RC1:

The paper "Exploring biogenic secondary organic aerosol using a PTRMS-CHARON in laboratory experiments: characterization and fingerprint analysis" applies the PTRMS-CHARON instrument to investigate the chemical composition of SOA obtained from the oxidation of well-known biogenic reactive organic precursors i.e. isoprene, limonene and beta-caryophyllene. The study employed the DouAir atmospheric simulation chamber to simulate ambient aerosol formation. The CHARON data is also supported by additional gas- and particle-phase measurements. The paper is well-written and research discussion is appropriately supported with citations of relevant previous measurements. However, I felt the study is a bit lacking in casting a proper scope to justify the work. It can be considered for publication after the following concerns are resolved:

1. The scope of the study is not clear. The introduction section is quite large and the authors use only the last paragraph of the section to show that PTRMS-CHARON has been in existence for nearly 10 years already and used in ambient as well as chamber/lab measurements. Several studies are cited to support this. However, the nuances of its use in these studies are not properly laid out. It'd be good to provide some more detail on how was the CHARON instrument used in previous work that leaves open a gap for a systematic investigation of BVOC oxidation products. If the paper is about the application of PTRMS-CHARON, then it should somehow be the focus element of the introduction, especially since the oxidation of BVOCs in itself is not a new thought.

We thank the reviewer for this insightful comment regarding the scope and structure of the introduction. We agree that the initial focus was too heavily weighted towards general BVOC oxidation. We have restructured the introduction to better define the scope. Instead of a general overview of BVOC oxidation, we now focus more specifically on the application of the PTR-MS/CHARON. We have enhanced the references to highlight why a systematic investigation of BSOA formation pathways was necessary to fill the current knowledge gap.

"Globally, organic aerosol (OA) particles account for an average of ~50 % of the submicron particulate matter (PM_1), however, with values ranging from 10 to 90 %, depending on the nature of the site (forested, urbanized, etc.) and atmospheric conditions (de Gouw and Jimenez, 2009; Tsimpidi et al., 2025). PM largely affects radiative forcing, climate, air quality, and public health, and has therefore been the subject of intense research (Hallquist et al., 2009; Shrivastava et al., 2017; Nault et al., 2021; Pye et al., 2021). While primary sources contribute to this burden, a dominant fraction originates from the atmospheric oxidation of volatile organic compounds (VOC), with biogenic VOC (BVOC) being widely accepted as the most significant precursors globally (Yáñez-Serrano et al., 2020; Dada et al., 2023). The chemical complexity of biogenic secondary organic aerosol (BSOA) formation is high. Terpenoids such as monoterpenes and sesquiterpenes are key precursors in boreal environments due to their rapid reactivity (Hakola et al., 2012; Zhou

et al., 2017; Roldin et al., 2019). Conversely, in tropical regions like the Amazon, isoprene dominates emissions, where its oxidation pathways, varying drastically between low-NO and high-NO conditions, dictate the resulting aerosol composition (Martin et al., 2010; Leppla et al., 2025). Unraveling these distinct chemical pathways requires precise identification of the oxidation products, which serve as unique tracers for source apportionment.

Mass spectrometric techniques such as Aerosol Mass Spectrometers (AMS) have been extensively used in the scientific community to understand OA loadings and dynamics (Hu et al., 2015; Kristensen et al., 2017). However, the high fragmentation associated with electron impact ionization hinders molecular characterization and reduces the source/process identification capabilities. In recent years, new soft ionization techniques have been implemented in mass spectrometry techniques to reduce fragmentation, allowing the identification of low-volatility compounds at the molecular level, such as chemical ionization mass spectrometry (CI-MS) (Lopez-Hilfiker et al., 2014; Eichler et al., 2015). Molecular ionization is achieved by the transfer of an electron/proton/adduct of various reagent ions (e.g., Br^-, H_3O^+, NH_4^+, I^-, Huang et al., 2021). CI-MS equipped with a H_3O^+ source (Proton-Transfer-Reaction Mass Spectrometry, PTR-MS) has been the main tool for fast and precise quantification of small organic gaseous compounds for several decades (de Gouw and Warneke, 2007). More recently, the system has been coupled with thermo-desorption (TD) aerosol inlets, termed CHemical Analysis of aeRosol ONline (CHARON-PTRMS, Eichler et al., 2015).

However, the application of CHARON to date has left specific gaps regarding BSOA. Previous field deployments have successfully quantified bulk OA or identified specific tracers in urban and biomass burning plumes (Müller et al., 2017; Piel et al., 2019; Song et al., 2024). Similarly, laboratory applications have largely focused on anthropogenic precursors like toluene (Lannuque et al., 2023) or vehicle emissions (Kostenidou et al., 2024). While isolated studies have touched upon biogenic precursors (Gkatzelis et al., 2018a, b), a comprehensive spectral library covering the major isoprene and terpene oxidation pathways is lacking.

To address this gap, we characterized the formation of SOA from the most relevant biogenic precursors in the new Teflon DouAir atmospheric chamber. We systematically investigated five distinct SOA formation pathways, namely monoterpene (limonene) and sesquiterpene (β-caryophyllene) ozonolysis, the isoprene-OH oxidation via the HO_2 route, favoring or suppressing the epoxidiol route (IEPOX-SOA and non-IEPOX-SOA) under low-NO conditions, and the isoprene-NO oxidation promoting the isoprene-NO-SOA in high polluted environments."

2. Lines 104-115: No citation is provided for previous characterization tests of the DouAir chamber in section 2.1. Is this a new chamber? If so, it should be stated as such since this may introduce uncertainties in measurements. Is the chamber mixed mechanically? The schematic in figure 1 does not show the mixer.

The DouAir chamber is indeed a new facility described here in its first peer-reviewed publication, though preliminary characterization results have been presented at international conferences (e.g., Bouzidi et al., EGU 2021). We have updated Section 2.1 to explicitly state this status.

Line 81: *"The experiments were conducted in the new 9 m^3 mobile DouAir Teflon chamber (Fig. 1), housed at IMT Nord Europe, Douai, France."*

Regarding mixing, the chamber operates without a mechanical stirrer to minimize wall losses. However, characterization tests for both gaseous and liquid species (the latter injected via rapid vaporization in a heated injector) confirmed that homogeneity is reached in less than 4 minutes via airflow dynamics.

The following sentence has been added to the SI:

"The DouAir chamber operates without a mechanical stirrer to minimize wall losses. Characterization tests for both gaseous and liquid species (the latter injected via rapid vaporization in a heated injector) confirmed that homogeneity is reached in less than 4 minutes via airflow dynamics, as indicated in Figure S2."

3. Line 123: The thermodesorption unit of the CHARON was operated at 140C. How was this operating temperature set for your instrument and up to what volatility range is evaporated from the particle-phase at this setting?

The more recent Fusion-CHARON instrument from Ionicon Analytik operates at around 170C to evaporate up to ELVOCs.

The temperature of 140°C was selected based on manufacturer recommendations for our specific model. Our own optimization tests confirmed that higher temperatures did not increase OA mass recovery but indicated potential increased fragmentation. Importantly, at the low operating pressure (~8 mbar), 140°C is considered sufficient to evaporate species down to 10^{-14} Pa (ELVOCs) (Peng et al., 2023), which is consistent with previous deployments in the literature (e.g., Leglise et al., 2019; Tan et al., 2018)

4. Line 144-145; 152-153: EF was determined as a ratio of the flows before and after the ADL. It is not clear what the term "flow" here means. Is it the particle count or the volumetric flow rate? In line 152, it is unclear what the authors mean by "PTRMS-CHARON measurements". The CHARON provides chemical speciation of the incoming aerosol sample. CPC on the other hand provides particle number/ mass count for monodispersed particles. The authors should specify

what CHARON measurement is being ratioed with the CPC data. Citations are provided in lines 145-146 but there should be a brief description to help the reader.

Yes, it is the volumetric flow rate. Theoretical EF can be calculated using the following equation:

$$EF = \frac{F_{DT}}{F_{ADL}}$$

Where, F_{DT} is the flow into the drift tube and the F_{ADL} is the flow before the aerodynamic lens.

The text was modified accordingly:

Line 125: *"The theoretical EF is defined as the ratio of the volumetric sampling flow rate entering the Aerosol Dynamic Lens (ADL) to the volumetric flow rate entering the drift tube. However, to account for transmission efficiency and wall losses, the experimental size-dependent EF was determined by introducing a known number concentration of monodispersed particles, as described in Eichler et al. (2015) and Peng et al. (2023)."*

Line132: *"The monodisperse particles were sampled by a condensation particle counter (CPC; TSI 3750) and the PTRMS-CHARON. The mass concentration of size-selected particles measured by the CPC was determined assuming a shape factor of 0.8 and 1 for ammonium nitrate and levoglucosan, respectively. This mass concentration was subsequently converted into a Volume Mixing Ratio (VMR, in ppbv). Finally, the size-dependent EF was calculated as the ratio between the VMR measured by the PTRMS-CHARON and the equivalent VMR derived from the CPC data."*

5. I could not find information about the accuracy of mass calibrations in this study. It should be stated to ascertain confidence in peak identifications/molecular formulas.

We agree that stating the mass accuracy is essential for confidence in our peak identification. We have revised the manuscript to specify the internal calibration method. The following text has been added:

Line 113: *"To ensure high mass accuracy and confidence in molecular formula identification, mass calibration was performed internally using four ubiquitous peaks spanning the measured mass range. These included the hydronium water isotope (H_3O^+ at m/z 21.022), the second water cluster (at m/z 55.039), and the diiodobenzene peaks ($C_6H_5IH^+$ at m/z 203.943 and $C_6H_4I_2H^+$ at m/z 330.848). This continuous internal calibration resulted in a mass accuracy of better than 5 ppm across the detection range".*

6. Line 242: A maximum of 5 ppb for a total injection of 60 ppb is interesting. The half life of SQT with ozone would be a few seconds following pseudo first order kinetics. In order to say that the loss is primarily due to high reactivity, the timescale of mixing of the precursor inside the chamber should also be stated.

We agree with the reviewer's analysis. The characteristic mixing time in the chamber is < 4 minutes (now stated in the text). Since the chemical lifetime of SQT with ozone is on the order of seconds, the reaction timescale is indeed significantly shorter than the mixing timescale. This rapid consumption - occurring faster than the chamber can become well-mixed - explains why the measured concentration never reaches the theoretical injected values. It is also important to clarify that the total amount introduced was not 60 ppb, but 70 ppb (this value was corrected based on the number of injections shown in Figure 2). The SQT was added in seven separate injections of ~10 ppb each to maintain low concentrations.

7. Figure 2: Since the paper is CHARON focused, the PTR-CHARON data in this figure should be made clearer visually. I also raise the following points:

We have revised Figure 2 to enhance the visual distinction of the PTR-CHARON data as requested.

(a) Why the OA exhibits two modes while the isoprene injection occurred only once. (b) Isoprene injection occurred twice but three modes appear in OA.

Response to (a) & (b): The stepwise increase (or "modes") in OA concentration is driven by oxidant availability rather than the precursor injection. In these experiments, OH radicals were generated via TME ozonolysis. Since the precursor (Isoprene) was already present in the chamber, SOA formation occurred in bursts triggered by each discrete injection of Ozone (added to maintain O_3 levels for TME reaction).

For (a): Two Ozone injections were performed, resulting in two distinct periods of rapid SOA formation.

For (b): Three Ozone injections were performed, resulting in the three observed steps. We have clarified this oxidant generation strategy in the revised manuscript.

The text has been revised to clarify the interpretation of these results.

Line 227: *"It is important to mention the stepwise increases ("modes") in OA concentration during ISOP-IEPOX-SOA and ISOP-non-IEPOX-SOA reflect bursts of SOA formation driven by oxidant availability rather than the number of isoprene injections. Because OH radicals were generated through discrete O_3 injections for TME ozonolysis, each addition of O_3 triggered a new period of rapid SOA formation, producing the observed modes in the OA time series."*

We also described the ozone injections used to maintain the concentration between 100 and 110 ppbv

Line 182: "To maintain ozone concentrations between 100–110 ppbv, additional ozone was injected as needed, and TME was injected every 5 minutes for approximately 4 hours."

(c) Three injections of monoterpene but a smooth enhancement in the OA signal.

The "smooth" appearance of the OA signal during the MT experiment, despite three distinct injections, is due to the timescale of mixing relative to the reaction kinetics. The injections occurred all within the first hour. The chamber mixing time (~4 minutes) acts to smooth out the instantaneous effect of each injection. Unlike the Isoprene experiment (where OH bursts caused sharp steps), the MT oxidation proceeded more steadily, resulting in a gradual cumulative increase in OA rather than sharp steps.

(d) SQT-SOA and the precursor SQT signal are positively correlated. Should the precursor not reduce over time as OA grows? Or am I not understanding this correctly.

The reviewer is correct that in a single-pulse decay experiment, precursor and product should be anti-correlated. However, in this experiment, SQT was introduced via sequential injections over time (up to minute ~350). Consequently, the total SQT burden in the chamber was increasing (positive slope in gas signal) while simultaneously reacting to form SOA (positive slope in OA signal). The expected decay of the precursor is indeed observed, but only after the injections stopped (after minute 400). The alternation between Gas and Particle measurement cycles in the instrument may also contribute to the visual fragmentation of this trend.

8. Is C4H8O a real peak or a fragment in figure 5c? Similarly for the C5H6O trace in the CHARON measurements in figure 4a. In AMS measurements, C5H6O is a fragment produced from electron ionization of parent species, which should be interpreted differently than a C5H6O trace signal in PTRMS-CHARON measurements. These compounds appear prominently in the CHARON mass spectra in figures 5a and c and therefore should be carefully discussed. I am not sure whether such oxidation products partition enough to the particle phase to appear so strongly in the aerosol spectra.

We agree with the reviewer that these signals likely arise from fragmentation or thermal decomposition within the instrument, rather than from parent compounds partitioning directly into the particle phase.

Regarding C_4H_8O: We attribute this signal to ionic fragmentation. As demonstrated by Gkatzelis et al. (2018) using separation techniques for parent and fragment ions in CHARON-PTR-ToF-MS, C_4H_8O in the particle phase is a characteristic fragment observed in Isoprene-NO experiments, distinct from its gas-phase isomer (MEK).

Regarding C_5H_6O: We interpret this signal (attributed to methylfuran) as a product of thermal decomposition occurring during the desorption process. As described by the reviewer, this mechanism is well-documented in AMS studies (e.g., Allan et al., 2014; Lin et al., 2012) and filter-based GC-MS analysis (Robinson et al., 2011), where it forms from the decomposition of IEPOX-SOA. However, a key finding in our study is that the CHARON inlet detected this ion in both the IEPOX-SOA and the non-IEPOX-SOA (both low-NO_x) experiments. This contrasts with AMS

results where it is strictly an IEPOX tracer. Consequently, we suggest that for CHARON measurements, C_5H_6O acts as a broader potential tracer for low-NO_x isoprene SOA, rather than being specific to the IEPOX pathway. We have added a cautionary note in the text regarding the robustness of this tracer.

9. Figure 3 caption should clearly note whether this is AMS data. Add units/ (e.g. # or fraction) to the y-axis label in figure 3 if there is one on the x-axis. The x-axis unit ‰ is a bit confusing. Is it a percentage?

Both axes are now expressed in percentages. For improved clarity now the figure caption now reads as:

"Figure 3: AMS scatter plot of f_{CO_2} vs. $f_{C_5H_6O}$ (expressed in percentage, %) for ISOP-SOA experiments conducted in the DouAir atmospheric chamber. The successful production of IEPOX-SOA was achieved by increasing relative humidity (from 20% to 50%) and using acidic seed particles. For comparison, data from literature laboratory experiments characterizing IEPOX uptake and isoprene oxidation pathways are also included."

10. Figure 4: (b) "AMS/SMPS" can be confused as a ratio. A comma or "and" would be more appropriate.

It has been corrected.

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RC2

The paper of Ramírez-Romero et al., “Exploring biogenic secondary organic aerosol using a PTRMS-CHARON in laboratory experiments: characterization and fingerprint analysis” describes 5 SOA experiments with precursors isoprene, limonene and b-caryophyllene in a smog chamber. The particle phase was measured by the newly developed inlet CHARON coupled to a PTRMS. Limonene SOA has also been measured by Gkatzelis et al. (2018), but isoprene and b-caryophyllene SOA have not been characterized by the CHARON-PTRMS system. However, the manuscript is quite weak as it is: a lot of details have not been discussed thoroughly; the experiment section needs to be reorganized. The results should be rewritten. It seems that the paper has a lot of information hidden but it is fast and informally written. The conclusion section is quite weak, and the reader feels confused. I believe these results deserve publication but only after a major revision.

We sincerely thank the reviewer for their critical and constructive assessment of our manuscript. We appreciate that you recognized the potential value of the dataset, particularly regarding the novel characterization of Isoprene and beta-caryophyllene SOA using the CHARON-PTRMS system. We acknowledge that the presentation of the results was not sufficiently rigorous and that valuable information was indeed "hidden" due to the structure and writing style. In response to this "Major Revision" decision, we have performed a comprehensive overhaul of the paper:

Reorganization: The Experimental Section has been restructured to provide a clearer, more logical flow of the methodology (including chamber characterization and instrument settings).

Depth of Discussion: The Results Section has been largely rewritten. We have moved away from a "fast" description to a thorough scientific discussion, carefully addressing the identification of fragments vs. parent molecules and the interpretation of temporal trends (as detailed in the specific responses below).

Formalization: We have carefully edited the text to ensure a formal, academic tone throughout, removing the "informal" phrasing noted by the reviewer.

Conclusion: The Conclusion has been expanded to better synthesize the findings and their implications for the atmospheric science community, ensuring the reader is left with a clear take-home message. We believe that this revised version reveals the full potential of the data and meets the standards required for publication.

Comments:

1) Page 2, lines 40-43: please use more recent literature.

Following the suggestion of reviewer #1, we have revised the introduction which encompassed adding more recent references.

2) Page 3, line 108: “artificial UV lamp” you need to explain what kind of lamps were used (range of radiation), number of lamps, JNOx etc…

The paragraph below was added to the chamber description (Section 2.1, DouAir Atmospheric Simulation Chamber, first paragraph).

Line 85: *“DouAir can be operated under dark conditions or irradiated either via natural solar light or artificial UV lamps, allowing the simulation of a wide range of atmospheric conditions. The chamber is equipped with 48 UVA actinic lamps (365 nm, 40 W, 1.2 m in length), with 24 lamps mounted on each side. The photolysis frequency for NO_2, $J(NO_2)$, was determined by actinometry and measured to be 1.42×10^{-3} s^{-1}.”*

3) Page 5, lines155-156: “To ensure consistency across experiments, an EF value of 21 was applied, as specified by the manufacturer's certified documentation”. Why didn’t you apply the EF that you found for levoglucosan (24.1)? An EF of 21 is what is suggested and has been measured for a specific instrument. It doesn’t mean that EF is the same across all CHARON systems. How much do the results change applying an EF of 21? Shouldn’t NH4NO3 EF be near 21 as well? Please explain.

The value of 21 was found in the instrument certification by the manufacturer for our model, as well in agreement with the theoretical EF from the measured volumetric flows. Given the experimentally determined calibration for levoglucosan has been close to this value, we decided to apply it across the experiments. We have modified the text to improve its clarity:

Line 137: *“The EF using levoglucosan (a non-volatile marker) yielded an EF of 24.1 ± 0.5, demonstrating efficient particle enrichment. In contrast, semi-volatile ammonium nitrate yielded a significantly lower EF (~6.5 ± 1.2), likely due to particle evaporation within the sub-atmospheric pressure region of the CHARON inlet. Given that the measured EF for stable particles (24.1) was in reasonable agreement with the theoretical EF, as well as the manufacturer's certified documentation (21), the latter was applied to all datasets.”*

4) Page 5, lines 159-162: “Other mass spectrometers were used to complement PTRMS-CHARON observations, such as a second PTRMS (second generation, Kore Technology Inc.) for VOC measurements (Michoud et al., 2017).” Are there any data from the second PTRMS presented in the paper? If not, then there is reason to mention it. Please explain.

Yes, the VOC measurements related to the isoprene-derived SOA formation pathways (ISOP-IEPOX-SOA, ISOP-non-IEPOX, and ISOP-NO-SOA) and MT-SOA were conducted using the second PTR-MS, as the PTR-MS-CHARON was operated in particle-phase mode. This clarification has been included in the main text, described below.

Line 152: *”Other mass spectrometers were used to complement PTRMS-CHARON observations, such as a second PTRMS (second generation, Kore Technology Inc.; Michoud et al., 2017) for VOC measurements during ISOP-SOA and MT-SOA experiments.”*

5) Page 5: Experimental protocol: This part is very confusing. It should contain only the experimental procedure. If needed you may add a methodology section, but in my opinion it should not be named experimental protocol. Most of it consists of theory mentioning previous literature. Please remove the theory as it is not the appropriate place. If you need the theory in this part either transfer it to the theory part (with the corresponding modifications) or use it later to explain your observations.

We have now revised the text accordingly. The theoretical background has been incorporated into the Results and Discussion section, and the corresponding changes have been made to the experimental protocol. Below is the updated version of that section.

"Three different terpenoids were used as precursors for SOA production: isoprene (ISOP, Sigma-Aldrich, 99%), limonene (MT, Sigma-Aldrich, 97%), and β-caryophyllene (SQT, Sigma-Aldrich, > 80%). All experiments were conducted at 15–50% RH and roughly 20 °C. Following each experiment, the DouAir chamber was flushed with purified air (40 L min $^{-1}$) for at least 24 hours. Table 1 summarizes the specific conditions for each experiment.

Isoprene experiments

ISOP-SOA formation was investigated under three configurations: ISOP-IEPOX, ISOP-non-IEPOX, and ISOP-NO-SOA:

- *Low-NO Conditions (IEPOX/non-IEPOX): Hydroxyl radicals (OH) were generated via tetramethylethylene (TME, C_6H_{12}) ozonolysis, as described in Berndt et al. (2019). The OH concentration was calculated based on the decay of the dilution-corrected isoprene signal, following the approach described by Barmet et al. (2012) and detailed in the SI. Seed particles and the initial ozone injection were introduced prior to isoprene addition. To maintain ozone concentrations between 100–110 ppbv, additional ozone was injected as needed, and TME was injected every 5 minutes for approximately 4 hours. The ISOP-IEPOX-SOA experiments utilized acidic seed particles (0.005 M ammonium sulfate + 0.1 M sulfuric acid) at 50% RH, with continuous seed injection to maintain acidity. The ISOP-non-IEPOX-SOA experiments used neutral seed particles (0.005 M ammonium sulfate) at 15–30% RH.*

- *High-NO Conditions (ISOP-NO-SOA): OH was generated via HONO photolysis. These experiments employed neutral seed particles (0.005 M ammonium sulfate) and initial mixing ratios of NO (~8 ppbv) and NO_2 (~5 ppbv).*

Monoterpene and sesquiterpene experiments

MT-SOA and SQT-SOA were generated via the ozonolysis of limonene and β-caryophyllene, respectively, without seed particles. For all experiments, chamber humidification was the initial step, followed by background measurements. Ozone was injected prior to the precursor.

- *Limonene (MT): Three injections were performed at 20-minute intervals.*
- *β-caryophyllene (SQT): Seven injections were performed at intervals between 20 and 45 minutes.*

***Table 1**. Summary of experimental conditions during the chamber experiments. Maximum SOA mass concentrations were determined using AMS for the ISOP-SOA experiments and SMPS for the MT- and SQT-SOA experiments.*

Experiment (# of repetitions)	Seed particles	Injection of biogenic precursor in ppbv (# of injections)	Ozone (ppbv)	Injection of TME in ppbv (# of injections)	OH (molecules cm^{-3})	RH (%)	NO and NO_2 (ppbv)	Maximun SOA formed (μgm^{-3})	SOA formation conditions
ISOP-IEPOX-SOA (3)	$(NH_4)_2SO_4+H_2SO_4$	200 (1)	80-100	10 (27)	~4 x 10^5	50	< 1	~5	Reaction with OH
ISOP-non-IEPOX- SOA (2)	$(NH_4)_2SO_4$	100 (2)	80-100	10 (19)	~4 x 10^5	15-30	< 1	~4	Reaction with OH
ISOP-NO-SOA (1)	$(NH_4)_2SO_4$	90 (1)	~100	----	~4 x 10^6	30	7.5 and 5.3	~3	Reaction with OH
MT-SOA (5)	----	18 (3)	80 initial	----	----	30	----	~120	Ozonolysis
SQT-SOA (3)	----	10 (7)	100 initial	----	----	30	----	~83	Ozonolysis

”

In the experimental part you need to be clear in which experiments you used seeds, how OH was produced and how did you calculate the concentrations of OH in Table 1. Also please add information about the precursors used (purity, company).

The requested information has been added into the revised protocol section, described on the previous comment. The following information has also been added into the Supplementary Information:

“OH Concentration Calculation

During the ISOP-SOA experiments, OH radicals were generated through the ozonolysis of TME. The OH concentration was previously calculated from the decay of the dilution and wall loss-corrected isoprene signal, following the method described by Barmet et al. (2012). The slope of the plot of the natural logarithm (ln) of the dilution-corrected isoprene concentration versus time corresponds to -k·[OH], where k is the isoprene reaction rate constant with OH and [OH] is the OH concentration.

$$[OH] = \frac{-slope}{k}$„$$

In addition, the purity and supplier of the compounds were included in the experimental protocol.

6) Page 5, Lines 230-231: “All the measurements were corrected for dilution and wall losses as detailed in the SI.” In the SI there is an equation that corresponds to dilution correction. But there are no details about the wall losses appart from the phrase “First order wall loss rates were determined for gases, O3, and particles and are reported in Table S2.” What kind of particles did you use? (organics, ammonium sulfate?) Were they polydisperse (please give the diameter range), monodispersed (please give the diameter)? Between each experiment? At the beginning of the campaign? How long did the wall losses measurements last (e.g. 4 hours?). Did you use a protocol (may refer to previous literature?). Were these chamber wall losses measured by the CHARON-PTRMS, by the AMS, by an SMPS? If there were from AMS or SMPS how did you apply them on CHARON-PTRMA data?

Wall-loss characterization experiments were conducted prior to these chamber experiments. The wall-loss monitoring period was approximately 4 hours for particle characterization and about 13 hours for the VOCs studied. The determination of k_{wall} followed the methodology described in Smith et al. (2019), Guo et al. (2022), and Wang et al. (2018). The particle wall-loss rate was derived from SMPS measurements and subsequently applied to the AMS and PTRMS–CHARON (particle phase) data using the correction described by Wang et al. (2018).

This information has been added to the SI:

Particle wall-loss rate k_{wall} was determined from the first-order decay of the total polydisperse SOA mass concentration measured by the SMPS after chemical reactions had fully completed following the protocol proposed by Wang et al. (2018). For this correction, the SOA was produced from dark ozonolysis of ~16 ppbv of α-pinene with ~50 ppbv of O_3. Wall-loss monitoring was conducted for approximately 4 hours for particle phase and 13 hours for the VOC studied (table S1), providing a sufficiently long exponential decay period for reliable determination. This mass-based approach assumes that the wall-low rate is size-independent over the size range of particles produced in the atmospheric chamber and that it remains constant throughout each experiment (Wang et al., 2018). Previous studies (e.g., Smith et al., 2019; Guo et al., 2022) estimated the total first-order decay rate constant $k_{total} = k_{(wall+dilution)}$ by fitting the natural logarithm of the normalized concentration $Ln\left(\frac{[A]_0}{[A]_t}\right)$ as a function of time. The slope of this linear fit corresponds to k_{total}, where $[A]_0$ and $[A]_t$ represent the initial and time-dependent concentrations of VOC (in ppbv) or particle mass (in μg m^{-3}), respectively.

The equations used in this study are:

$$Ln\left(\frac{[A]_0}{[A]_t}\right) = k_{(wall+dilution)} \cdot t$$

$$k_{wall} = k_{(wall+dilution)} - k_{dilution}$$

The particle lifetime with respect to wall deposition was calculated as:

$$\tau = \frac{1}{k_{wall}}$$

7) Page 7, Table 1: Please add RH, NO kai NO2 and seeds concentrations for each experiment. Is the maximum SOA formed, obtained by the CHARON?AMS?SMPS? Please explain.

The requested information has been added to table 1. The following sentence has been added to the caption.

"Maximum SOA mass concentrations were determined using AMS for the ISOP-SOA experiments and SMPS for the MT- and SQT-SOA experiments."

Table 1. *Summary of experimental conditions during the chamber experiments. Maximum SOA mass concentrations were determined using AMS for the ISOP-SOA experiments and SMPS for the MT- and SQT-SOA experiments.*

Experiment (# of repetitions)	Seed particles	Injection of biogenic precursor in ppbv (# of injections)	Ozone (ppbv)	Injection of TME in ppbv (# of injections)	OH (molecules cm^{-3})	RH (%)	NO and NO_2 (ppbv)	Maximun SOA formed (μgm^{-3})	SOA formation conditions
ISOP-IEPOX-SOA (3)	$(NH_4)_2SO_4$+H_2SO_4	200 (1)	80-100	10 (27)	~4 x 10^5	50	< 1	~5	Reaction with OH
ISOP-non-IEPOX- SOA (2)	$(NH_4)_2SO_4$	100 (2)	80-100	10 (19)	~4 x 10^5	15-30	< 1	~4	Reaction with OH
ISOP-NO-SOA (1)	$(NH_4)_2SO_4$	90 (1)	~100	----	~4 x 10^6	30	7.5 and 5.3	~3	Reaction with OH
MT-SOA (5)	----	18 (3)	80 initial	----	----	30	----	~120	Ozonolysis
SQT-SOA (3)	----	10 (7)	100 initial	----	----	30	----	~83	Ozonolysis

8) Page 8, Figure 2a: At the beginning of the experiment there is organic phase appearing along with the ammonium sulfate. Is this organic contamination from seeds? (it has the same trend). As it is quite high (~1/3) of the total mass concentration it can affect the data quality. Did you correct the time series and the mass spectra for this contamination? How? Please explain.

The reviewer is correct that an initial organic fraction appears concomitantly with the ammonium sulfate seed injection (~1/3 of total mass). Given that this specific experimental protocol had been repeated several times in the preceding days, we attribute the initial organic fraction observed on the seed particles to the condensation of residual oxidized species from the previous days.

Crucially, a comparison of the mass spectral signatures revealed that this background is chemically identical to the SOA formed later in the experiment, that condensed extremely efficiently into the acidic seed particle. Since the primary objective of this study is chemical fingerprinting rather than quantitative yield determination, we chose not to perform a background subtraction. Instead, we analyzed the mass spectra at the peak SOA concentration, which occurred several hours after the precursor injection, ensuring the reported signatures are dominated by the target chemistry.

9) In Figure 2 is the gas phase measured by the second PTRMS? Please explain.

Yes, for the isoprene-derived SOA and MT-SOA experiments we used the measurements from the second PTRMS instrument in response to comment number 4.

10) How did you convert the signal of the PTRMS/CHARON in ug/m3 (left y axis)? What k rate did you use? Please explain in the text.

The following section was added to the SI, where the calculation of the mass concentration of the detected species in PTRMS-CHARON is described.

Mass concentration calculation with PTRMS-CHARON

The particle phase concentrations of a given species i was calculated based on Müller et al. (2017) and Peng et al. (2023).

$$Pi = \frac{I_i \times (\frac{m}{z}_i - 1)}{\frac{V_m \times S_i}{EF}}$$

Where Pi is the mass concentration (ng m^{-3}) of the compound i, I_i the normalized signal (ncps) of the ion detected $\frac{m}{z}_i$ is the mass over charge of the protonated ion i. V_m is the the molar volume (22.4 L mol^{-1}), S_i is the sensitivity of the compound i (ncps/ppbv) and EF is the enrichment factor. The total OA mass concentration is calculated by summing the contribution of all individually detected ions (Pi). For the ions detected in the particle phase, a k-rate of 3×10^{-9} cm s^{-1} was used.

11) Why SOA formation increase is not continuous in Figures 2a and 2b? The are 3 and 2 "bumps" but there is no precursor added just before. Please explain.

The stepwise increase (or "modes") in OA concentration is driven by oxidant availability rather than the precursor injection. In these experiments, OH radicals were generated via TME

ozonolysis. Since the precursor (Isoprene) was already present in the chamber, SOA formation occurred in bursts triggered by each discrete injection of Ozone (added to maintain O_3 levels for TME reaction).

We have included the following paragraph in the main text:

Line 227: "*It is important to mention the stepwise increases ("modes") in OA concentration during ISOP-IEPOX-SOA and ISOP-non-IEPOX-SOA reflect bursts of SOA formation driven by oxidant availability rather than the number of isoprene injections. Because OH radicals were generated through discrete O_3 injections for TME ozonolysis, each addition of O_3 triggered a new period of rapid SOA formation, producing the observed modes in the OA time series.*"

For figure 2a: Two Ozone injections were performed, resulting in two distinct periods of rapid SOA formation.

For figure 2b: Three Ozone injections were performed, resulting in the three observed steps. We have clarified this oxidant generation strategy in the revised manuscript.

12) How well do the AMS organic mass concentrations match with the CHARON concentrations for each experiment? What was the CE of the AMS (or what was assumed?)

The OA concentrations measured by the AMS and the PTR-MS-CHARON showed a Pearson correlation of 0.9, indicating a very strong temporal agreement between the two techniques. However, the CHARON inlet accounted for approximately 20% of the total OA mass reported by the AMS (calculated using a CE of 1, given the high acidity of the seed particles). We attribute this quantitative discrepancy to two main factors:

Particle Size Cut-offs: The AMS efficiently transmits particles down to ~80 nm, whereas the CHARON inlet has a lower cut-off efficiency below ~125 nm. Since chamber-generated SOA often has a significant mass fraction in the accumulation mode below 125 nm, the CHARON physically samples a smaller subset of the aerosol population.

Quantification Uncertainties: While the CHARON is expected to effectively evaporates ELVOCs (as noted in response to Reviewer #1), the subsequent detection via PTR-MS is subject to uncertainties in reaction rate constants (k-rates) for complex, high-molecular-weight oxidized species. Furthermore, ionic fragmentation (e.g., loss of neutral fragments or formation of ions below the measured mass range) leads to an underestimation of the total mass. Therefore, while the absolute mass is lower in CHARON, the high temporal correlation confirms that the instrument captures the bulk of the chemical evolution. This reinforces the utility of CHARON-PTRMS as a tool for chemical fingerprinting and spectral signature analysis, even if total mass closure with AMS remains challenging due to these physical and fundamental differences.

The following information was included in Section 2.2.

Line 160: *"The HR-AMS has been calibrated using monodispersed ammonium nitrate and ammonium sulfate particles from the corresponding solutions at 0.005 M. HR-AMS data were corrected using the parametrization of Middlebrook et al. (2012). A collection efficiency (CE) of 1.0 was used for the ISOP-IEPOX-SOA experiment, due to the presence of acidic seed particles, while a CE of 0.5 was applied to the ISOP-non-IEPOX-SOA and ISOP-NO-SOA experiments with neutral seed aerosol."*

13) Page 8, lines 268-276: "The HR-AMS……Morgan et al., 2020)". This part does not belong to the results section. It is again a theory. You may use it to explain your results but as it is right now it looks irrelevant with the rest of the text.

Thank you for your comment. This section has been revised for improved clarity:

Line 245: "To characterize the contribution of IEPOX-SOA and to distinguish it from the ISOP-non-IEPOX-SOA pathway, we used the established AMS marker $f_{C_5H_6O}$, defined as the ratio of C_5H_6O (m/z 82 at unit mass resolution) to total OA (Hu et al., 2015). This ion corresponds to methyl furan, a thermal decomposition product of 3-MeTHF-3,4-diols formed via IEPOX reactive uptake (Robinson et al., 2011; Lin et al., 2012; Hu et al., 2015). Additionally, f_{CO_2} (or f_{44} at unit mass resolution) was used to evaluate the OA oxidation state and degree of aging (Cubison et al., 2011; Milic et al., 2017; Morgan et al., 2020)."

14) Page 8, lines 279-281: Here the reader does not understand much. What are you referring to? What is the result shown in Fig 3? What does Fig 3 mean? Please explain Fig 3 and then use the theory (maybe in the previous paragraph) support your results. However, I don't understand why Figure 3 is important or why it should be shown in the paper. What is it relationship with RH or acidic particles?

We have revised the text to better explain the purpose of Figure 3, which serves as a crucial validation step for our experimental protocols. Since this study aims to characterize specific SOA regimes, we used the AMS data in Figure 3 to prove that our experimental adjustments (acidic seeds and increased RH) successfully triggered the IEPOX reactive uptake pathway. The figure demonstrates that these conditions lead to a distinct increase in the established AMS marker f_{C5H6O} (a tracer for IEPOX-SOA), clearly distinguishing these experiments from the standard low-NOx isoprene oxidation. This "sanity check" ensures that the subsequent CHARON fingerprints correspond to the intended chemical regimes.

The importance of acidity and relative humidity in the formation of IEPOX-SOA along the ISOP-IEPOX pathway has been included in the following section:

Line 250: *As shown in Fig. 3, $f_{C_5H_6O}$ increased substantially under IEPOX-reactive uptake conditions compared to the ISOP-non-IEPOX-SOA pathway, confirming the formation of IEPOX-derived aerosol. This enhancement is driven by the acidity of the seed particles, which catalyzes the ring-opening of the epoxide functional group, accompanied by the addition of particle-phase*

nucleophiles such as sulfate and water (Liu et al., 2015; Wong et al., 2015). The RH also played an important role in the reactive uptake of IEPOX. Wong et al. (2015) demonstrated that under high-RH conditions, particle-phase water strongly enhances SOA formation. These conditions promote the dissolution of soluble species, facilitating aqueous-phase oxidation and leading to the formation of low-volatility products such as C_5-alkene triols (e.g., 2-methyltetrols and $C_5H_{10}O_3$ compounds; Frauenheim et al., 2022), 1,4-diols, 1,3-diols, 3-methyltetrahydrofuran-3-ol, oligomers, and organosulfates (Kuwata et al., 2015; Liu et al., 2015; D'Ambro et al., 2019).

15) Page 9, Figure 4: The time series of *m/z* 83.049, m/z 119.07 and m/z 137.081 (Figure 4a) have completely different trends from the AMS organic phase (Figure 4b). They also do not agree with the time series of CHARON organics (Figure 2a). All these 3 figures refer to the same experiment but they are different between each other. Please explain.

We thank the reviewer for closely examining these trends. First we want to clarify that Figure 2 displays roughly the first 8 hours, while Figure 4 includes the full ~20-hour experiment. Focusing solely on figure 4 we clarify that the difference in trends is driven by the nature of the signal being monitored (Bulk Mass vs. Specific Tracers) and the initial state of the seed particles.

Residual Background vs. Fresh Production: As noted in our response to Comment 8, the AMS detects a residual organic background (approx. 1.2 ug/m3) on the seed particles immediately upon injection (visible in Figure 4b from t=0). This signal is attributed to residual oxidized species from previous identical experiments condensing on the seeds. While this background is chemically similar to the SOA formed later, the AMS measures the total organic burden and thus registers this mass immediately.

Chemical Induction Time: In contrast, the CHARON tracers shown in Figure 4a (e.g., m/z 119, 137) track the active formation of fresh second-generation products. Even if similar species exist in the background, the sharp rise in these specific molecular signals corresponds to the onset of the new photochemical cycle (Isoprene to ISOPOOH then IEPOX). The ~1-hour delay represents the chemical induction time required for this fresh production to generate sufficient quantities to dominate the signal.

Confirmation via the "Bump": This interpretation is confirmed by the second injection event (the "bump" at the end of the time series). During this phase, the rapid injection of precursors and oxidants created a high flux of new SOA. Because this was a fresh, high-intensity event, both the AMS (bulk) and CHARON (tracers) registered the increase simultaneously. This synchronization confirms that the instruments respond temporally to the same active chemical events.

The following sentence has been added to the main text:

Line 275: *"The initial offset between the AMS and CHARON signals is attributed to a residual organic background on the seed particles, which is detected immediately by the AMS as bulk mass, whereas the CHARON tracers track the kinetic induction of fresh oxidation products."*

16) Why is the number concentration of the SMPS necessary in Figure 4b? It is not even discussed in the text.

The SMPS concentration was removed.

17) Page 10, lines: 299-300: “Figure 5 depicts the signature spectrum for the experiments studied here. For ISOP-Non-IEPOX-, MT-, and SQT-SOA, the signature spectra were chosen for the period when OA peaked.” Do you mean when the uncorrected OA mass concentration peak? Did you apply the wall-losses and dilution corrections to check when is the real maximum? Did you compare the mass spectra with the final ones? Moreover, did you compare between the initial and final mass spectra for the rest of the experiments? Please explain.

We confirm that wall-loss and dilution corrections were applied to the entire dataset. The "peak" period selected for the spectral analysis corresponds to the maximum organic mass concentration determined after these corrections were applied. We selected this specific period because it represents a moment of chemical stability where the SOA population is mature. The primary objective of this study is to establish a distinct "spectral signature" for these specific BSOA types. This is crucial because, unlike AMS (which often yields similar bulk spectra for most of those precursors), CHARON-PTRMS provides some molecular-level detail that distinguishes these pathways. Therefore, the selected spectrum is intended to serve as a reference fingerprint for the "characteristic" SOA formed.

Regarding the comparison between initial and final spectra: while some temporal evolution occurs, a detailed analysis of these mechanisms and the resulting spectral shifts is complex. It represents a distinct scientific question that will be the subject of a forthcoming study also looking at the gas-particle partitioning of those organic compounds. For the scope of this manuscript, focusing on the chemically stable peak provides the most robust reference for identification purposes.

Proposed Revision (Line 286): *“Figure 5 depicts the signature spectrum for the experiments studied here. For ISOP-non-IEPOX-, MT-, and SQT-SOA, the signature spectra were extracted from the period corresponding to the maximum OA concentration (corrected for wall losses and dilution). This period was identified as a period of chemical stability, representing the mature SOA composition. For ISOP-IEPOX-SOA, the signature spectrum was selected during the second injection of acidic seed particles, after the onset of gas-phase oxidation, when the C_5H_6O signal measured by CHARON reached the highest concentration.”*

18) Page 10, lines: 300-301: “strongly dependent on seed particle acidity” what does this mean?
That paragraph was rewritten for improved clarity, and the sentence in question was removed, as shown in the previous comment (14)

19) Page11, Figure 5: Did you correct for any organic contamination in the first (Figure 5a) mass spectrum

This comment has already been addressed previously (comment number 8)

20) Page11, lines 337-352: "Similar…. Jaoui et al., 2013). Here you need to identify these ions: you need to look for previous literature (which used analytic instrumentation) and link the measured characteristic m/zs to possible compounds. Right now, this paragraph, it is just describing what was observed.

To address this comment, the following text has been modified

Line 328: "*Similar to the ISOP-SOA experiments, the contribution of compounds to MT- and SQT-SOA is distributed between main ions and likely fragments, several of which have been previously reported in the literature. Using PTRMS–CHARON, Gkatzelis et al. (2018a) observed highly oxidized semi-volatile compounds during limonene ozonolysis, including $C_8H_{12}O_{4,5}$, $C_9H_{14}O_{3,4}$, and $C_{10}H_{16}O_{3,4}$. These species were also detected in our MT-SOA experiments in the DouAir chamber, as well as their potential fragments (detailed in Table S2). The $C_9H_{14}O_{3,4}$ ions are attributed to multifunctional oxygenated C_9 products, dominated by carboxylic acids and aldehydes formed during limonene ozonolysis (Gkatzelis et al., 2018a; Jacob et al., 2023). These compounds are produced via alkoxy-radical (e.g., $C_9H_{13}O_3$) and RO_2 chemistry followed by intramolecular isomerization, as described by Kundu et al. (2012). The $C_9H_{12}O_4$ ion may also represent a fragmentation product of $C_9H_{14}O_5$ (m/z 203.091), a compound previously identified by Jacob et al. (2023) using liquid chromatography–mass spectrometry (LC-MS). The $C_{10}H_{16}O_{3,4}$ ions are attributed to larger multifunctional carboxylic acids and aldehydes (Gkatzelis et al., 2018a; Wong et al., 2021), while lower-carbon-number oxidation products (e.g., $C_8H_{12}O_{4,5}$) correspond to highly oxygenated C_8 carboxylic acids (Hammes et al., 2019; Jacob et al., 2023). During the SQT-SOA experiments, the composition was dominated by multifunctional oxygenated sesquiterpene products, consistent with previous PTRMS–CHARON observations of β-caryophyllene ozonolysis (Gao et al., 2022).The most abundant signals corresponded to $C_{15}H_{24}O_{2,3}$ and $C_{14}H_{22}O_{2,3}$ ions, typically associated with first-generation ozonolysis products such as aldehydes and carboxylic acids (Li et al., 2011). In addition, more highly oxygenated species, including $C_{15}H_{24}O_4$ and $C_{15}H_{26}O_4$, were detected and are consistent with hydroxy- and hydrated carboxylic acids formed (Chan et al., 2011; Li et al., 2011; Jaoui et al., 2013; Gao et al., 2022). Lower-carbon-number oxidation products (e.g., C_{11} compounds) were also observed, consistent with second-generation oxidation products formed during β-caryophyllene ozonolysis (Li et al., 2011; Jaoui et al., 2013). A comprehensive list of the detected main ions, their likely fragments, and corresponding compound assignments is provided in Table S3."*

We also included the main ions, their molecular formulas, tentative compound assignments based on the literature, and the corresponding potential dehydration fragments for the MT-SOA and SQT-SOA experiments, as summarized in Tables S2 and S3 of the Supplementary Information, respectively.

***"Table S 2:** Main ions detected during limonene ozonolysis (MT-SOA) experiments using PTRMS-*

CHARON, including their molecular formulas, tentative compound assignments based on literature, and the corresponding potential dehydration fragments $[M+H-H_2O]^+$.

MT-SOA: Limonene ozonolysis			
Main ion (m/z)	**Formula**	**Compound assignment from literature**	**Potential fragments $[M+H-H_2O]^+$ (m/z; formula)**
171.102	$C_9H_{14}O_3$	Limonalic acid; norlimononic acid; ketolimononaldehyde	153.091 ($C_9H_{12}O_2$)
173.081	$C_8H_{12}O_4$	Norlimonic acid	155.070 ($C_8H_{10}O_3$)
185.117	$C_{10}H_{16}O_3$	Limononic acid; 4-isopropenyl-1-methyl-1,5-hydroxy-2-oxocyclohexane; 7-hydroxylimononaldehyde	167.106 ($C_{10}H_{14}O_2$)
187.096	$C_9H_{14}O_4$	Ketolimononic acid; limonic acid	169.086 ($C_9H_{12}O_3$)
189.075	$C_8H_{12}O_5$	Ketolimonic acid	171.065 ($C_8H_{10}O_4$)
201.112	$C_{10}H_{16}O_4$	5-hydroxylimononic acid; 7-hydroxylimononic acid	183.102 ($C_{10}H_{14}O_3$)
203.091	$C_9H_{14}O_5$		185.080 ($C_9H_{12}O_4$)

(Gkatzelis et al., 2018a; Hammes et al., 2019; Wong et al., 2021 Jacob et al., 2023)

Table S 3: *Main ions detected during β-caryophyllene ozonolysis (SQT-SOA) experiments using PTRMS-CHARON, including their molecular formulas, tentative compound assignments based on literature, and the corresponding potential dehydration fragments $[M+H-H_2O]^+$.*

SQT-SOA: β-caryophyllene ozonolysis			
Main ion (m/z)	**Formula**	**Compound assignment from literature**	**Potential fragments $[M+H-H_2O]^+$ (m/z; formula)**
237.185	$C_{15}H_{24}O_2$	β-caryophyllon aldehyde	219.174 ($C_{15}H_{22}O$)
239.164	$C_{14}H_{22}O_3$	β-nocaryophyllon aldehyde	221.154 ($C_{14}H_{20}O_2$)
253.18	$C_{15}H_{24}O_3$	β-caryophyllonic acid	235.169 ($C_{15}H_{22}O_2$)
255.159	$C_{14}H_{22}O_4$	β-caryophyllinic acid	237.149 ($C_{14}H_{20}O_3$)
269.175	$C_{15}H_{24}O_4$	β-hydroxycaryophyllonic acid	251.164 ($C_{15}H_{22}O_3$)
271.19	$C_{15}H_{26}O_4$	Hydrated β-caryophyllonic acid	253.180 ($C_{15}H_{24}O_3$)
199.133	$C_{11}H_{18}O_3$	3,3-dimethyl-2-(3-oxobutyl) cyclobutane carboxylic acid	

(Chan et al., 2011; Li et al., 2011; Jaoui et al., 2013; Gao et al., 2022). ”

21) Page 12, lines 367-374: “Non-sulfated dimers….. ISOP-Non-IEPOX-SOA route.” What are you trying to support in the paragraph? I can’t understand the meaning here. Please rewrite.

We wanted to clarify that the formation of dimers, their possible decomposition, and PTRMS-CHARON fragmentation may contribute to the broader and more diverse molecular distribution observed in Fig. 6 compared with the non-IEPOX-SOA pathway. The text has been rewritten accordingly as follows:

Line 365: *“The ISOP-IEPOX-SOA mass spectrum (Figure 6) exhibits a notably broader and more diverse molecular distribution compared to the non-IEPOX pathway. This complexity is likely driven by the formation and subsequent processing of low-volatility oligomers. Previous studies have established that acidic conditions promote the formation of non-sulfated dimers, such as $C_{10}H_{22}O_7$ and $C_{10}H_{20}O_6$ (Surratt et al., 2006; Lin et al., 2014). Furthermore, Armstrong et al. (2022)*

suggested that these oligomers can decompose via OH oxidation into lower molecular weight compounds. Although the PTR-MS/CHARON cannot directly resolve these high-mass oligomers, their decomposition, combined with ionic fragmentation within the drift tube, provides a plausible mechanism for the dense array of ions observed in the IEPOX-SOA spectrum."

22) Page 13, line 394: "mass loadings from 3-5 µg m-3". Is these concentrations with or without wall loss and dilution corrections?

All mass-loading concentrations include both wall-loss and dilution corrections – see comments by reviewer #1.

23) Page 13, line 408: "under varying NO conditions". But you didn't try various NO conditions.

We acknowledge the reviewer's point regarding the phrasing. While we did not perform a continuous variation of NOx concentrations, our experimental matrix explicitly included two distinct regimes: High-NO (ISOP-NO experiment) and Low-NO (ISOP-IEPOX and Non-IEPOX experiments). These two conditions were selected to represent the extreme ends of the RO_2 fate spectrum (RO_2 + NO vs. RO_2 + HO_2), which effectively bounds the "varying" chemical pathways relevant to isoprene oxidation. We have amended the text to be more precise.

Line 405: "Overall, this work provides a robust experimental framework and a spectral database that enhances the capability of PTRMS-CHARON for source identification. These reference spectra will be essential for disentangling complex ambient mixtures in forested and urbanized environments, offering a higher molecular-level resolution than traditional bulk aerosol monitoring techniques."

24) General comment:

Since you have nice particle phase (CHARON/PTRMS) and gas phase (PTRMS) data for the b-caryophyllene experiment as shown in Figure 2e, I suggest you should calculate the volatility of the measured species using for example the approach of Gkatzelis et al. (2018) or Kostenidou et al. (2024). I suggest you to focus only to major m/z's.

We thank the reviewer for this excellent suggestion. We have decided to keep this analysis outside the scope of the current manuscript given that its primary objective is the qualitative chemical characterization (fingerprinting) of specific SOA regimes. We aim to establish robust spectral signatures for identification purposes. Given the depth required to perform this analysis correctly, we have reserved the quantitative volatility and partitioning assessment for a dedicated follow-up study. Including it here would significantly expand the length and complexity of the current manuscript, potentially distracting from the core message regarding the spectral fingerprints.

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