Ion mobility in Neon-based mixtures

Dezső Varga
Wigner RCP, Budapest

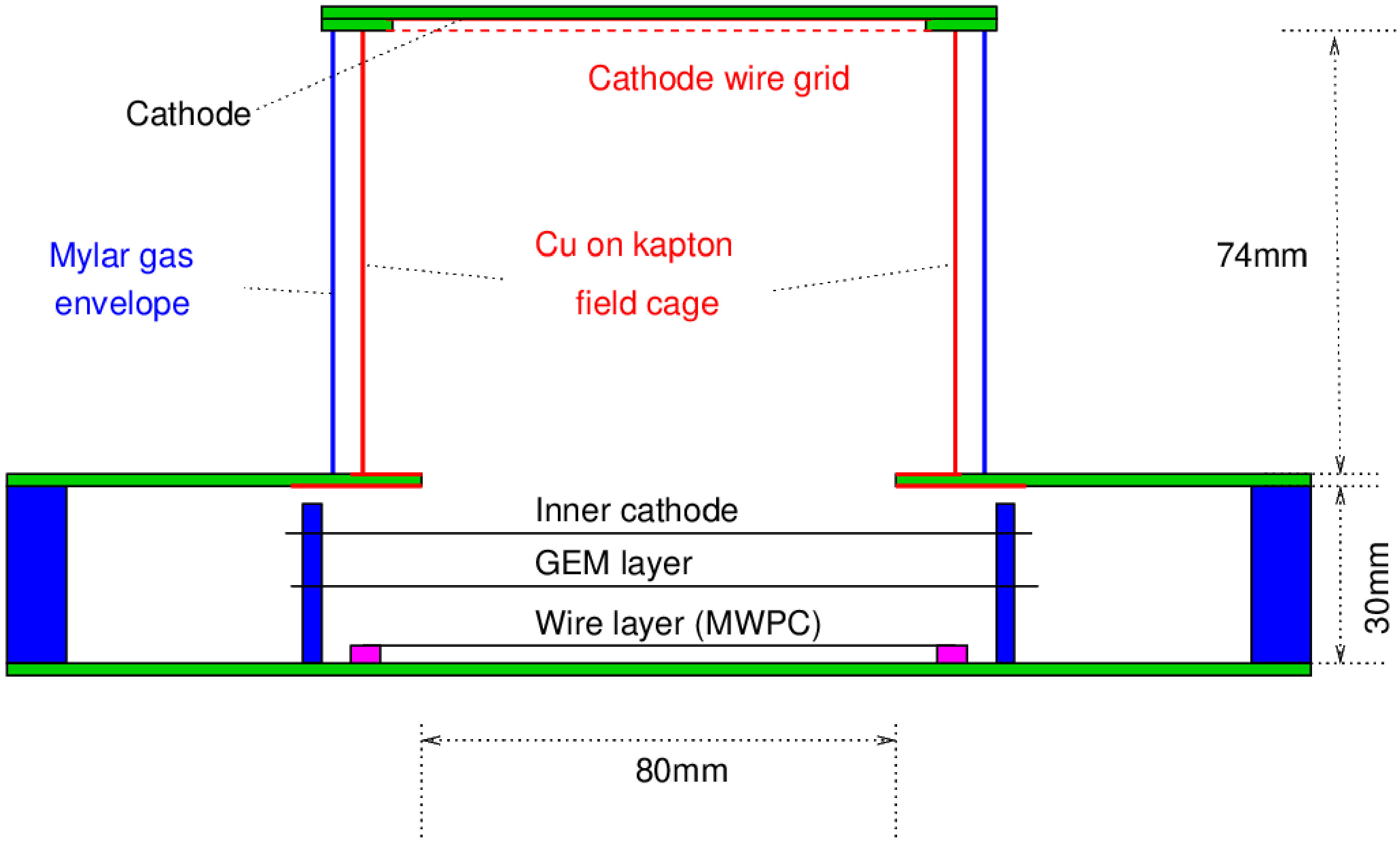
- Experimental setup
- Preliminary results on Ne CO_2 and Ne CH_4 mixtures
- Consistency with earlier data and with Blanc-rule
- What migrates in CO_2? Existence of ion clusters
- Lessons from Ion Mobility Spectrometry, a well established technique

Motivation

- Ion mobility is a key parameter for tracking detectors: defining rate capability, track distortion in large volumes
- Earlier data are sometimes inconclusive: results depend on measurement conditions
- Neon: promising candidate as TPC gas with low density and expected high ion mobility

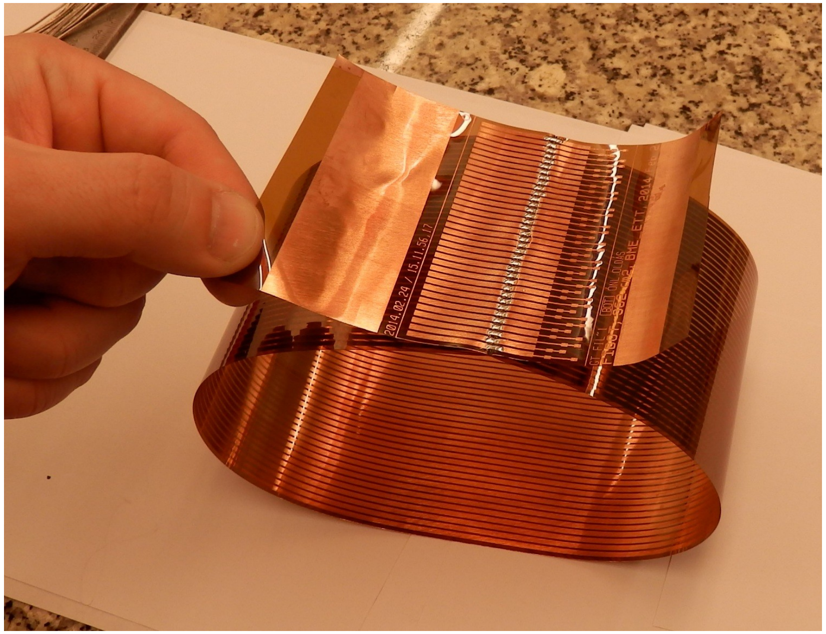
Detector outline

- Drift from GEM to GRID: 87.5mm (+/-0.5mm) at variable field of few 100V/cm
- Higher field (1kV/cm, variable) from MWPC to GEM



Construction aspects

- Double wall for improved gas quality
- Fine spaced field cage (printed on kapton) for uniform field over the sensitive volume (8cm by 8cm by 8cm)



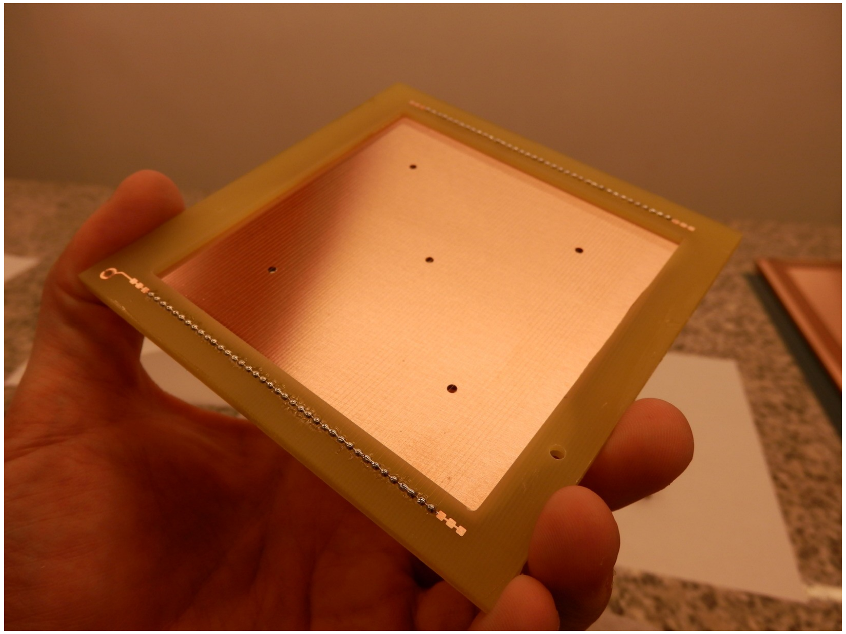
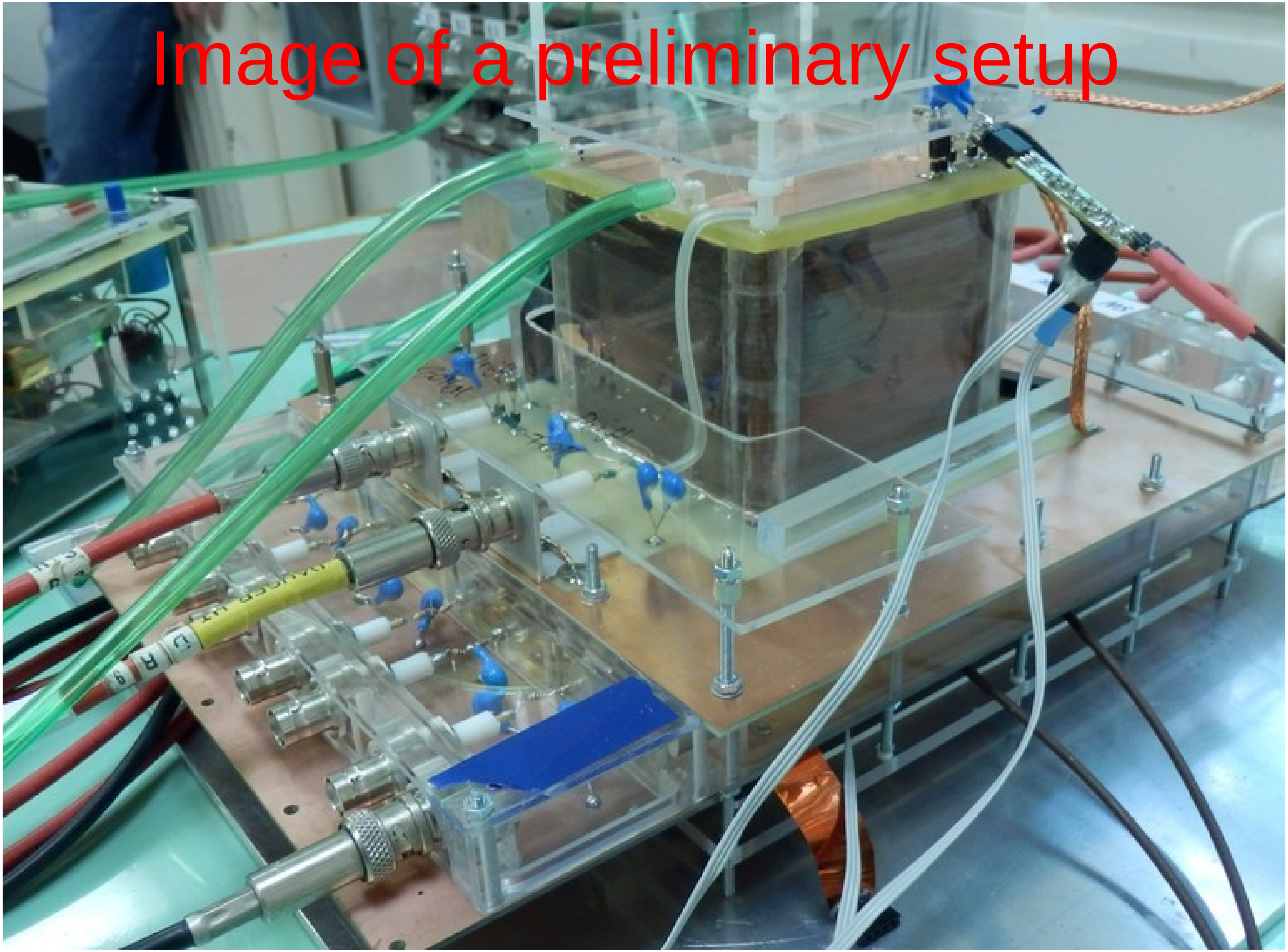


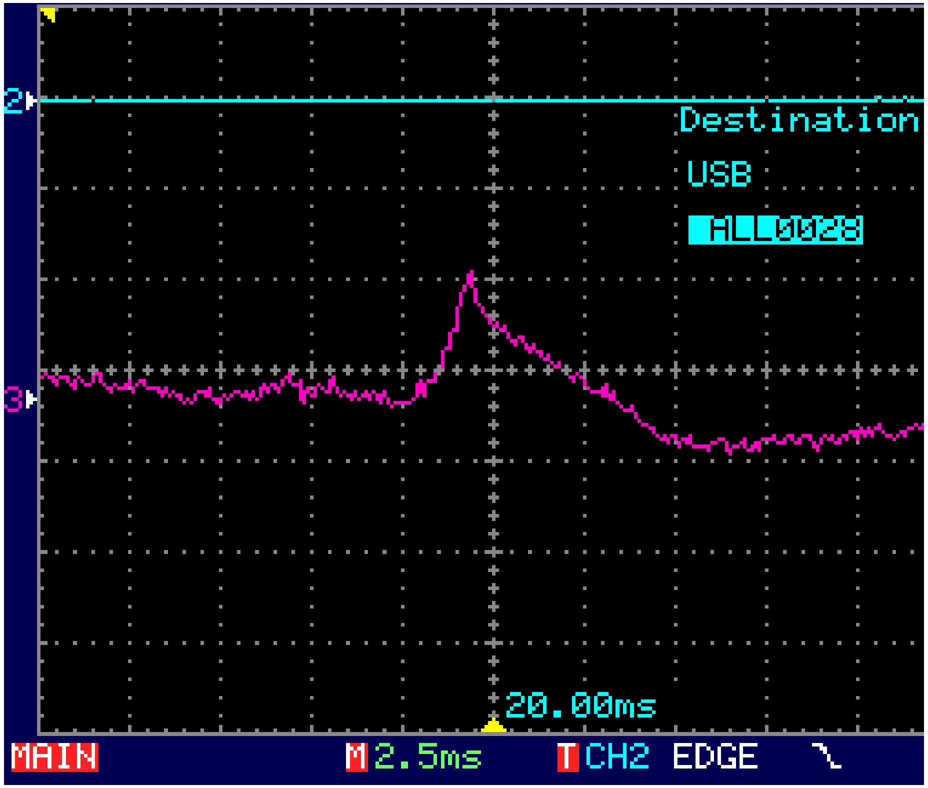
Image of a preliminary setup



Arrival signal shape

- Needs more understanding, and even more, a **well designed preamp** (note signals on ms timescale)

- **Starting** electron pulse from a high ionization
- **Sharp rise** (contains timing information), collection of ions
- **Decay**, undershoot due to electronics



Calculating mobility value

- Time = transfer to GEM + drift

$$t = \frac{1}{\mu}\left(\frac{5.7\text{mm}}{E_{transfer}} + \frac{(87.5\text{mm} - 1.3\text{mm})}{E_{drift}}\right)$$

- $E_{transfer}$ typically 1kV/cm, small contribution
- Correction for accelerating wire grid: high field causes -1.3mm effective length shortening
- Electron drift time negligible

Mobility values for $ArCO_2$ 80:20

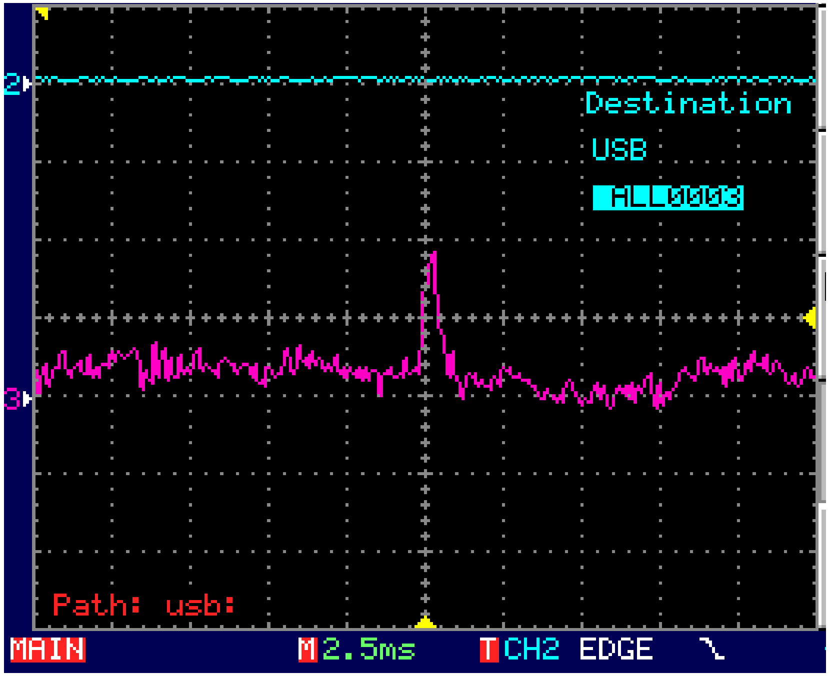
- **400V/cm: 1.580 (t=14.0)**
- **300V/cm: 1.601 (t=18.3)**
- **200V/cm: 1.582 (t=27.6)**

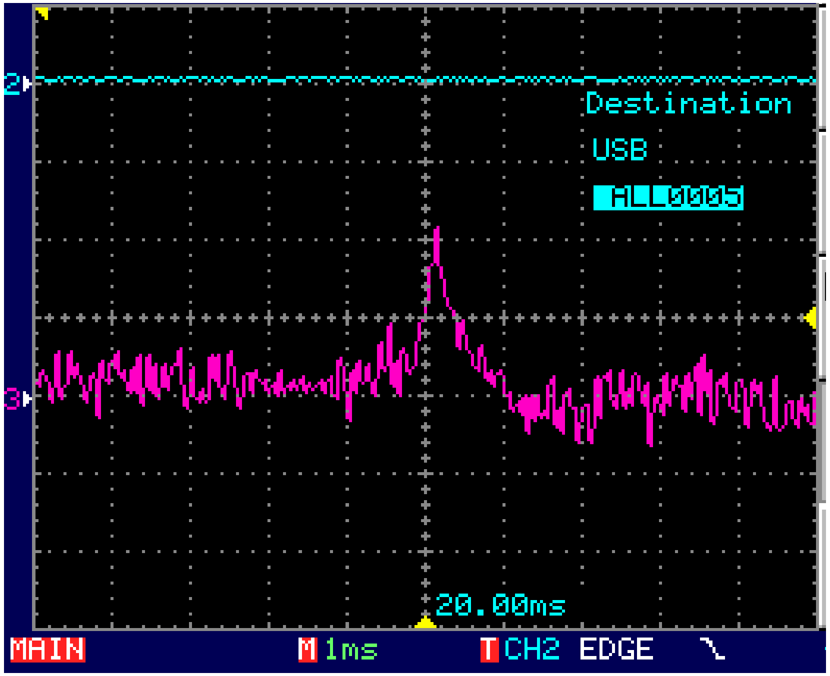
  (units always $cm^2/s/V$)

- Linearity expected in the low-field limit against E_{drift}, which is precisely confirmed

Arrival peak in pure CO_2

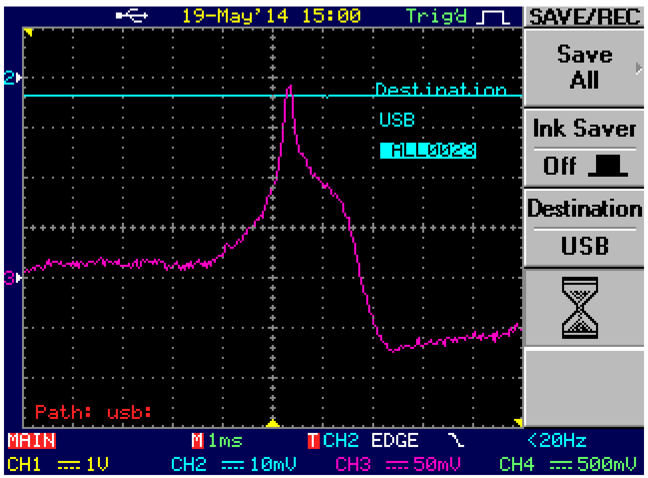
- Very sharp, shows that broadening in other cases is physical!
- Extracted mobility: **1.11 +/- 0.02** (ambient), consistent with [3]



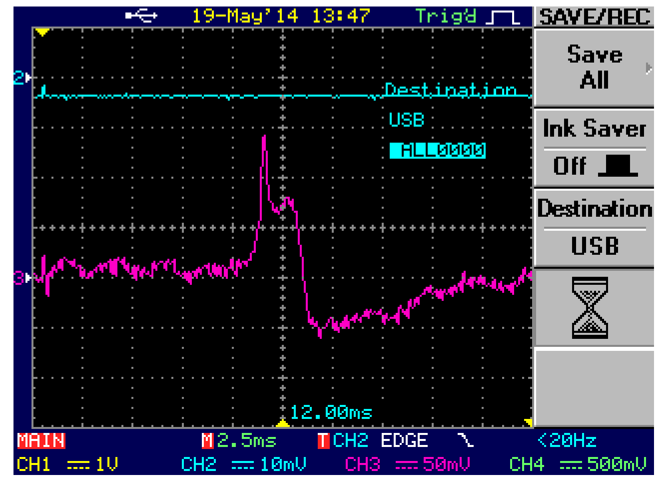


Arrival time signal in $NeCO_2$

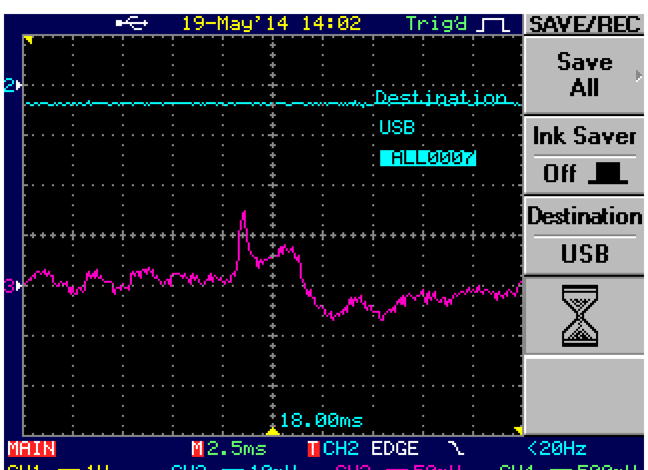
- 400V/cm



300V/cm



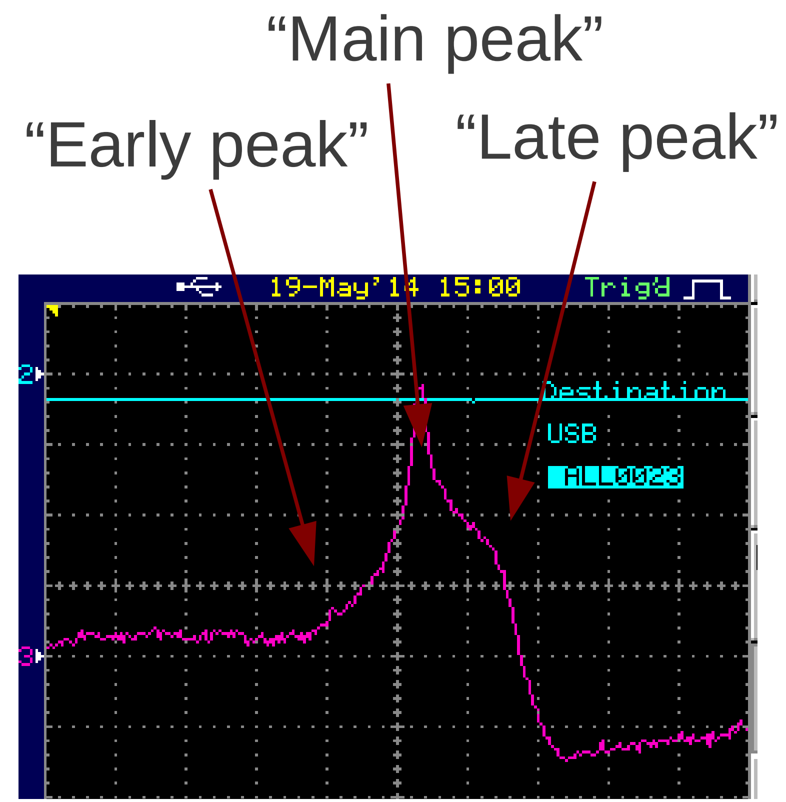
- 200V/cm



150V/cm

Main “peak” mobility values (ambient) for $NeCO_2$ 90:10

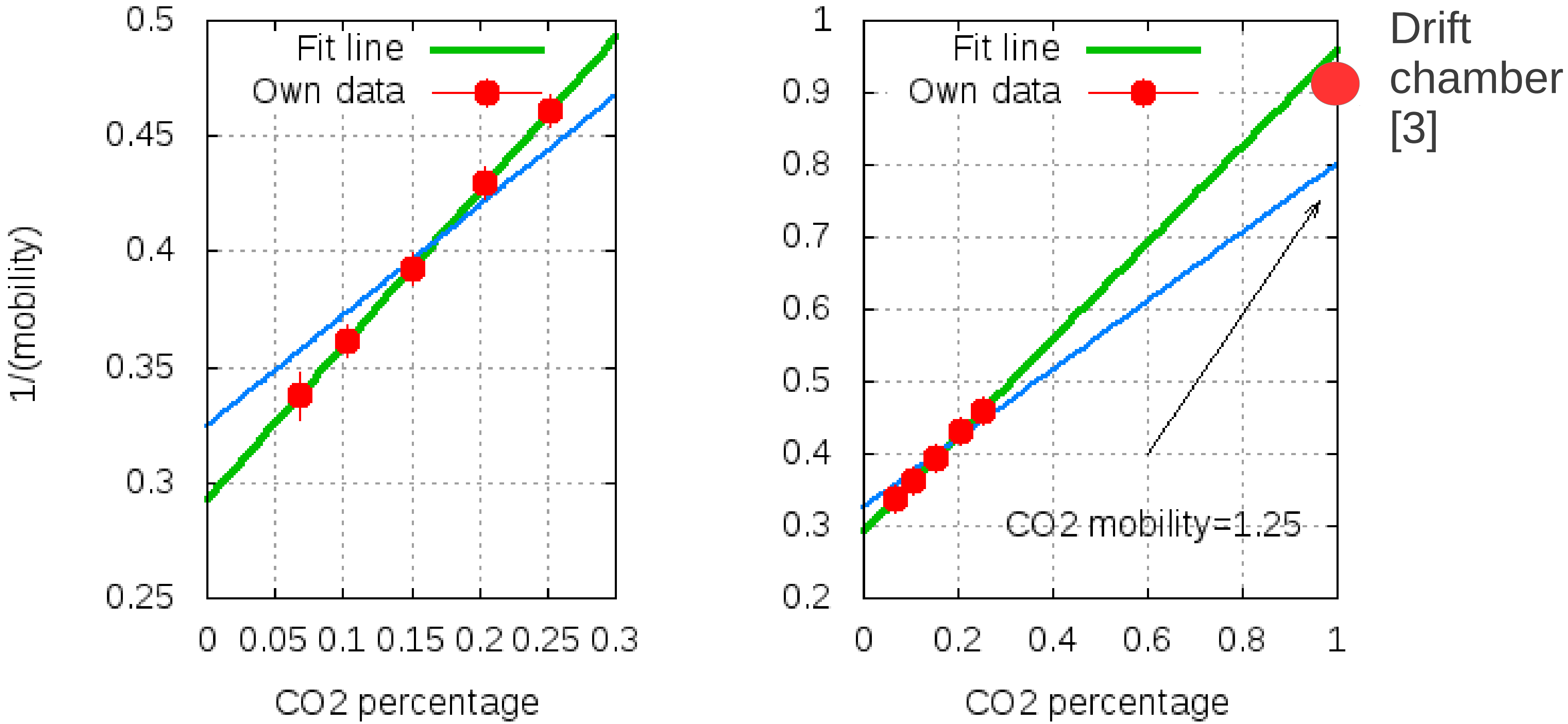
- **400V/cm: 2.731 (t=8.1)**
- **300V/cm: 2.764 (t=10.6)**
- **200V/cm: 2.729 (t=16.0)**
- **150V/cm: 2.725 (t=21.3)**



- (Late peak mobility around 2.4)
- (Early peak mobility around 3.1)

Blanc rule for Ne-CO_2 mixtures (main peak)

- CO_2 percentage of about 7, 10, 15, 20, 25

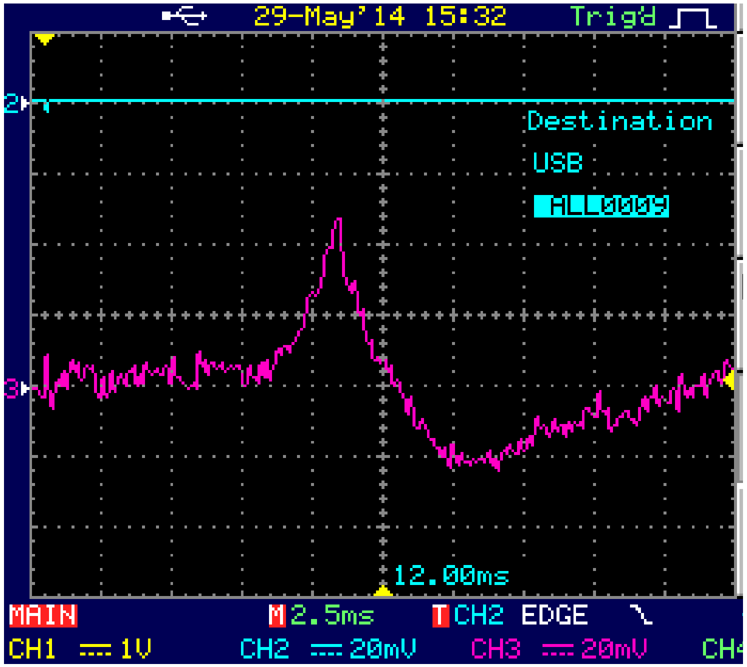


- Charge carriers may be the same in pure CO_2 and NeCO_2 mixtures

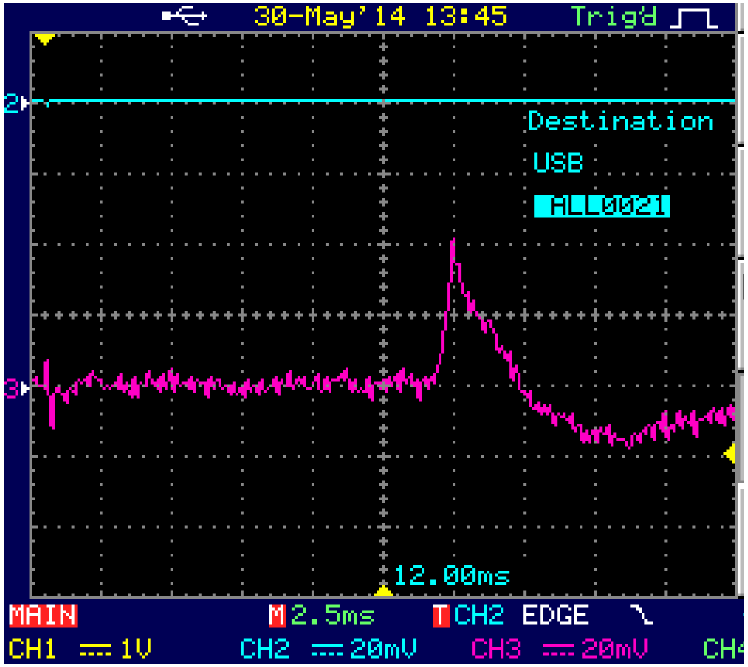
Arrival peaks in Ne-CH_4

- Sharp only for pure CH_4, otherwise blurred like earlier; so preliminary values extracted

Ne CH_4 50:50

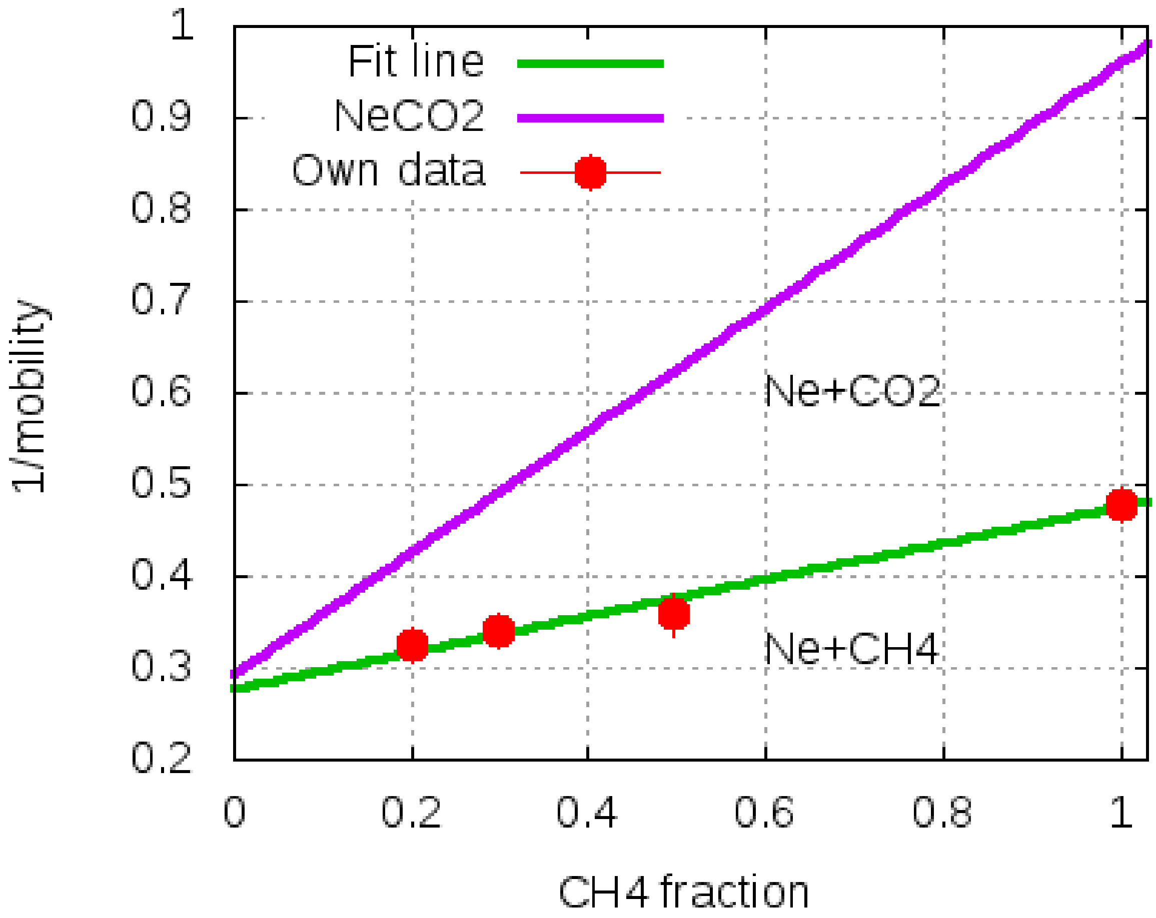


pure CH_4



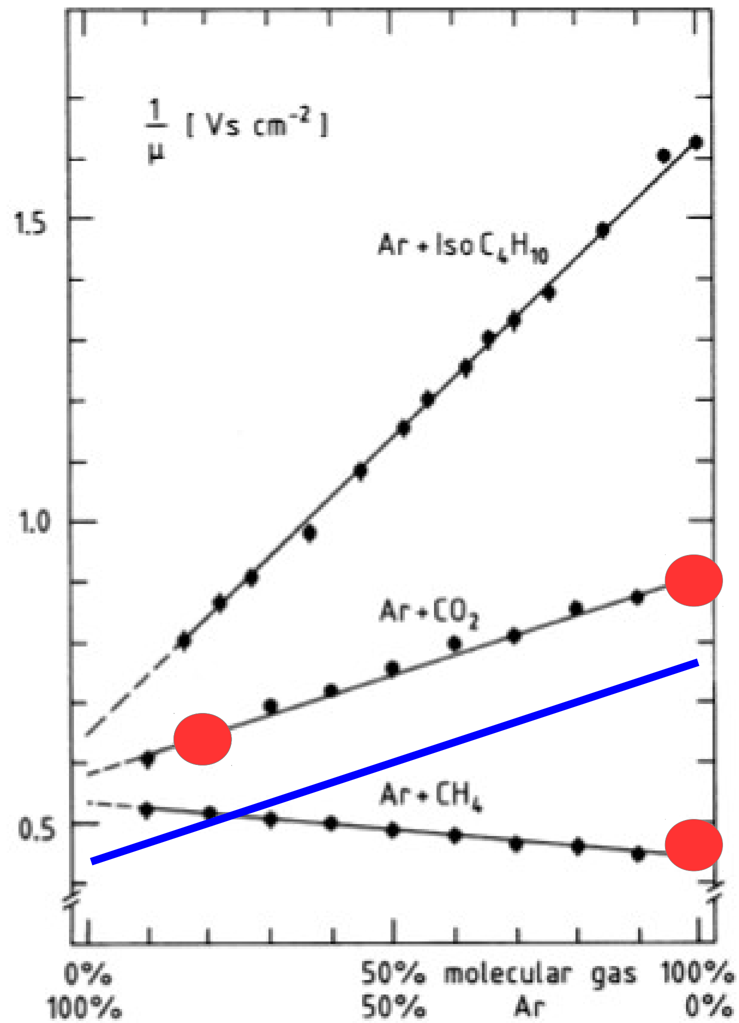
Blanc rule check for Ne CH_4

- Rather well fulfilled, note agreement again with [3] !



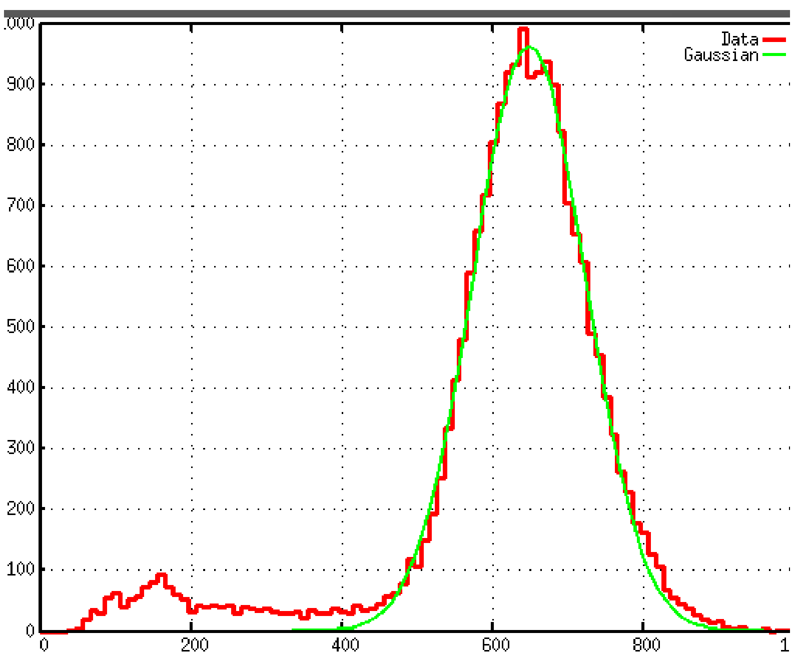
Consistency with earlier data

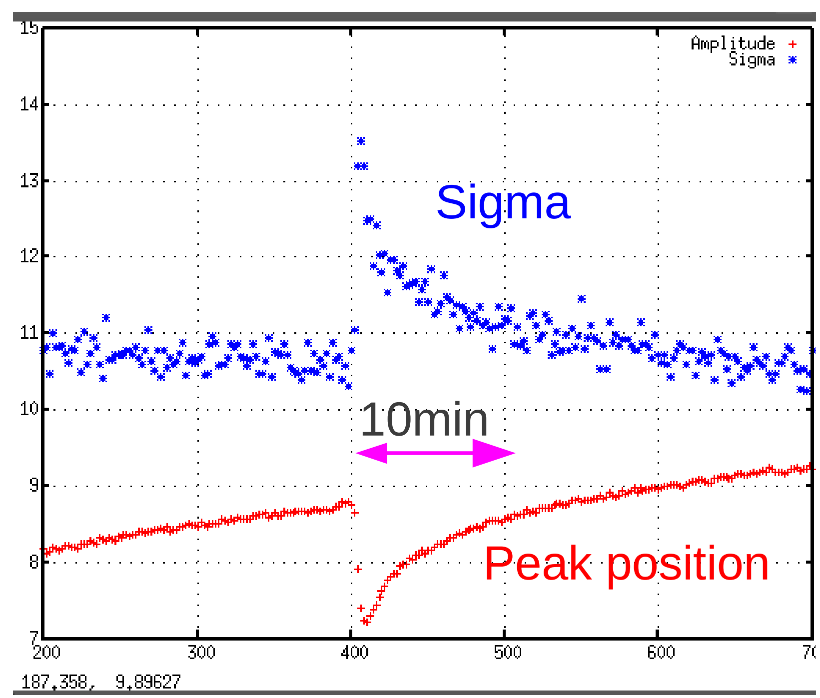
- Blanc's rule
- Measured by “Charpak group” in '77 Schulz [3]
- Red dots confirmed (ambient, 22-24 ^{o}C)
- Pure CO_2^+ ions [2](blue line) inconsistent with experimental values: ion clusters appear (see later)



Oxygen content dependence test

- Oxygen content in chamber < 25ppm, not yet conclusively measured
- Direct **insertion of air** in a bypass: 0.7ml for a chamber of 1400ml volume: **100ppm** Oxygen for about 8 min.
- Upper limit confirmed by little Fe55 peak position change and broadening

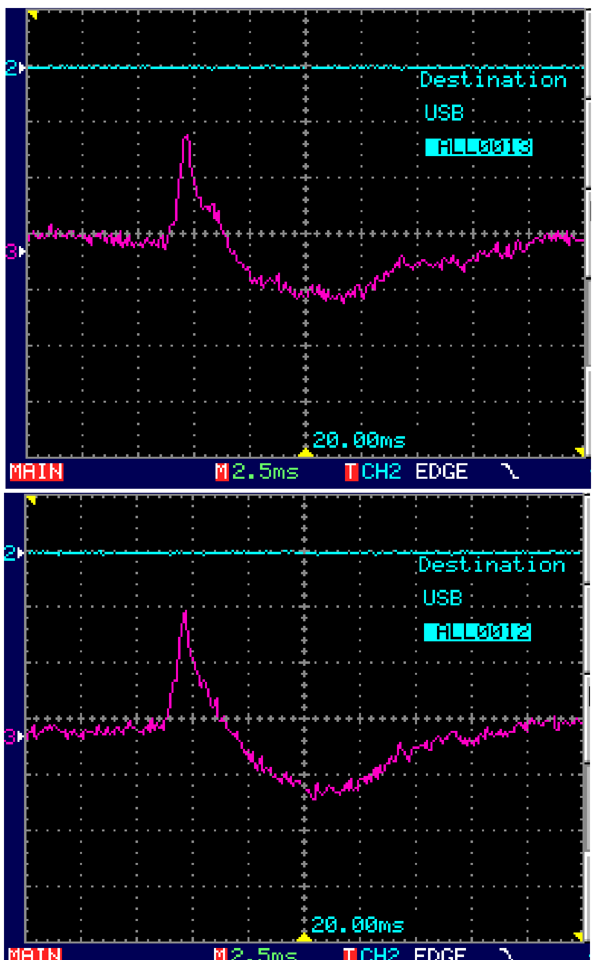




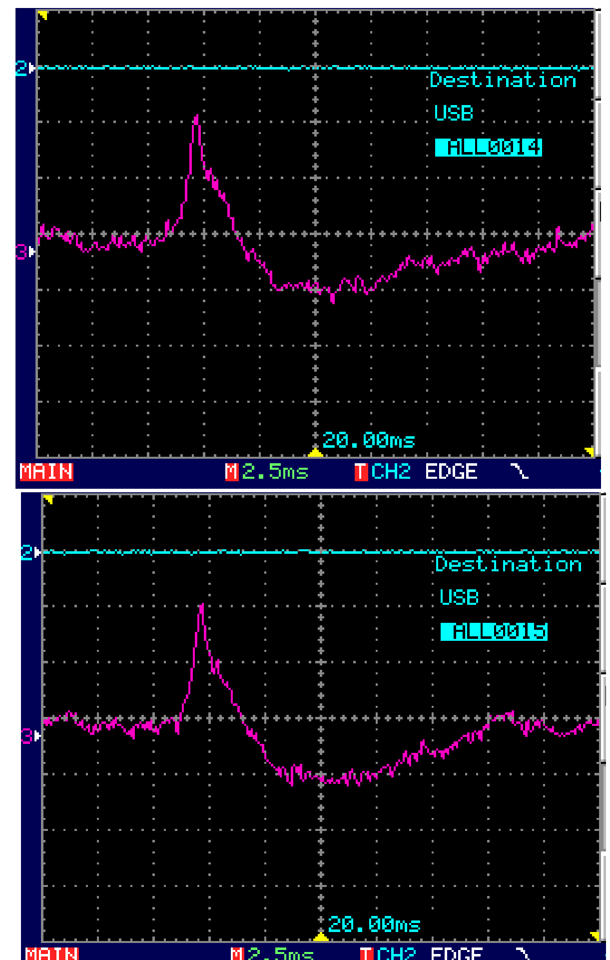
Oxygen content (non)dependence in Ar CO_2 mixture

- Arrival distribution is untouched: **100ppm O_2**

CLEAN GAS



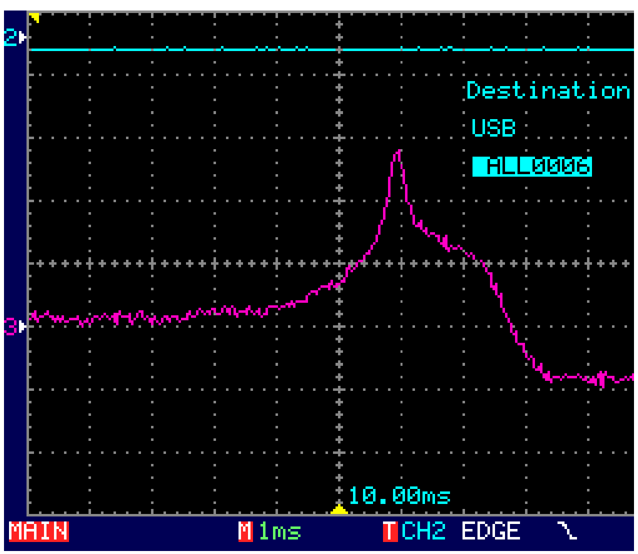
CONTAMINATED WITH O2



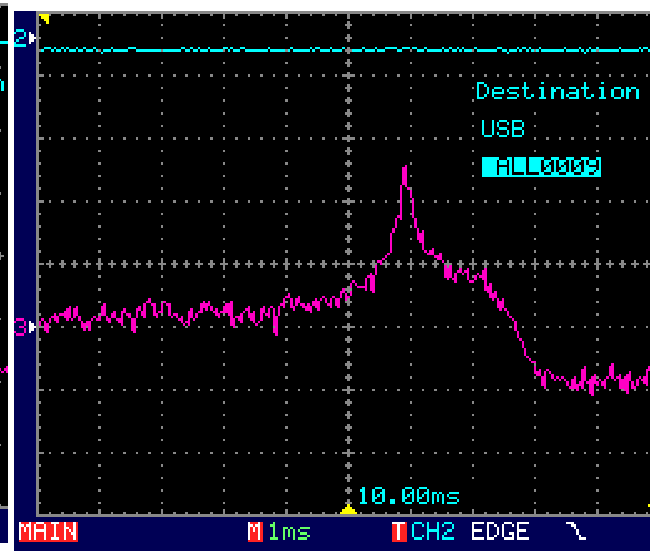
Oxygen (non)modification again in $Ne+CO_2$ mixture

- Injecting ambient air to chamber (300V/cm)

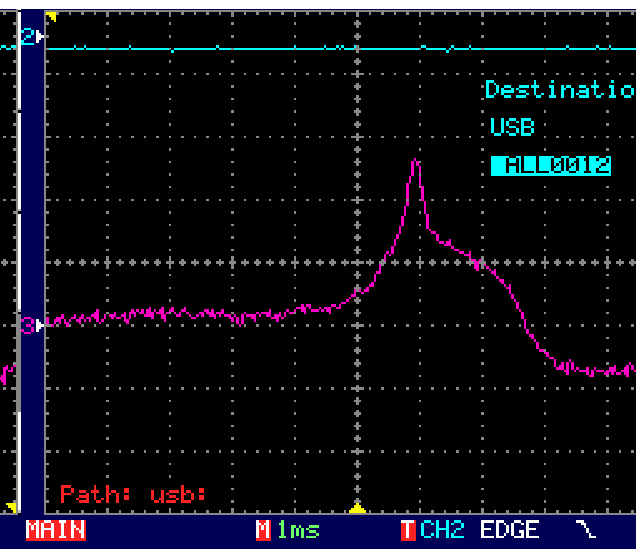
CLEAN GAS



200ppm O_2



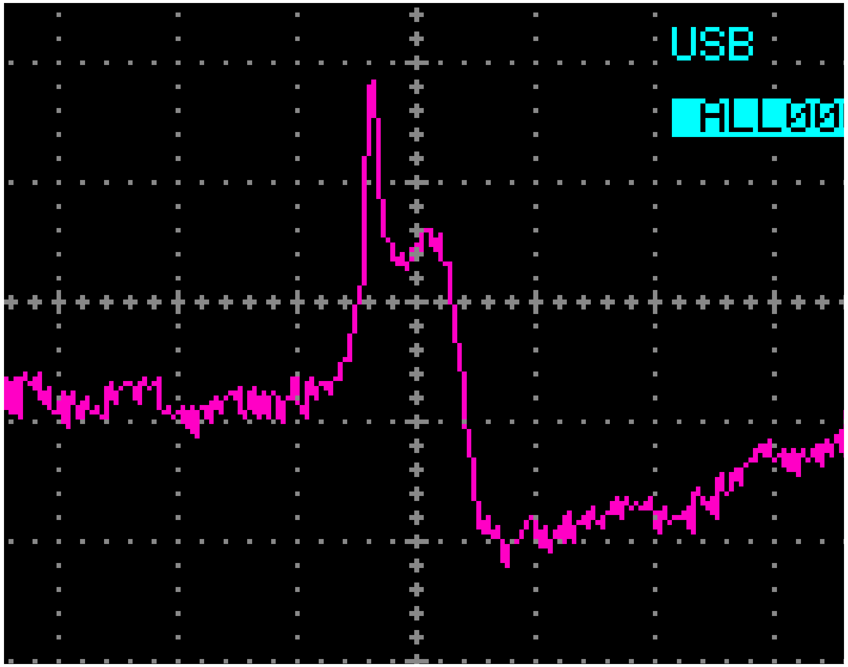
AFTER (15min)



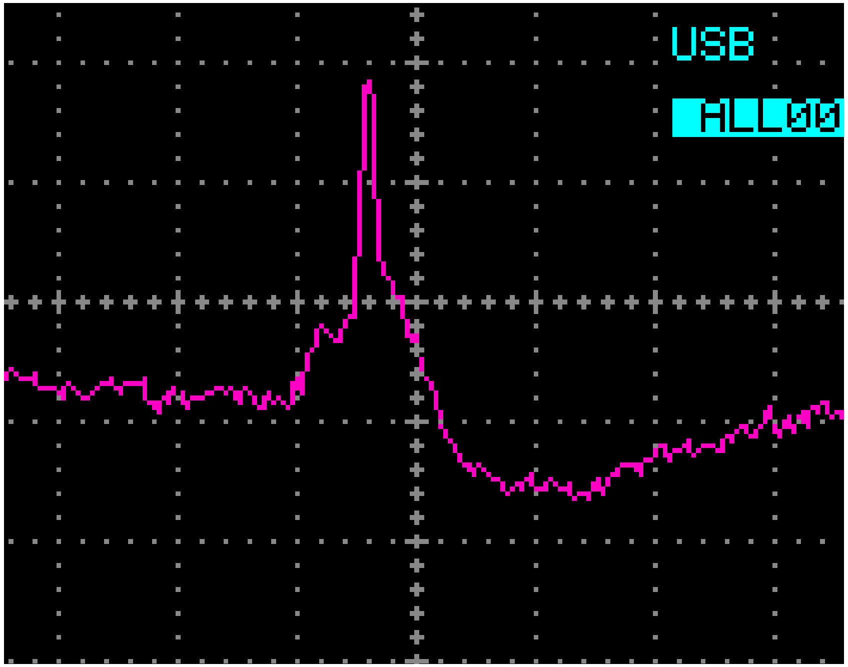
Water content (300V/cm)

- adding water (MUCH) with a bubbler, order of 1000ppm – “early peak” sharpens! (300V/cm)

NO WATER



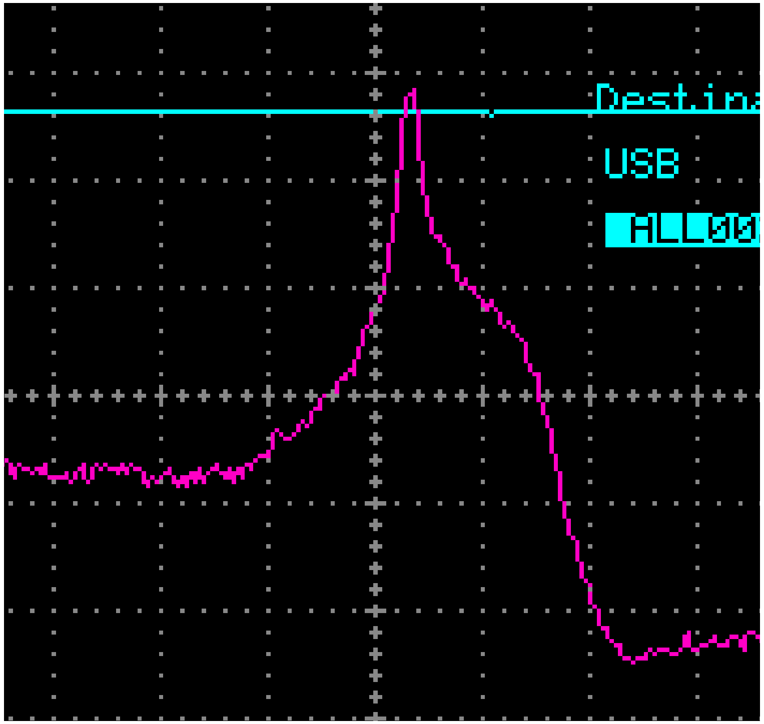
WITH WATER



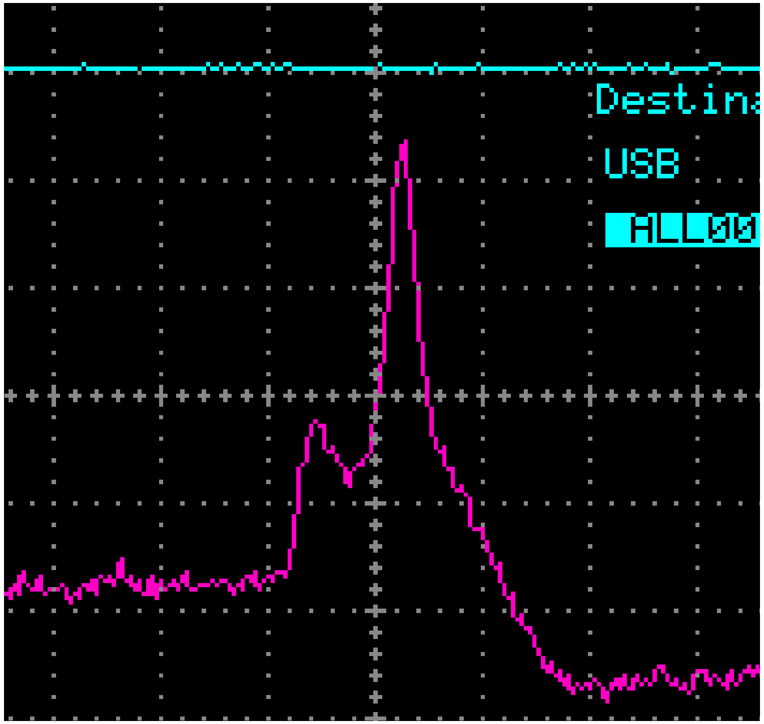
Water content (400V/cm)

- Possibly “late peak” reduces??

NO WATER



WITH WATER



Which ion migrates – naïve approach

- Common belief states “lowest ionization potential becomes soon dominant”.

Ionization energies, eV:

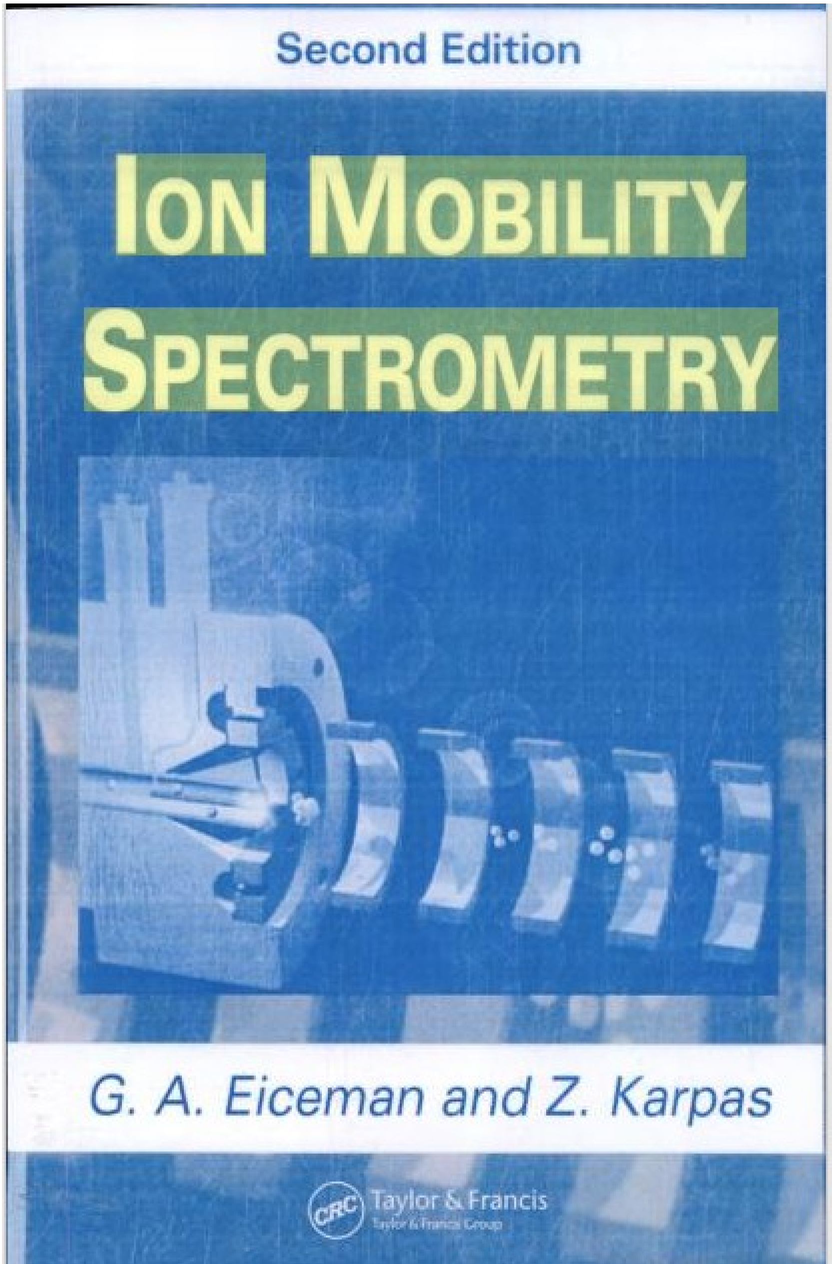
- Ne 21.56
- N_2 15.6
- CH_4 12.61
- O_2 12.1

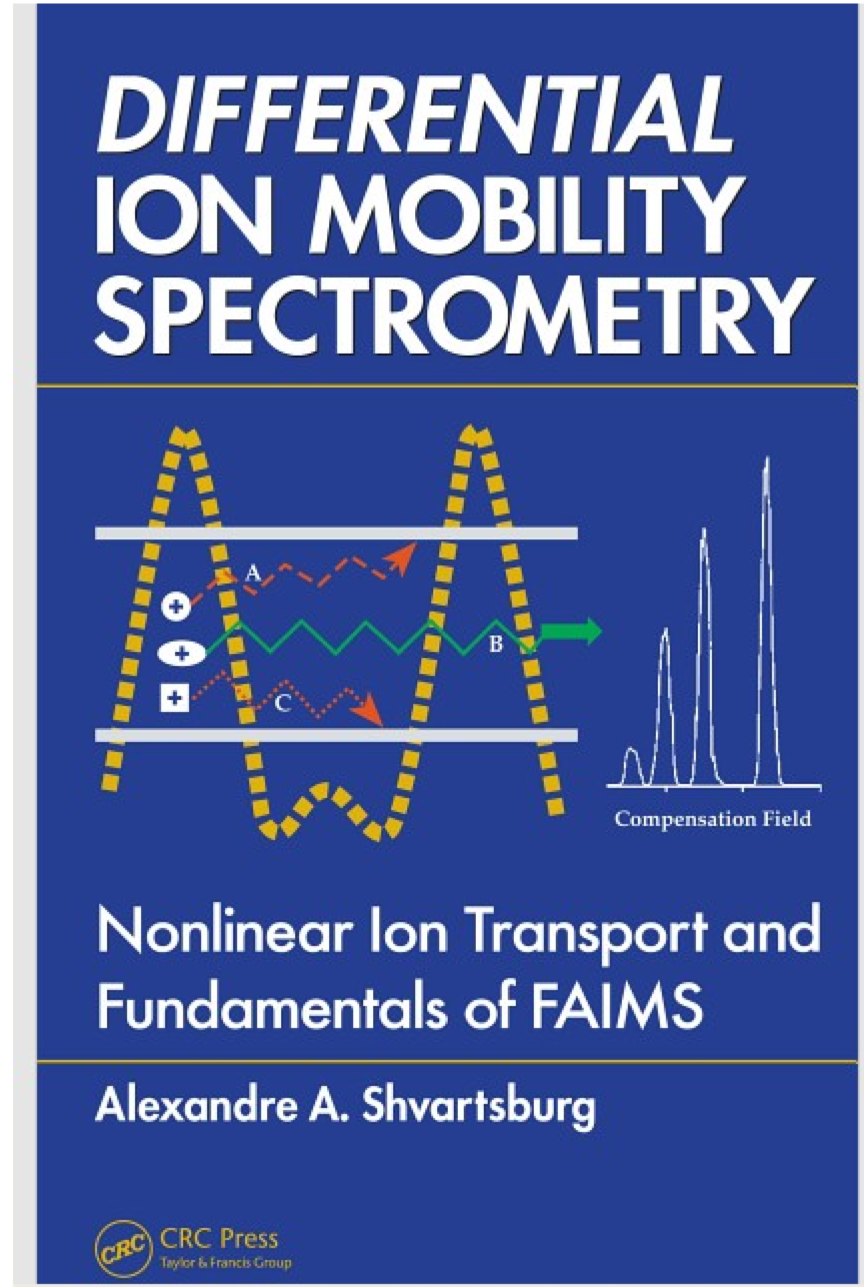
- Ar 15.76
- CO_2 13.8
- H_2O 12.62

Ion Mobility Spectrometry: commonly known method in chemistry

- Also at Wikipedia. Mostly ambient pressure, often in air, mostly heated
- Used in security systems; 50000 (!) IMS detectors have been sold worldwide (also to the US Army), well established, multi-100M$ business
- Ions of water (in air) or “reactant” (in pure gases) pick up the molecule to be analysed, multiple peaks identify molecule types

Textbooks


Second Edition
ION MOBILITY SPECTROMETRY
G. A. Eiceman and Z. Karpas
CRC Taylor & Francis


DIFFERENTIAL ION MOBILITY SPECTROMETRY
A
B
C
Compensation Field
Nonlinear Ion Transport and Fundamentals of FAIMS
Alexandre A. Shvartsburg
CRC Press
Taylor & Francis Group

Ion mobility spectrometry in pure CO_2 from [5] (example)

- 8cm drift, 200V/cm, atmospheric pressure, mostly elevated temperature
- Need of **dry** reactant gas!

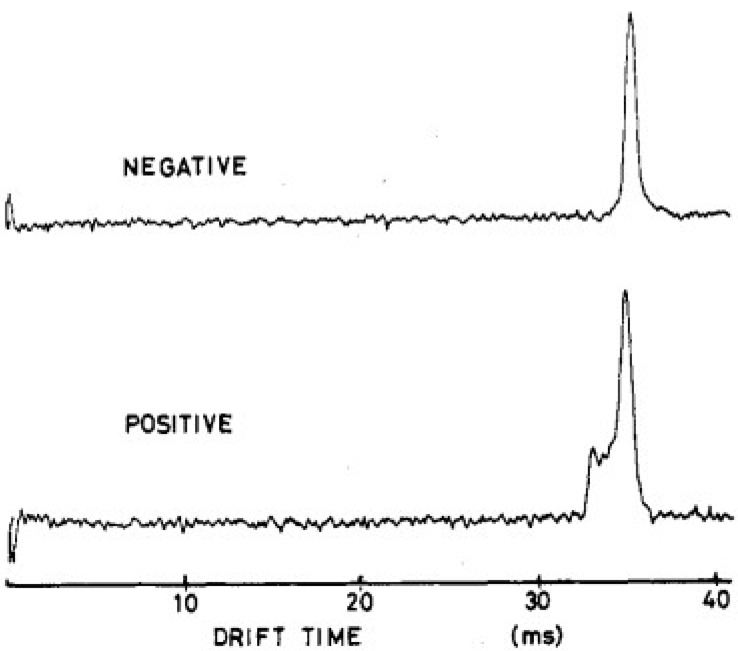


Figure 1. CO_2 reactant ion spectra at 25 °C. The upper spectrum is of the negative reactant ions. The lower spectrum is of the positive reactant ions. The operating conditions different from those listed in Table I were as follows: pressure, 748 torr; repetition period, 60 ms; dwell time, 60 μs.

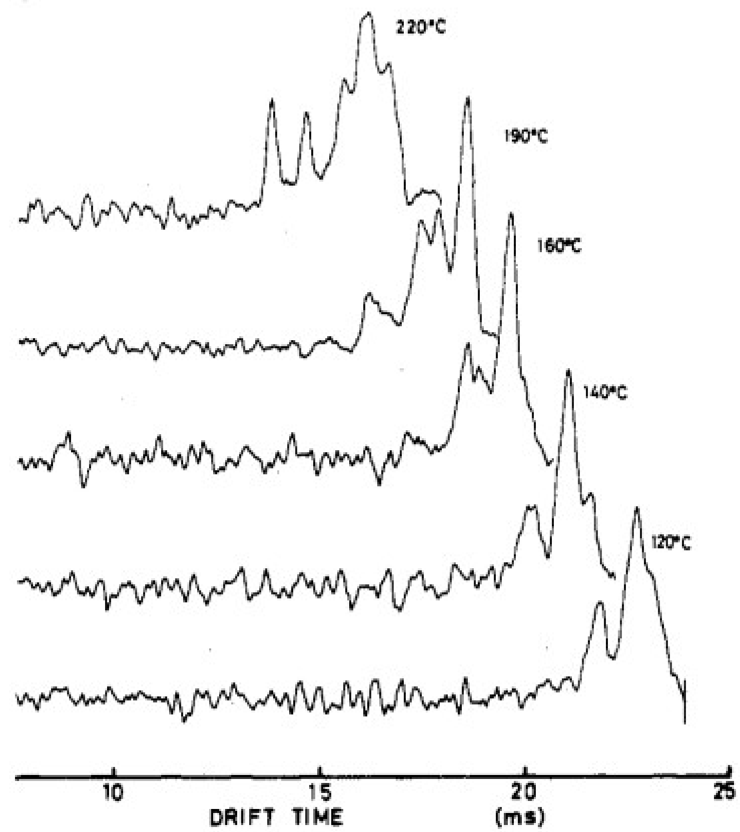


Figure 3. CO_2 positive reactant ions at various temperatures. Operating conditions different from those listed in Table I were as follows: pressure, 753; vertical display, 8.192; autostop, 2048; gate width, 0.1 ms.

Ion identity in CO_2

- For CO_2 from low (<1 torr) to atmospheric pressure many measurements exist, [2], [5]
- **The classical reference**: Ellis [2] measures CO_2+ and **CO_2 * CO_2+** cluster mobilities: conclusions is that the **latter** is the dominant even at low pressures (below 1torr)! See also Coxon [4]
- At **higher** (few torr) **pressures**, oxygen ionizes and clusterizes: dominant ion is (**O_2^+ * nCO_2**) , clusters with n = 5-10 (reason not clarified)
- Mobility **independent of cluster size**, 1.06 - 1.09

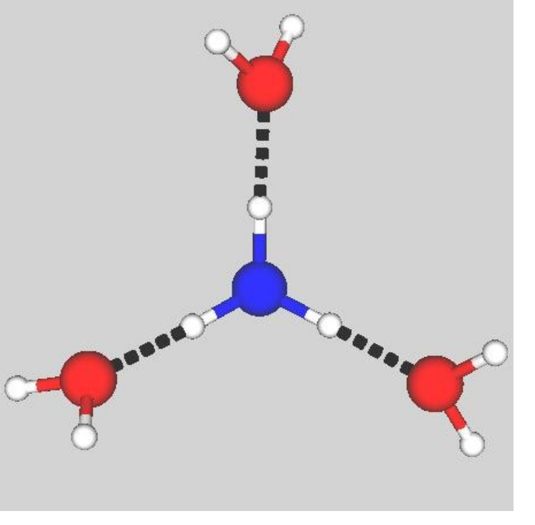
CO_2 at atmospheric pressures [2]

- Mobility largely **independent of cluster size**, 1.05 – 1.08 for pressures above 100 torr, due to CO_2 “surrounding” the small ion “core”.
- From mass spectroscopy: ion masses are 117, 161, 205, 249, … note **odd** masses (protonating)
- Conclusion would be: water content very important! Seemingly **quickly H_3O+** or similar takes over and makes cluster with CO_2 molecules!

How such an ion cluster can look like – pure speculations!

- Mass of 117+44n can be like this:

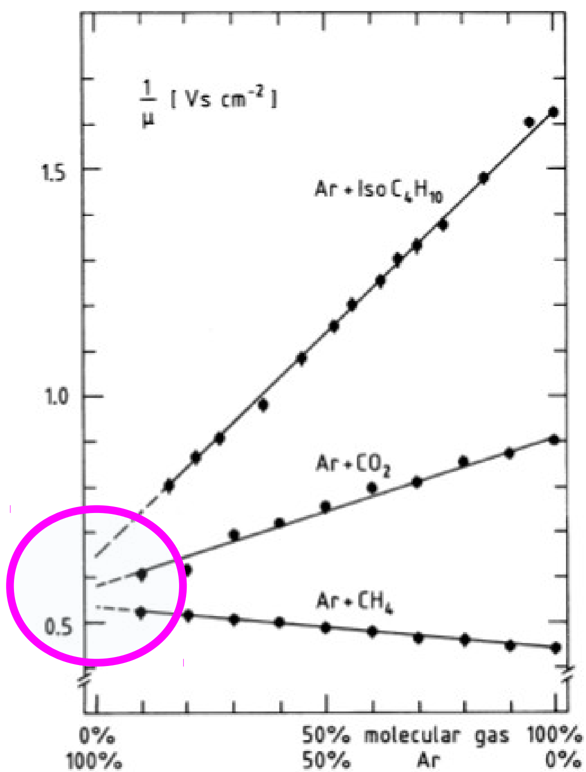
  $(H_3O^+) + (H_2O)_3 + (CO_2)_n$ with n=1
- "Eigen-cation" with high binding energy 3.2eV
- Clustered by CO_2 molecules
- Needs trace amounts of water!
- Alternative: $(HCO^+) + (CO_2)_n$

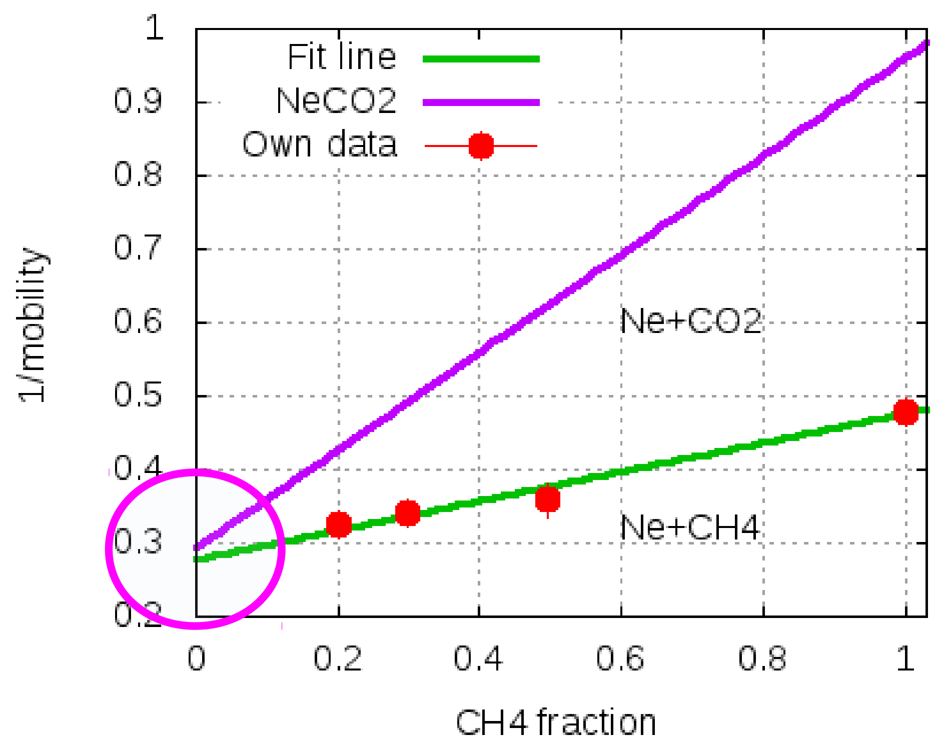


The Cambridge Cluster Database, D. J. Wales, J. P. K. Doye, A. Dullweber, M. P. Hodges, F. Y. Naumkin F. Calvo, J. Hernández-Rojas and T. F. Middleton, URL http://www-wales.ch.cam.ac.uk/CCD.html

Limit of large size clusters: "Rayleigh limit" or "Langevin limit"

- Prediction: all clusters with similar mobility, depending only on buffer gas (mass, polarizability)





Polarizability limit: only charge-dipole reaction contributes to collision cross section

- K = 13.85 /sqrt($\alpha\mu$) where K is mobility, μ is reduced mass, α is atomic polarizability

	Polarizability	limit-K	"experimental" K
Neon	0.396	4.9	3.3 – 3.6 (this work)
Argon	1.671	1.69	1.7
N_2	1.76	1.97	
CO_2	2.9	1.23	1.05
CH_4	2.6	2.14	2.2

Conclusions

- Effective ion mobility in $ArCO_2$ consistent with earlier reference in drift chambers [3], also pure CO_2 and methane
- In $NeCO_2$ structures appear, far from conclusive. “Main peak” mobility (ambient temperatures) around 2.73
- Blanc rule nicely followed by Ne-based mixtures
- **No change** in migration pattern for 25-200ppm of **Oxygen**, variation with **water** apparent
- CO_2 is an established IMS gas, ion clusters known to exist, with inconclusive measurements on their nature

References

- [1] H. Ellis et al., Transport properties of gaseous ions over a wide energy range IIV, Atomic Data And Nuclear Data Tables
- [2] Ellis, Ion identity and transport ... in CO2, J. Chem. Phys 64, (1976) 3935, doi: 10.1063/1.432024
- [3] G. Schultz, G. Charpak and F. Sauli, Mobilities of positive ions in some gas mixtures used in proportional and drift chambers, Rev. Phys. Appl. (France) 12, 67 (1977)
- [4] Coxon, Moruzzi, J.Phys. D: Appl. Phys. Vol 10, 1977
- [5] Rokushika, Hill, Anal. Chem. 58 (1986) 361-365

- See A. Cortez talk in the same session for a nice theoretical discussion and making the Ar+CO2 case
- + textbooks...

Backup slides

Cross section; Gas flow