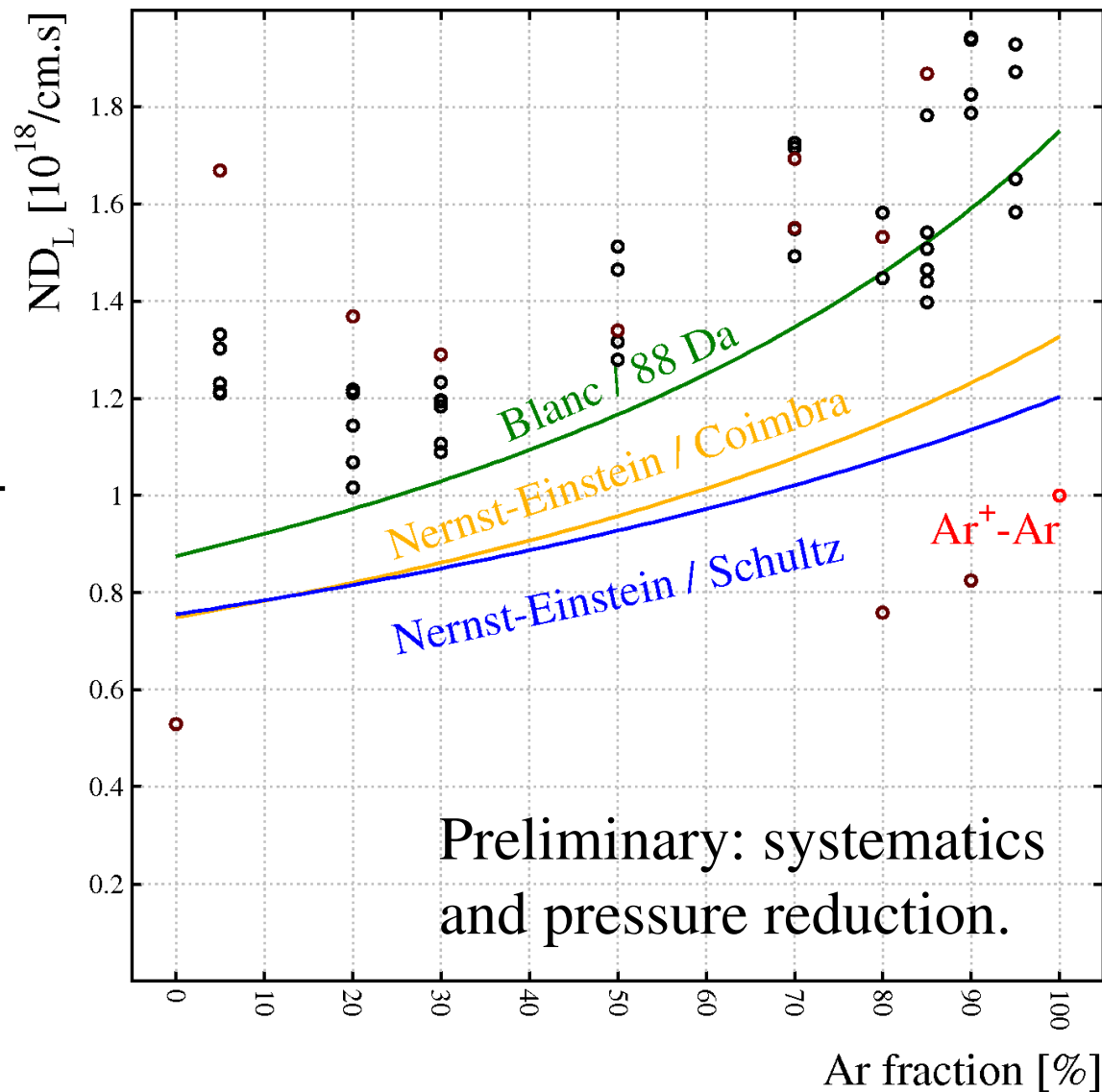
Arrival time spread in Ar-CO₂: Coimbra

- Higher Ar fractions lead to faster ion transport and a correspondingly smaller arrival time spread.



Diffusion coefficient in Ar-CO₂

- ▶ Mass-diffusion relation for 88 Da (CO₂⁺•CO₂) 25 % lower than data.
- ▶ Einstein relation using mobility from Schultz + Coimbra data: 40 %.
- ▶ Likely due to poor understanding of instrument effects.



Conclusions

- ▶ Alkane ions, noble gas ions and CO_2^+ react with the carrier gas to form molecular ions and cluster ions.
- ▶ Measurements of the ion mobility in Ar- CO_2 , Ne- CO_2 and N₂- CO_2 mixtures show that the ions are compatible with being heavier objects.
- ▶ Measurements of ion diffusion are scarce. LIP-Coimbra is working to fill the gap. Initial data is, within error bars, consistent with other measurements and theory, but systematics remain to be understood.

Spares

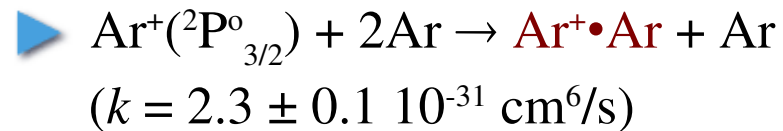
Situating cluster ions

- ▶ 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]

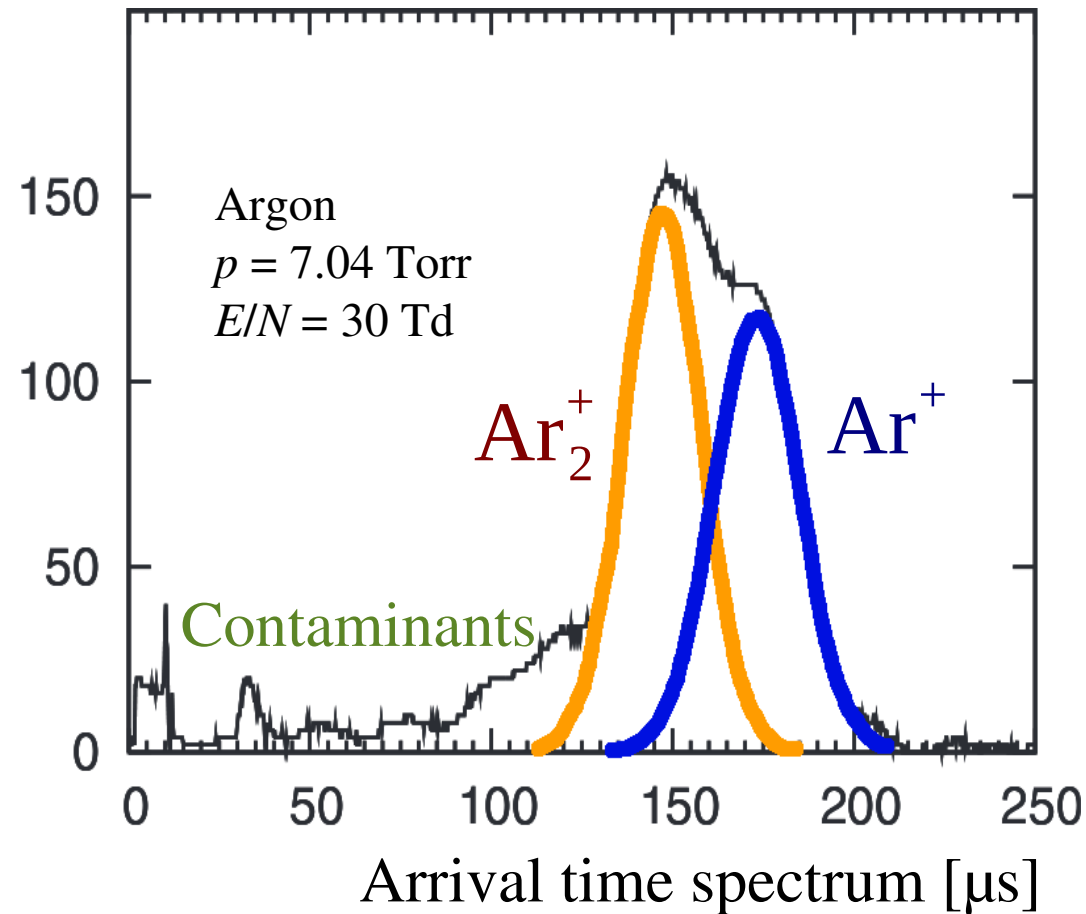
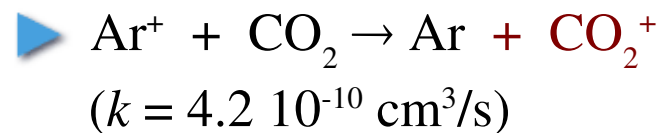
Ions drifting in pure Ar

▶ In pure argon, dimers are formed:



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

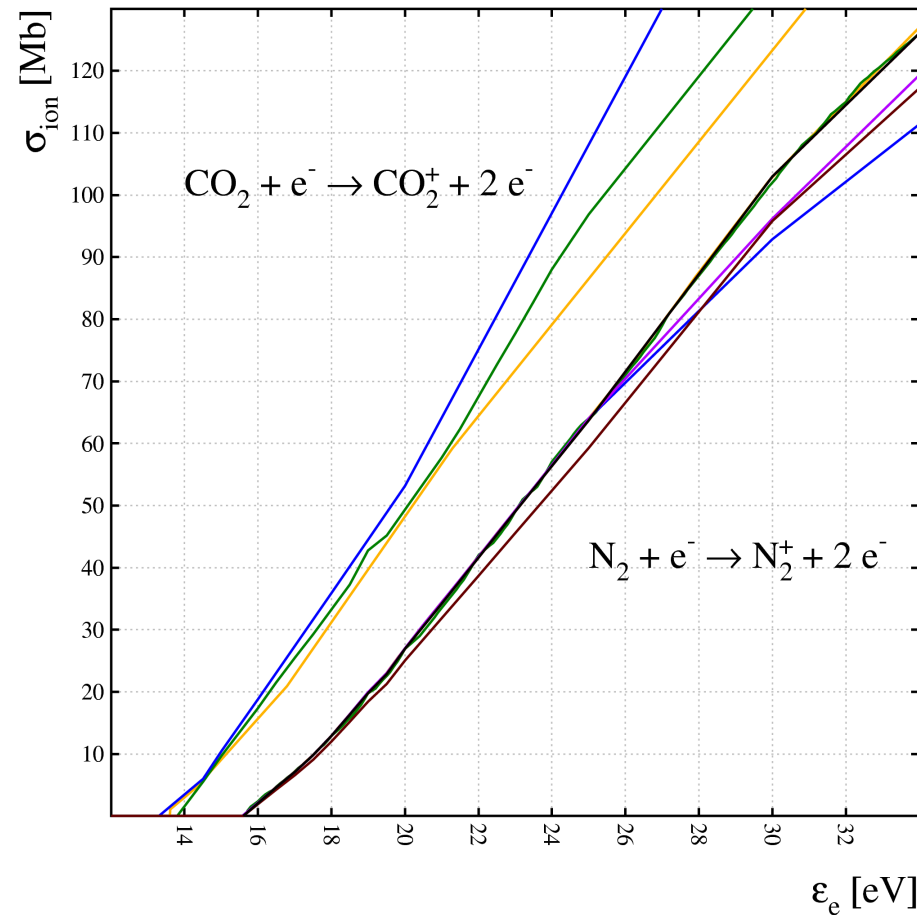
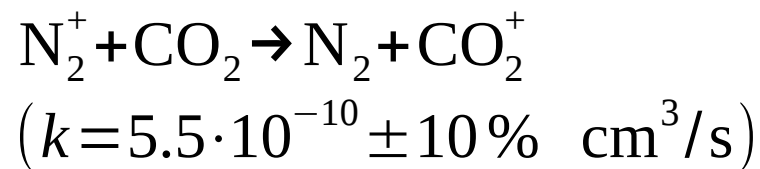
▶ In mixtures, charge exchange dominates:



Electron impact ionisation in N₂-CO₂

▶ CO₂ has a lower IP (13.8 eV) than N₂ (15.6 eV) and a higher ionisation cross section.

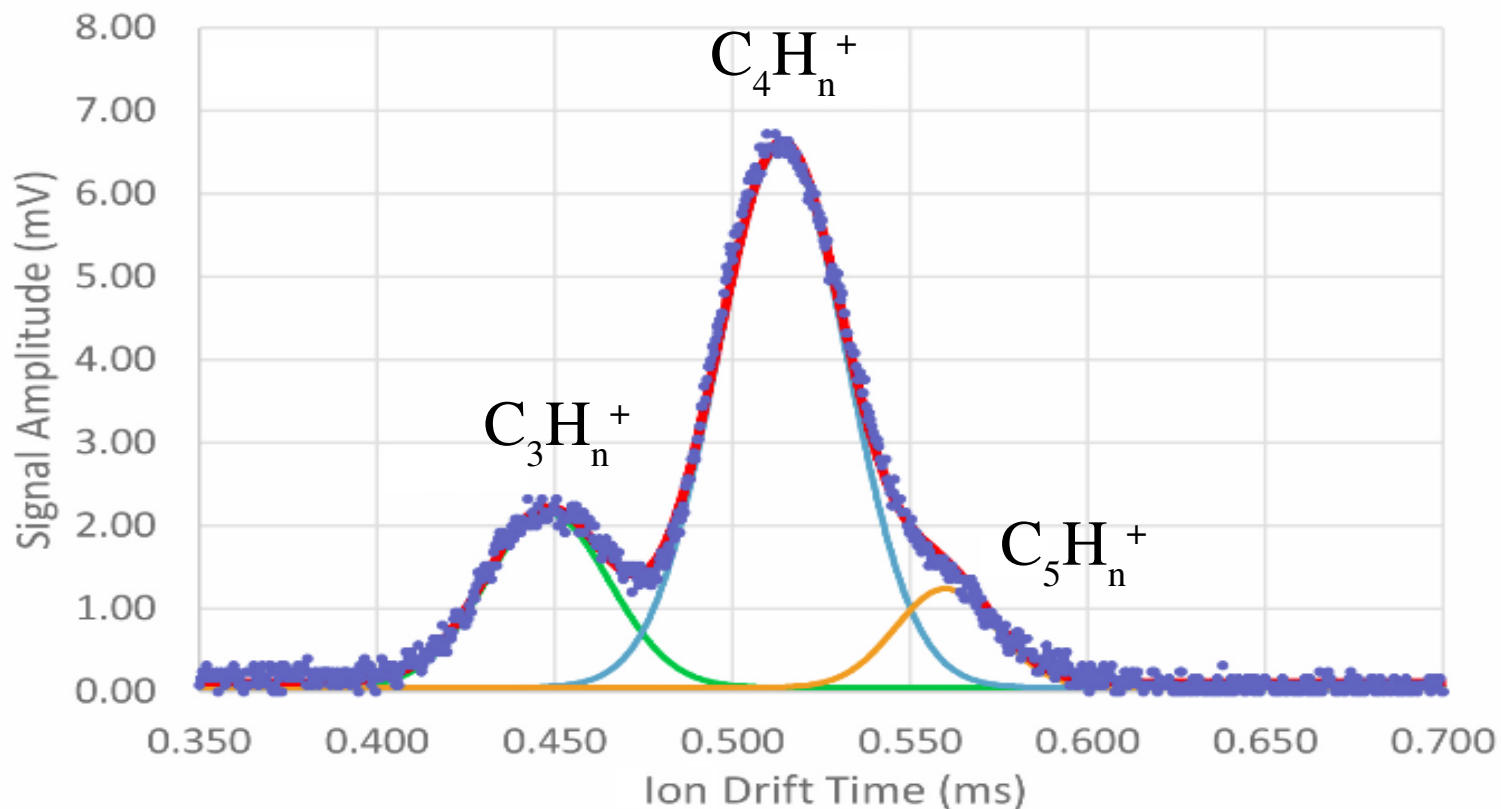
▶ N₂⁺ transfers its charge to CO₂:



[www.lxcat.net, retrieved on September 28th 2015,
see paper for detailed database references;
VG Anicich and WT Huntress Jr., 10.1086/191151]

Alkane ion reactions

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



Potential energy: induced dipoles

- ▶ Electric field due to a point charge: $E = q/r^2$
- ▶ Induced dipole: $\mu_{\text{ind}} = \alpha E = \alpha q/r^2$
- ▶ Point charge – induced dipole: $U = \mu_{\text{ind}} q/r^2 = \alpha q^2/r^4$

- ▶ Electric field due to a dipole: $E = \mu/r^3$
- ▶ Induced dipole: $\mu_{\text{ind}} = \alpha E = \alpha \mu/r^3$
- ▶ Permanent dipole - induced dipole: $U = \mu_{\text{ind}} \mu/r^3 = \alpha \mu^2/r^6$

- ▶ Induced dipoles are necessarily aligned with the permanent dipoles that create them.

- ▶ In the above numeric factors, signs and $1/4\pi\epsilon_0$ have been left out.

Polarisability – examples

Gas	Polarisability
He	0.2/0.208
Ne	0.4/0.381
Ar	1.63/1.664
N ₂	1.72/1.710
CH ₄	2.600/2.448
C ₂ H ₆	4.470/4.226
C ₃ H ₈	6.290/5.921
<i>n</i> -C ₄ H ₁₀	8.200
CO ₂	2.507
CF ₄	2.590
C ₂ F ₆	4.430

[Mostly from http://openmopac.net/Polarizability_table.html
<http://cccbdb.nist.gov/polcalccomp2.asp?method=3&basis=4>]

Dipole forces

- ▶ Dipole forces tend to be attractive. Induced dipoles are always aligned and hence attractive.
- ▶ Permanent dipoles have no fixed orientation. Forces can due to heat momentarily be repulsive. Except for water, none of our gases has a permanent dipole moment.
- ▶ Illustrated by the higher boiling point of polar liquids.

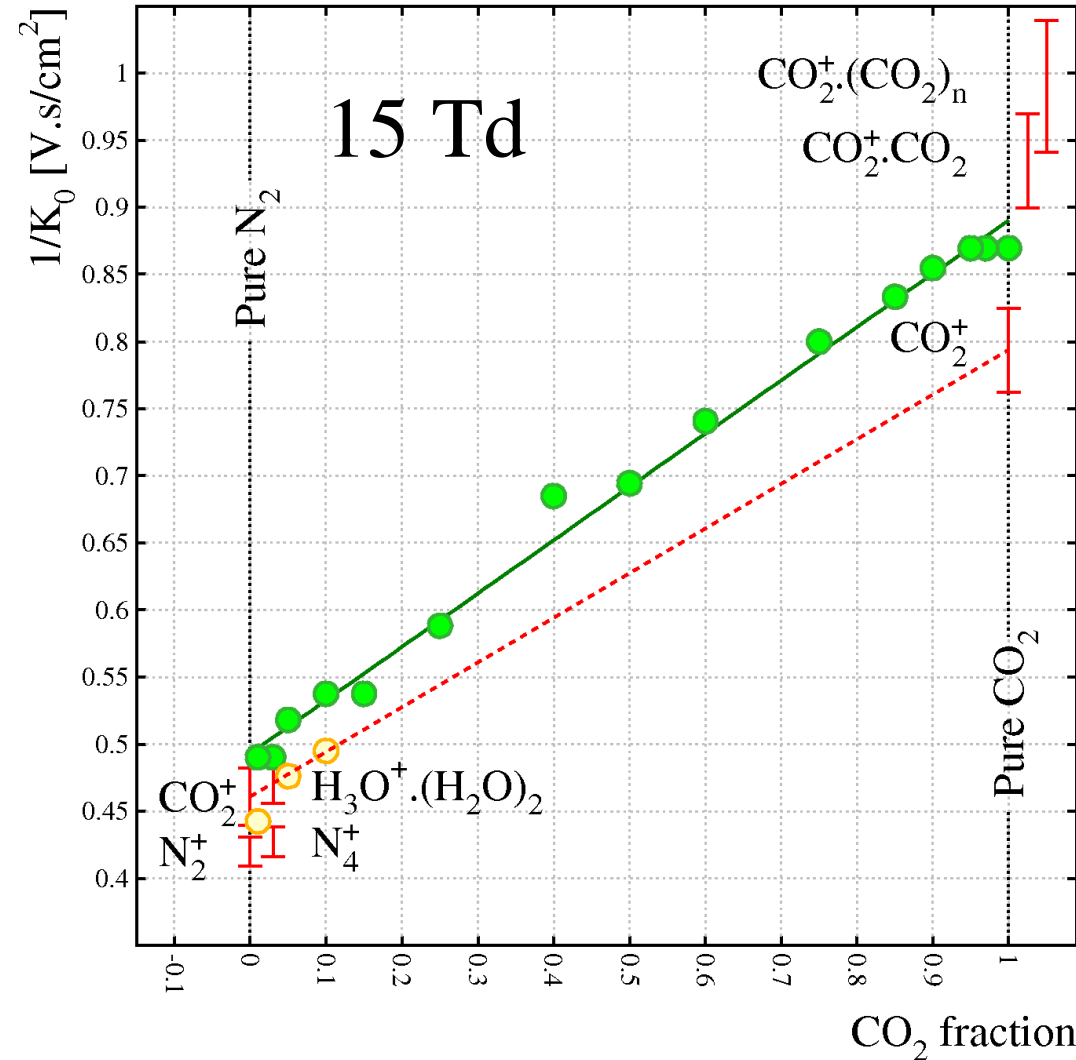
Ions drifting in $\text{CO}_2\text{-N}_2$: $E/N = 15 \text{ Td}$

▶ Reference mobilities in CO_2 :

- ▶ CO_2^+ 1.26 ± 0.05
- ▶ $\text{CO}_2^+\cdot\text{CO}_2$ 1.07 ± 0.04
- ▶ N_2^+ in CO_2 : charge exchange

▶ Mobilities in N_2 :

- ▶ $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ 2.28 ± 0.1 (15 Td)
- ▶ $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ 2.27 ± 0.1 (20 Td)
- ▶ $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$ 2.13 ± 0.1
- ▶ CO_2^+ 2.17 ± 0.1
- ▶ N_2^+ $2.38 \pm ?$
- ▶ N_4^+ 2.34 ± 0.06 (15 Td)
- ▶ N_4^+ 2.35 ± 0.06 (20 Td)



Mobility in weak electric fields

- ▶ Model assumptions:
 - ▶ the ion, like the gas, is in random *thermal motion*;
 - ▶ weak E field: the energy picked up by the ions from E is *much smaller* than their thermal energy: $v_{\text{ion}} = v_{\text{thermal}}$;
 - ▶ gas and ions have equal mass m ;
 - ▶ on colliding with gas, an ion loses all its energy.
- ▶ Applicable ?
 - ▶ thermal energy at stp: ~ 30 meV,
 - ▶ mean free path: ~ 2 μm .
 - ▶ i.e. $E < 150$ V/cm.

Weak field mobility – accurate ?

- ▶ Inserting the thermal velocity and re-arranging:

$$K = \sqrt{\frac{\pi}{8}} \frac{1}{\sqrt{k_B T}} \frac{q}{N \sigma} \frac{1}{\sqrt{m}}, \quad v_{\text{thermal}} = \sqrt{\frac{8 k_B T}{m \pi}}$$

- ▶ How accurate ?
 - ▶ Temperature dependence, density dependence, mass dependence and electric field dependence are correct (for weak fields).
 - ▶ The numerical factor 0.63 differs by 6 % from the one in the Chapman-Enskog equation 0.66 (see following slides).
 - ▶ Otherwise, it is the kinetic theory expression .

More careful averaging ...

- ▶ Start at stand-still and travel a free path x :

- ▶ time and mean velocity: $x = \frac{1}{2} \frac{qE}{m} \tau^2, \quad v = x/\tau = \sqrt{\frac{qEx}{2m}}$

- ▶ probability free path x : $P(x) = e^{-x/\lambda} / \lambda$

- ▶ average over free paths:
$$\bar{v} = \int_0^{\infty} dx \sqrt{\frac{qEx}{2m}} \frac{e^{-x/\lambda}}{\lambda}$$
$$= \sqrt{\frac{\pi}{8} \frac{qE\lambda}{m}}, \quad \lambda = \frac{1}{N\sigma}$$

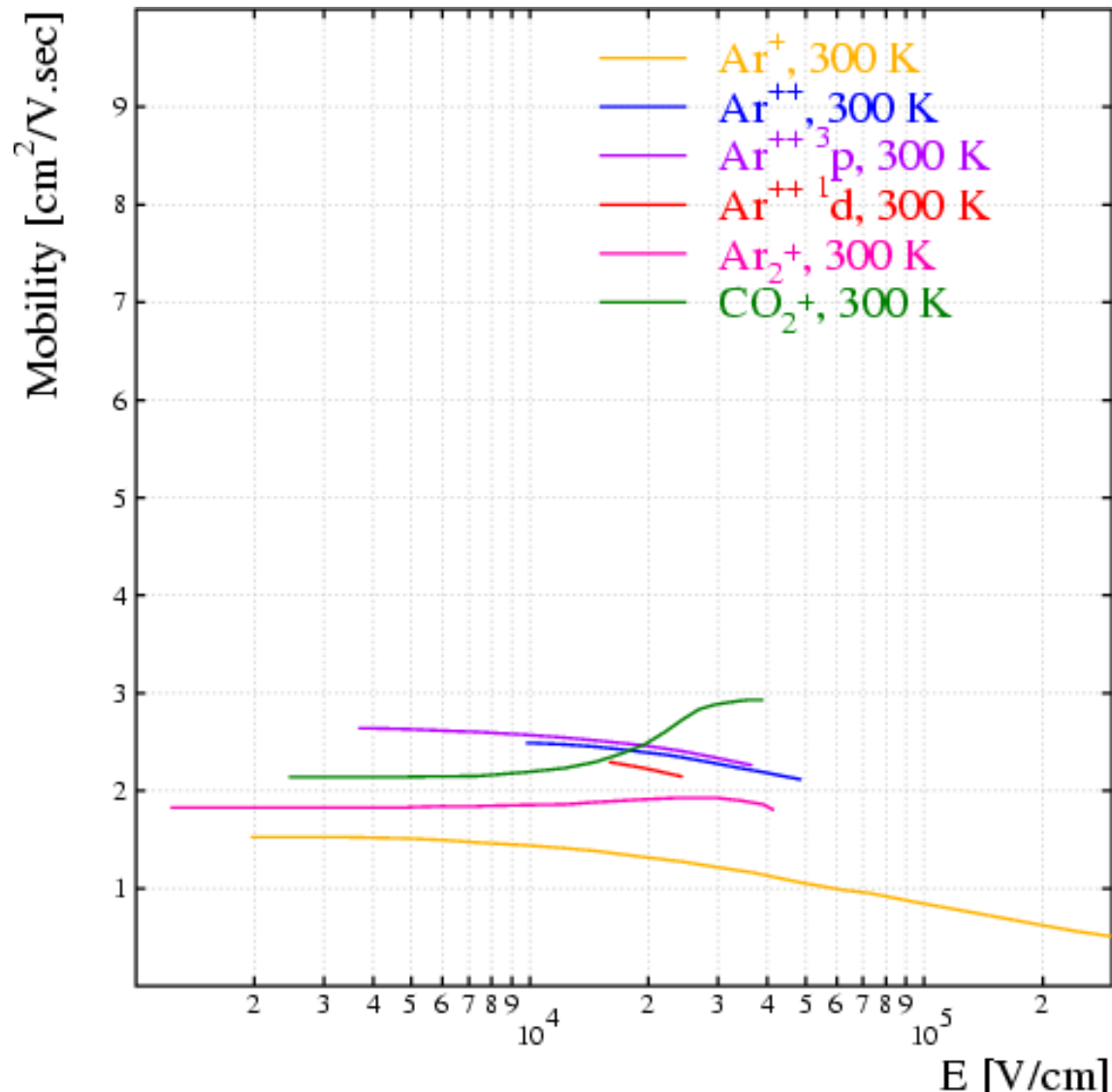
- ▶ mobility:

$$K = \sqrt{\frac{\pi}{8}} \sqrt{\frac{q}{mN\sigma} \frac{1}{E}}$$

- ▶ The ion stops on collision and the cycle restarts ...

Comparison with Ar data

- ▶ There are several things wrong with this model:
 - ▶ $K \propto 1/\sqrt{E}$ holds for large E – but K is constant at low E .
 - ▶ In reality $K \propto 1/N$, not $K \propto 1/\sqrt{N}$.
 - ▶ K is not independent of T but scales in $1/\sqrt{T}$.



$\Omega^{(1,1)}$ [10^{-16} cm²] tabulated for noble gases

	He	Ne	Ar	Kr	Xe
He ⁺	73.4				
Ne ⁺	28.8/30.2*	82.5	88.7 *		
Ar ⁺	27.1	only 77 K	157		
Kr ⁺	29.4/29.0*	-	~94 +	~190 +	
Xe ⁺	32.9 *	44.6	93.2 *	-	~245 +

At $T = T_{\text{eff}} = 300$ K except when marked * (294 K) or + (extrapolated).

Comparison with van der Waals radii

- ▶ The cross section for ions in their parent gas is approximately 2 times larger.
- ▶ The effective cross section for He is nearly compatible with the van der Waals radii. The effective cross sections for Ne and Ar are up to 2.5 times larger.

$\Omega^{(1,1)}$ / van der Waals cross section

	He	Ne	Ar	Kr	Xe
He ⁺	2.98				
Ne ⁺	1.09	2.77	2.41		
Ar ⁺	0.80	-	3.53		
Kr ⁺	0.79	-	1.97	3.79	
Xe ⁺	0.83	1.04	1.82	-	4.18

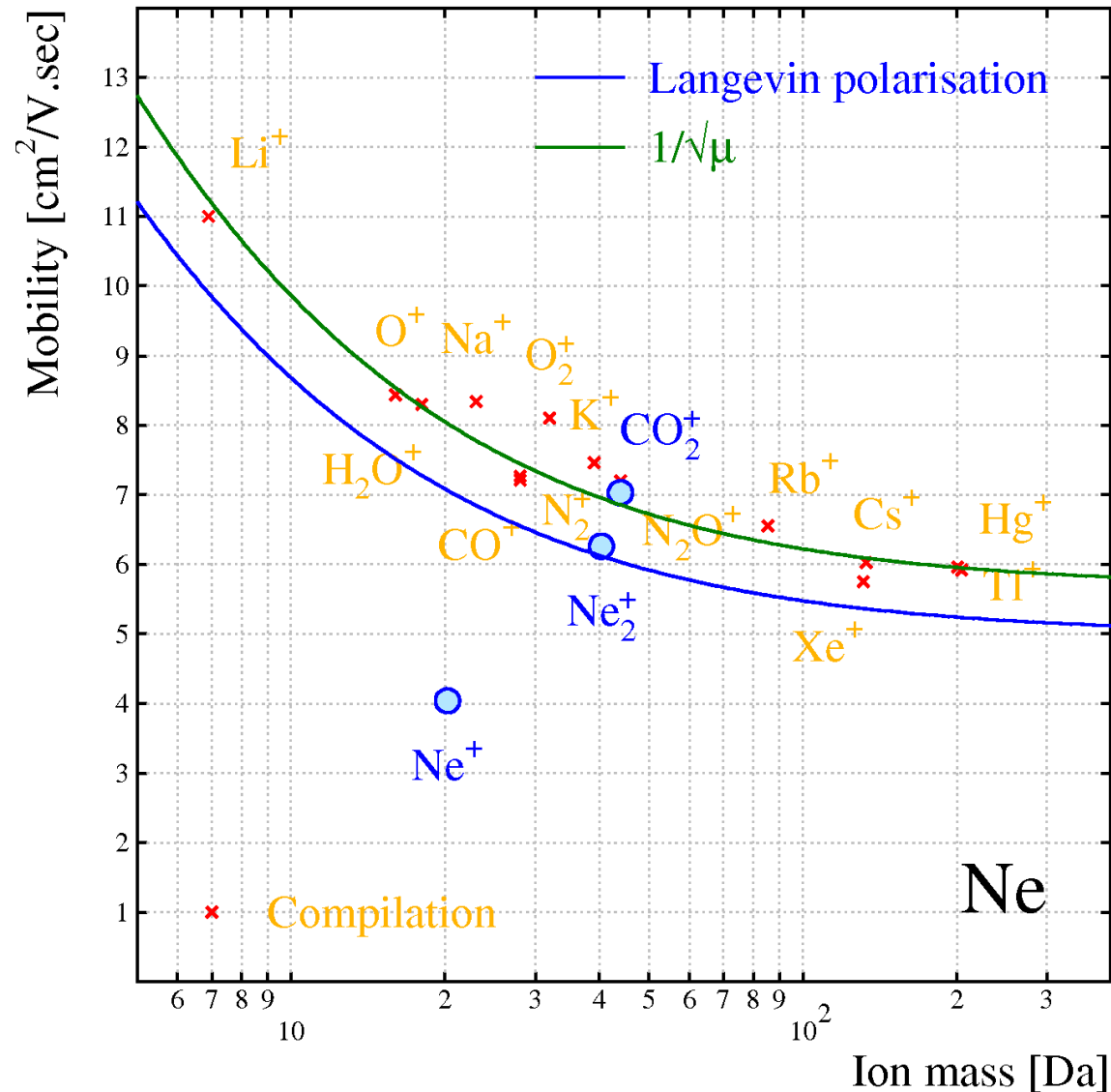
At $T = T_{\text{eff}} = 300$ K except when marked * (294 K) or + (extrapolated).

Cross section modifications

- ▶ In some polarisable gases, ions tend to be surrounded by clusters of gas molecules. This increased the effective mass and the effective diameter of the ions.
- ▶ In the proximity of an ion, most gases – also those without permanent dipole – will have an induced dipole. This results in an attractive force which increases the cross section.

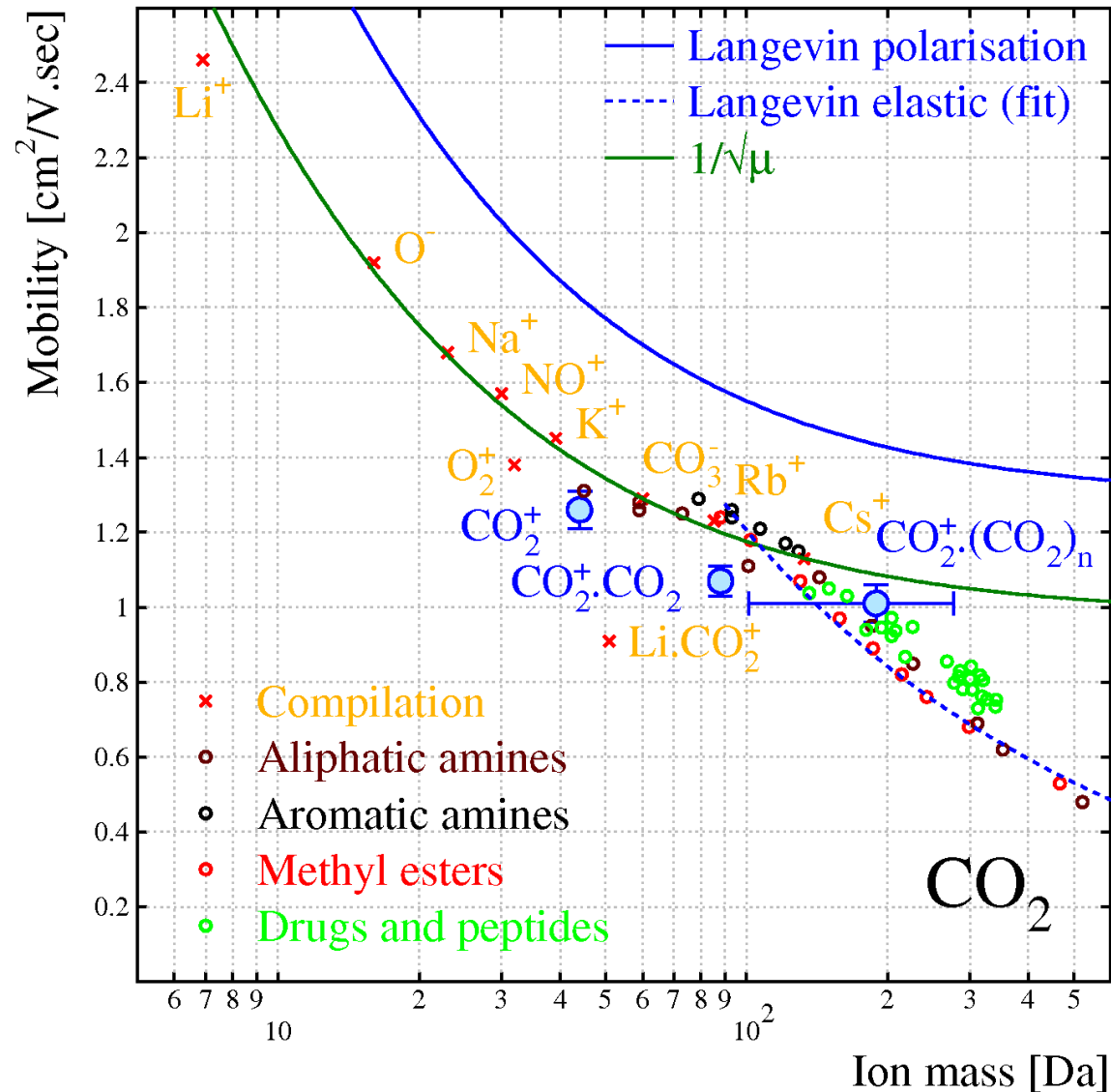
Mass-mobility relation: Ne

- ▶ Langevin polarisation underestimates K in the case of Ne.

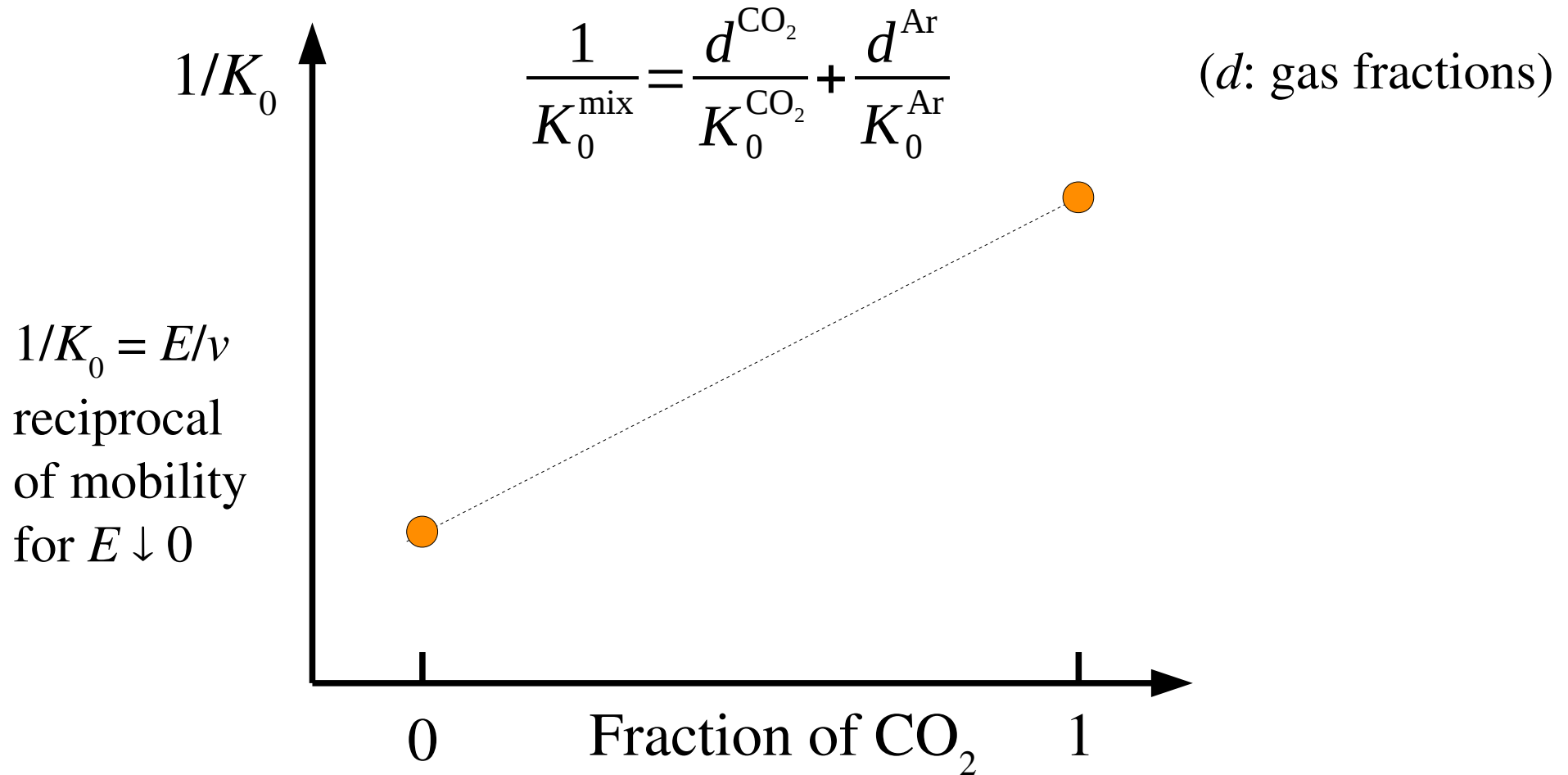


Mass-mobility relation: CO₂

- ▶ Langevin polarisation overestimates K in the case of CO₂.
- ▶ CO₂⁺ in CO₂ follows the trend of foreign molecules.



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](https://doi.org/10.1051/jphystap:019080070082501)]

Blanc's law for diffusion: a naive try

- ▶ Tempting to try the decoupling approach for diffusion:
 - ▶ Gas layer i has thickness: d_i , time needed to traverse: t_i
 - ▶ Diffusion in space and time in this gas layer:

$$\sigma_i^x = \sqrt{2 D_i t_i} \quad \sigma_i^t = \frac{\sqrt{2 D_i t_i}}{E K_i} = \frac{\sqrt{2 D_i d_i}}{(E K_i)^{3/2}}$$

- ▶ Summing the layers:

$$\sigma_{\text{mix}}^t = \sum_i \frac{2 D_i d_i}{(E K_i)^3} = \frac{2}{E^3} \sum_i d_i \frac{D_i}{K_i^3}$$

- ▶ Hence, the sum rule would be:

$$d \frac{D_{\text{mix}}}{K_{\text{mix}}^3} = \sum_i d_i \frac{D_i}{K_i^3}$$

- ▶ But ...

Diffusion: link between D and σ_{diff}

- ▶ Flow equation (Fick):

$$u_t = D u_{xx}$$

- ▶ Insert in flow equation:

$$\sigma_t(t) = D / \sigma(t)$$

- ▶ Solve:

$$\sigma(t) = \sqrt{2Dt}$$

- ▶ Growing Gaussian cloud with spatial size $\sigma(t)$:

$$u(t, x) = \frac{1}{\sqrt{2\pi}\sigma(t)} e^{-\frac{1}{2} \frac{x^2}{\sigma(t)^2}}$$

- ▶ Replace time dependence by position, via velocity:

$$r = v_D t$$

$$\sigma(r) = \sigma_{\text{diff}} \sqrt{r}, \quad \sigma_{\text{diff}} = \sqrt{2D/v_D}$$

- ▶ Dimensions:

$$[D] = \text{length}^2 \text{time}^{-1}$$

$$[\sigma_{\text{diff}}] = \sqrt{\text{length}}$$

Wannier's diffusion proposal

- ▶ Gregory Wannier suggested in 1953:

$$D_{\parallel} = \frac{d v_D}{d a} \text{RMS}(v - v_D), \quad a = \frac{q E}{m}, \quad v_D = K E$$

- ▶ The proportionality with $\text{RMS}(v - v_D)$ is plausible.
- ▶ If dv_D/dE is large, then any increase of E leads to a large increase of v_D . This implies a large mfp and hence large diffusion. Conversely, at low dv_D/dE , even a large E field barely manages to accelerate ions, typical for low diffusion.
- ▶ Probably inspired by dimensional arguments.

E : electric field

K : mobility of the ion

D : diffusion coefficient

k_B : Boltzmann constant

T : temperature

λ : mean free path

Einstein equation

m : mass of a gas atom

q : charge of the ion

τ : time to travel free path

v : (mean) velocity

- ▶ A priori, it is surprising there would be a relation between the mobility – driven by the electric field - and the diffusion coefficient – driven by temperature.

- ▶ Recall kinetic energy; mobility K ; and relation between mean free path λ , collision time τ and velocity v :

$$\frac{3}{2} k_B T = \frac{1}{2} m \bar{v}^2 \quad v = \frac{q E}{m} \tau, \quad K = \frac{q \tau}{m}$$

- ▶ With some debatable juggling:

$$\lambda = \bar{v} \tau$$

$$\frac{k_B T}{q} K = \frac{m \bar{v}^2}{q} \frac{q \tau}{m} = \bar{v}^2 \tau = \lambda \bar{v} = D$$

Einstein-Smoluchowski
except for factor of 2

- ▶ Trick: v (thermal motion) and τ (mobility) are related via λ .

Recovering the Einstein relation

▶ Simplifying assumptions:

▶ v_D may be neglected in $\text{RMS}(v v_D)$,

▶ mobility K does not depend on E ,

$$v_D = K E, \quad a = \frac{q E}{m} \quad \rightarrow$$

▶ equate $\text{RMS}(v)$ and energy:

$$\frac{1}{2} m \overline{v^2} = \frac{1}{2} k_B T \quad \rightarrow$$

$$D_{\parallel} = \frac{d v_D}{d a} \overline{(v - v_D)^2}$$

↓

$$D_{\parallel} = \frac{m K}{q} \overline{v^2}$$

↓

$$D_{\parallel} = K \frac{k_B T}{q}$$

▶ Valid if:

▶ drift velocity \ll instantaneous ion velocity

▶ drift velocity does not contribute to ion energy;

▶ mobility independent of E .

Longitudinal moments & temperature

- ▶ The 1st longitudinal moment is the drift velocity: v_D

$$\bar{v} = v_D$$

- ▶ The 2nd moment is the mean velocity² relative to v_D .

$$\text{RMS}(v) = \overline{(v - v_D)^2} = \bar{v}^2 - 2\bar{v}v_D + v_D^2 = \bar{v}^2 - v_D^2$$

- ▶ Similar to the kinetic energy of an ion, $k_B T = \frac{1}{2} m v^2$, we can define a longitudinal energy and temperature T_{\parallel} :

$$\frac{1}{2} k_B T_{\parallel} = \frac{1}{2} m \overline{(v - v_D)^2}$$

Transverse moments & temperature

▶ There is no net transverse motion, hence the 1st transverse moment vanishes.

▶ The 2nd moment is the mean velocity².

$$\text{RMS}(v) = \sqrt{\overline{v^2}}$$

▶ Analogously to T_{\parallel} we can introduce a transverse energy and temperature T_{\perp} :

$$\frac{1}{2} k_{\text{B}} T_{\perp} = \frac{1}{2} m \overline{v^2}$$