Supplement of Atmos. Chem. Phys., 16, 12945–12959, 2016
http://www.atmos-chem-phys.net/16/12945/2016/
doi:10.5194/acp-16-12945-2016-supplement

Supplement of

A novel framework for molecular characterization of atmospherically relevant organic compounds based on collision cross section and mass-to-charge ratio

Xuan Zhang et al.

Correspondence to: Manjula R. Canagaratna (mrcana@aerodyne.com)

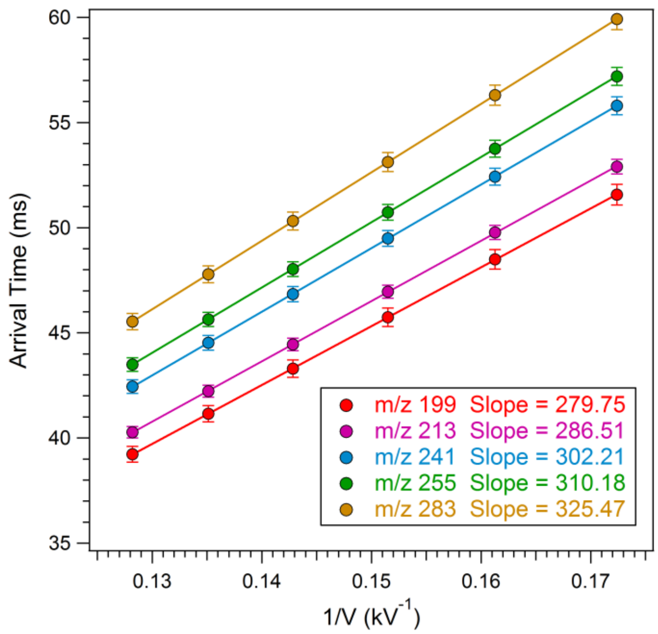

Figure S1. Linear regression of the recorded arrival time (t_a) for the deprotonated C_{12} (*m/z* 199), C_{13} (*m/z* 213), C_{15} (*m/z* 241), C_{16} (*m/z* 255), and C_{18} (*m/z* 283) *mono*-carboxylic acids on the inverse of the drift voltage in ~ 781.5 *Torr* of nitrogen gas at 340.4 K. Three replicate mobility measurements were performed and the deviations in the calculated mobility constants are within ±0.95%, ±0.67%, ±0.77%, ±0.74% and ±0.84%, respectively.

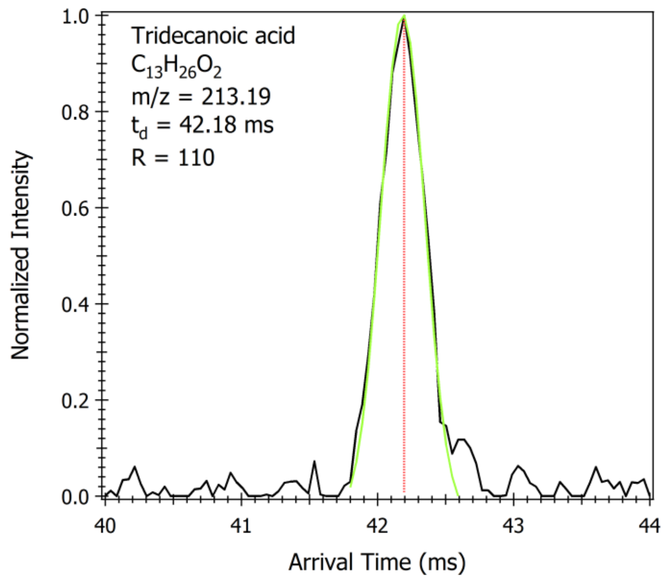

Figure S2. Arrival time distribution for the deprotonated tridecanoic acid (*m/z* = 213.19) with a drift voltage of 7.42 kV in ~ 781.5 *Torr* of nitrogen gas at 340.4 K.

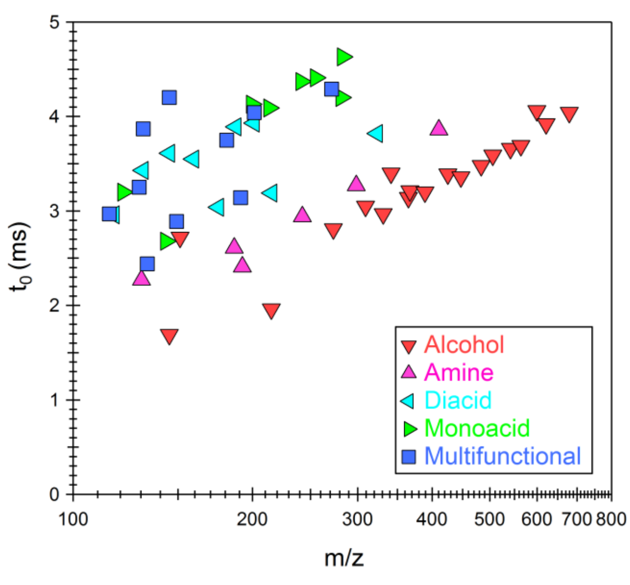

Figure S3. Time of the ion spent from the exit of the drift tube to the MS detector (t_0) as a function of mass-to-charge ratio (*m/z*). For a selected organic class, t_0 is proportional to $\sqrt{m/z}$ due to the time-of-flight separation. For different organic classes, t_0 values span a large range under the same *m/z* value due to different CID voltages applied (0 – 6 V) at the quadruple interface during the measurement.

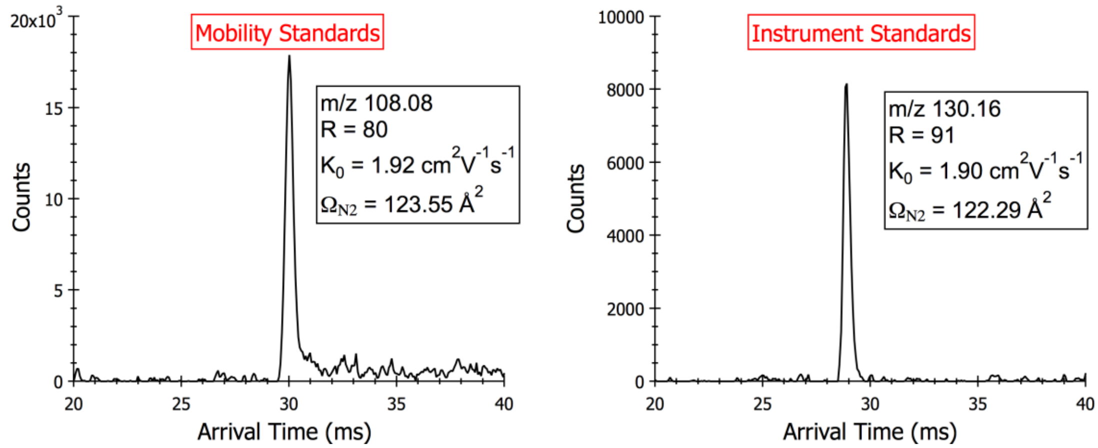

Figure S4. Arrival time distributions for the mobility standard 2,4-lutidine (*m/z* = 108.08) and the instrument standard tetraethyl ammonium iodide (*m/z* = 130.16) with a drift voltage of 7.42 kV in ~ 781.5 *Torr* of nitrogen gas at 340.4 K. Also shown are their calculated reduced mobility constants (K_0) and collision cross sections (Ω_{N_2}).

Table S1. Comparison of collision cross section values (Ω_{N_2}) for small ionic compounds measured from this study with those reported in literatures.

Name	*m/z*	Ω_{N_2}		% Diff.
		This study	Literatures	
Tetraethylammonium chloride	130	122.09	122.2[a]	-0.09
Tetrapropylammonium chloride	186	143.75	143.8[a]	-0.03
Tetrabutylammonium iodide	242	165.77	166.0[a]	-0.14
Tetrapentylammonium chloride	298	189.96	190.1[a]	-0.00
Tetraheptylammonium chloride	410	236.46	236.8[a]	-0.14
Malic acid	133	111.41	113.9[b]	-2.24
Citric acid	191	123.02	125.5[b]	-1.80

Data source: [a] Campuzano et al. (2012) and [b] Forsythe et al. (2015).

Table S2. Predicted collision cross sections ($\Omega_{N_2\_mod}$) by the (12-4) core model with best-fit parameters.

	m/z	r_m (Å)	*a* (Å)	ε (J)	$\Omega_{N_2\_mod}$ (Å²)	$\Omega_{N_2\_exp}$ (Å²)	% Diff.
Amine	130.16	7.35	2.20	1.91e-21	122.02	122.29	-0.22
	186.10	8.24	2.47	1.21e-21	144.18	143.97	0.14
	242.17	9.06	2.72	8.25e-22	166.62	166.01	0.37
	298.35	9.84	2.95	5.92e-22	189.48	190.20	-0.38
	410.47	11.34	3.40	3.36e-22	236.86	236.71	0.06
Carboxylic acid	143.11	7.55	3.02	3.16e-21	144.92	144.91	0.00
	199.17	8.20	3.28	2.28e-21	162.01	162.19	-0.11
	213.19	8.34	3.34	2.13e-21	166.18	166.37	-0.11
	241.22	8.62	3.45	1.87e-21	174.41	173.97	0.25
	255.23	8.75	3.50	1.76e-21	178.46	178.14	0.18
	283.26	9.01	3.60	1.56e-21	186.46	185.64	0.44
	281.25	8.99	3.60	1.58e-21	185.90	187.13	-0.66
Alcohol	273.17	8.02	3.21	2.49e-21	157.15	156.68	0.30
	309.23	8.31	3.32	2.16e-21	165.27	165.98	-0.43
	331.21	8.48	3.39	1.99e-21	170.20	169.90	0.17
	367.27	8.74	3.50	1.76e-21	178.25	179.45	-0.67
	389.24	8.90	3.56	1.64e-21	183.13	181.95	0.65
	425.31	9.15	3.66	1.47e-21	191.11	191.10	0.00
	447.28	9.30	3.72	1.38e-21	195.94	194.27	0.86
	483.35	9.54	3.82	1.24e-21	203.85	204.99	-0.56
	505.32	9.68	3.87	1.17e-21	208.64	206.52	1.03
	541.39	9.91	3.96	1.07e-21	216.49	218.82	-1.07
	563.36	10.05	4.02	1.01e-21	221.25	219.62	0.74
	599.42	10.27	4.11	9.27e-22	229.06	231.63	-1.11
	621.40	10.40	4.16	8.80e-22	233.80	232.15	0.71
	679.44	10.74	4.30	7.73e-22	246.31	246.65	-0.14

Matlab codes for calculating collision cross section Ω_{N_2}:

```
% Constants

q = 1.6e-19; % Ionic charge; unit: kg m2 V-1 s-2
kb = 1.3806e-23; % Boltzman constant; unit: m2 kg s-2 K-1
N0 = 2.69e25; % Number density of an ideal gas at 0 ∞C and 1 atm; unit: m-3
T0 = 273.15; % Standard temperature; unit: K
P0 = 1013.25; % Standard pressure; unit: mbar
M = 28; % N2 molecular weight; unit: amu
fc = 0.5; % Fraction of collisions in the cooling classes;
fh = 0.5; % Fraction of collisions in the heating classes;


% Instrument parameters
% !! Need to be constrained using instrument standard by Equation (5) !!

L = 21.5; % Drift tube length; unit: cm
T = 340.35; % Drift tube temperature; unit: K
P = 1041.91; % Drift tube pressure; unit: mbar
Ud = 8815; % Potential gradient on the drift tube; unit: V


% Measurements
m = 130.16; % Molecular weight of the ion; unit: amu
z = 1; % Number of charges on the ion;
slope = 200.51; % Linear regression of Equation (3)


% Calculations

K0 = (T0/T)*(P/P0).*(L^2./slope); % Reduced ion mobility constant; unit (cm^2/s/V)
Vd = (Ud/L/100).*K0; % Drfit velocity of the ion; unit: m s-1
Vt = ((8*kb*T)/(3.14*1.66E-27*(m*M)./(m+M))).^0.5; % Termal velocity of the ion; unit: m s-1
alpha = (2/3)*(1+fc*m./(m+M)+fh*M./(m+M)); % Correction coefficients for collision frequency
beta = (2./(m./(m+M))./(1+(m./(m+M)))).^0.5; % Correction coefficients for  momentum transfer
CCS = 10^20*(3*z*q/16/N0).*(2*3.14/kb/T0)^0.5.*((m+M)/m/M/1.66e-
27).^0.5.*(10^4./K0)*(1+(beta/alpha)^2*(Vd./Vt).^2)^0.5; % Collision cross section; unit: A^2
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