

Supporting Information for An Examination of Reduced Mobility, Collision Cross Section, and Alpha Values at Varying Reduced Electric Field Strengths in Ion Mobility

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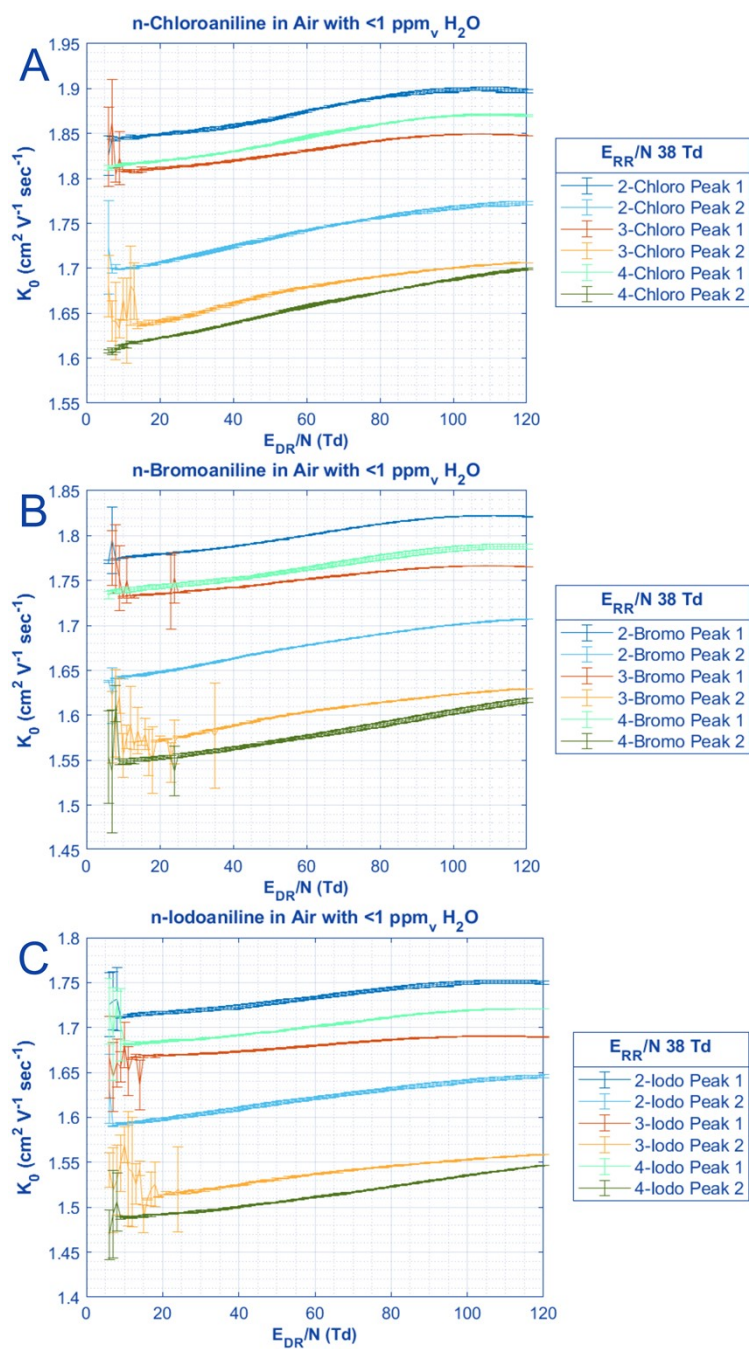


Figure S1: The mobilities of n-chloroanilines (A), n-bromoanilines (B), and n-iodoanilines (C) in air are plotted as a function of reduced electric field strength. The general trends for all species are similar to what is plotted in Figure 3. All experimental parameters are in Table 1.

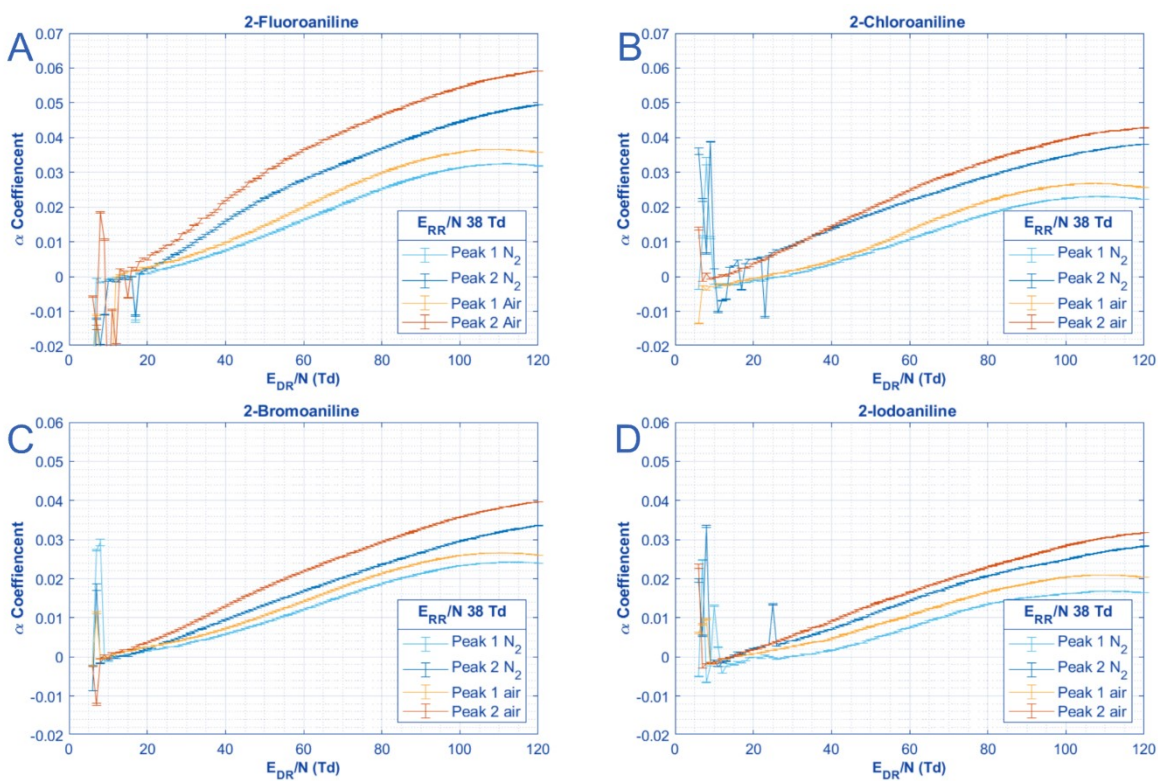


Figure S2: All alpha functions for the ortho halogenated anilines are graphed as a function of E/N . The respective $K_{0,E=0}$, α_2 , and α_4 are listed in Table 2 and S1. All experimental parameters are listed in Table 1.

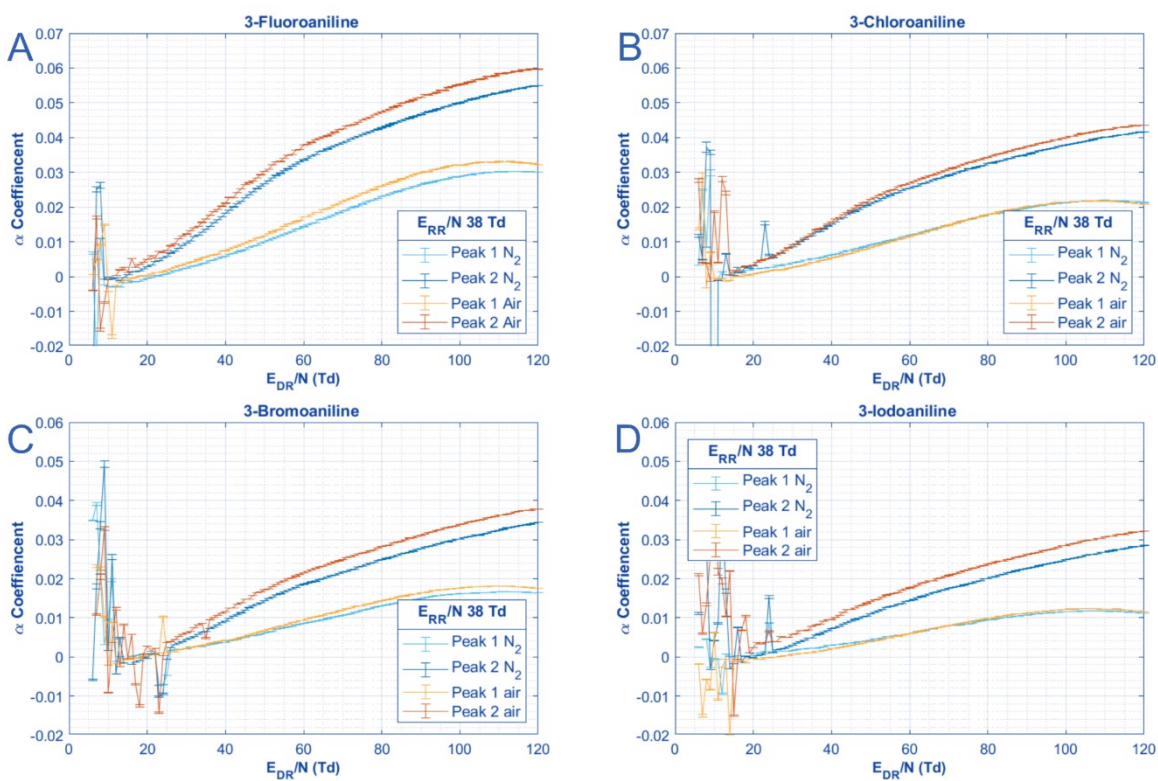


Figure S3: All alpha functions for the meta halogenated anilines are graphed as a function of E/N . The respective $K_{0,E=0}$, α_2 , and α_4 are listed in Table 2 and S1. All experimental parameters are listed in Table 1.

Table S1: The first 2 alpha coefficients plus the low-field mobility for the alpha function for all halogenated anilines in both peaks in air are given

	Peak 1 $K_{0,E=0}$	Peak 1 α_2 (*10 ⁻⁶)	Peak 1 α_4 (*10 ⁻¹⁰)	Peak 2 $K_{0,E=0}$	Peak 2 α_2 (*10 ⁻⁶)	Peak 2 α_4 (*10 ⁻¹⁰)
2-fluoro	1.925	10.9 ± 0.3	-5.1 ± 0.3	1.745	6.4 ± 0.3	-2.8 ± 0.3
3-fluoro	1.905	11.1 ± 0.2	-5.2 ± 0.2	1.71	5.43 ± 0.09	-2.22 ± 0.09
4-fluoro	1.905	10.2 ± 0.2	-4.4 ± 0.2	1.705	7.03 ± 0.07	-2.99 ± 0.06
2-chloro	1.85	7.6 ± 0.1	-3.4 ± 0.1	1.7	4.4 ± 0.1	-1.76 ± 0.09
3-chloro	1.81	8.1 ± 0.3	-3.8 ± 0.2	1.635	3.8 ± 0.2	-1.6 ± 0.1
4-chloro	1.815	8.9 ± 0.2	-3.8 ± 0.2	1.61	5.45 ± 0.02	-2.38 ± 0.02
2-bromo	1.775	7.1 ± 0.1	-3.1 ± 0.1	1.642	4.62 ± 0.06	-1.99 ± 0.05
3-bromo	1.735	6.3 ± 0.2	-2.7 ± 0.2	1.57	4.0 ± 0.2	-1.9 ± 0.2
4-bromo	1.74	5.0 ± 0.2	-1.4 ± 0.2	1.55	4.26 ± 0.02	-1.66 ± 0.02
2-iodo	1.715	6.1 ± 0.2	-2.7 ± 0.2	1.595	3.47 ± 0.07	-1.43 ± 0.06
3-iodo	1.67	5.3 ± 0.3	-2.3 ± 0.3	1.51	3.9 ± 0.1	-2.0 ± 0.1
4-iodo	1.68	4.21 ± 0.09	-1.13 ± 0.08	1.49	4.1 ± 0.2	-1.7 ± 0.2

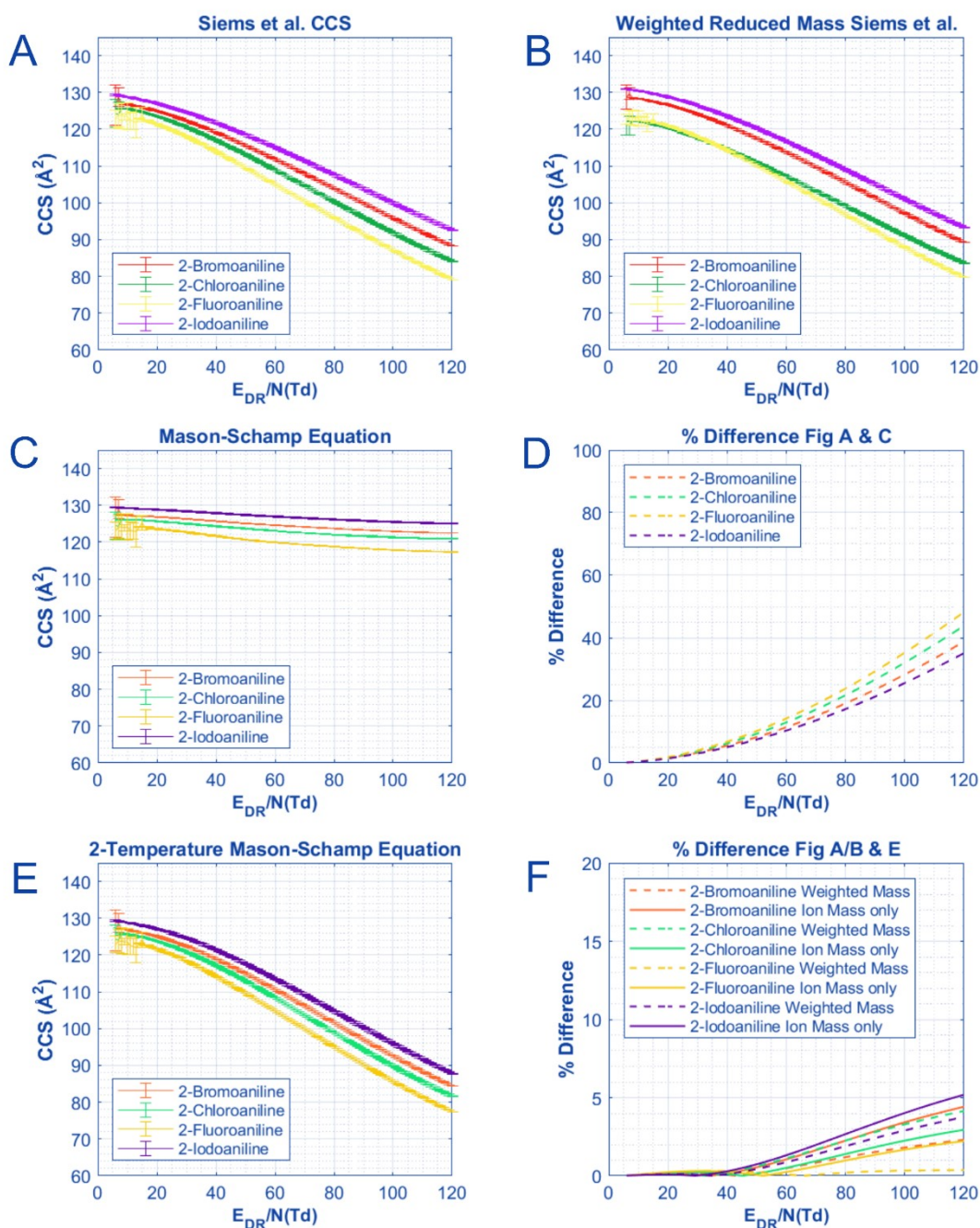


Figure S4: For each of the ortho-halogenated anilines, the CCS values and % difference between methods are shown with the corrections from Siems et al. (A) used as the basis for comparison. If the reduced mass is treated as non-static (i.e. gradually losing 18 from water declustering) with the corrections from Siems et al. the difference is 1-2 Å depending on analyte mass (B). Depending on if temperature in the Mason-Schamp equation is assumed to be the same as the drift gas (C) or calculated from the reduced field strength using the Wannier equation (E) the results are drastically different from the corrections made from Siems et al. (D & F).

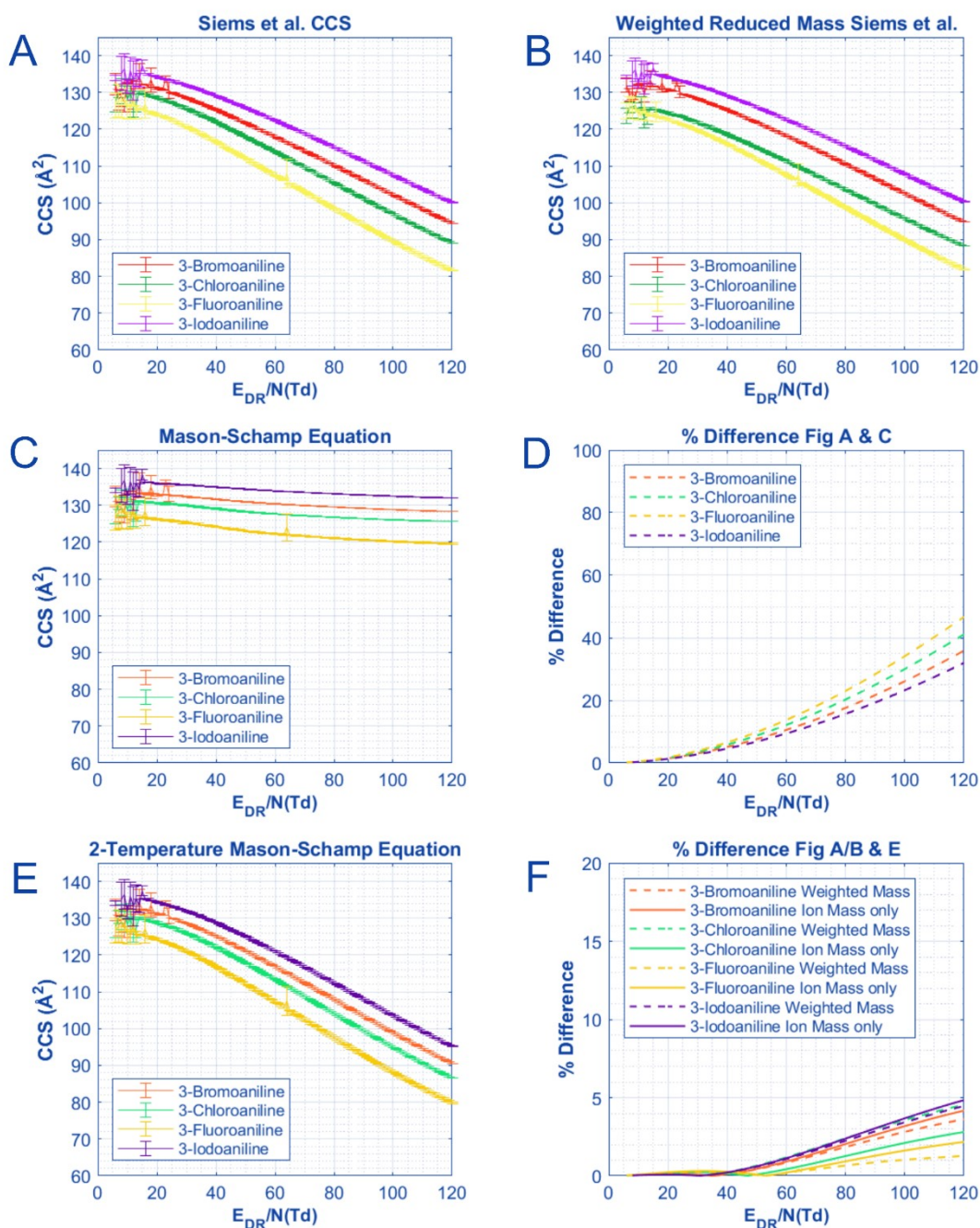


Figure S5: For each of the meta-halogenated anilines, the CCS values and % difference between methods are shown with the corrections from Siems et al. (A) used as the basis for comparison. If the reduced mass is treated as non-static (i.e. gradually losing 18 from water declustering) with the corrections from Siems et al. the difference is 1-2 \AA depending on analyte mass (B). Depending on if temperature in the Mason-Schamp equation is assumed to be the same as the drift gas (C) or calculated from the reduced field strength using the Wannier equation (E) the results are drastically different from the corrections made from Siems et al (D & F).

Table S2: A brief description of each column in the accompanying spreadsheet of mobilities. Each distinctive ion is represented with “#” here where in the table the # corresponds to Peak 1, 2, or 3. For names marked with a *, these values are at the end of the table with the reduced masses treated as non-static based upon cluster equilibrium.

Column title	Description
Drift Region E/N (Td)	(E_{DR}/N) The reduced electric field strength in the drift region for the measurement
Reaction Region E/N (Td)	(E_{RR}/N) The reduced electric field strength in the reaction region for the measurement
Pressure (mbar)	The pressure inside the reaction and drift region for the measurement
Temperature (C)	The temperature in Celsius for the measurement
Drift Voltage (V)	The voltage applied to the drift region for the measurement whereas the other end of the drift tube is grounded
Effective Temperature # (K)	The effective temperature of the ion according to the corrected Wannier equation described by Siems et al. and using E_{DR}/N to calculate the field ¹
Drift Time # (ms)	The drift time of the ion in ms (this is converted into K_0 and 2 variants of CCS)
Drift Velocity # (m/s)	The drift velocity of the ion as described by Siems et al. (drift length/ drift time) ²
Thermal Velocity # (m/s)	The thermal velocity of the neutral carrier gas as described by Siems et al. ² $(8k_b T/(\mu\pi))^{0.5}$
Ion Mass # (Da)*	The mass of the ion (protonated or the molecular ion) in Daltons
K_0 Ion # ($\text{cm}^2 \text{m}^{-1} \text{s}^{-1}$)	Reduced mobility of the ion where one half of the gate pulse width is subtracted from the ion’s drift time
CCS Ion # (Mason-Schamp, Å^2)	Ion-neutral collisional cross section according to the Mason-Schamp equation
Alpha Ion #*	(α_{MT}) coefficient as described by Siems et al. ² (See Eqn S2 below)
Beta Ion #*	Transverse velocity coefficient as described by Siems et al. ² (See Eqn

	S3 below)
Fc Ion*	The fraction of cooling (ratio of cooling vs heating collisions between ion and neutral)using the table from Siems et al. ¹
CCS Ion # (BLH Corrected, A ²)*	Ion-neutral collisional cross section as corrected by Siems et al. ²

Equations:

The derivations as described by Siems et al.^{1,2} begins with breaking up the reduced mass of the ion neutral pair into the mass fractions of the ion and neutral collision (Equations S1-S2) which allows for weighting the reduced mass of the ion/neutral pair based on the energy of the collision:

$$\hat{m} = \frac{m}{m + M} \quad \text{Equn S1}$$

$$\hat{M} = \frac{M}{m + M} \quad \text{Equn S2}$$

Where m is the mass of the ion and M is the mass of the neutral gas. Here \hat{m} represents the mass fraction of the ion and \hat{M} represents the mass fraction of the neutral. In later calculations, all units are converted in to SI to simplify things, but since each of the mass fractions are ratios, the conversion from amu to grams is unnecessary for their purpose. For the momentum transfer between ion and neutral along the axis of the drift tube (Equation S3), the fraction of ion cooling and heating are used with the mass fractions above:

$$\alpha_{MT} = \frac{2}{3} * (1 + f_c \hat{m} + \hat{M}(1 - f_c)) \quad \text{Equn S3}$$

α_{MT} is the momentum transfer coefficient as determined from the mass of the ion and neutral (Eqns S1-S2). f_c is the fraction of cooling from the number of collisions of ion and neutral and is obtained via a field dependent probability distribution as described by Siems et al.¹ f_c is always between 0.5 to 1 where at $E/N=0$ Td, $f_c=0.5$ and approaches 1 as E/N increases. For practical purposes in calculation the fraction of cooling is found in Table S1 in the Supporting Information for Siems et al.¹ and additionally found in the ion mobility calculator worksheet (Ion Mobility MoCal v3.xlsm) or corresponding Jupyter notebook (Ion Mobility Calculator 2) on Github (<https://github.com/bhclowers/DAMS/tree/master/Ion%20Mobility%20Calculator>).

The other variable to consider (Equn S4) represents the transverse velocity coefficient which is solely a function of the mass fraction of the ion:

$$\beta = \sqrt{\frac{2}{\hat{m} * (1 + \hat{m})}} \quad \text{Equn S4}$$

Beta is the transverse velocity coefficient and is the degree of ion movement perpendicular to the electric field from neutral scattering. Beta combined with the velocity of the ion (v_d , Equn

5) and the thermal velocity of the neutral drift gas (v_T , Equn 6) and gives the rotational velocity of the ion but relies on a few additional calculations first:

$$v_d = \frac{t_d}{l} \quad \text{Equn S5}$$

$$v_t = \sqrt{\frac{8k_b T}{\pi\mu}} \quad \text{Equn S6}$$

Where l is the length of the drift tube in meters, t_d is the time the ion packet reaches the detector in seconds, k_b is Boltzmann's constant ($1.3807 \cdot 10^{-16}$ erg/K), T is the thermal temperature of the drift gas in Kelvin, and μ is the reduced mass in grams. These variables give the rotational velocity (v_r) in Equation S7 below:

$$\hat{v}_r = v_T + \beta v_d \quad \text{Equn S7}$$

Also called the average speed of the ion from thermal motion alone, i.e. without the presence of an electric field and only from Brownian diffusion. The variable used in the corrections to the Mason-Schamp equation is the correlation coefficient defined in Equn S8-S9 (depending on field):

$$\xi = \sqrt{1 + \left(\frac{\beta v_d}{\alpha v_T}\right)^2} \quad \text{Equn S8}$$

$$\xi = \sqrt{1 + \frac{8}{3\pi\hat{m}}\left(\frac{v_d}{v_T}\right)} \quad \text{Equn S9}$$

Which is the "correlation coefficient" and can be defined either according to momentum transfer theory (Equn S8) or two temperature theory (Equn S9). Then the results can be plugged into Equation 5 to give the corrected cross sections in Figure 5.

References

- (1) Siems, W. F.; Viehland, L. A.; Hill, H. H. Correcting the Fundamental Ion Mobility Equation for Field Effects. *Analyst* **2016**, *141* (23), 6396–6407.
- (2) Siems, W. F.; Viehland, L. A.; Hill, H. H., Jr. Improved Momentum-Transfer Theory for Ion Mobility. 1. Derivation of the Fundamental Equation. *Anal. Chem.* **2012**, *84* (22), 9782–9791.