

## SUPPLEMENTAL MATERIAL

Figure 1S: Photograph of components of reactive stage tandem differential mobility spectrometer (top frame) and completed assembly (bottom frame). Components from center to sides include 0.5 mm thick Teflon gasket to direct gas flow and ions through the analyser, planar DMS layers including metal sections (DMS1, reactive stage, DMS2, and detector) on insulator, Teflon retaining blocks, and aluminum frame to compress components into a single unit (bottom frame). Sample and gas flow enters the tandem DMS from right into a Swagelok union into which the  $^{63}\text{Ni}$  foil fitted. Flow is vented from top surface of analyser into a radioactive particulate filter.

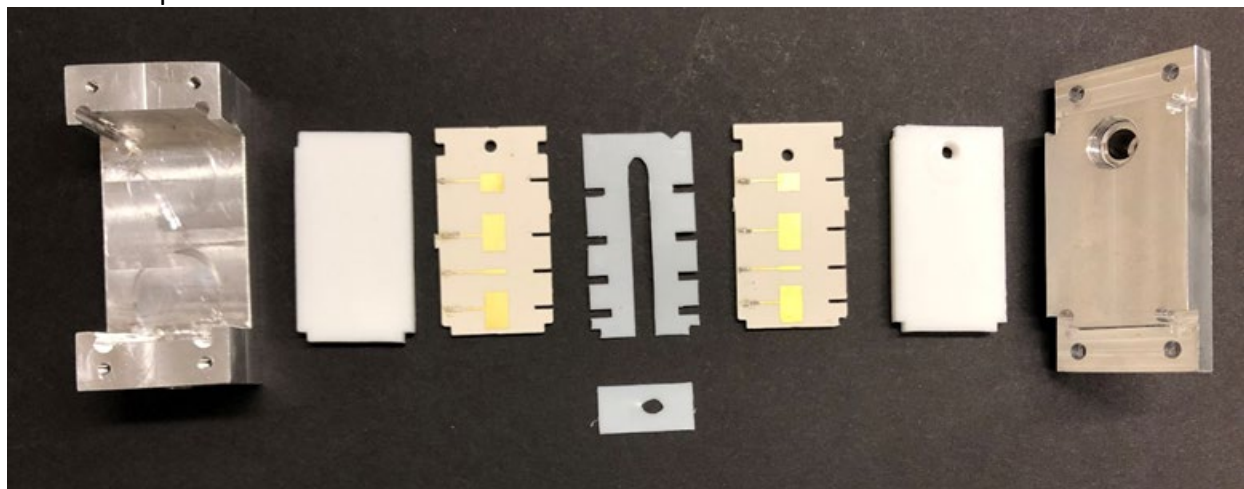


Figure 2S: Plot of ion intensity, chromatographic retention time, and DMS compensation voltage for mobility isolated proton bound dimers of n-aldehydes from butanal to nonanal. This graphic follows from Figure 2 when the protonated monomers are isolated without a reactive stage and leads into Figure 3 with fields in the reactive stage. Note the absence of measurable intensities for the RIP and minor intensity for proton bound dimer of octanal and nonanal.

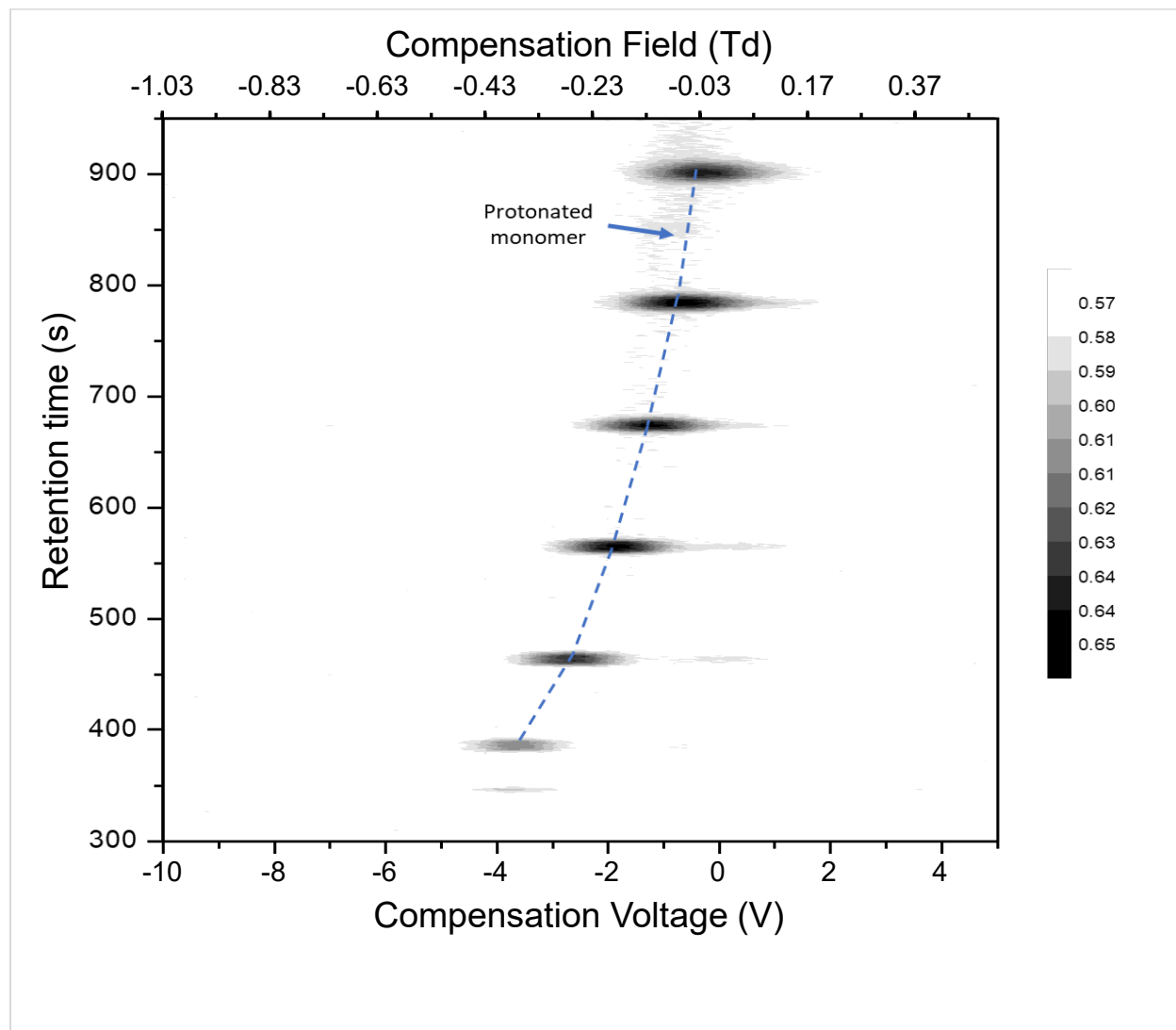


Figure 3S. SIMION model of electric field lines between the DMS and fragmenter plates in two different voltage configurations. DMS 1 and 2 plates are held 400 V apart (1 and 5 in the figure at -200V, 2 and 6 at 200V), while one plate of the fragmenter is shown at 1 and -1 kV (plate 3) and the other is held at ground (plate 4).

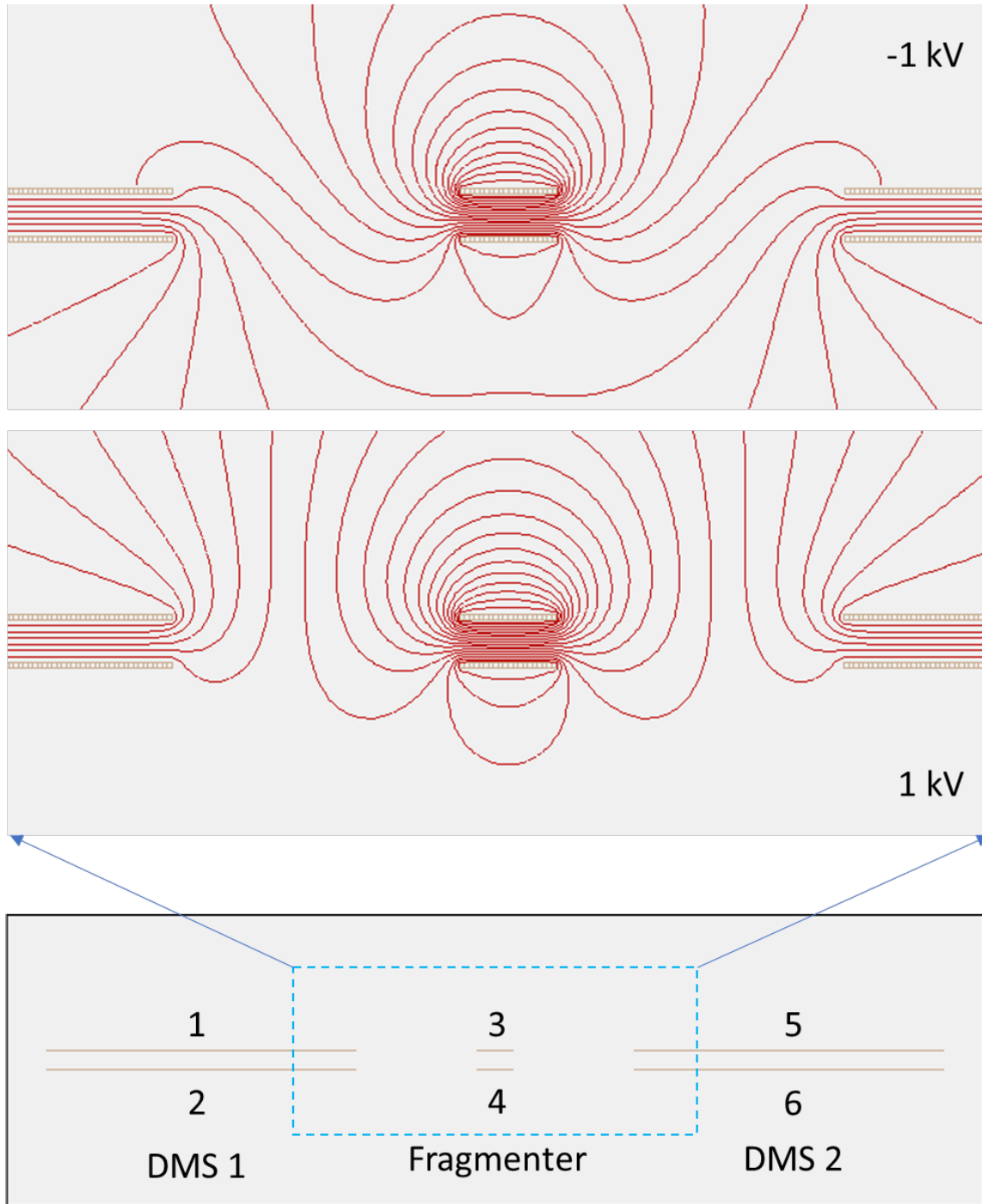


Table 1S: Summary of mass analysis of ions from ethers and ketones with a reactive stage at 179 Td. Fragmentation of ethers was observed in the tandem DMS yet ion intensities were below the limits for identification for all but two ethers. Ketones did not undergo measurable fragmentation up to 155 Td.

Ethers	M <sub>2</sub> H <sup>+</sup>	MH <sup>+</sup> (H <sub>2</sub> O) <sub>n</sub>			C <sub>3</sub> H <sub>7</sub> O <sup>+</sup>
Diethyl Ether	-6%	6%	-	-	-
Dipropyl Ether	-22%	3%	-	-	7%
Dibutyl Ether	-7%	-6%	-	-	-
Dipentyl Ether	-19%	-1%	-	-	-
Diethyl Ether	1%	3%	-	-	-
Diisopropyl Ether	-9%	-25%	-	-	21%
Ketones	M <sub>2</sub> H <sup>+</sup>	MH <sup>+</sup> (H <sub>2</sub> O) <sub>n</sub>	(MH <sup>+</sup> )-H <sub>2</sub> O		
2-pentanone	-17%	11%	-	-	-
2-hexanone	-9%	9%	3%	-	-
2-heptanone	-12%	15%	-	-	-
2-octanone	-2%	5%	-	-	-
2-nonanone	0%	2%	-	-	-
2-decanone	7%	-6%	-	-	-
MIBK	-31%	10%	3%	-	-
Pinacolone	-13%	17%	-	-	-

Table S2. More text. Could be from 12 to 24W depending on round error. Software fits the range at 13 W.

Power for reactive stage

GAA power (W)*	Voltage (V)	Field (V/cm)	Field (Td)	Amps (AC)**	Power (W)**
13.4	3000	30000	155	0.3	36
9.3	2500	25000	129	0.3	36
5.9	2000	20000	103	0.2	24
3.3	1500	15000	77	0.2	24
1.5	1000	10000	52	0.2	24
0.4	500	5000	26	0.2	24
0	0	0	0	0.1	12

\*taken from software controlling the reactive stage

\*\*taken from True RMS Clamp Meter (Fluke model 323) with 0.1 amp accuracy.