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Reply on RC2

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Author comment on "Mass spectrometric measurements of ambient ions and estimation of gaseous sulfuric acid in the free troposphere and lowermost stratosphere during the CAFE-EU/BLUESKY campaign" by Marcel Zauner-Wieczorek et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-238-AC2, 2022

(**Comments by the referee are in bold font**, answers by the authors are in regular font)

The manuscript entitled "Mass spectrometric measurements of ambient ions and estimation of gaseous sulfuric acid in the free troposphere and lowermost stratosphere during the CAFE-EU/BLUESKY campaign" by Zauner-Wieczorek and co-authors presents ion measurements in the UTLS region. To this end, an API-ToF-MS was operated onboard the HALO aircraft and sampled air masses primarily over Western Europe. The negative ion mode was found to be dominated by NO3- and HSO4- as well as clusters thereof. Based on the measured ion concentrations the number concentration of sulfuric acid was derived. The positive ion mode was studied in less detail but protonated pyridine was identified as a major ion. Based on the data presented an increase of nitrate ions with altitude was found while hydrogen sulfate ions as well as sulfuric acid showed a more evenly distributed trend. My overall assessment of this manuscript is quite positive and it clearly fits the scope of ACP. Especially the introduction is well written and gives a nice overview of previous work, however, a few things need clarification and improvement before final approval.

We would like to thank the Referee for their valuable feedback. We believe that, thanks to the Referee's suggestions, the manuscript could be improved significantly.

Let me start with section 3.1.3 which I feel least comfortable with. While the in-cloud measurement shows some interesting features, the interpretation seems speculative and immature to me. In a way the section sounds vague and does not quite fit the rest of the manuscript. Apart from the fact that this was a one-time signal over 30 seconds only, there are a couple of questions that need clarification.

We agree with the Referee's view that section 3.1.3 holds the least firm results of our manuscript. We are, nevertheless, convinced that also observations that cannot be explained in full detail yet should be communicated to the scientific community to raise awareness of open questions and stimulate future research. By using terms like "we speculate that" we clearly mark our attempt to explain the observations as hypotheses that are still to be debated. To emphasise this, we also added this opening sentence to the section:

p. 14, l. 353: "In this section, we report an interesting finding that may be attributed to an artefact."

As I understand this measurement took place at an altitude of >5km. I actually can't believe that outside temperature at this height and latitude will be positive. What does the temperature reading refer to? What were temperatures during other flights/altitudes?

The reported temperature is the ambient temperature measured by the BAsic HAlo Measurement And Sensor system (BAHAMAS), which is HALO's standard system to collect basic meteorological and flight data. In the initial manuscript, we had erroneously used the Total Air Temperature, which is the uncorrected temperature measured outside the aircraft. We are thankful to the Referee for pointing out this mistake. In the revised manuscript, we use the Static Air Temperature instead, which is the corrected, "true" ambient temperature. The value now reads 261 K instead of 275 K and is, thus, clearly below the freezing point. We changed Fig. 3, the main text in Sect. 3.1.3, the abstract, and the conclusion accordingly:

p. 2, l. 21ff.: "During the transit through a mixed phase cloud, we observed an event of enhanced ion count rates and aerosol particle concentrations that can largely be assigned to nitrate ions and particles, respectively; this may have been caused by the shattering of liquid cloud droplets on the surface of the aircraft or the inlet."

p. 15, l. 363ff.: "The temperature, however, was constant at 261 K, only decreasing by less than 1 K during the humidity peak events. At this temperature, mixed-phase clouds consist mainly of liquid cloud droplets because the most common ice nucleating particles, consisting of mineral dust, become active at lower temperatures (Hoose et al., 2010; Hoose and Möhler, 2012; Kanji et al., 2017)."

p. 15, l. 373ff.: "Because the aircraft passed through a mainly liquid mixed-phase cloud during this event, it is likely that the shattering of liquid cloud droplets on the surface of the aircraft or the sampling system…"

p. 16, l. 404: "During the transit through a mixed-phase cloud, we observed an event…"

Furthermore, we adapted the values for n_+ and t_{rec} in the main text that were re-calculated based on the new values for α (after Eq. (2) and (5)):

p.13, l. 308f.: "The average t_{rec} = 136 s (129 to 151 s) and the average n_+ = 4090 cm^{-3} (3880 to 4540 cm^{-3})."

This mistake also influenced the calculated values of [H_2SO_4] after Eq. (1b) because the parameterised value for the ion-ion recombination coefficient, α, is dependent on the temperature. We corrected the temperature values and, simultaneously, changed the parameterisation of α from the one by Brasseur and Chatel (1983) to the one by Israël (1957). This is because, in the meantime, we have found a misprint in Israël's formula, which, if corrected, yields an even more favourable parameterisation than the one by Brasseur and Chatel (Zauner-Wieczorek et al., 2021). However, the corrected values for

[H_2SO_4] do not differ significantly from the previously reported ones. For instance, the average concentration for the altitude bin of 13.4 km is now $1.9 \cdot 10^5$ cm^{-3} (instead of $1.8 \cdot 10^5$ cm^{-3}) and for the altitude bin of 8.7 to 9.2 km, it is now $7.8 \cdot 10^5$ cm^{-3} (instead of $9.1 \cdot 10^5$ cm^{-3}). The conclusions drawn from these results are still the same.

In the revised manuscript, the parameterisation by Israël (1957) is introduced (Sect. 2.4), Fig. 3 is updated for the newly calculated values of [H_2SO_4] and the values in the main text (Sect. 3.1.2), in the abstract, and in the conclusion are corrected accordingly.

On the other hand, reported values of RH exceeding 130% sound completely unfamiliar to me. Basic literature (e.g. Seinfeld & Pandis) reports supersaturations in convective clouds not exceeding 2%, so I'd expect RH to be clearly below 110%. Even if the reported numbers are correct they must be put into context otherwise readers will get confused.

The relative humidity over water is measured by the Sophisticated Hygrometer for Atmospheric ResearCh (SHARC), which employs a tuneable diode laser (TDL). Indeed, the value for *RH* cannot be used reliably during the passage of clouds. We had, therefore, added the sentence "Within clouds, the measurement of the relative humidity can be influenced by the evaporation of cloud particles, thus, relative humidities exceeding 100 % are possible." (old manuscript, p. 6, l. 152f.) to the initial manuscript. While the absolute values are certainly not correct, the relative increase in *RH* during the event of interest can, nevertheless, be demonstrated well. To put this into context, we added the following remarks to the main text:

p. 15, l. 359ff.: "Between 11:01:57 and 11:02:20 UTC, the relative humidity over water (*RH*) showed three peaks of 132–136 % compared to 114 % before and after this event (see Fig. 4 (b)). Please note that the measurements of the relative humidity are influenced by the evaporation of cloud droplets during in-cloud measurements. Thus, the absolute numbers of *RH* are strongly overestimated here. Nevertheless, one can observe the increased peaks in *RH* during the event relative to the measured *RH* values before and after the event."

In addition, I'd be surprised that during such a number of flights there was only one period of 30 s in-cloud flight. What makes this cloud different from the others?

During the measurement campaign, we operated the instrument in the Chemical Ionisation (CI) mode for the majority of time, which is subject to other publications. Especially during periods of constant flight levels, we operated the instrument in the Atmospheric Pressure inlet (APi) mode, which is presented in this manuscript. In the APi measurement periods, we rarely changed the flight altitude or passed clouds. Thus, the in-cloud measurement of flight segment 06.2 is unique to our data set despite the large number of flights. We are looking forward to study this phenomenon in more detail in future measurement campaigns where dedicated vertical profiles and cloud-passing flights in the APi mode may be performed.

Unless this section is improved considerably I'd recommend putting this topic into supplemental material or keep it for another publication when data are clearer.

We are convinced that, thanks to the valuable feedback by the Referee, this section could be improved and sheds light on a research topic that invites to future research activities.

Along these lines the introduction of C-TOF-AMS and OPC in the instruments section appears quite unexpectedly as they do not relate to the ion (distribution) measurements. These should better be mentioned together with the in-cloud measurements.

We are thankful for this suggestion. Section 3.1.3 is concerned with the results and discussion of the in-cloud measurement, while Section 2.1 is concerned with the description of all instruments whose data are discussed within the manuscript. We believe that the description of the instruments should be placed within the Methods section (2.1) to enable interested readers to quickly find the information they are looking for.

A few minor issues:

Page 8, line 182: "…data were averaged to 30 s". What distance does this period relate to at cruise speed? Again, put numbers into context.

We added the information accordingly:

p. 8, l. 185ff.: "The uncorrupted data were then averaged to 30 s. For typical groundspeeds of 160 to 240 m s^{-1}, this relates to a covered ground distance of 5 to 7 km for one averaged data point."

Page 9, line 239: "… the value of q applied here MUST be 90%…" This is quite a strong formulation that should be relaxed, maybe by giving a range.

We chose a less strong formulation:

p. 10, l. 250: "…therefore, we estimated a value for *q* of 90 % of the maximum polar value of *q* (Bazilevskaya et al., 2008) for this data set."

Page 11, Table 2: the exact mass is only given for one ion. Why not show all exact masses for reference? Or do all measured masses agree exactly with the nominal masses?

All measured masses agree with the expected masses except for the signal at 95.973 that could be assigned to SO_4^-. Therefore, we added the exact mass of SO_4^- in the remarks. The exact masses of all observed signals are given in the first column. For more clarity, we changed the caption of Table 2:

p. 11, l. 275: "Table 2: Observed signals in the negative mass spectra with, their exact mass-to-charge ratio, *m*/*z*, and the assigned ions."

Regarding section 3.2 "Positive ions": For me and probably for many other

readers it would be interesting to see an averaged mass spec of the positive ions. It is shown for negative ions (Figure 2) but not for positive ones. I would very much appreciate it if such a plot could be added.

We agree that a positive mass spectrum is very interesting. Based on the limited data we have in the positive mode, we, however, refrained from adding such a mass spectrum to the manuscript because we want to avoid the impression of a false confidence. Besides the peak for protonated pyridine, the interpretation of the other peaks in the mass spectrum are not yet resolved with confidence. We are looking forward to future studies where we can focus on the positive APi measurements more strongly.

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