

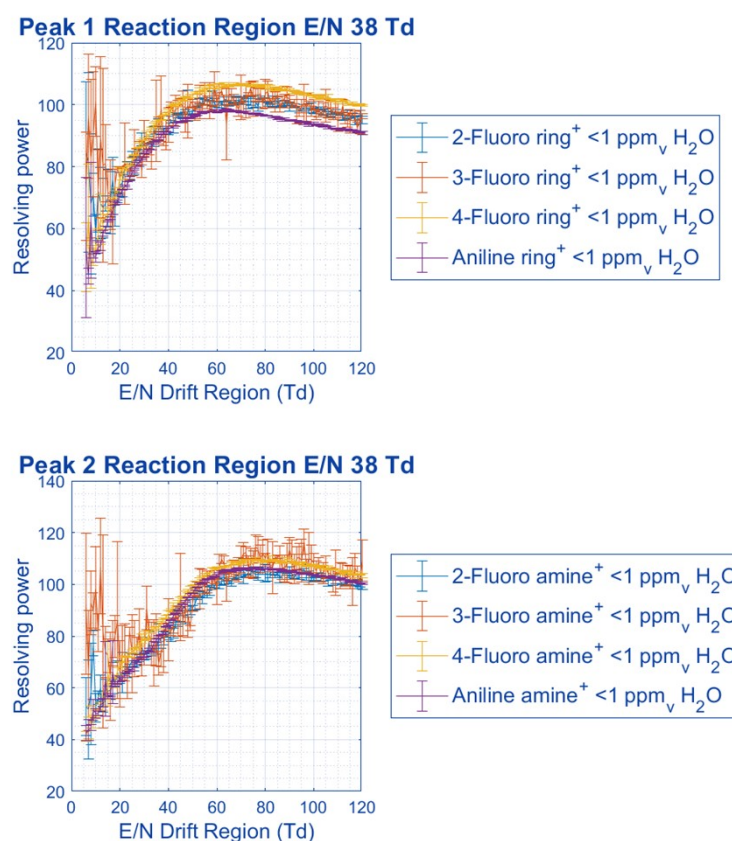
# Supporting Information for the Origin of Isomerization of Aniline Revealed by High Kinetic Energy Ion Mobility Spectrometry (HiKE-IMS)

Cameron N. Naylor,<sup>1\*</sup> Christoph Schaefer,<sup>1</sup> Ansgar T. Kirk,<sup>1</sup> Stefan Zimmermann<sup>1</sup>

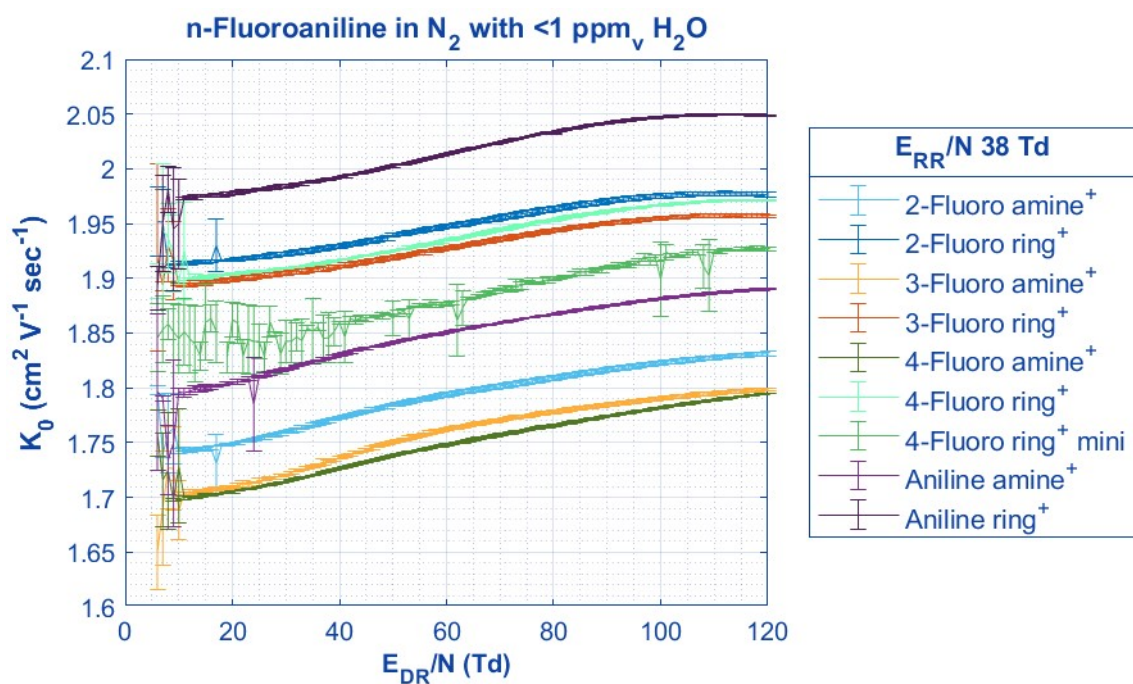
<sup>1</sup> Leibniz University Hannover, Institute of Electrical Engineering and Measurement Technology, Department of Sensors and Measurement Technology, 30167 Hannover Germany

\*Corresponding Author: [naylor@geml.uni-hannover.de](mailto:naylor@geml.uni-hannover.de)

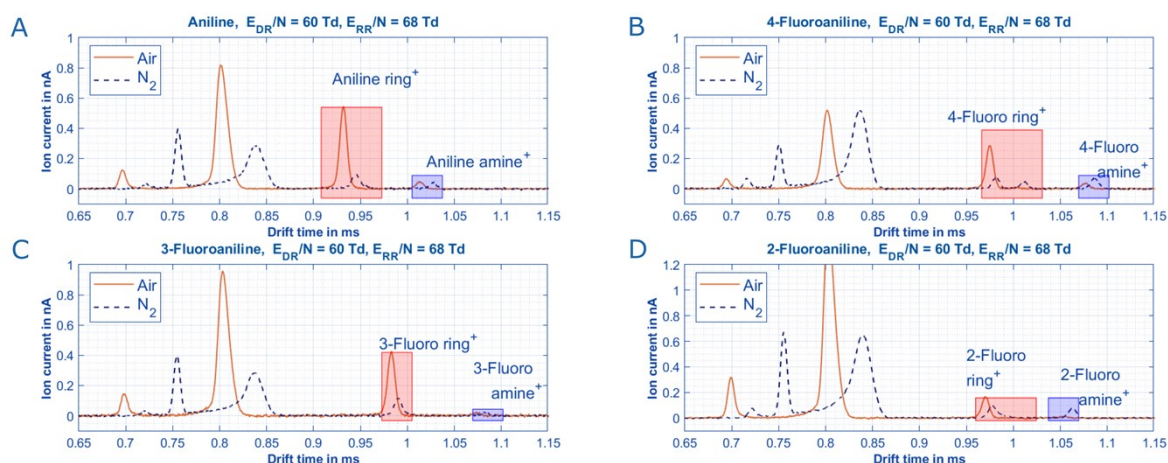
## Figures



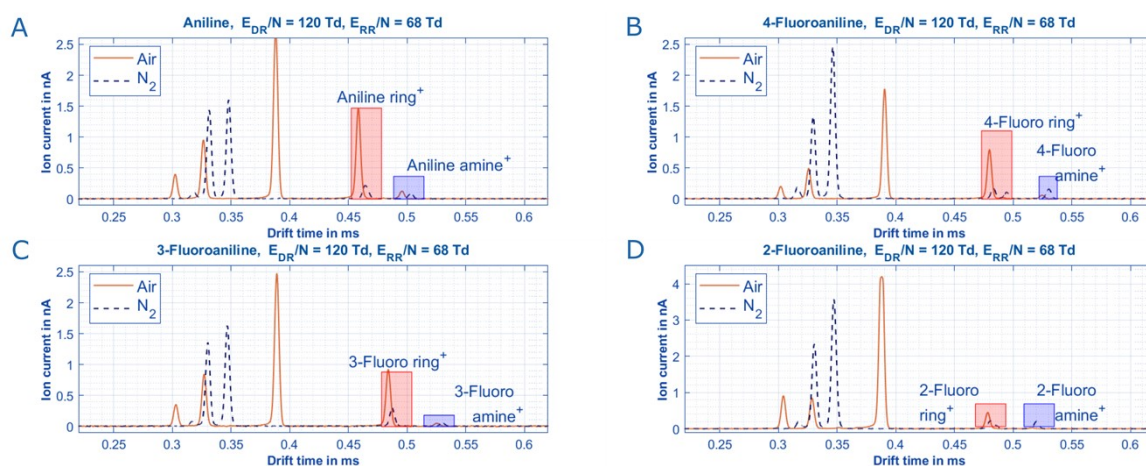
**Figure S1:** The resolving power of each aniline peak. Interestingly for aniline and all fluoroanilines, the maximum resolving power of each peak is reached at different  $E_{DR}/N$  values. Additionally, the resolving powers for the amine-charge located aniline does not have a constant increase, but instead remains constant between 20-30 Td before increasing again. The inflection points in the mobility changes might originate from dehydration of the amine peak.



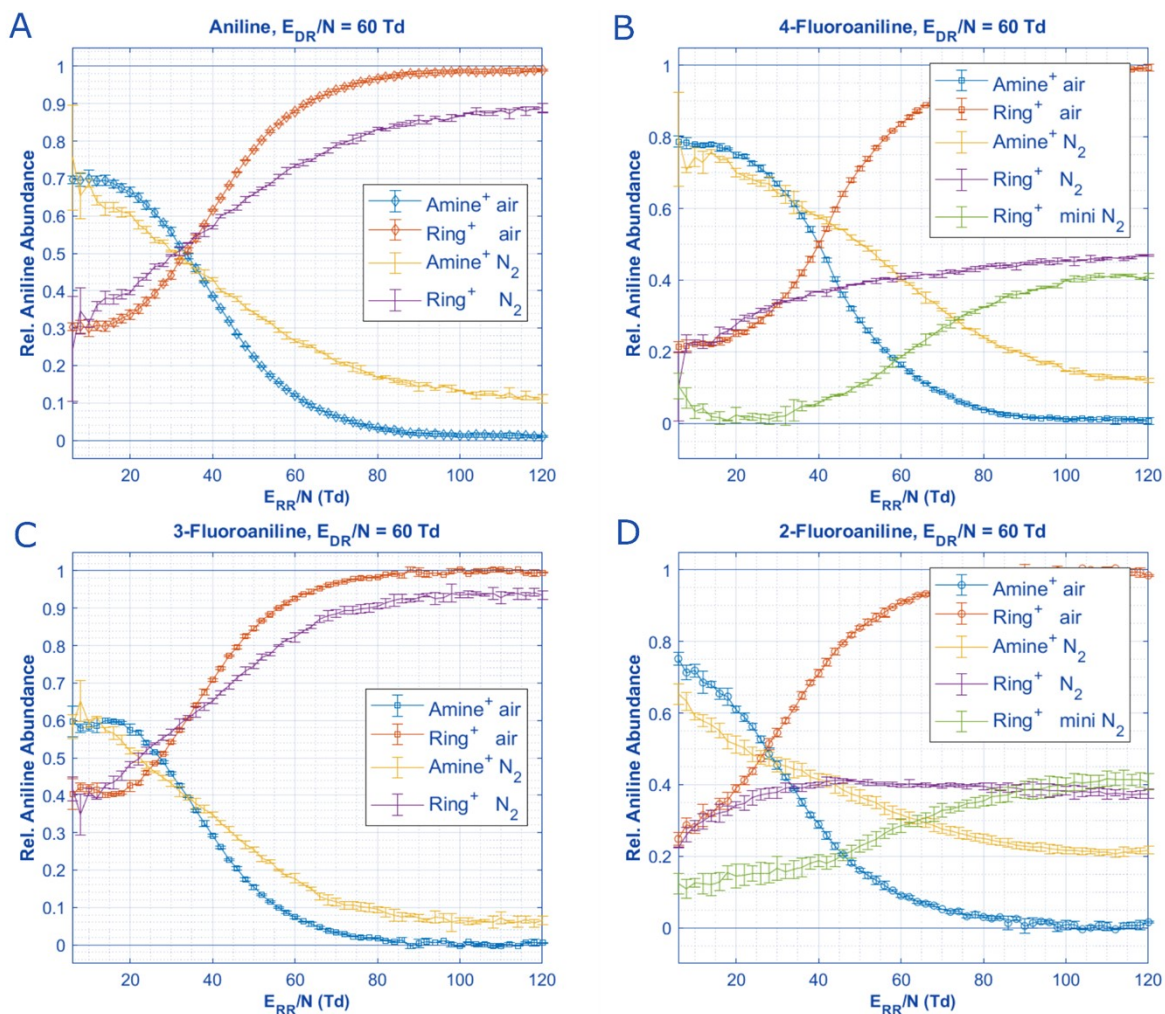
**Figure S2:** The reduced mobilities of each aniline peak as measured in nitrogen. The third peak of 4-Fluoroaniline is added to the graph is labeled as “4-fluoro ring mini.”



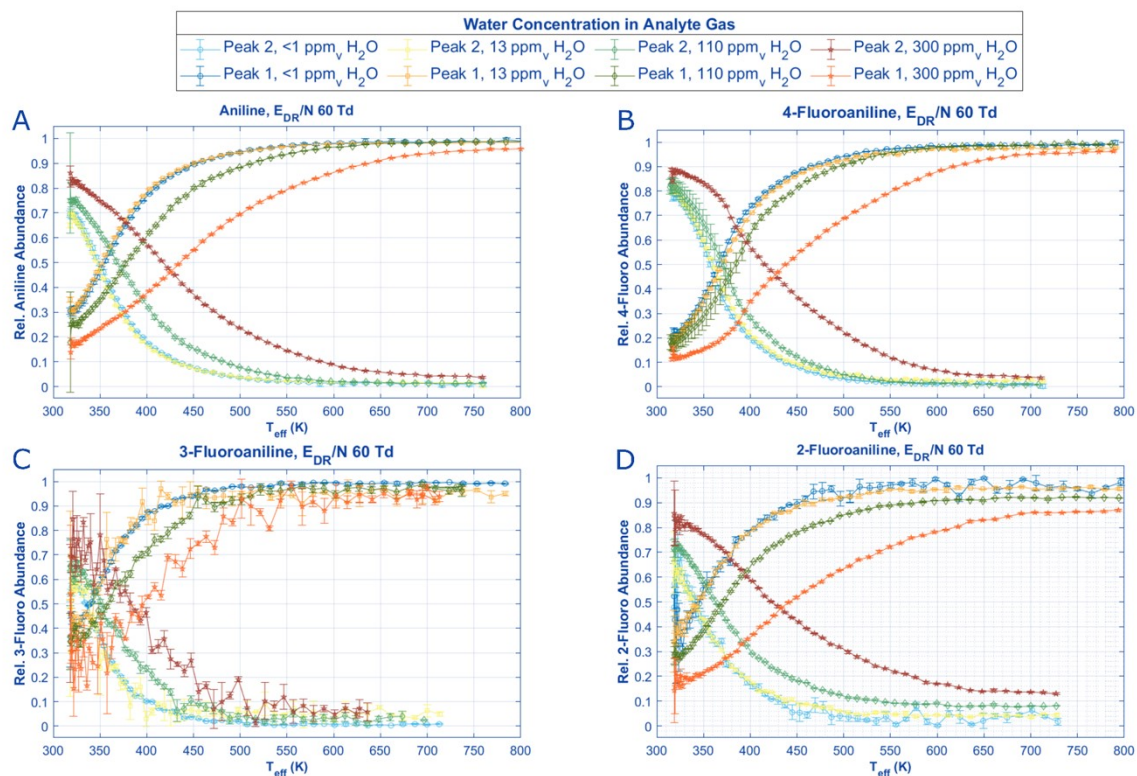
**Figure S3:** When the  $E_{DR}/N$  across the is 60 Td the abundances of each peak as the drift gas changes is shown. The aniline ring<sup>+</sup> peak is still in the most abundance when oxygen is present (i.e. in air) but much less abundant in nitrogen. Also like in Figure S4, the abundance of the proton transfer peak remains roughly the same in both gases. Lastly, the third peak of 4-fluoroaniline in nitrogen is present at this  $E_{DR}/N$ , as well.



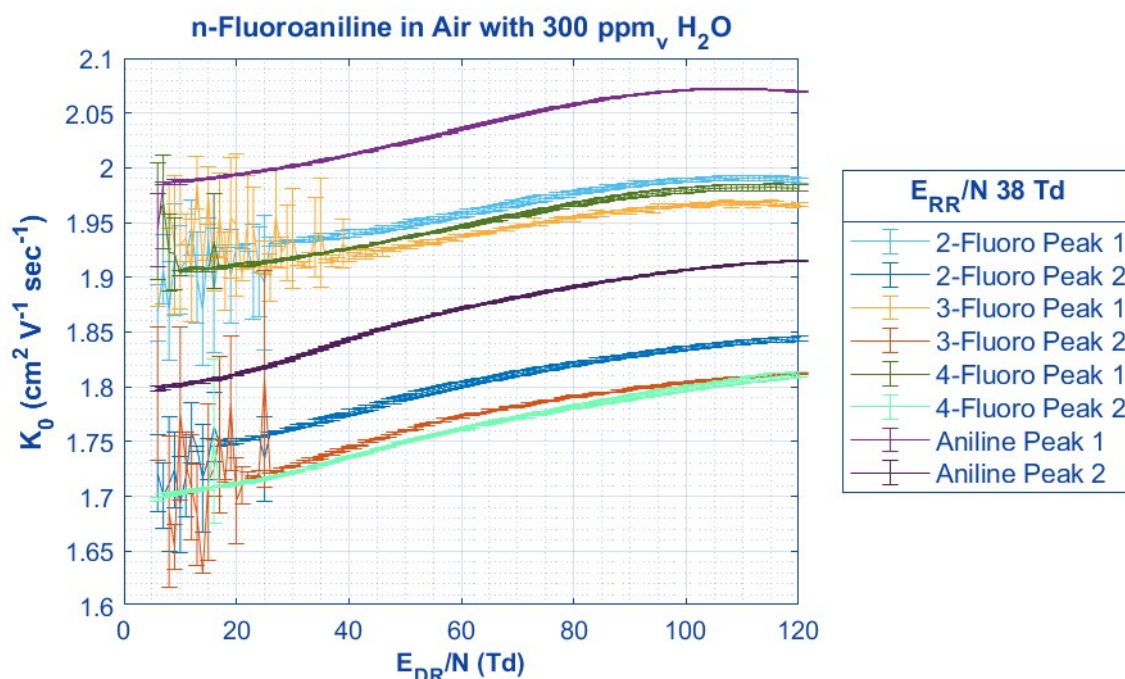
**Figure S4:** Example spectra of aniline and the n-fluoroaniline measured in air (orange, solid line) and nitrogen (blue dashed line) are plotted. Although this is one spectrum with  $E_{DR}/N$  of 120 Td, both aniline peaks are separated and present in significant abundance. Interestingly, the impact of the reactant ions on the intensities of the aniline peaks is visible here, where the ring conformer is significantly more abundant in air than in nitrogen. This suggests the presence of  $O_2^+$  and  $NO^+$  in the drift tube is responsible for the charge transfer ionization mechanism of this conformer. Additionally, 4-fluoroaniline, when measured in nitrogen (B), has an additional peak with a mobility value slightly smaller than the ring conformer, suggesting there is another possible conformation for the molecular ion peak.



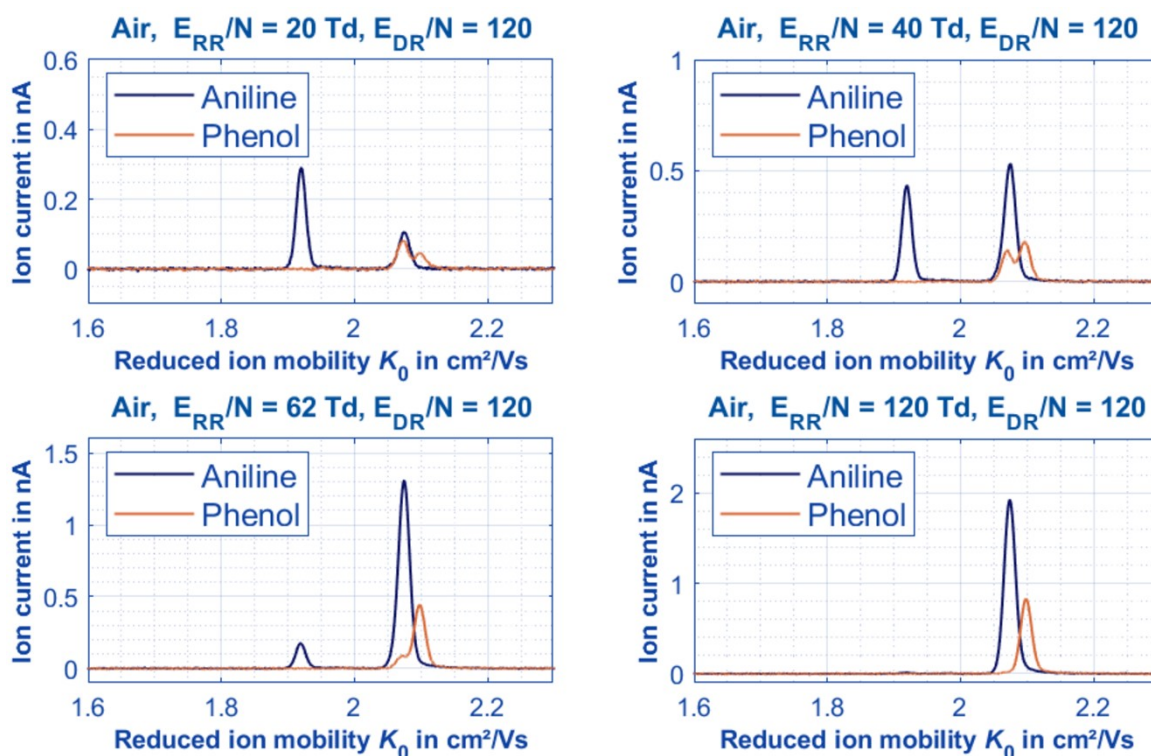
**Figure S5:** When the  $E_{DR}/N$  is held constant at 60 Td and the  $E_{RR}/N$  is scanned for each analyte in air and nitrogen, the abundance of the species can be monitored. These abundances are largely the same as those in Figure 6 when the  $E_{DR}/N$  is 120 Td which indicates that the drift region reduced electric field strength has no effect on speciation in either drift gas.



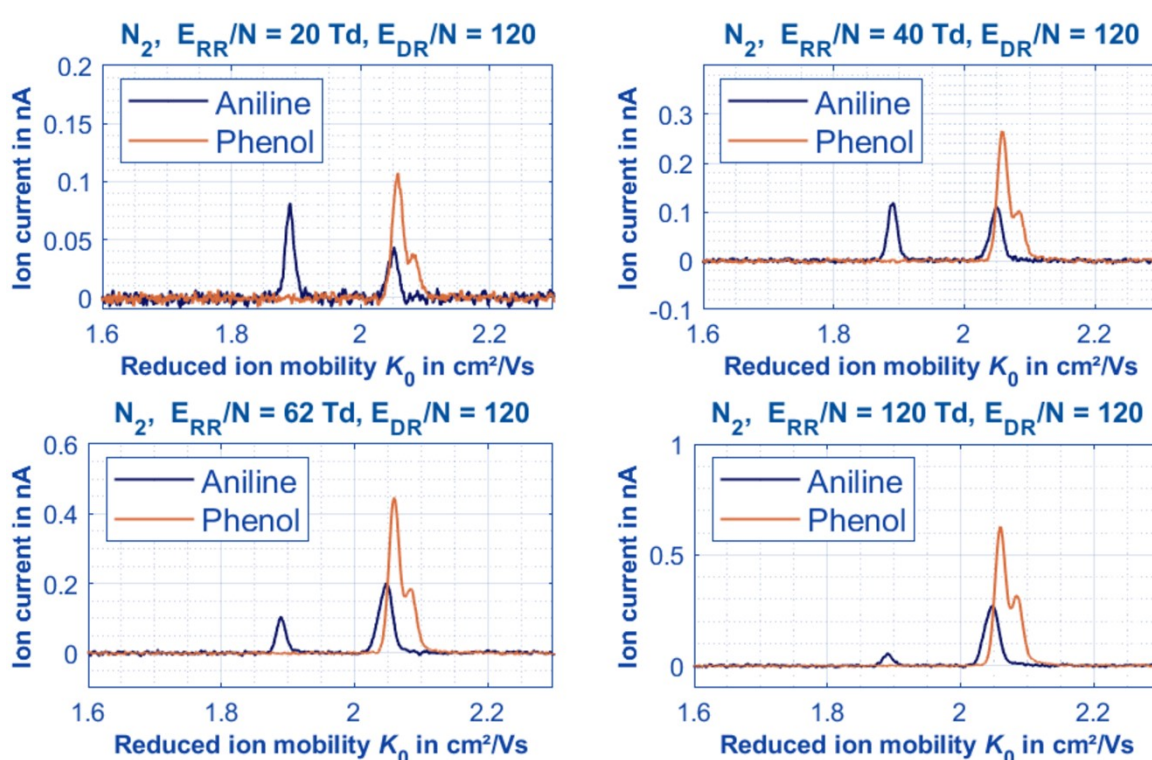
**Figure S6:** With the  $E_{DR}/N$  at 60 Td instead of 120 Td in Figure 5, the change in effective temperature as the  $E_{RR}/N$  is scanned can be graphed. The inflection points and abundances are largely the same what is shown in Figure 5. However, low signal to noise ratio for 3-fluoroaniline is due to the lower reduced electric field strength in the drift region.



**Figure S7:** The mobilities of aniline and n-fluoroanilines in air with 300 ppm<sub>v</sub> H<sub>2</sub>O present in the reactant gas. This graph is nearly identical to the one in Figure 2 except for the error associated with some of the measurements. The maximum difference in  $K_0$  values between these measured in 300 ppm<sub>v</sub> H<sub>2</sub>O and those in <1ppm<sub>v</sub> H<sub>2</sub>O is 0.008, or 0.5% difference. This difference is not larger than the experimental error between triplicates of mobility measurements within the same moisture content.



**Figure S8:** Spectra of aniline and phenol (Sigma part: W322318) measured in air at varying  $E_{RR}/N$  settings. Similar to aniline, phenol has 2 peaks that vary in intensity as a function of ionization conditions in similar abundances between the two peaks. Unlike aniline, the two phenol peaks are unable to be baseline separated at the highest possible reduced electric field strength in the HiKE-IMS. Furthermore, while the protonated phenol peak has a similar mobility to Aniline's Peak 1, Phenol's molecular ion peak has a distinctly different mobility from aniline. Given that we see no shoulder on Aniline's Peak 1 and the mass spectra in Figures 2 and 7 have no 95 Da or 113 Da peak respectively, the nucleophilic substitution as observed by Kune et al. is not happening in our HiKE-IMS.<sup>1</sup>



**Figure S9:** Spectra of aniline and phenol measured in nitrogen at varying  $E_{RR}/N$  settings. The mobilities of Aniline's Peak 1 and Phenol's Peak 2 are noticeably different in this gas compared to air (Fig. S8). Another stark difference between aniline and phenol, is that phenol speciation does not change as a function of  $E_{RR}/N$  but aniline does. Further investigation of why this occurs is out of the scope of this manuscript.

## References

- (1) Kune, C.; Delvaux, C.; Haler, J. R. N.; Quinton, L.; Eppe, G.; De Pauw, E.; Far, J. A Mechanistic Study of Protonated Aniline to Protonated Phenol Substitution Considering Tautomerization by Ion Mobility Mass Spectrometry and Tandem Mass Spectrometry. *J. Am. Soc. Mass Spectrom.* **2019**, *30* (11), 2238–2249.