Response to reviewer #1's comments

We would like to thank the reviewer for the positive reception of our work and constructive comments that helped us to improve our manuscript. In this document we provide our replies to the reviewer's comments. Page and line numbers in the responses correspond to those in the AMTD paper.

1. ***P5, L15-16. The authors stated that organic compounds with lower sensitivities under dry conditions exhibit a stronger humidity dependence and that higher molecular weight molecules show a weaker humidity dependence. It would be interesting to plot the sensitivity of calibrated compounds versus their molecular weight to check if there is a clear relationship between sensitivity and molecular weight. It is also interesting to check if there is a connection (relationship) between water dependence and V_{50} or $KE_{cm\ 50}$ values for OVOCs.***

   On average, heavier molecules are detected at the higher sensitivity, however the connection between the sensitivity of calibrated compounds and their molecular weights is relatively weak ($R^2 = 0.35$) as shown in Fig. S5.

   We include the following sentence to the manuscript (P5 L9):

   "There is no strong correlation between the sensitivity to the calibrated compounds and their molecular weight ($R^2 = 0.35$, Fig. S5)."

   We include the following figure in the Supporting Information (Fig. S5, SI P7):

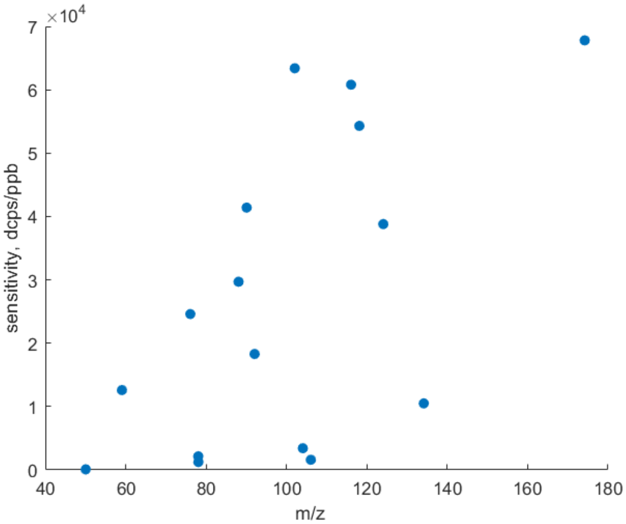

   Figure S5: The relationship between the measured sensitivity for calibrated compounds and their molecular weight.

   Similarly, more stable NH_4^+-VOC clusters (the ones that have higher $KE_{cm\ 50}$) show slightly smaller sensitivity dependence on RH, but this connection is also relatively weak ($R^2 = 0.29$) as shown in Fig. S6.

   We modify the last two sentences of the section 3 of the manuscript (P5 L15):

“~~Generally, a stronger humidity dependence is observed for components with lower sensitivities at fry conditions. Higher molecular weight molecules have weaker humidity dependence.~~ Humidity dependence of sensitivity does not show a strong correlation to cluster stability, as quantified by $\mathrm{KE}_{50\,\mathrm{cm}}$ ($R^2 = 0.29$, Fig. S6). In addition, correlation between humidity dependence of sensitivity and polarity of analyte molecules is relatively weak ($R^2 = 0.31$).”

We include the following figure in the Supporting Information (Fig. S6, SI P8):

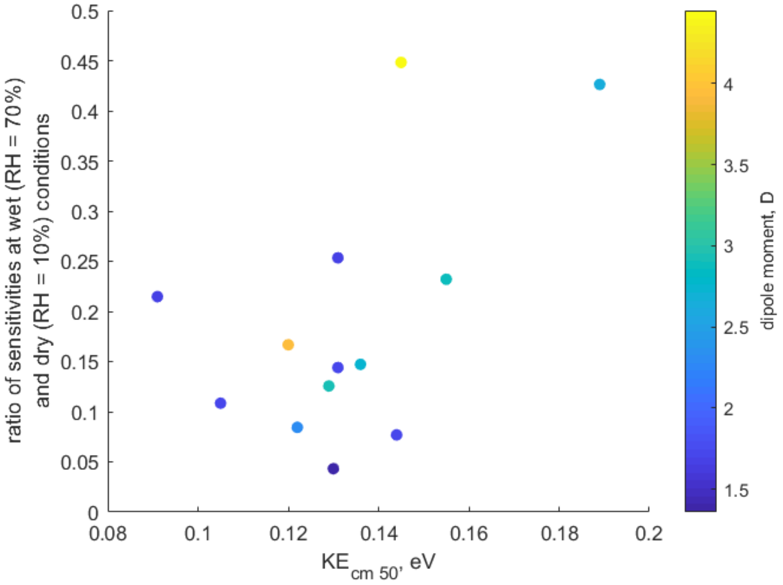

Figure S6: The relationship between the NH_4^+-CIMS sensitivity dependence on RH and $\mathrm{KE}_{\mathrm{cm}\,50}$. Data points are color-coded using the permanent dipole moment of the species.

2. ***P5, L18. Are there any evidence for protonated ions of organic molecules, especially for aerosol samples?***
   There are several molecules that were observed as protonated ions as well as ammonia-organic clusters. Some of these molecules, detected in the particle phase, are shown in Fig. R3.

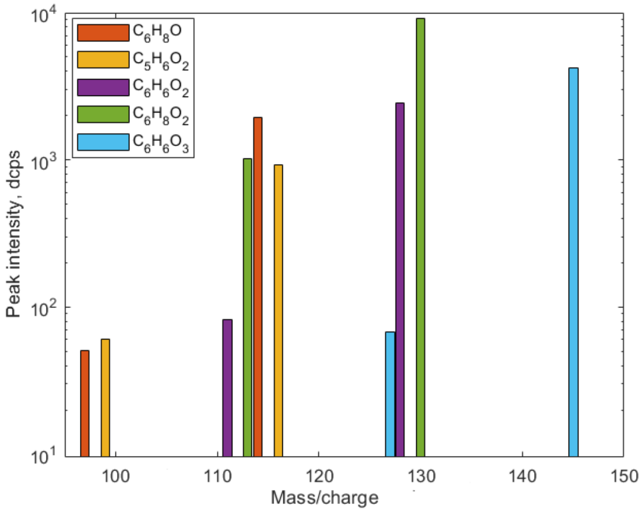

Figure R3: Peak intensities for molecules detected as ammonia-organic clusters as well as protonated ions.

This plot contains five molecules each of which was detected as a protonated ion (i.e., $C_6H_8O{\cdot}H^+$) and an ammonia-organic cluster (i.e., $C_6H_8O{\cdot}NH_4^+$).

We include the following discussion to the manuscript (P4 L29):

"Most organic molecules are detected as ammonium-organic clusters $NH_4^+{\cdot}VOC$ with a few exceptions for which protonated ions $VOC{\cdot}H^+$ are also observed. The protonated ions could be produced through proton switching reaction either from $H_3O^+{\cdot}(H_2O)_n$ or NH_4^+. However, for all of these molecules the intensity of the ammonia-organic cluster is at least one order of magnitude higher than the intensity of the corresponding protonated ion."

3. ***P6, L25-28. What are the RH conditions for the measurements presented in Fig. 4? Is the relationship between the $KE_{cm\ 50}$ and sensitivity of calibrated compounds probed under varying RH conditions? Given that the sensitivity of NH_4^+-CIMS greatly depends on RH (Fig 2), the relationship between the $KE_{cm\ 50}$ and sensitivity may also be RH dependent. This issue merits additional discussions in the manuscript, as it determines whether the relationship obtained at a certain RH can be applied to measurements performed at a different RH.***

We modify the following sentence by adding the RH conditions for the measurements presented in Fig. 4 (P6 L25):

"Fig. 4 shows the relationship between the calculated kinetic energy $KE_{cm\ 50}$ and measured sensitivity for 16 calibrated compounds at 10% RH and 20 °C."

We include the following discussion of the dependence of the relationship between $KE_{cm\ 50}$ and sensitivity on RH (P7 L4):

"As shown in Fig. 2, the sensitivity of NH_4^+-CIMS to many calibrated compounds is RH dependent, thus we observe that the relationship between the calibrated kinetic energy $KE_{cm\ 50}$ and the measured sensitivity also depends on the humidity of the sampled air (Fig. S7). Therefore, the values of the collisional limit and other calculated sensitivities reported herein are unique to the instrument setup (i.e., pressures and voltages in the reaction chamber) and vary with the humidity of the sampled air."

We include the following figure in the Supporting Information (Fig. S7, SI P9):

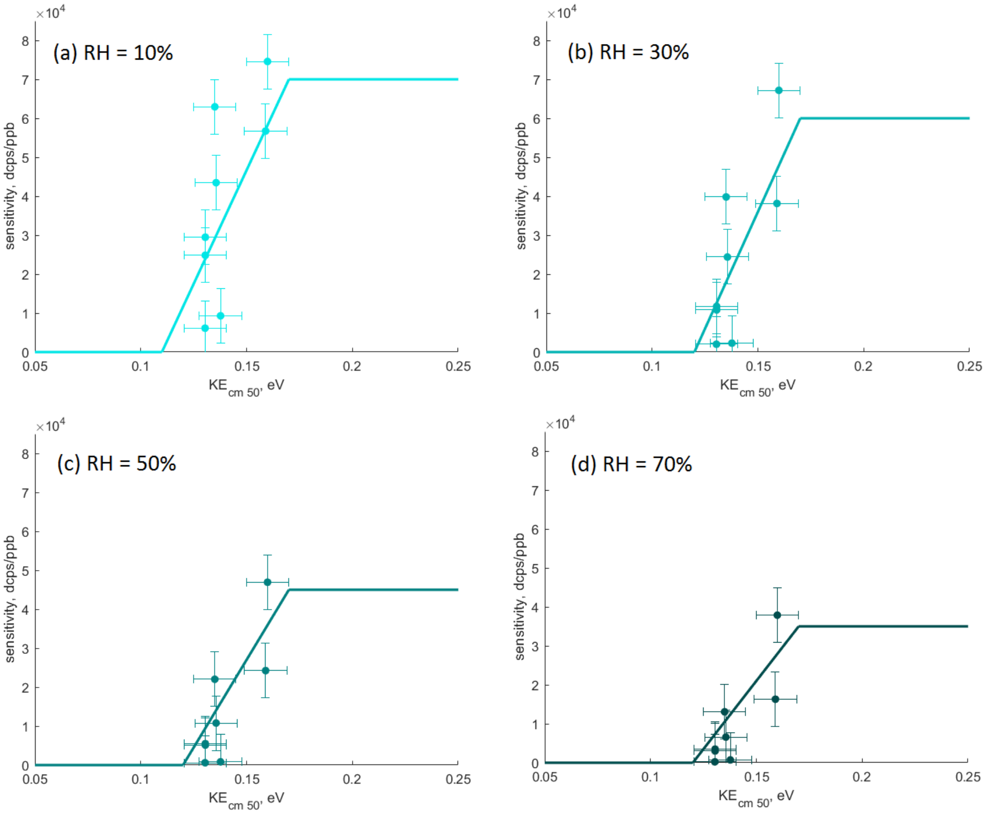

Figure S7: The relationship between calculated kinetic energy of the ammonium-organic clusters $KE_{cm\ 50}$ and measured sensitivity to calibrated compounds obtained at different RH of the sampled air.

4. ***It is not clear how the reaction time in the reaction chamber was determined based on the sensitivities observed in H_3O^+ mode. An elaboration about this should be included in the manuscript.***

We modify the description of the method of calculating the kinetic sensitivity and include the following description of the procedure used to estimate the reaction time in the reaction chamber (P6 L31):

“We calculate this limit by using experimentally-determined pressure and reaction time in the reaction chamber, and kinetic limit of ion-molecule reaction rate. We estimate the reaction time in the reaction chamber using the instrument sensitivity to specific compounds in the H_3O^+ mode. For polar compounds with proton affinity much higher than of water (i.e., acetone), we can assume that reverse proton transfer reactions do not occur. In this case, the instrument sensitivity to those compounds is given by (Lindinger et al., 1997):

$$\frac{i(\mathrm{RH}^+)}{[\mathrm{R}]} = i_{primary} \cdot k \cdot t_{react} \cdot \frac{p_{react}}{1013\ \mathrm{mbar}} \quad (9)$$

where $\frac{i(\mathrm{RH}^+)}{[\mathrm{R}]}$ is the component sensitivity, $i_{primary}$ is the primary ion current, k is the rate constant for the proton-transfer reaction (e.g., k=3.6·10^{-9} cm^3 s^{-1} for acetone, Cappellin et al., 2012) , t_{react} and p_{react} are the reaction time and pressure in the reaction chamber, respectively. By measuring the instrument sensitivity to acetone in the H_3O^+ mode, we estimate t_{react} to be 3 ms.”

5. ***P7, L2-4. Again, is there a RH dependence of the kinetic sensitivity or the maximum sensitivity of NH_4^+-CIMS?***

   We include the following discussion of the dependence of the relationship between $KE_{cm\ 50}$ and sensitivity on RH (P7 L4):

   “As shown in Fig. 2, the sensitivity of NH_4^+-CIMS to many calibrated compounds is RH dependent, thus we observe that the relationship between the calibrated kinetic energy $KE_{cm\ 50}$ and measured sensitivity also depends on the humidity of the sampled air (Fig. S7). Therefore, the values of the collisional limit and other calculated sensitivities reported herein are unique to the instrument setup (i.e., pressures and voltages in the reaction chamber) and to the humidity of the sampled air.”

6. ***P7, L20. Can the sensitivity of H_3O^+ reagent ions to acetone represent the sensitivities to other OVOCs? Did the authors make any measurements and comparisons of sensitivities in H_3O^+ mode for different calibration compounds as listed in Table 1?***

   We include to the following discussion about the instrument sensitivity in the H_3O^+ mode (P7 L20):

   “Breitenlechner et al. (2017) showed that due to the enhanced reaction time and the increased pressure in the reaction chamber the equilibrium between the forward and reverse proton reactions can be achieved. Hence, many compounds require careful calibration over a broad humidity range. Since PTR3 has the highest detected sensitivity to ketones, we use the acetone sensitivity to calculate the lower limit concentration of OVOCs.”

7. ***P7, L24-26. Similar or relevant observations about the sensitivity and selectivity of NH_4^+ and H_3O^+ reagent ions have been reported in previous studies. For example, Aljawhary et al. (2013) showed that $(H_2O)_nH^+$ reagent ions are more selective to organic compounds with lower oxygen content. Zhao et al. (2017) showed that NH_4^+ reagent ions are sensitive to a wide range of oxidized organic compounds including highly oxygenated and higher molecular weight***

molecules formed from ozonolysis of alpha-pinene. The findings in these studies should be discussed in relation to the current work.

The following discussion is included in the manuscript (P7 L28):

“Similar observations about the selectivity of NH_4^+-CIMS and PTR-MS have been reported in the previous studies. Aljawhary et al. (2013) showed that $H_3O^+\cdot(H_2O)_n$ primary ions are more selective to the detection of less oxidized water-soluble organic compounds (WSOC) extracted from alpha-pinene SOA comparing to acetate $CH_3C(O)O^-$ and iodide water clusters $I^-\cdot(H_2O)_n$ used as primary ions. Zhao et al. (2017) demonstrated that multiple positive reagent ions (NH_4^+, Li^+, Na^+, K^+) have higher selectivity to a wide range of highly oxygenated organics with higher molecular weights formed from ozonolysis of alpha-pinene, while negative reagent ions (I^- and NO_3^-) are more selective towards smaller species (e.g., CH_2O_2, CH_2O_3, $C_2H_2O_3$, and $C_2H_4O_3$).”

8. ***P8, L7. Since the authors never discuss the third ion source in the manuscript, I would suggest removing the statement “the instrument is equipped with three corona discharge ion sources”.***

   We change the sentence as suggested (P8 L7):

   “The instrument can be operated in both NH_4^+ and H_3O^+ modes as NH_4^+-CIMS and PTR-MS, respectively, while switching between the two modes can be done within two minutes.”

9. ***Table 1. The detection limit is usually defined as the concentration that gives rise to a signal of 3 sigma. I wonder why the authors use 2 sigma.***

   We replace 2σ-LOD by 3σ-LOD in Table 1:

Species	Ion formula	m/z	Sensitivity		3σ-LOD [pptv] (1s)	V_{50} [V]	$KE_{cm\,50}$ [eV]
			[cps/ppb]	[dcps/ppb]			
methanol	$CH_4ONH_4^+$	50.06	59	83	93	27.8	0.091
acetonitrile	$C_2H_3NNH_4^+$	59.0604	9700	12600	9	34.5	0.120
acetone	$C_3H_6ONH_4^+$	76.0757	21400	24600	2.75	36.4	0.129
acetic acid	$C_2H_4O_2NH_4^+$	78.055	1890	2140	99	31.4	0.105
isopropanol	$C_3H_8ONH_4^+$	78.0913	1100	1240	23	36.5	0.131
MVK	$C_4H_6ONH_4^+$	88.0757	27900	29700	20	36.9	0.131
MEK	$C_4H_8ONH_4^+$	90.0913	39300	41400	8	37.8	0.136
hydroxyacetone	$C_3H_6O_2NH_4^+$	92.0706	17600	18300	14	35.8	0.126
furanone	$C_4H_4O_2NH_4^+$	102.055	64000	63400	57	40.3	0.149
biacetyl	$C_4H_6O_2NH_4^+$	104.0706	3490	3420	35	36.6	0.130
pyruvic acid	$C_3H_4O_3NH_4^+$	106.0499	1650	1600	53	34.8	0.122
angelica lactone	$C_5H_6O_2NH_4^+$	116.0706	65500	60800	0.86	39.6	0.145
hexanone	$C_6H_{12}ONH_4^+$	118.1226	59000	54300	8	41.5	0.155
benzaldehyde	$C_7H_6ONH_4^+$	124.0757	43200	38800	2.03	36.7	0.130
heptanol	$C_7H_{16}ONH_4^+$	134.1539	12150	10500	2.28	39.5	0.144
decanone	$C_{10}H_{20}ONH_4^+$	174.1852	89400	67800	2.49	47.1	0.189

Table 1: Sensitivities and detection limits of NH_4^+-CIMS for various VOC species; voltage (V_{50}) and corresponding kinetic energy ($KE_{cm\,50}$) at which half of the ions have dissociated.

References:

Cappellin, L., Karl,T., Probst, M., Ismailova, O., Winkler, P. M., Soukoulis, C., Aprea, E., Märk, T.D., Gasperi, F., Biasioli, F.: On Quantitative Determination of Volatile Organic Compound Concentrations Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry, Environ. Sci. Technol., 46 (4), 2283–2290, doi: 10.1021/es203985t, 2012