FRAGMENTATION, AUTO-MODIFICATION AND POST IONISATION PROTON BOUND DIMER ION FORMATION: THE DIFFERENTIAL MOBILITY SPECTROMETRY OF LOW MOLECULAR WEIGHT ALCOHOLS

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SUPPLEMENTAL TABLES AND FIGURES

TABLES

Table S1 **Properties of the alcohols used in the studies, with their molecular mass (*M*), proton affinity (*PA*), boiling point (Bp), density (ρ) and CAS number. [a] ChemSpider and [b] NIST**

Compound	M^b / g.mol^{-1}	PA^b / kJ.mol^{-1}	Bp^b / °C	ρ^a / g.cm^{-3}	CAS
Methanol	32.0	754.3	64.7	0.79	67-56-1
Ethanol	46.1	776.0	72.6	0.79	64-17-5
Propan-1-ol	60.1	786.5	95.8	0.80	71-23-8
Butan-1-ol	74.1	789.2	117.0	0.81	71-36-3

Table S2 **Instrumental parameters used in capturing dispersion plots, during studies on effect of Teff on alcohol DMS responses.**

Symbol.	Parameter	Value	
F_1	DMS transport gas flow	300-320	cm^3.min^{-1}
F_2	Test-atmosphere flow into the DMS transport gas	1-5	cm^3.min^{-1}
split	F2 split		1:10
T_{HS}	headspace vial temp.	40	°C
T_{DMS}	DMS temp / °C	45-130	°C
T_H	Transfer line temp	100	°C
H_d	d-IMS humidity / pmv	25-35	ppm(v/v)
RF	radio-frequency voltage (Dispersion field strength control)	500-1500	V
E_c	Compensation field scan range	-860 to 300	V.cm^{-1}
N_s	Number of steps in compensation field scan	100	
δ_t	Step duration	10	ms

Table S3 **Details of permeation sources used in experiments on effect of T_{eff} on n-alcohols DMS responses, with membrane thickness ($d$mem), calibration time ($t$cal), initial and final masses of permeation sources ($m$in and $m$fin),and mean calculated rate of diffusion (Q).**

Compound	d_{men} **/ mm**	t_{cal} **/ min**	m_{in} **/ g**	m_{fin} **/ g**	**Q / ng.min^{-1}**
MeOH	0.5	53,155	2.67243	2.66958	65.2
EtOH	0.5	90,250	2.84192	2.83294	99.50
PrOH	0.1	90,265	2.83331	2.82049	142.03
BuOH	0.1	56,202	2.48272	2.47757	63.96

Table S4 **Theoretical calculations of ROH ions formation in DMS at Teff between 391 and 523 K (effective temperatures of ions presented in Figures 1 and 2) where [i] is the concentration of the ROH at which specific ionclusters and their ratios are formed.**

ROH	Teff	[i] / mg m^{-3}	[i] / mg m^{-3}	[i] / mg m^{-3}	[i] / mg m^{-3}	[i] / mg m^{-3}
	/ K	PBT	PBT/PBD	PBD	PBD/PM	PM
		≥95%	1:1	≥95%	1:1	≥95%
Methanol	523	Out of range	2605	121	0.11	0.009
	458	Out of range	130	6.6	0.001	Out of range
Ethanol	481	Out of range	569	39.7	0.0005	Out of range
	391	110	3.5	0.17	Out of range	Out of range
Propan-1-ol	505	Out of range	2143	111	0.06	0.003
	441	Out of range	53.8	2.74	Out of range	Out of range

FIGURES

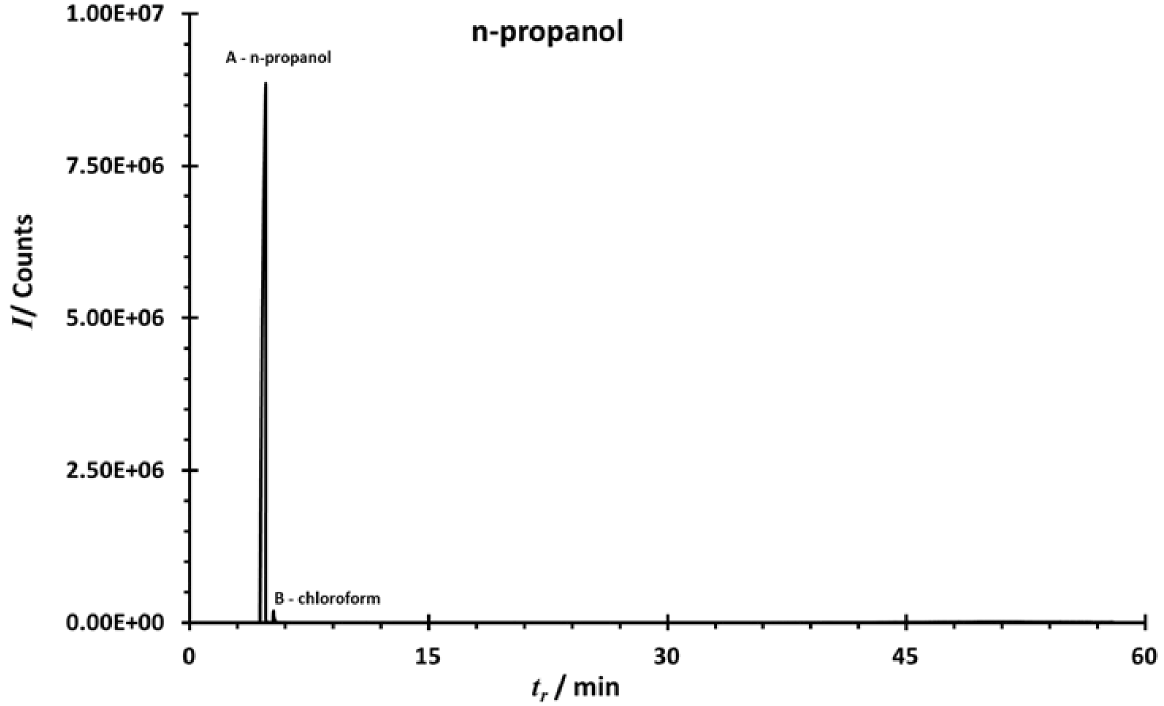

Figure S 1. An example total ion chromatogram of a 0.5 mg.g^{-1} propan-1-ol in methanol. Both solvents had been purged with high purity nitrogen before use. The chloroform residue from the syringe clean may be discerned at an estimated concentration of 0.1µg.g^{-1} in methanol.

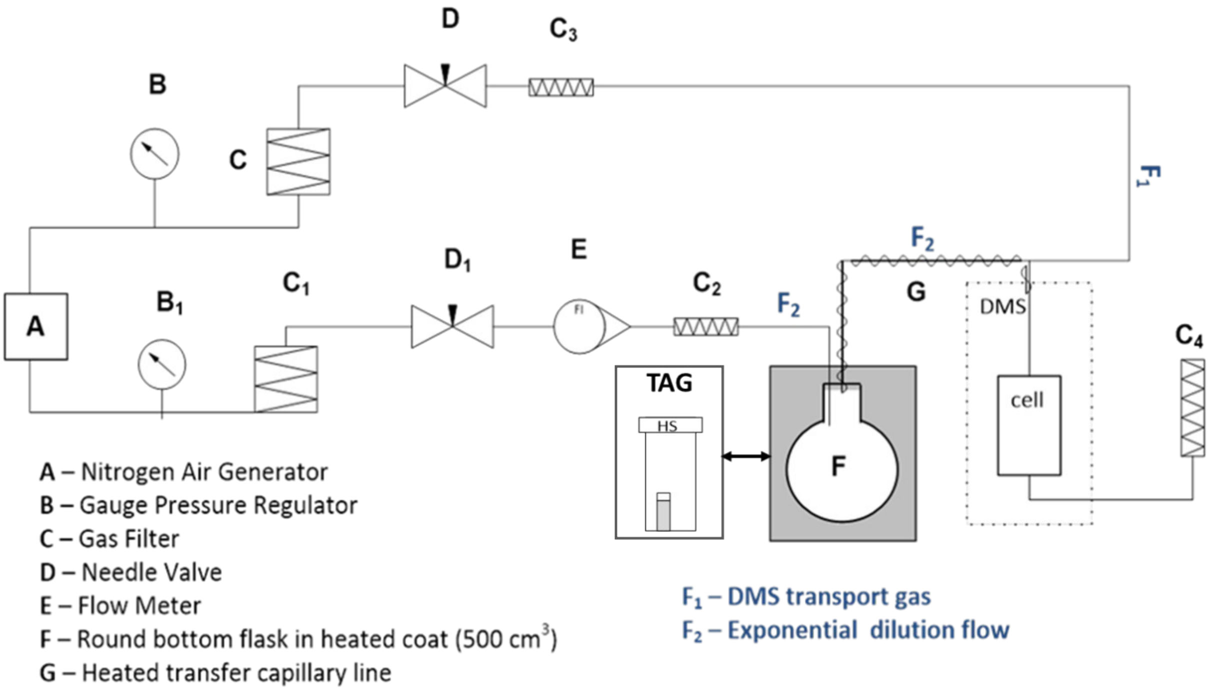

Figure S1. **Schematic of the System used in effect of concentration and T_{eff} on DMS spectra of alcohols from C_1 to C_5. Nitrogen carrier gas was distributed from nitrogen generator (A) and regulated using pressure regulators with gauge (B_1 and B_2). The gas passed through moisture (C and C_1) and purification (C_2 and C_3) filters and flow was controlled with stainless steel needle valves (D_1 and D_2) (Swagelok, UK). Nitrogen flow was split into two streams. F_1 provided around 300 ml min^{-1} DMS transport gas flow and F2 was connected to 500 cm^3 exponential dilution flask or TAG, transferring the vapors of the analyte into the transport gas. At the experiment another carbon trap was installed (C_4).**

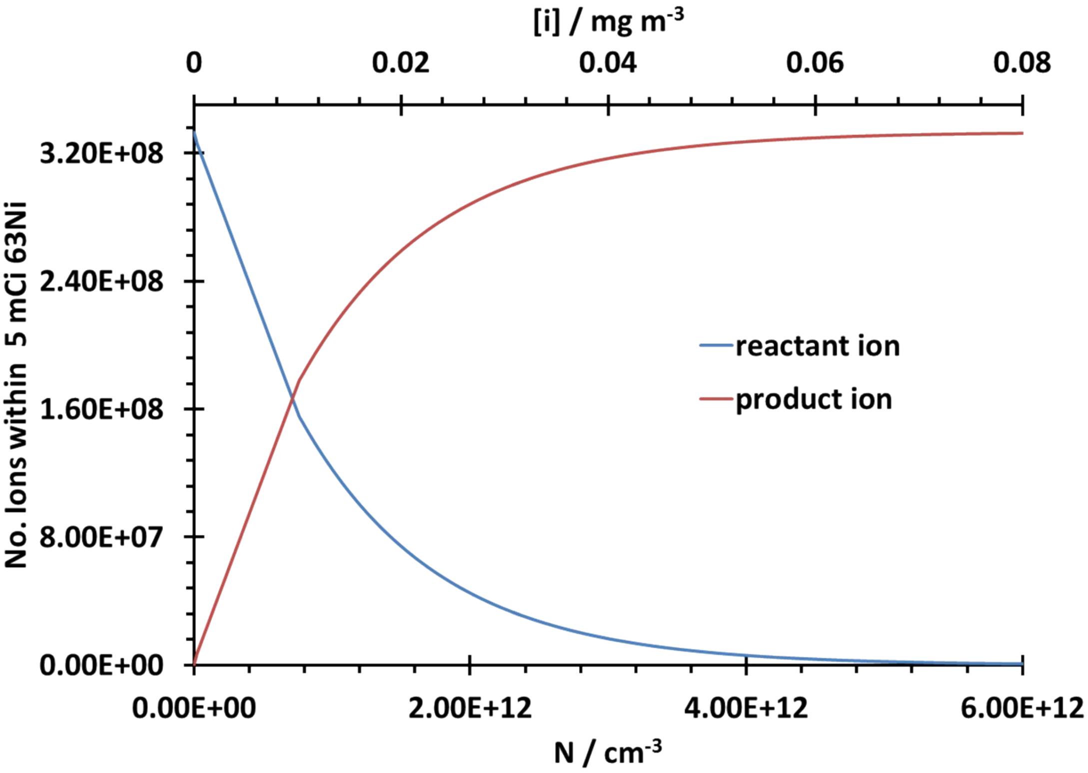

Figure S2. Formation of product ion and depletion of reactant ion as a function of number density [N]. Plots demonstrate relationship between DMS product ion formation (i_p), calculated for methanol ions, in relation to concentration [N], showing that 50% of RIP ions is expected to disappear at around 0.01 mg m^{-3} level of analyte concentration and to be completely lost at around 0.03 mg m^{-3}, where only PI should be observed.

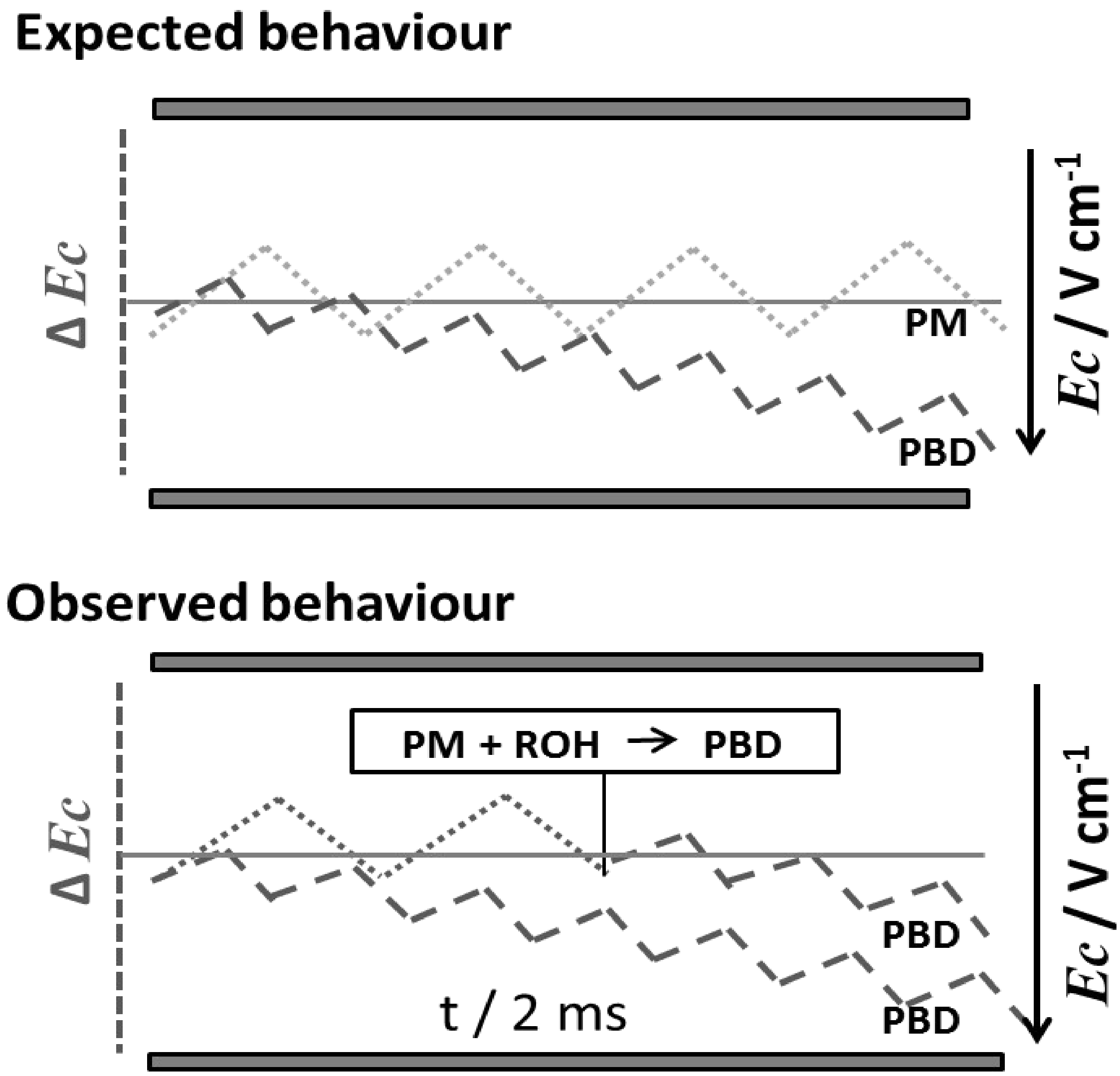

Figure S3. Schematic of the mechanism explaining the convergence of proton bound dimer (PBD) and protonated monomer (PM) signals observed with the increasing concentration of methanol ethanol). ΔE_C is a change of the position on the E_C scale, t is a travel time of an ion through the DMS cell. Dotted lines trajectory of protonated monomer. Dashed lines trajectory of proton bound dimer.

Top: non compensated ion trajectories for ions formed outside the ion filter in the reaction region.

Bottom: A collision between a protonated monomer and a neutral alcohol molecule within the ion filter generates a proton bound dimer and creates a new trajectory that will result in a shift in the E_C observed for the ion that falls between the values observed for the protonated monomers and proton bound dimers produced in the reaction region at the entrance to the ion filter.