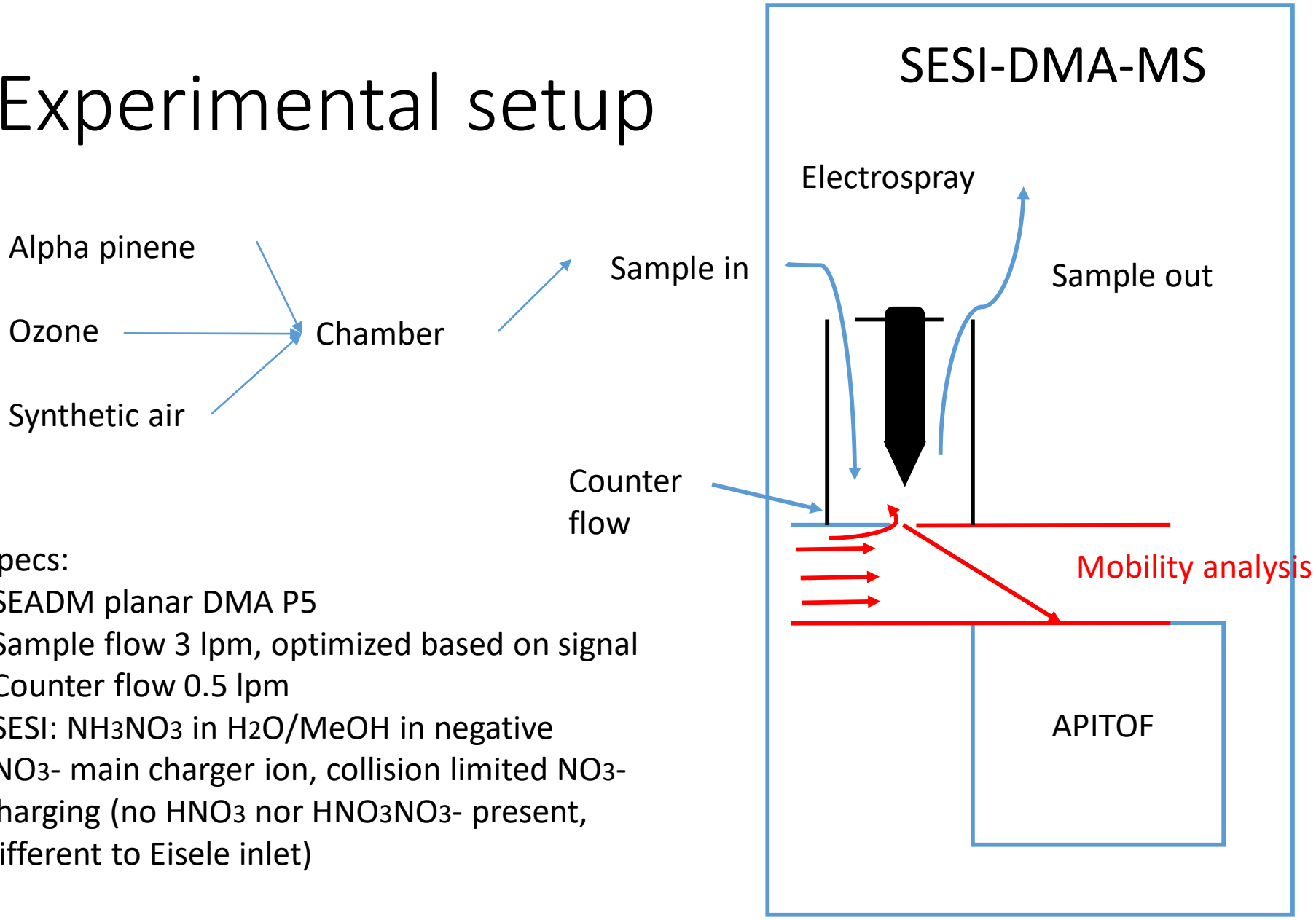
Electrical mobilities of alpha pinene oxidation product+NO_3^- clusters

Juha Kangasluoma, Aurora Skyttä, Lauri Ahonen, Runlong Cai, Angelica Bianci, Theo Kurten

University of Helsinki

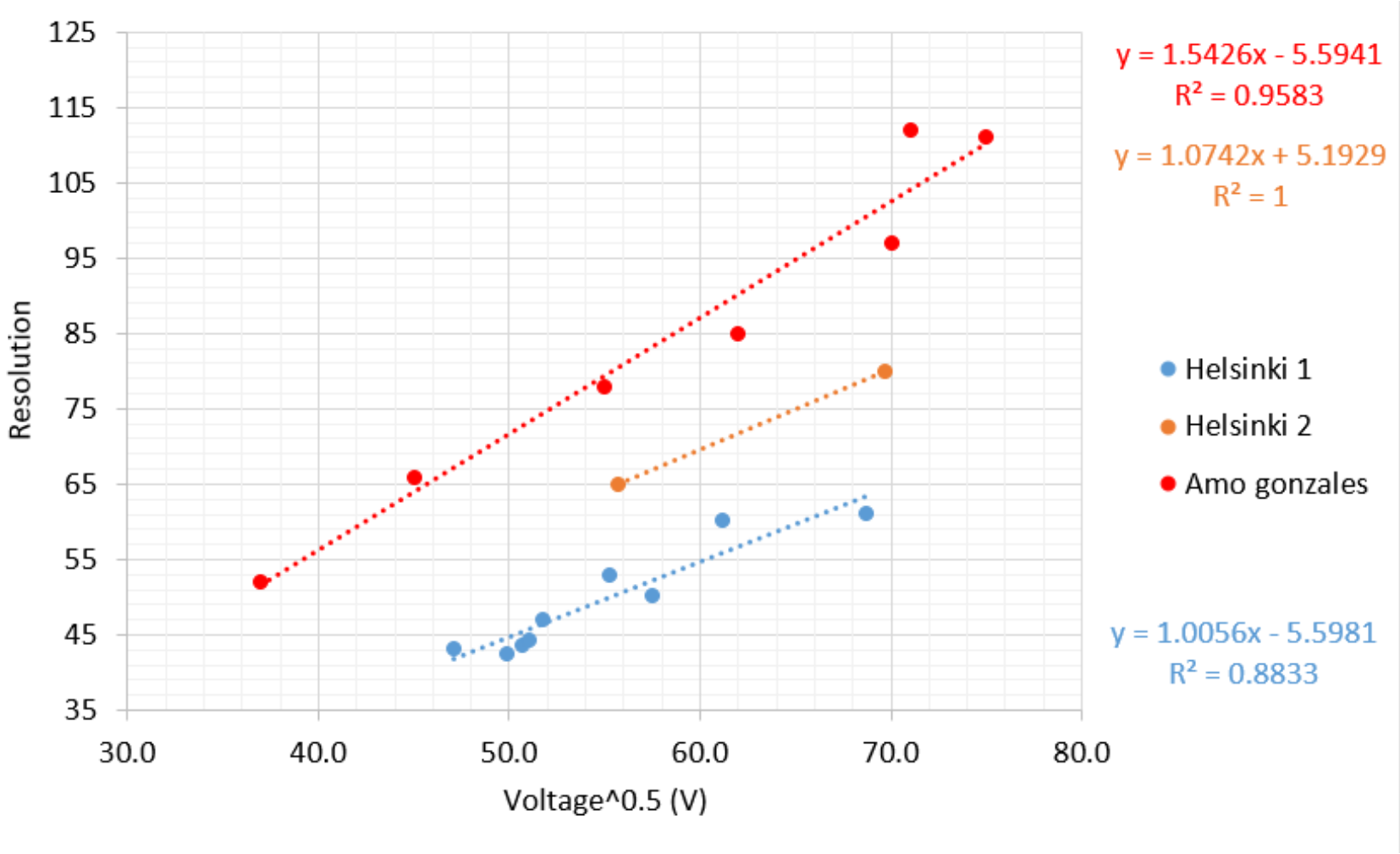
Experimental setup



Specs:
-SEADM planar DMA P5
-Sample flow 3 lpm, optimized based on signal
-Counter flow 0.5 lpm
-SESI: NH_3NO_3 in H_2O/MeOH in negative
-NO_3^- main charger ion, collision limited NO_3^- charging (no HNO_3 nor $HNO_3NO_3^-$ present, different to Eisele inlet)

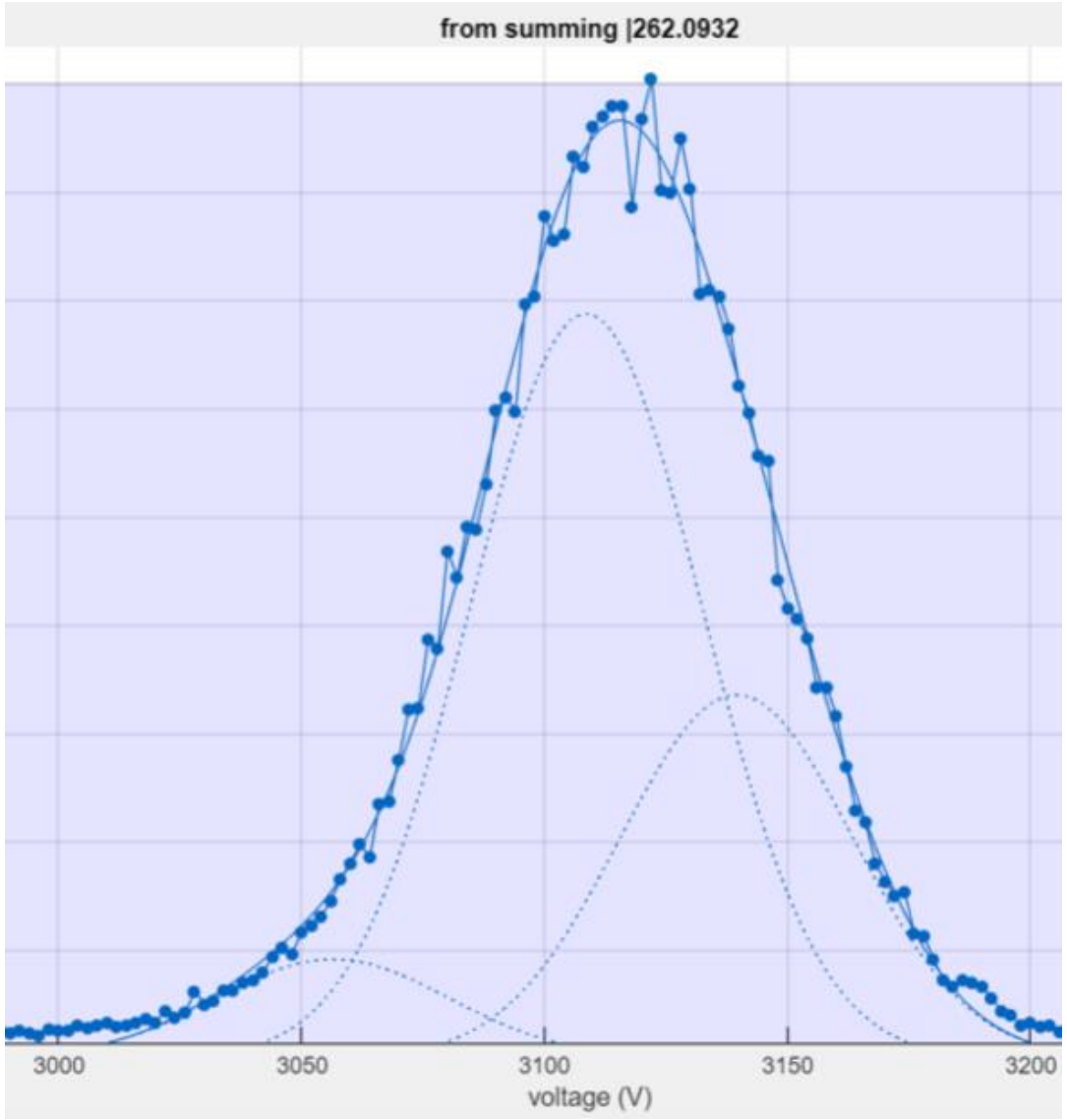
Mobility resolution

-Some work to do in optimizing the mobility resolution



Example mobility spectra for selected compounds

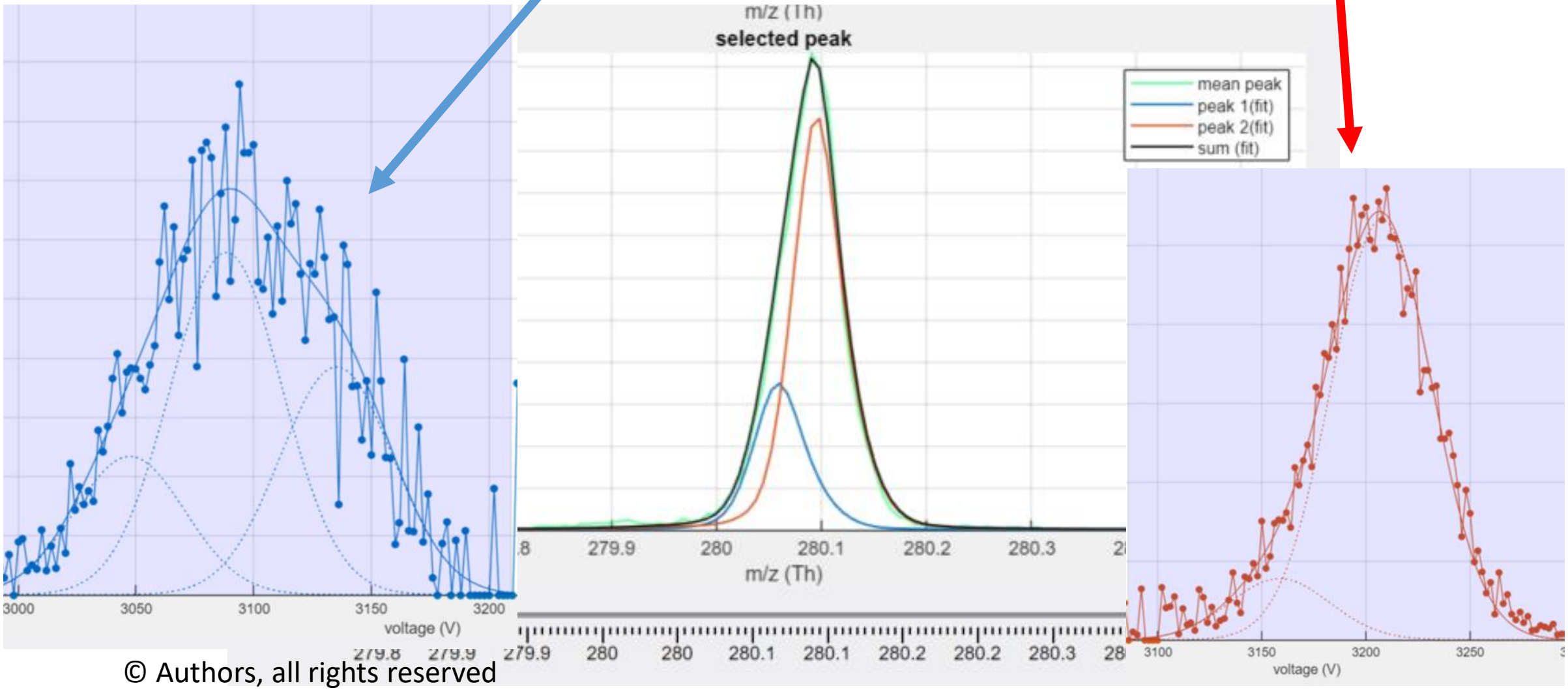
-C10H16O4NO3-
-Three isomers



Example mobility spectra for selected compounds

Blue: C9 H14 O6 (NO3)1-, 3 isomers

Red: C10 H18 O5 (NO3)1-, 2 isomers



Observed clusters

Formula	With NO3-	isomers
C9 H14 O3 (NO3)1	232.0827	1
C10 H18 O2 (NO3)1-	232.1190	2
C8 H12 O4 (NO3)1-	234.0619	2
C10 H14 O3 (NO3)1-	244.0827	2
C10H15O3NO3-	245.0905	2
C10H16O3NO3	246.0983	1
C9 H14 O4 (NO3)1-	248.0776	2
C10 H18 O3 (NO3)1-	248.1140	2
C8 H12 O5 (NO3)1-	250.0568	2
C10 H14 O4 (NO3)1-	260.0776	3
C10 H16 O4 (NO3)1-	262.0932	3
C9 H14 O5 (NO3)1-	264.0725	2
C10 H18 O4 (NO3)1-	264.1089	2
C8 H12 O6 (NO3)1-	266.0518	1
C9 H16 O5 (NO3)1-	266.0881	2
C10 H13 O5 (NO3)1-	275.0647	3
C10 H14 O5 (NO3)1	276.0725	3
C11 H18 O4 (NO3)1-	276.1089	2
C10 H16 O5 (NO3)1-	278.0881	4
C9 H14 O6 (NO3)1-	280.0674	3
C10 H18 O5 (NO3)1-	280.1038	2
C10 H14 O6 (NO3)1-	292.0674	3
C10H15O6NO3	293.0752	3
C10H16O6NO3	294.0831	3--5
C10 H14 O7 (NO3)1-	308.0623	n
C10H16O7NO3	310.0780	2
C10 H14 O8 (NO3)1	324.0572	3

This study

Number of detected isomers affected by different charging?

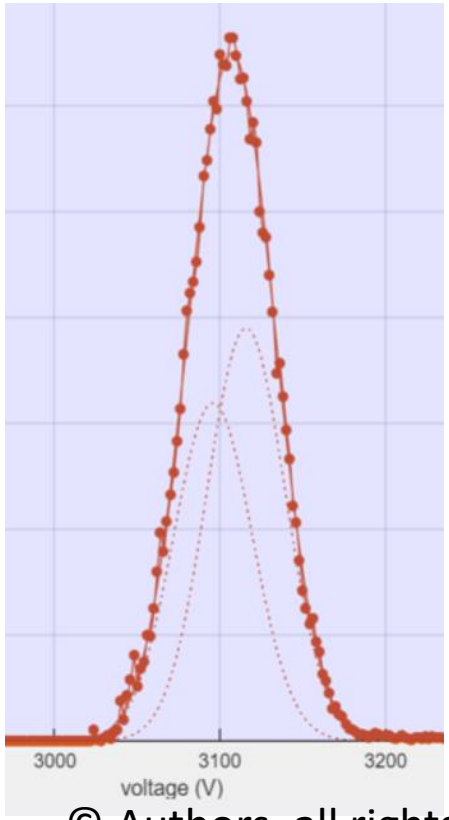
Krechmer et al 2016 using Tofwerk IMS-APITOF

Formula	with NO_3^-	isomers
$C_7H_{10}O_4$	220.05	1
$C_5H_6O_6$	224.00	1
$C_5H_6O_7$	240.00	1
$C_7H_8O_8$	282.01	1
$C_8H_{12}O_7$	282.05	1
$C_8H_{12}O_8$	298.04	1
$C_{10}H_{14}O_7$	308.06	1
$C_9H_{12}O_8$	310.04	1
$C_{10}H_{16}O_7$	310.08	1
$C_8H_{12}O_9$	314.04	1
$C_{10}H_{14}O_8$	324.06	1
$C_{10}H_{16}O_8$	326.04	1
$C_9H_{12}O_9$	326.07	1
$C_9H_{14}O_9$	328.05	1
$C_{10}H_{14}O_9$	340.05	2
$C_9H_{12}O_{10}$	342.03	2
$C_{10}H_{16}O_9$	342.07	1
$C_{10}H_{14}O_{10}$	356.05	2
$C_{10}H_{16}O_{10}$	358.03	2
$C_9H_{12}O_{11}$	358.06	1
$C_{10}H_{14}O_{11}$	372.04	1
$C_{10}H_{16}O_{11}$	374.02	1
$C_{10}H_{14}O_{13}$	404.03	1

C10H18O3NO3- structures

-Two isomers

-Voltage ratio = 1.0065



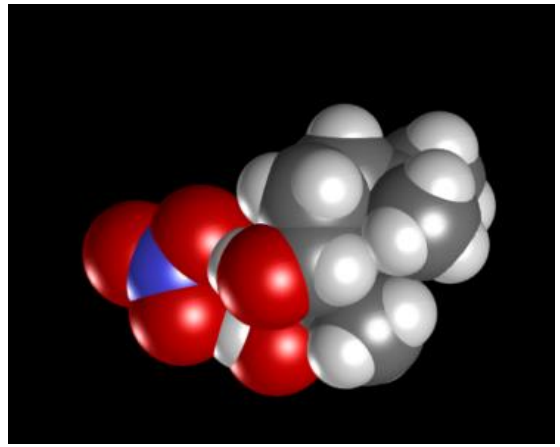
- Simulate structures for isomers 1 and 2, calculate mobility using IMOS by Prof. Larriba

Structure	COLLISION CROSS SECTION	MOBILITY
1	148.759019 A^2	1.523912 cm^2/Vs
2a	149.923028 A^2	1.512081 cm^2/Vs
2b	149.741265 A^2	1.513916 cm^2/Vs
2c	154.808106 A^2	1.464366 cm^2/Vs

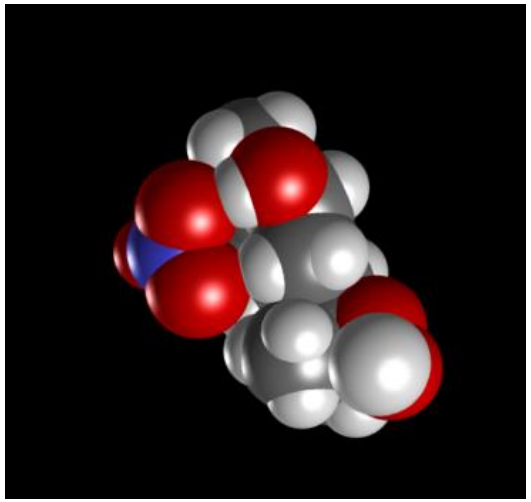
- Simulated mobiity ratios
- 1/2a = 1.0078
- 1/2b = 1.0066
- 1/2c = 1.0407

- Experiment matches almost perfectly ratio 1/2b
- Experimental mobilities for the two peaks 1.475 and 1465 which are too low but can be due to offset in THAB calibration

Sturcture1



Sturcture2b



Conclusions

- With combination of DMA-MS and computational chemistry possible to resolve initial oxidation steps
- NO3- SESI charging detects a-pinene oxidation states < O7
- Closure between experiment and model suggests structural identification
- Main problem: how to verify experiment vs model is not in agreement by accident?