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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular Insights into New Particle Formation in Barcelona, Spain" *by* James Brean et al.

Anonymous Referee #1

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General comments

The authors present a set of data collected in summer 2018 in Barcelona, Spain. Using state-of-the-art instrumentation, they study new particle formation (NPF), analyzing particle formation rates, gas concentrations and composition of highly oxygenated organic molecules (HOM). The authors conclude that the NPF at the site proceeds via SA-H2O-DMA and/or SA-H2O-Organic nucleation, while HOM are needed for particles to grow beyond 10nm. The results are novel and valuable for understanding physics and chemistry of NPF in different environments. The text is well-written. However, few discussion and conclusions need to be addressed before paper can be published.

The paper starts very well with comparison of formation rates and sulfuric acid dimer-to-monomer ratios to chamber studies. In addition, gas concentrations and conden-

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sation sink on different days are compared. When discussion goes to composition of HOM, their sources, and their contribution to particle growth, it becomes somewhat out of focus, the reader is lost in HOM influence on NPF versus growth. Some conclusions are presented in much stronger way than the results can support. The text suffers from too many general comparisons, such as “relatively larger/smaller/low”, “broadly similar”, “broadly dependent”, which makes the results less clear and leaves a lot of figure interpretation to the reader.

I suggest that authors 1) check their calculations, 2) provide a clearer (consistent) discussion and interpretation of HOM results and 3) rethink how final conclusions are presented regarding “molecular insights” in accordance with presented evidence. Please see specific comments below.

Specific comments

Major:

1. **Values for condensation sink (CS), J1.5, J5, growth rates (GR).**
There is a mistake in CS formula (line 181). The coefficient 4 should be 2, as in Kulmala et al. (2001).

J1.5 and J5 are very high, but in line (within some uncertainty) with calculated kinetic limit sulfuric acid nucleation (Kurten et al. 2018). However, during the observed NPF, the temperature is close to 30 degC. At this high temperature, I would expect lower formation rates. Please, check the values and provide a comment on this.

It would be beneficial, if more information was included how CoagS and GR were calculated (shortly from which instrument and with which method GR was calculated). Would it be beneficial to include GR values to results as important physical parameter of NPF?

2. **“Burst event”/ “full-event” discussion’**
The discussion what separates these event types is hard to follow for the following

reasons

1) In Fig. 2-6, how the data was produced? Are these values during certain part of the day or is whole day included? Are these hourly values? Please specify this in Methods or Results.

For instance, in terms of CS comparison, CS over whole day may not show any difference (lines 205-206, 209-210 and Fig. 2a). On the other hand, daily profile of CS may show that on "burst event" (Figure 1c), 100nm mode appears around 14:00, which I assume increases afternoon CS during that day.

2) The discussion about differences in meteorology is incomplete. In lines 246 and 397, it is mentioned that south and south-west air masses were responsible for NPF, while in Fig. S6, air masses on 3/5 NPF days came from North. Could change in air mass (wind direction) be responsible for no growth during "burst events"? Please clarify.

3) Please provide information on which day, what type of NPF was seen.

3. **Discussion about HOM sources/formation/influence on particle growth**
The presentation and discussion on HOM results is very valuable. To make the section 3.3 more clear, I suggest to separate it in two subsection: 1) HOM composition and sources and 2) How HOM change on different days in relation to NPF. The following are my main concerns regarding HOM discussion:

1) Interpretation of Figure 7. Are there really dependencies seen?

Fig. 7a to me shows correlation between T and global radiation. If night and day are separated, there is no dependency on T, or is there?

In Fig. 7b, dependency is discussed when all points are taken together. But is there a point to do that if different groups of HOMs are plotted against different VOCs? For C7/C9 I don't see any dependence.

Therefore, the conclusion that HOM has "strong dependence of their concentration on

both temperature and VOC concentration" (line 394) is not supported.

In Fig. 7a HOM C5-10 are plotted, while in Fig. 7b, only C5/C7 /C9 are shown. What is the reason for excluding for instance C6,C8,C10?

Please clarify this section and harmonize the text (abstract-discussion-conclusions).

2) Sudden statement in conclusion regarding HOM effect on NPF and growth:

In lines 395-399, it is stated "aromatic organic compounds are more important compounds which initiate new particle formation and growth than oceanic emissions". Which data leads to this conclusions? Especially, the part in which aromatic compounds initiate NPF. In line 377, it is actually mentioned that biggest difference between the two event types are in fact C9/C10 compounds. Please clarify this aspect.

3) Please clarify what is the effect of HOM on NPF vs growth, if such can be distinguished from the data.

4. **Strong conclusions regarding pathway for NPF**
Based on the results from the analysis, the results are not as conclusive as claimed both by title ("molecular insights") and in the text (slightly different in abstract/discussion/conclusions). I would, therefore, suggest to rephrase the statements in text.

line 111: related to problem with title: "we examine molecular level evidence ... at the critical diameter"- even the authors state "cluster identity cannot be identified" (line 276), so this wording is not appropriate.

line 293: It is clear that the results are similar to Kurten 2016 (except really high J). Mind that they conclude that SA-H2O-DMA or other pathway could not be confirmed with their data.

lines 301-302: I suggest softening this conclusion. Also check abstract (lines 38-39) for consistency.

line 387: The first and main conclusion is that NPF “plausibly proceeds by the formation of clusters involving sulphuric acid and highly oxygenated organic molecules, with likely involvement of bases”. You clearly state earlier in line 276 that cluster identity cannot be directly identified and suggest that HOM is important for growth (not NPF, as far as I understood from text). So I am not sure what “plausibly” refers to. Please rephrase to reflect that results are not so conclusive, but the hypothesis is as follows (. . .).

Minor:

line 63: I appreciate the use of very recent references, but surely there are older references/review that appropriate to be referenced here (from other groups).
line 74: near-kinetic limit is achieved at certain DMA concentrations, can be specified here (Almeida et al. 2013).
line 143: In Brean et al. 2019, calibration coefficient of 7e8 cm-3 was used. Were any further adjustments done in this work to get 3e9 cm-3?
lines 216-217: Sulfuric acid time series/dial profile are discussed, which is not shown anywhere. Consider including time series of measured parameters in the Supplementary.

Figure 3: Was it possible to reliable fit amines and ammonia from the spectra? Kurten et al. 2016 mentions that at high RH, nitrate-water cluster interferes with the fitting of C2 amines. Please comment and preferable provide a figure of the peak fitting. Please also include Kurten et al. 2016 into references when talking about detecting ammonia with nitrate CI-APi-TOF.

lines 234-236: You probably mean to say that TMA won’t efficiently cluster with nitric acid and won’t be detected. It is not very clear, please rephrase.
line 267 and Fig. 5: I think CLOUD data presented here is J1.7 for 278 degC, isn’t it? Please mention it in the text and/or caption.
line 282-283: “Sulphuric acid dimer roughly represents the strength of sulphuric acid

clustering in the nitrate CI-APi-TOF". - I am not sure what this means. Did you mean it tracks atmospheric clustering?
line 287: "lower limit" – do you mean upper? Please explain how IIC was calculated, or was it taken directly from Kurten et al. (2016)? I would like to note that the reaction time in drift tube in Kurten et al. (2016), is 50ms, what is it in your instrument?
line 318: Is this a relevant reference for C10 HOMs that are coming with inland air mass?
lines 323-328: a series of unconnected sentences. please rephrase to make more logical. "condensational growth being a reversible, step-wise kinetic process" – I am not sure what you mean, please rephrase. Do you mean "higher HIO3 cannot account for stopped growth beyond 10nm?. rephrase it to fit in HOM discussion or move it to section 2.2.
In line 334, it is said that "precursors for these HOMs are presumed to be largely isoprene, alkylbenzenes and monoterpenes". However, in abstract (line 40) and in conclusions (line 394), isoprene is lost.
line 346: include also isoprene reference.
line 369: you mention that HOM>500 m/Q are increased during "full-events", however no data above 500m/Q is shown. Or do you mean HOM within 400-500 m/Q? This has to be clarified as this is also mentioned in conclusions. It can be shown as time series (or dial) of the sum of unit mass resolution peaks above 500 m/Q or box plot (I understand high masses are hard to fit/identify).
line 389-390: "multiplicity of mechanisms has been shown to occur in chamber studies but has not been observed in the real atmosphere previously."- for instance Yan et al. (2018) showed two regimes for NPF at SMEAR II station, Finland. Kurten et al. 2016 shows very similar results to this study and analogously (lines 390-391) points out high J, similarity to CLOUD for both SA-DMA-H2O and SA-OxOrg studies. Please rephrase.

Figure 7: Why HOM is shown in normalized signal, while in Fig. 3 it is in cm-3? How many days and in what time resolution are the data in this plot? Caption: "Influencing

factors on VOC concentration" – on HOM concentration?

Figure 8: Please provide a list of identified peaks in Supplementary and please explain what are the HOM observed at m/Q below 200 (quite high signals). Are they deprotonated species fitting with the "HOM" criteria?

I suggest the authors would look into following and add more quantitative interpretation of results in the text.
-line 44: "significantly lower" – here easy to specify exactly how much, a factor of X.
-line 87-89: phrase "despite (extremely) high condensation sinks" repeats twice in a row. For comparison here, it would be nice what is meant by "extremely high".
-line 100: please specify what is "frequent", 40-lines 101-105, 195: "relatively high ozone", "relatively low ozone (high compared with the rest of the year)"-can you rephrase or provide values as example? I also got lost in logic related to "relatively high" ozone during NPF and "maximum ozone episodes" with no NPF.
-line 244-245: "HOM ... greatly enhanced", "lower during burst". Please provide values or a factor for HOM difference between days.
-line 248: "...HIO3 and ...MSA are low". I assume you refer to Fig S5d and e here? Relative to what are these concentrations low?
-line 270: instead of "extremely high" provide actual numbers from Fig. 5.
-line 271: what does "broadly similar" mean?
-line 349: what does "broadly dependent" mean?

Technical corrections

line 125: "interface" with small i.
line 222: remove empty line
line 333: "temperature plotted against the signal of HOMs". Isn't it the other way around? Also see caption to Fig. 7.
line 368: insert: "enhancement" in comparison "to smaller alkylbenzene derived

HOMs".
line 401: repetition of line 394-395.
Figure 8. In-text (line 355), you mention that Fig. 8 has same days as Fig. 1. On Fig 1, there is 11/07/2018, while caption to Fig. 8 says 12/07/2018. Is it a typo? Please fix.

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