



A Br-MION2-Orbitrap and flow-reactor modelling framework for interpreting and quantifying organic photochemical oxidation

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Abstract. Isoprene-derived oxygenated organic molecules (IP-OOM) drive new particle formation in the upper troposphere (Shen et al., 2024; Curtius et al., 2024), but the mechanisms that produce them, and the role of photochemistry in shaping their distribution, remain poorly constrained. These products are both hard to quantify, owing to isobaric and isotopic interferences that conventional time-of-flight mass spectrometers cannot resolve, and hard to interpret, as their formation pathways cannot be established from the measured product distribution alone. We address both with a combined measurement and modelling framework, which we demonstrate through chamber and flow reactor experiments. On the measurement side, we optimise a high-resolution Q Exactive Plus Orbitrap mass spectrometer, coupled to a bromide multi-scheme chemical ionisation inlet (the Br⁻-MION2-Orbitrap), by tuning three operating parameters that change individual-species signals by 10-90 %. Benchmarked side by side against a Br⁻-MION2-APi-TOF in chamber experiments, it agrees to within a factor of two for the oxygenated oxidation products while resolving isobaric interferences the time-of-flight instrument cannot. This comparison also shows that the Orbitrap's apparent non-linearity at low concentrations, sometimes regarded as an intrinsic limitation, is rather an artefact of post-acquisition data processing: averaging that assigns zero intensity to non-detections biases the signal low near the detection limit. Disregarding the non-detections gives a conservative upper-bound detection limit of $\sim 1.3 \times 10^5 \text{ cm}^{-3}$, comparable to that of the APi-TOF. On the modelling side, we extend MARFORCE from simple inorganic chemistry to comprehensive organic mechanisms of hundreds of species coupled to transport, and add a continuous, spatially distributed OH source; the same model can also run as a well-mixed box model for chamber experiments. Applying the framework to the OH oxidation of 1,2-ISOPOOH in the flow reactor, we detect several abundant products absent from the current isoprene mechanism, and find that photolysis of the hydroperoxide-bearing products, a previously underappreciated process, shapes the product distribution.



These experiments show how pairing molecular-level measurement with a model that resolves chemistry and transport provides a quantitative and transferable basis for studying the photochemical oxidation of isoprene and other volatile organic compounds relevant to upper-tropospheric aerosol formation.

1 Introduction

Isoprene is the most abundant biogenic non-methane volatile organic compound (NMVOC) in the atmosphere, with global emissions exceeding 500 Tg C per year (Guenther et al., 1995), primarily released by deciduous and broad-leaved evergreen trees. Once emitted, it is removed mainly by reaction with the hydroxyl radical (OH), with a daytime lifetime of an hour or two, and this oxidation strongly influences the oxidising capacity of the atmosphere, including the radical recycling that sustains OH over low-nitrogen-oxide (NO_x) forests (Lelieveld et al., 2008). Isoprene oxidation is also a major global source of secondary organic aerosol (SOA), formed largely through reactive uptake of isoprene epoxydiol (IEPOX) (Claeys et al., 2004; Kroll et al., 2006; Paulot et al., 2009). More recently, measurements in the CLOUD chamber at CERN and from a research aircraft have shown that oxygenated molecules formed during isoprene oxidation (IP-OOM) can also drive new particle formation (NPF, consisting of aerosol nucleation and initial growth), particularly under upper tropospheric conditions (Shen et al., 2024; Curtius et al., 2024).

The impact of isoprene on atmospheric chemistry and climate hinges on oxidant levels and the resulting oxidation product distribution and abundance - both governed by the gas-phase and multiphase chemistry of isoprene and its products. Among these products, those most relevant to aerosol nucleation are the nitrogen-free IP-OOM (Shen et al., 2024). Such nitrogen-free products are favoured under the low- NO_x conditions typical of pristine rainforests and remote marine regions, where the isoprene peroxy radicals (ISOPOO) formed by OH addition react predominantly with HO_2 rather than NO, yielding isoprene hydroxy hydroperoxide (ISOPOOH), mainly as the 1,2-ISOPOOH and 4,3-ISOPOOH isomers. Subsequent OH oxidation of these first-generation hydroperoxides produces IEPOX (Paulot et al., 2009) together with a wide range of multifunctional IP-OOM (Wennberg et al., 2018; Berndt et al., 2016). Because these IP-OOM form via multi-step OH oxidation, they span a broad volatility range with formation pathways that are difficult to resolve, leaving the resulting distributions only partially characterised. The gap is especially significant for the OH oxidation of ISOPOOH, the dominant first-generation isoprene oxidation product under low NO_x , which yields a complex IP-OOM mixture still poorly constrained by direct measurement. A further, poorly constrained control on this distribution is the photolysis of the oxidation products themselves, many of that separates genuine chemical kinetics from the loss processes experimental setups isoprene-driven NPF is most significant, the near-UV radiation reaching these altitudes drives only slow photolysis (for H_2O_2 , for example, a photolysis frequency of order 10^{-5} s^{-1} ; Allen et al. 2022); because the competing condensation sink there is comparably small, however, this photolysis can still shape which products persist - unlike nearer the surface, where faster losses suppress it. Closing this gap therefore requires controlled experiments that pair molecular-level product detection with a kinetic model capable of separating genuine chemical kinetics from the loss processes that experimental setups themselves introduce.



The molecular-level detection of isoprene oxidation products is analytically challenging: IP-OOM are chemically complex and present at low ambient concentrations, requiring instruments with both high sensitivity and high chemical specificity. Chemical ionisation atmospheric pressure interface time-of-flight mass spectrometers (CI-APi-TOF) are widely used for the real-time detection of trace atmospheric compounds owing to their versatility and sub-pptv level sensitivity (Munson and Field, 1966; Eisele and Tanner, 1993; Kirkby et al., 2011; Ehn et al., 2014). A variety of reagent ions have been employed in CI-APi-TOF systems to selectively target different chemical classes, including nitrate (NO_3^-), bromide (Br^-), iodide (I^-), acetate ($\text{C}_2\text{H}_3\text{O}_2^-$), and ammonium (NH_4^+) ions (Jokinen et al., 2012; He, 2017; Veres et al., 2008; Hansel et al., 2018). Among these, nitrate-based CI-APi-TOF (NO_3^- -APi-TOF) is commonly employed for the detection of highly oxygenated organic molecules (HOMs), particularly those formed during monoterpene ozonolysis, but exhibits relatively low sensitivity toward less oxidised compounds. Therefore, combining multiple CI techniques has become a necessary approach to achieve broader chemical coverage (Stolzenburg et al., 2018; Simon et al., 2020). In the context of isoprene oxidation, Shen et al. (2024) demonstrated that the multi-scheme chemical ionisation inlet (MION2) operated with a bromide (Br^-) reagent ion provides a powerful complement to both NO_3^- -APi-TOF and NH_4^+ -based proton transfer reaction (PTR3) mass spectrometry. The Br^- -MION2-APi-TOF is particularly sensitive to IP-OOM: these molecules typically carry fewer oxygen atoms than monoterpene-derived HOMs and are therefore detected only with poor sensitivity by NO_3^- -based ionisation. The Br^- chemical ionisation is also very sensitive to key first-generation products such as ISOPOOH and IEPOX, making it well-suited for investigating isoprene oxidation and the IP-OOM-driven aerosol nucleation and initial growth.

A key limitation of the Br^- -MION2-APi-TOF of this study, however, is its moderate mass resolving power (10,000). The bromide ion has naturally occurring isotopes that differ by two atomic mass units, which are present at nearly equal abundance. Since target analytes are usually detected as bromide adducts (e.g., $\text{C}_5\text{H}_{10}\text{O}_3\text{Br}^-$), analyte signals can therefore overlap with isotopic peaks from compounds differing by two atomic mass units, particularly within the crowded m/z range of 150-300 from isoprene oxidation. This is especially problematic for the detection of low-concentration intermediates such as peroxy radicals (RO_2), which may be indistinguishable from background or interfering signals.

Replacing the time-of-flight analyser with a high-resolution Orbitrap mass spectrometer has recently been shown to substantially improve molecular identification (Riva et al., 2020; Cai et al., 2022), providing mass resolving power of 280 000 at m/z 200 and enabling confident separation of isobaric and isotopic interferences. Early studies, however, reported comparatively high limits of quantification, on the order of 10^5 to 10^6 molecules cm^{-3} at 10 min integration (Riva et al., 2019a, 2020). Subsequent work progressively improved this sensitivity: Cai et al. (2022) showed that increasing the number of ions in the analyser, the number of microscans and the averaging time improved the signal-to-noise ratio, and Cai et al. (2024) found that separating the reagent-ion from the analyte-ion measurements further lowered the threshold for truncation to zero. Together, these refinements lowered the detection limit to $\sim 5 \times 10^4$ molecules cm^{-3} with 1 h averaging, comparable to that of CI-APi-TOF instruments (Jokinen et al., 2012). However, achieving this sensitivity requires specific software licenses from Thermo Fisher Scientific not generally provided with the instrument. Moreover, as we will show in this study, the detection limits reported in these earlier works may have been overestimated as a result of how the software (Orbitool) processes the data, and further optimisation is needed to actually achieve this level of sensitivity.



A separate limitation concerns the instrument's intensity response linearity at low concentrations. The same early studies reported an apparent non-linear response below 1×10^6 molecules cm^{-3} (Riva et al., 2020); because atmospheric analytes of interest are frequently present at concentrations at or below this level, this putative non-linearity was long perceived as a fundamental limitation of the Orbitrap. The refinements introduced by Cai et al. (2022) extended the linear detection range
90 down to $\sim 1 \times 10^5$ molecules cm^{-3} , although non-linearity persisted below this threshold. It remained unclear, however, whether this reported non-linearity reflects an intrinsic instrument limitation or an artefact of specific data-processing choices: although the two instruments have been compared before (Riva et al., 2020; Liu et al., 2026), no comparison has yet tested the Orbitrap response against an independent linear reference across the relevant concentration range.

These advances and improvements in chemical ionisation, instrument sensitivity and measurement linearity substantially
95 extend what molecular-level measurements can reveal about IP-OOM composition, but detection alone cannot fully resolve the pathways that produce them: a given molecular formula can often arise from several distinct oxidation sequences, so identifying the products is not the same as establishing the kinetics that connect them. Disentangling these pathways therefore still relies on controlled experiments, typically in environmental chambers or flow reactors, combined with kinetic modelling.

Flow reactors, in particular, offer the advantage of short reaction times, which allow specific reaction steps to be isolated
100 rather than capturing the full evolving chemistry. Simulating that chemistry within a flow reactor is, however, inherently challenging: it develops within a non-uniform flow field, in which concentration gradients, radial and axial diffusion and convection, and wall losses can shape the measured distributions independently of the underlying chemical mechanism. A common workaround is to minimise these effects through careful reactor design, so that the data can be interpreted with a zero-dimensional, well-mixed box model (Berndt et al., 2016, 2025). However, wall-loss-free reactors remain scarce and are
105 available to only a limited number of research groups (Berndt et al., 2015; Huang et al., 2017; Scholz et al., 2022). Moreover, achieving wall-loss-free conditions typically restricts the range of residence times and oxidant exposures that can be explored. For the majority of flow reactor experiments, which lack wall-loss-free conditions, disentangling genuine chemical kinetics from these transport effects instead requires a model that explicitly resolves chemistry alongside convection and diffusion. To meet this need, He et al. (2023) developed the MARFORCE model, which resolves coupled convection–diffusion–reaction
110 processes in cylindrical flow reactors. In its original form, however, MARFORCE was applied mainly to simple inorganic chemistry - such as sulfur and iodine species - under a fixed initial OH concentration at the reactor entrance. This design limits the model's applicability, making it incompatible with flow reactor experiments under complex photochemical conditions - such as isoprene oxidation, which involves tens of organic species and requires OH to be produced photolytically along the length of the tube, rather than introduced at a single inlet point.

115 In this work, we develop both the measurement and the modelling capabilities required to study isoprene photochemical reactions using flow reactors. We optimise the Br^- -MION2-Orbitrap for isoprene oxidation products and benchmark it directly against the Br^- -MION2-APi-TOF under identical conditions and across a wide range of products and concentrations. In parallel, we substantially extend the MARFORCE model beyond its current limitations: coupling comprehensive organic mechanisms with diffusion and convection in the reactor and representing a continuous OH source as an option. The resulting MARFORCE model is now capable of simulating a broad range of flow reactor experiments, involving both organic and
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inorganic chemistry. We apply this combined approach to the OH oxidation of synthesised 1,2-ISOPOOH, comparing the measured product distribution with simulations using the Wennberg et al. (2018) mechanism. Additionally, we explore how deep-UV irradiation could photolyse organic molecules containing hydroperoxide functional groups, a pathway that could represent a major loss process for organics in the upper troposphere but not at ground level.

125 2 Methods

2.1 Instrumentation

2.1.1 Br⁻-MION2-Orbitrap and Br⁻-MION2-API-TOF

Both Br⁻-MION2-Orbitrap and Br⁻-MION2-API-TOF used multi-scheme chemical ionisation inlet 2 (MION2), coupled either to a long-flight-path Atmospheric Pressure Interface Time-of-Flight (API-TOF) mass spectrometer (Tofwerk AG, Switzerland) (Junninen et al., 2010) or to a Q Exactive Plus Orbitrap mass spectrometer (Thermo Fisher Scientific Inc.) (Cai et al., 2022),
130 respectively. In this study, the Orbitrap mass resolution was set to 280 000 at m/z 200. The automatic gain control (AGC) target and microscan number were set to 3×10^6 ions and 10, respectively, with a maximum injection time of 100 ms. In addition to these scan parameters, the Source DC offset and the S-lens RF in the ion-transfer region were adjusted to -10 V and 40 %, respectively, with licensed access provided by Thermo Fisher Scientific Inc. The Orbitrap sampled ions through a heated
135 capillary maintained at 40 °C. To maximise sensitivity, the Orbitrap was operated with a mass scan range of m/z 82-700 for 8 minutes within each 10-minute cycle, with reagent ions selectively excluded. This strategy improves sensitivity by removing reagent ions (Cai et al., 2024) and is more effective for the Br⁻ system than for the nitrate system. In the Br⁻ system, reagent ions are mainly concentrated at low m/z , enabling their selective exclusion without sacrificing critical chemical information. In contrast, the nitrate system contains reagent ions distributed over a much broader mass range (62-188 m/z). Consequently,
140 effective exclusion of these ions requires shifting the lower bound of the scan range to m/z 126 (nitrate trimer is not excluded), resulting in the loss of information below this threshold. In contrast, the Br⁻ system can retain the full scan range starting from m/z 82 without significant information loss in the m/z 82-126 range.

A detailed description of the inlet and the Br⁻-MION2-API-TOF is provided in our previous work (He et al., 2023; Finkenzeller et al., 2024). Both inlets were operated with identical settings, including a nitrogen carrier gas flow of 2 standard cubic
145 centimetres per minute (sccm) over a liquid reagent (dibromomethane, CH₂Br₂). A purge flow of 100 sccm was used to prevent electrically neutral reagent molecules from entering the sampling tube, and the exhaust flow was set to 50 sccm. The voltages for the MION inlet (-3000 V and -200 V) were optimised to improve the reagent ion signal and then kept constant during the experiments. The measured sample flows for the Br⁻-MION2-Orbitrap and Br⁻-MION2-API-TOF were 22.4 standard L min⁻¹ and 20.8 L min⁻¹, respectively. We performed independent H₂SO₄ calibrations for both instruments using the same
150 setup described in He et al. (2023), yielding calibration factors of 1.33×10^{10} and 1.27×10^{10} cm⁻³ per normalised signal for the Br⁻-MION2-Orbitrap and Br⁻-MION2-API-TOF, respectively. Here, the normalised signal is defined as the ratio of the



analyte ion signal to the primary ion signal. The calibration factor obtained for the Br^- -MION2-API-TOF is consistent with the value ($1.9 \times 10^{10} \text{ cm}^{-3}$) reported by Shen et al. (2024).

Before all experiments, the operating parameters of both instruments were optimised in dedicated chamber tests, so that each instrument performed at its best and the direct comparison between them reflects genuine differences between the two mass analysers rather than differences in tuning. For the Br^- -MION2-Orbitrap, this was done by varying one parameter at a time (for example, Source DC offset from -20 to 0 V) while holding the others constant, as detailed in Sect. 3.1. The Br^- -MION2-API-TOF was likewise tuned to its optimal operating settings beforehand.

2.1.2 Data processing

The data-processing workflows for the two instruments differ in both the software employed and the strategy applied: API-TOF data were processed with Tofware (version 3.3.0, TOFWERK AG) and Orbitrap data with Orbitool (v2.5.3) (Cai et al., 2021). They also differ in how the raw signal is recorded, which determines how it should be processed. The Br^- -MION2-API-TOF records the full mass spectrum in every extraction, including the baseline noise, so its spectra were averaged over 10 min intervals to enhance the signal-to-noise ratio (SNR) and thereby maximise detection sensitivity. The Br^- -MION2-Orbitrap, by contrast, delivers data that are already averaged and denoised at the point of acquisition, and this dictates how they must be treated afterwards. Each recorded scan is itself the average of 10 microscans, so a degree of signal averaging is built into every stored spectrum. The instrument then applies an internal noise threshold (set to 4.63 here) before the data are written: within each scan, only peaks exceeding this threshold are retained, whereas the baseline noise and any peak falling below the threshold are removed rather than stored (Riva et al., 2019a, 2020; Cai et al., 2022). A sub-threshold peak is therefore not recorded for that scan and appears as a zero only when a time series is reconstructed (in Orbitool) from the individual scans. This signal filtering before saving data files results in files being significantly smaller on Orbitrap instruments and simplifies further data logistics. Because the baseline is already excluded and the signal already averaged at acquisition, applying a further post-acquisition temporal average across scans - as is necessary for the API-TOF, which stores the full spectrum including baseline noise - would combine these threshold-induced zeros with the scans in which the peak was genuinely detected and bias the reported mean low. For this reason the Orbitrap data were used at their native, per-scan time resolution, without any additional indiscriminate averaging or denoising; the consequences of this acquisition behaviour for the instrument's linearity and detection limit are examined in Sect. 3.3.

The limit of detection (LOD) was likewise determined differently for the two instruments: for the Br^- -MION2-API-TOF we followed the approach of previous studies (He et al., 2023), whereas for the Br^- -MION2-Orbitrap only the scans above the noise threshold were averaged over a given period, so that the zero-valued scans do not bias the mean low.

2.1.3 Synthesis, storage and quantification of 1,2-ISOPOOH sample

A 1,2-ISOPOOH standard was synthesized following the procedure described by Ríos and Carlos (2018). An ethereal hydrogen peroxide solution ($\text{H}_2\text{O}_2 \cdot \text{Et}_2\text{O}$) was prepared by saturating 30 % aqueous H_2O_2 with NaCl and extracting diethyl ether with the salt-saturated H_2O_2 solution. The resulting organic phase was dried over anhydrous MgSO_4 and filtered. 2-



185 Methylvinylloxirane (200 μL) was then added to the $\text{H}_2\text{O}_2 \cdot \text{Et}_2\text{O}$ solution, followed by addition of phosphomolybdic acid (5 mg) as the catalyst. The reaction mixture was stirred at room temperature for approximately 6 h, during which its color changed from dark blue to pale yellow.

After reaction, the mixture was diluted with diethyl ether and passed through a short silica plug to remove the phosphomolybdic acid catalyst. The solvent was evaporated under reduced pressure, and the crude product was purified by flash column
190 chromatography using 90:10 hexane:ethyl acetate as the mobile phase. Product-containing fractions were identified by thin-layer chromatography with potassium permanganate staining, combined, and carefully concentrated under reduced pressure. The purified 1,2-ISOPOOH sample was stored at -20°C .

The concentration of 1,2-ISOPOOH was determined by nuclear magnetic resonance (NMR) spectroscopy at two separate stages: first at Harvard, shortly after synthesis and before shipment, and then again in Helsinki, immediately before the calibration experiments. The second measurement was performed to verify that the concentration had remained stable during
195 the approximately one-week transport and subsequent storage. The sample was shipped under dry-ice cooling and remained cold upon arrival in Helsinki, providing confidence that the concentration had not changed substantially during transport. The concentration measured in Helsinki was therefore used for the calibration experiments. For this later measurement in Helsinki, the 1,2-ISOPOOH concentration was estimated by comparing its NMR signal integrals with those of the hydrogen peroxide
200 present in the sample, which served as an internal reference of known concentration. The spectrum was recorded at 25°C on a Bruker Avance NEO 400 spectrometer (^1H at 400 MHz), and the sample was analysed without further dilution, as additional dilution resulted in insufficient signal intensity. This re-evaluation indicated that the solution contained 5% (by mass) 1,2-ISOPOOH, a factor of approximately 3.4 lower than the original concentration in the sample prepared at Harvard. This reduction is likely due to sample degradation during transport and storage, as 1,2-ISOPOOH is known to be chemically unstable
205 and prone to decomposition over time (Rivera-Rios et al., 2014). The internal standard H_2O_2 also degrades over time, which may cause a slight overestimation of the calculated 1,2-ISOPOOH concentration. This overestimation was not corrected in the calibration but is considered in the uncertainty analysis.

2.1.4 Calibration of 1,2-ISOPOOH for Br^- -MION2-Orbitrap

The calibration setup for the Br^- -MION2-Orbitrap using the 1,2-ISOPOOH sample is illustrated in Figure A1. The instrument
210 was connected to a 1-inch stainless steel tube (59 cm in length), adapted to a 6 mm fitting and linked to a liquid calibration unit (LCU-a, Ionimed Analytik GmbH, Innsbruck) via a polyether ether ketone (PEEK) capillary tube.

The LCU-a uses an optimised evaporation technique for calibrating volatile and semi-volatile compounds from liquid standards. It generates trace gas phase concentrations with well-defined mixing ratios by evaporating aqueous solutions into a carrier gas stream. To prevent condensation of 1,2-ISOPOOH in the sampling tube at room temperature, the evaporator was
215 operated at 40°C , with a liquid flow rate between 0 and $10 \mu\text{L min}^{-1}$ and a carrier gas flow of 500 sccm. 1,2-ISOPOOH was detected as bromide adducts, $\text{C}_5\text{H}_{10}\text{O}^{79}\text{Br}^-$, at $196.98 m/z$ by the Br^- -MION2-Orbitrap. The calibration factor was derived from the normalised signal and the calculated concentration of the standard in the mixed inlet flow.



During the calibration experiments, no additional H₂O was introduced, and the system was kept at extremely low humidity (RH<0.1%). However, we also performed a separate set of experiments to evaluate the impact of water vapour on the detection of 1,2-ISOPOOH by the Br⁻-MION2-Orbitrap. In these experiments, water vapour levels were controlled by varying the flow of dry air through a water bubbler, enabling precise adjustment of relative humidity.

2.2 Experiments

2.2.1 OH-initiated isoprene oxidation chamber experiments

Data for the inter-instrument comparison were obtained from OH-initiated isoprene oxidation experiments in the COALA chamber. The COALA chamber is a 2 m³ cuboid reactor made of fluorinated ethylene propylene (FEP) (Riva et al., 2019b). The total chamber flow was maintained at 55 L min⁻¹ using zero air, corresponding to a residence time of approximately 36 min. Here, zero air denotes compressed and filtered ambient air that was then purified with a zero-air generator to remove residual water and volatile organic compounds. No additional H₂O was introduced during these chamber experiments.

Isoprene and tetramethylethylene (TME) were supplied from custom-made source bottles (547 ppmv and 36 ppbv, respectively), with flows controlled by mass flow controllers (MFCs) and delivered through polytetrafluoroethylene (PTFE) tubing. Because the isoprene concentration in the source bottle was uncertain due to the synthesis procedure, the chamber isoprene concentration was determined directly using a calibrated Vocus-PTR-TOF-MS (Krechmer et al., 2018). O₃ was generated by 185 nm UV photolysis of O₂ in the incoming zero air, and OH radicals were produced via ozonolysis of TME. The O₃ concentration was controlled in two ways: by adjusting the UV light intensity in the O₃ generator, and by adjusting the ratio at which the O₃-containing flow was diluted into the main inlet flow. The resulting concentration was monitored with a photometric O₃ analyser (model 400, Teledyne API).

The ozonolysis of TME used here to generate OH also co-produces acetone and organic peroxy radicals (RO₂), rather than OH alone; acetone, the dominant direct product, is not detected by Br⁻ chemical ionisation and so does not affect the measurements. These TME-derived RO₂ add to the radical pool and can undergo RO₂-RO₂ reactions, both among themselves and with the isoprene-derived peroxy radicals; although the TME fragments are individually small (largely C₃), such reactions can accrete into larger products - for example C₆ from two C₃ radicals - that may overlap the isoprene oxidation product range and perturb the measured distribution. For the inter-instrument comparison that these chamber experiments serve, however, this is not critical: the Br⁻-MION2-Orbitrap and Br⁻-MION2-API-TOF sampled the same chamber air simultaneously, so any TME-related species or perturbation appears identically in both datasets and does not bias their comparison. Because this inter-instrument comparison spans C₂-C₇ species, the detectable TME-derived products - the oxygenated C₃ species together with the larger accretion products formed through minor RO₂ channels - fall within the compared mass range, so not every compared species can be attributed to isoprene alone; those that cannot be positively assigned to isoprene oxidation are excluded from the quantitative comparison.

Both sampling lines of Br⁻-MION2-API-TOF and Br⁻-MION2-Orbitrap consisted of 3/4 inch PTFE tubes of similar length, minimising differences in vapour losses between the two instruments. Each experiment was run under constant conditions for



at least 1.5 h (approximately three chamber residence times), allowing the system to reach pseudo-steady state as confirmed by the time series. After reaching steady state, isoprene and O₃ levels were varied to scan different isoprene oxidation product distributions and concentrations.

2.2.2 Flow reactor experiments of OH-initiated 1,2-ISOPOOH oxidation

255 The experimental setup used to study OH-initiated oxidation of 1,2-ISOPOOH is shown in Figure A2. It follows the configuration in our previous work (He et al., 2023), with the main modification being the photochemical OH reactor design. The reactor consisted of a quartz tube (2.7 cm length, 3/4" inner diameter). In the H₂SO₄ calibration setup, the mercury lamp was housed in an aluminium block and fitted with a filter that transmitted only 184.9 nm UV radiation, thereby limiting the UV intensity delivered to the gas flow. Here, to enhance OH production, the lamp was positioned directly adjacent and parallel
260 to the quartz tube, with no shielding or filters between the lamp and the tube. This exposed the gas to the lamp's unfiltered mercury line emission - dominated by the strong 184.9 and 253.6 nm UVC lines, with weaker lines extending into the UVA and visible - rather than the single 184.9 nm line passed by the calibration filter, and provided uniform irradiation across the full 2.7 cm quartz section.

As the gas mixture passed through the irradiated quartz section, OH radicals were generated and reacted with 1,2-ISOPOOH.
265 Downstream, the gas stream flowed through a 26 cm stainless-steel tube (3/4" inner diameter), entered a Y-piece, and mixed with a secondary dilution flow (dry or humidified air). The mixed flow then travelled through a 68 cm stainless-steel sampling line (1-inch inner diameter) to the Br⁻-MION2-Orbitrap.

Generating OH photolytically, rather than from ozonolysis as in the chamber experiments, was a deliberate choice: it supplies OH without the co-produced peroxy radicals of a TME ozonolysis source. The trade-off is that the same UV that boosts OH
270 production also photolyses H₂O₂ and organic molecules carrying hydroperoxide (-OOH) chromophores (Badali et al., 2015). Whether this matters depends on the OH source: HONO, alkyl nitrites (e.g. C₃H₇ONO), and O₃/H₂O sources use weaker, longer-wavelength UV that photolyses the products only weakly, whereas short-wave-UV sources - notably the 185 nm photolysis of H₂O used in many oxidation flow reactors, including ours - also photolyse the -OOH-bearing products appreciably. The effect is therefore characteristic of strong short-wave-UV OH sources rather than unique to our setup or universal to UV-based
275 OH generation; rather than neglect it, we treat the photolysis explicitly (Sect. 2.3.2).

OH exposure was controlled by varying residence time in the quartz reactor (from tens to several hundred milliseconds) through flow adjustments, and OH concentration was further tuned by changing the water-vapour input via a bubbler. Under these conditions, simulations indicate OH concentrations of approximately 1×10^5 to 1×10^7 molecules cm⁻³ at 1,2-ISOPOOH concentrations above 1×10^9 molecules cm⁻³. The absolute OH production rate for these conditions was constrained using
280 separate calibration experiments based on H₂SO₄ formation in the same reactor configuration: by varying SO₂ concentration while keeping other conditions fixed, H₂SO₄ was generated through the SO₂ + OH reaction, and the corresponding OH production rate was derived (Sect. 2.3.1).

We characterised the oxidation of 1,2-ISOPOOH by varying each of these two OH controls in turn, and additionally evaluated the effect of relative humidity on product distributions by changing the humidity of the downstream dilution flow. The



285 LCU-a system supplied a constant gas-phase 1,2-ISOPOOH source throughout all experiments. Using the constrained OH production rate and the measured 1,2-ISOPOOH concentration, we then applied MARFORCE simulations based on the Wennberg et al. (2018) 'reduced plus mechanism' and compared model outputs with measurements.

2.3 Model developments

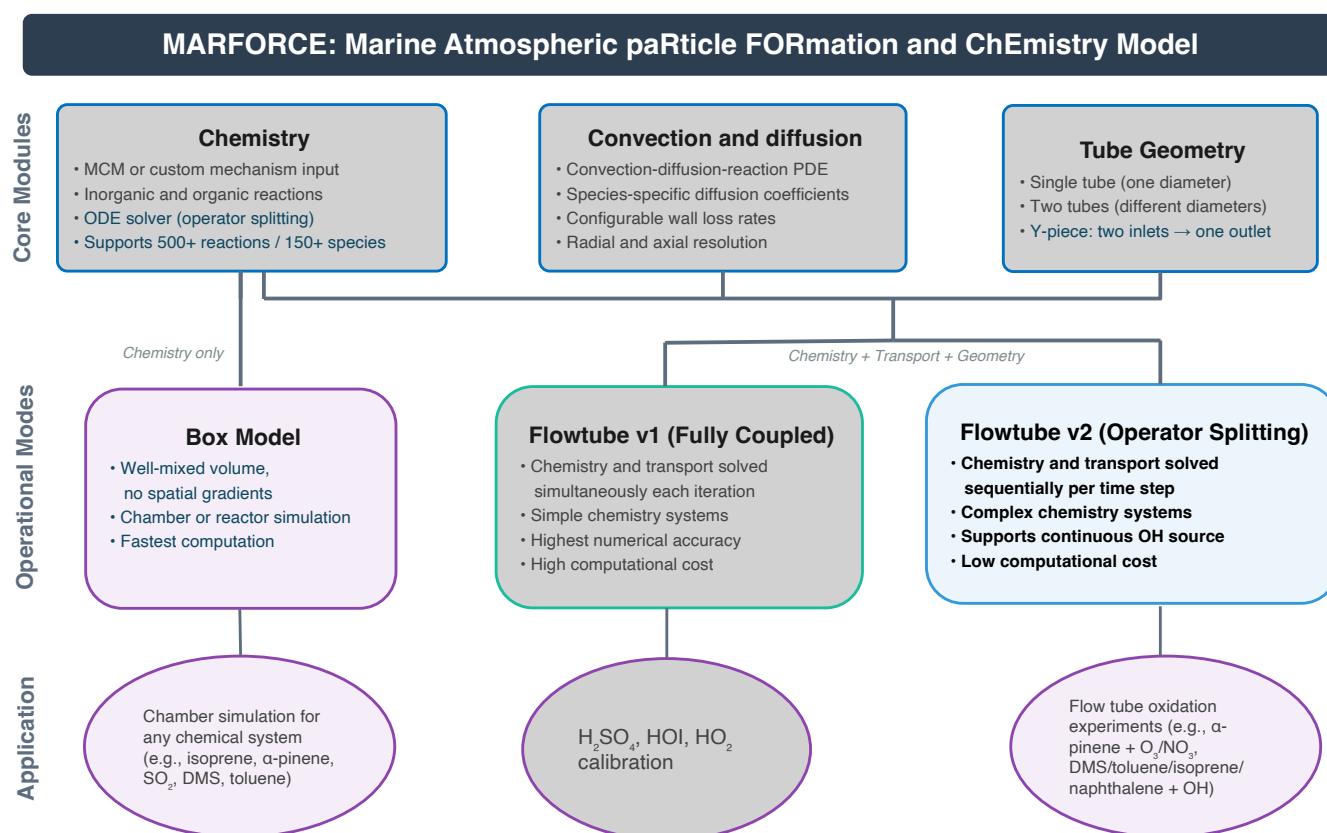


Figure 1. Current structure of the MARFORCE (Marine Atmospheric paRticle FORMation and ChEmistry) model following the developments presented in this work. The original framework comprises chemistry, transport, and tube-geometry modules described in previous studies. These modules are combined into three operational modes: a box model, a fully coupled flow-tube solver (v1), and an operator-splitting flow-tube solver (v2). The new developments introduced in this study primarily concern the operational capabilities of the model, including continuous OH production, unified multi-section reactor simulations, and support for large chemical mechanisms through operator splitting. Grey text denotes functionality available in previous versions of MARFORCE, whereas blue text highlights developments introduced in this study.

The Marine Atmospheric paRticle FORMation and ChEmistry model (MARFORCE) (He et al., 2023) is an open-source, two-dimensional flow reactor model developed by He and Shen (2025). It is designed to simulate diffusion, chemical reactions,



and convection processes within calibration sources, inlet tubes, or flow reactor systems. In our earlier study (He et al., 2023), MARFORCE was successfully used to simulate H_2SO_4 calibration experiments, reproducing both measured H_2SO_4 concentrations and their radial distributions. To extend MARFORCE to the more complex 1,2-ISOPOOH + OH system studied here, we introduce three major developments: (i) a continuous OH source from photochemical production, (ii) a unified treatment of multi-sectional (e.g., Y-shaped) reactors, and (iii) support for large chemical mechanisms through operator splitting.

Figure 1 summarises the updated MARFORCE framework. The model consists of three core modules responsible for chemistry, convection–diffusion transport, and tube geometry. These modules can be combined to operate MARFORCE as a box model, a fully coupled flow-tube model, or an operator-splitting flow-tube model. The blue text in Fig. 1 highlights the capabilities introduced in this study, whereas the remaining functionality was described previously.

In its original implementation, the model specified a fixed OH concentration uniformly across the entrance cross-section of the flow reactor, rather than treating OH production as a distributed source along the tube. This configuration was adequate for simulating the formation of species such as H_2SO_4 and hypoiodous acid (HOI), whose production pathways are relatively simple and require only limited OH exposure. For other chemical systems which require sustained OH exposure across an extended reaction region, the model should offer photochemical OH production as a selectable option. To address this limitation, the present study introduces OH as a continuous source along a defined section of the quartz tube, rather than prescribing OH at the inlet entrance. This modification provides greater flexibility in representing experimental conditions and enables sufficient OH exposure for the investigation of more complex chemical systems, such as the OH-initiated oxidation of 1,2-ISOPOOH.

In addition, MARFORCE has been extended to better represent flow reactors incorporating a Y-junction (or Y-piece), commonly used in atmospheric chemistry experiments to introduce dilution or auxiliary flows into the main reaction tube, or to modify flow conditions within the reaction zone. In the original model framework, the simulation domain was divided into two sequential sections, each representing a distinct flow condition. The first section was simulated to steady state, after which the resulting species concentrations were used as initial conditions for the second section. This modular approach reduced computational cost and memory requirements. However, this sequential treatment does not fully capture the continuity of boundary-layer conditions between the two sections; although usually a second-order effect, this can still influence convection, diffusion and chemistry. To remove this constraint, a unified simulation mode has been implemented in which both flow sections are solved simultaneously within each iteration. In this configuration, the species concentrations at the final cross-section of the first flow reactor section are used to update the first cross-section of the second flow reactor section at every iteration step. The transition between the two sections explicitly accounts for mass flux continuity, including changes in tube radius and volumetric flow rate. This approach provides a more physically consistent representation of interfacial diffusion processes while maintaining acceptable computational efficiency.

Finally, MARFORCE has been extended to handle complex chemical systems involving hundreds of species and reactions. In earlier applications, the model was sufficient for relatively simple chemical systems, such as H_2SO_4 calibration experiments. In contrast, comprehensive chemical mechanisms, for example, the isoprene oxidation mechanism of Wennberg et al. (2018) with more than 500 reactions and 149 species, exceed the practical limits of the original implementation. To enable simulations of such large chemical systems, an operator-splitting approach was implemented to decouple chemical reactions from trans-



port processes. Within this framework, chemical kinetics are solved using an ordinary differential equation (ODE) solver, after which the updated species concentrations are used in the convection-diffusion calculations over the same time step. This separation improves computational efficiency by permitting larger time steps, while maintaining numerical stability and accuracy for chemistry.

330 The updated MARFORCE retains the original approach - in which convection, diffusion, and reaction are solved on the same time scale - as an option for relatively simple chemical systems involving fewer than 20 reactions, while adopting the updated operator-splitting scheme as the default for more complex mechanisms. Despite these differences, both versions produced highly consistent H_2SO_4 concentrations under identical conditions. For example, simulations of OH-initiated oxidation of 1,2-ISOPOOH with continuous OH exposure require the updated version. In such cases, the computational cost is substantially
 335 reduced compared to the original implementation, decreasing from several days to hours to reach steady state for a single stage, depending on the system complexity, grid resolution, and computing resources. In addition, the updated MARFORCE model can be operated in a 'box-model' mode, in which the flow reactor is treated as a single, well-mixed volume without convection and diffusion. This option enables simulating smog chamber experiments. Detailed instructions for model setup and usage are provided in the user manual available in the GitHub repository (<https://github.com/momo-catcat/MARFORCE-flowtube>).

340 2.3.1 OH production rate estimation for the flow reactor experiments

As described above, accurate determination of the OH production rate is essential for simulating the OH-initiated oxidation of 1,2-ISOPOOH in the flow reactor experiments. In the H_2SO_4 calibration, OH production is constrained directly: the 184.9 nm-filtered UV intensity and the resulting H_2O photolysis rate are determined from a separate nitrous oxide (N_2O) photolysis experiment. However, the 1,2-ISOPOOH oxidation experiments instead use the mercury lamp's full spectral output, for which
 345 no equivalent direct method exists to determine the OH production rate.

We therefore constrained the OH production rate indirectly, using H_2SO_4 formation as a proxy. Calibration experiments were conducted using the configuration shown in Figure A2, in which SO_2 and H_2O were introduced at known concentrations and oxidised to H_2SO_4 by OH generated under the full-spectrum lamp. Because the H_2SO_4 measurement itself had already been calibrated using the standard H_2SO_4 calibration (He et al., 2023), and both SO_2 , O_2 and H_2O concentrations were known,
 350 the only remaining unknown in the model was the OH production rate. This rate was therefore adjusted iteratively until the simulated H_2SO_4 concentration - including its temporal evolution - matched the concentrations measured with the Br^- -MION2-Orbitrap.

Owing to the high SO_2 concentrations employed, the resulting H_2SO_4 concentrations exceeded $3 \times 10^9 \text{ molecules cm}^{-3}$, at which level H_2SO_4 dimers and higher-order clusters can form even at room temperature. To improve the robustness of the
 355 OH constraint, both H_2SO_4 monomer and dimer concentrations were included in the measurement-model comparison. The measured monomer and dimer concentrations differ by approximately one order of magnitude, indicating that dimer formation does not significantly perturb the monomer budget.

To estimate the uncertainty associated with this procedure, three optimisation strategies were applied, each prioritising agreement in a different portion of the time series (Figure A4): (1) the steady-state regime, yielding the best fit to the H_2SO_4



monomer and dimer plateaus but less well capturing the early ramp-up; (2) the early-ramp period ($t < 500$ s), which better reproduces the initial rise but overestimates the steady-state concentrations and (3) the overall trajectory, representing a compromise across the full time series. All three scenarios yield OH photolysis rates from H₂O within $\sim 22\%$ of each other ($It_x = 1.8\text{--}2.2 \times 10^{-10} \text{ s}^{-1}$), indicating that the result is robust against the choice of fitting window. The overall uncertainty in the derived OH production rate is estimated to be within a factor of ~ 2 , as it is largely dominated by the measurement uncertainty of H₂SO₄. The derived OH production rate is specific to the flow reactor conditions used in this study (lamp intensity, gas composition, and flow configuration) and was applied to the 1,2-ISOPOOH oxidation simulations described in Sect. 2.2.2.

2.3.2 Photolysis rate of isoprene oxidation products

As discussed above, besides the 185 nm wavelength, the mercury lamp also emits at 254 nm and longer wavelengths, which photolyse a range of isoprene oxidation products, in particular those carrying hydroperoxide (--OOH) groups. Photolysis of an --OOH group cleaves the O–O bond to yield an alkoxy radical and OH, and the alkoxy radical subsequently decomposes or reacts further to yield HO₂ (Badali et al., 2015). This recycling restores the radical pool and shifts the product distribution away from the terminal, highly oxygenated species that would otherwise accumulate, so it must be included when simulating these experiments.

Because the unfiltered lamp needed to sustain OH production also drives this photolysis, the absolute photolysis rates it produces are higher than atmospheric values, which is a limitation of the setup. It is less detrimental than it appears, however, because the product branching is governed by the ratio of the photolysis rate to the competing loss rate rather than by the absolute rate. In the clean upper troposphere, where isoprene-driven NPF is most significant (Shen et al., 2024), the condensation sink is of the order of 1×10^{-5} to $1 \times 10^{-4} \text{ s}^{-1}$ (Ranjithkumar et al., 2021), comparable to the photolysis frequency of H₂O₂ there ($\sim 1 \times 10^{-5} \text{ s}^{-1}$) (Allen et al., 2022), so photolysis competes with the condensation sink. In our flow reactor the dominant loss is instead wall deposition, at $\sim 0.3 \text{ s}^{-1}$, so the photolysis rate of our setup, for example for H₂O₂, must be of comparable magnitude to maintain the same photolysis-to-loss balance as in the atmosphere; we investigate whether this holds using the model (Sect. 3.6).

In the mechanism used here (the 'isoprene reduced plus' mechanism, v5 (Wennberg et al., 2018)), photolysis is represented in reduced form: the photolysis frequency of species i is taken as $J_i = f_i \times \text{SUN}$, where f_i is a fixed, species-specific scale factor (e.g., $5 \times 10^{-6} \text{ s}^{-1}$) that pre-integrates the cross section and quantum yield over a reference spectrum, and SUN is a single dimensionless intensity shared by all species (SUN=0 disables photolysis). The relative photolability of the species is therefore fixed by the f_i , whereas their absolute photolysis frequencies scale entirely with SUN. We cannot set SUN from first principles, because the photolysis rate of different molecules by the unfiltered mercury lamp could not be measured in our laboratory. We therefore treat SUN as a single tunable parameter and report the sensitivity of the modelled product distribution to it, rather than reporting absolute, constrained photolysis rates for individual species.



3 Results and discussion

3.1 Instrument tuning for optimised signal retention

To optimise the performance of the Br⁻-MION2-Orbitrap, we conducted a series of isoprene oxidation experiments and systematically evaluated the instrument's response under well-defined conditions. Oxidation was initiated by introducing isoprene together with TME and O₃, while all other experimental conditions were held constant. Under this stable chemical regime, we varied three key operating parameters of the Br⁻-MION2-Orbitrap in turn - the maximum injection time, the S-lens RF level, and the Source DC offset - to isolate their individual influence on the detected signal intensities of the isoprene oxidation products.

3.1.1 Maximum injection time

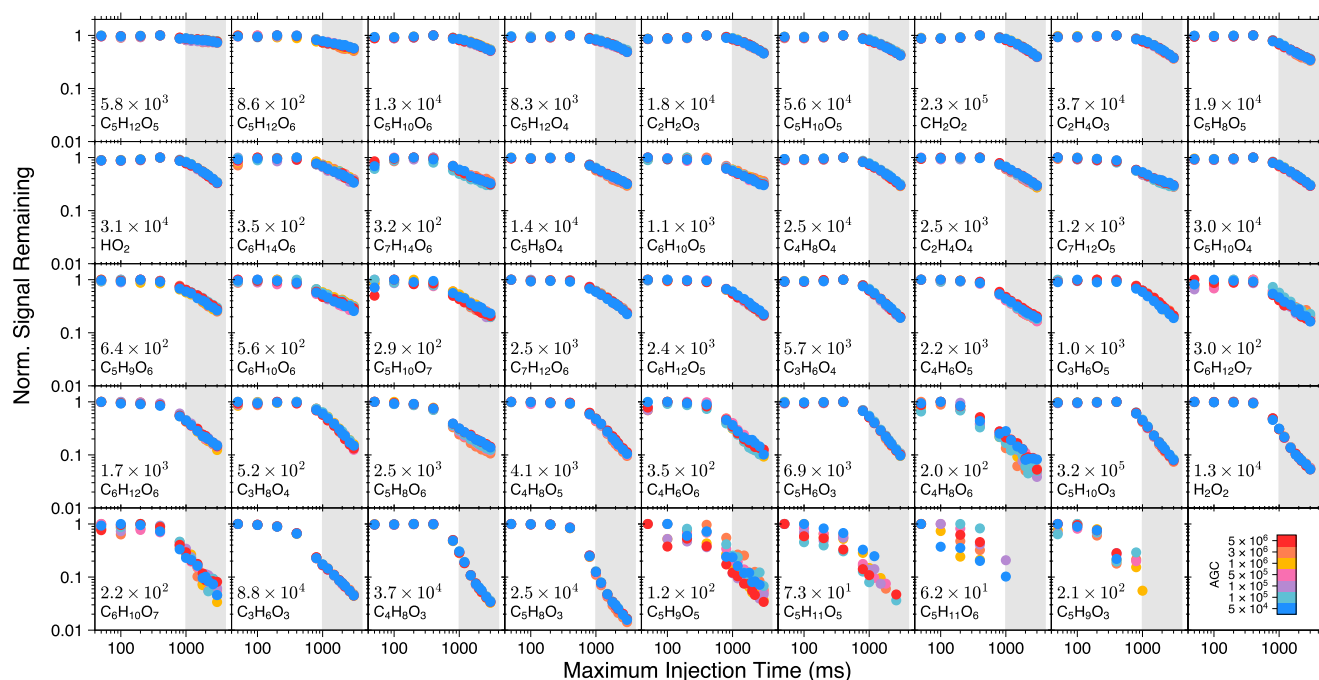


Figure 2. Normalised signal remaining as a function of maximum injection time, coloured by AGC target. For each species, the signal is normalised to its maximum value across all tested injection times at a fixed AGC target. The default maximum injection time is 100 ms. Values at the lower left corner of each panel indicate the peak signal intensity (cps) at 100 ms and an AGC target of 5×10^4 , representing the relative abundance of each species under reference conditions. Species are ordered by decreasing signal retention at 3000 ms injection time and an AGC target of 5×10^4 ; species with greater signal loss appear toward the lower right. The grey area indicates the range of injection times used in a previous study (Riva et al., 2020).



400 The maximum injection time is the longest period over which ions can accumulate in the C-trap before transfer to the Orbitrap analyser, and is coupled to the AGC target: accumulation stops when either the AGC target is reached or this time is reached (Thermo Fisher Scientific, 2010). In conventional Orbitrap applications, a longer maximum injection time can improve detection limits by allowing more ions to accumulate when the AGC target is not reached within the allotted injection period. Assuming negligible ion losses during storage, this does not change instrument sensitivity; instead, it increases the accumulated
405 ion signal and improves the signal-to-noise ratio, lowering the detection limit for the weakest, near-threshold signals by lifting them above the noise threshold; signals already above it gain no improvement in detectability.

In the Br⁻-MION2-Orbitrap, for the tested system, however, increasing the maximum injection time has the opposite effect (Figure 2). Across all species, signals remain stable for injection times up to about 400 ms but decline significantly at longer settings, with losses of 20-90 % at 1000 ms depending on the species. The total ion count (TIC) follows the same trend,
410 decreasing with increasing injection time at a fixed AGC target, indicating that longer accumulation reduces the number of ions ultimately detected. Ion losses that increase with trapping time are a well-established feature of ion-trap devices and can arise through several mechanisms, including collisional scattering and trajectory instability (Kai et al., 2011; Pedersen et al., 2002); they reflect an inherent trade-off, since accumulating for longer collects more ions but also raises the fraction lost before detection.

415 The magnitude of this loss varies considerably between species and correlates most clearly with ion abundance (Figure 2); in this set, however, the more abundant ions are also the lighter ones, so abundance and m/z co-vary and cannot be cleanly separated as drivers. High-abundance species (above approximately 1×10^4 cps), including HO₂Br⁻, C₂H₂O₃Br⁻, CH₂O₂Br⁻, and C₂H₄O₃Br⁻, retain relatively stable signals even at the longest injection times, despite comparatively weak bromide binding. Low-abundance species (below approximately 2.5×10^2 cps), including C₄H₈O₆Br⁻, C₆H₁₀O₇Br⁻, C₅H₉O₅Br⁻, C₅H₁₁O₅Br⁻,
420 C₅H₁₁O₆Br⁻, and C₅H₉O₃Br⁻, by contrast, show the greatest losses and the strongest sensitivity to the AGC target.

To achieve optimal signal retention, we adopted a maximum injection time of 100 ms for all subsequent measurements, as this setting minimises signal losses while maintaining sensitivity across the species studied. Because the optimum depends on instrument configuration, ion source characteristics, total ion flux, and analyte composition, this parameter should be optimised empirically for other chemical ionisation Orbitrap applications.

425 3.1.2 S-lens RF level

The S-lens RF level sets the radiofrequency amplitude applied to the stacked-ring ion guide (S-lens), which focuses ions from the source into the high-vacuum region of the mass spectrometer (Olsen et al., 2009). Higher RF amplitudes generally favour the transmission of heavier, higher m/z (> 200) ions, because collisional focusing in the ion guide is voltage dependent and heavier ions require stronger fields to be confined and transmitted efficiently (Kelly et al., 2010). At high amplitudes, however,
430 collisions become more energetic and can decluster weakly bound bromide adducts, which are more prevalent among the lighter, low m/z species, causing them to lose signal (Kelly et al., 2010). To characterise this trade-off for the Br⁻-MION2-Orbitrap, the S-lens RF level was scanned from 0 to 100 per cent (Figure 3) under controlled conditions.

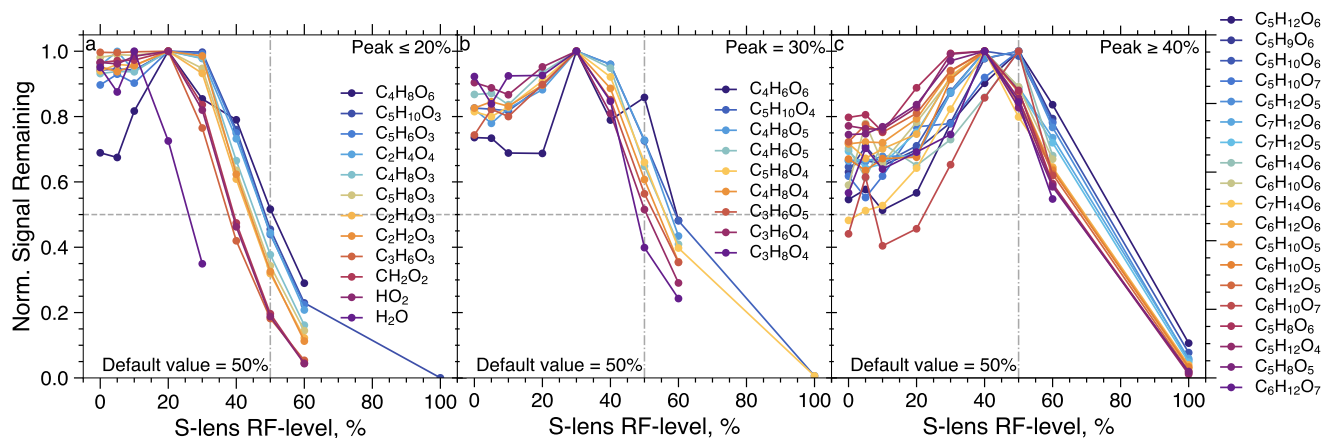


Figure 3. Normalised signal remaining as a function of S-lens RF level. For each species, the signal was normalised to its maximum value across the tested voltage range. The S-lens RF level adopted in this study is 40 %. Species are grouped by optimal RF level: panel a shows species with optima at or below 20 %, panel b at 30 %, and panel c at or above 40 %. Within each panel, colour indicates the normalised signal retained at an S-lens RF level of 60 %, from dark indigo (most) to purple (least).

The species fall into three groups according to the RF level at which their signal peaks (Figure 3, a–c). The first group (panel a) comprises small, light m/z species such as H_2OBr^- , HO_2Br^- , $\text{CH}_2\text{O}_2\text{Br}^-$, $\text{C}_2\text{H}_2\text{O}_3\text{Br}^-$, $\text{C}_2\text{H}_4\text{O}_3\text{Br}^-$, and several
435 C_3 – C_5 species, all peaking at $\leq 20\%$. These ions lose signal rapidly at higher amplitudes, most falling below 50 % of their maximum by ~ 30 – 40% and some disappearing almost entirely above 60 %. The second group (panel b) includes intermediate species such as $\text{C}_4\text{H}_6\text{O}_6\text{Br}^-$, $\text{C}_4\text{H}_8\text{O}_5\text{Br}^-$, $\text{C}_5\text{H}_{10}\text{O}_4\text{Br}^-$, and $\text{C}_3\text{H}_6\text{O}_4\text{Br}^-$, which peak near 30 % and remain strong between 20 and 40 % before declining. The third group (panel c) consists of larger, more highly oxidised isoprene products, mainly C_5 – C_7 species such as $\text{C}_5\text{H}_{12}\text{O}_6\text{Br}^-$, $\text{C}_5\text{H}_9\text{O}_6\text{Br}^-$, $\text{C}_5\text{H}_{10}\text{O}_6\text{Br}^-$, and $\text{C}_7\text{H}_{12}\text{O}_6\text{Br}^-$, which peak at $\geq 40\%$ and stay high over a broader
440 range (~ 30 – 60%). This progression toward higher optimal RF levels with increasing molecular size is broadly consistent with the expected m/z dependence of RF ion guides (Yan et al., 2023).

The grouping does not, however, follow m/z strictly: species of similar mass can have different optimal RF levels (e.g., $\text{C}_5\text{H}_{10}\text{O}_5\text{Br}^-$ peaks at 40 % whereas $\text{C}_5\text{H}_{12}\text{O}_5\text{Br}^-$ peaks at $\geq 50\%$), indicating that molecular structure also plays a role. Beyond optimising sensitivity, scanning the S-lens RF level may therefore carry structural information, since the optimal RF
445 level appears to depend on molecular properties such as the number and position of functional groups, the degree of oxidation, and the overall molecular geometry. Voltage-dependent transmission of halide adducts has likewise been reported for TOF-MS systems (Lee et al., 2014; He et al., 2023).

Considering the trade-off across all three groups, an S-lens RF level of 40 % was adopted as the best overall compromise, consistent with the value reported by Cai et al. (2022). At this setting, the third group is near its optimum and the second retains
450 ~ 80 – 90% of its peak signal, while the first already suffers substantial losses; this favours detection of the larger isoprene oxidation products most relevant to this study.

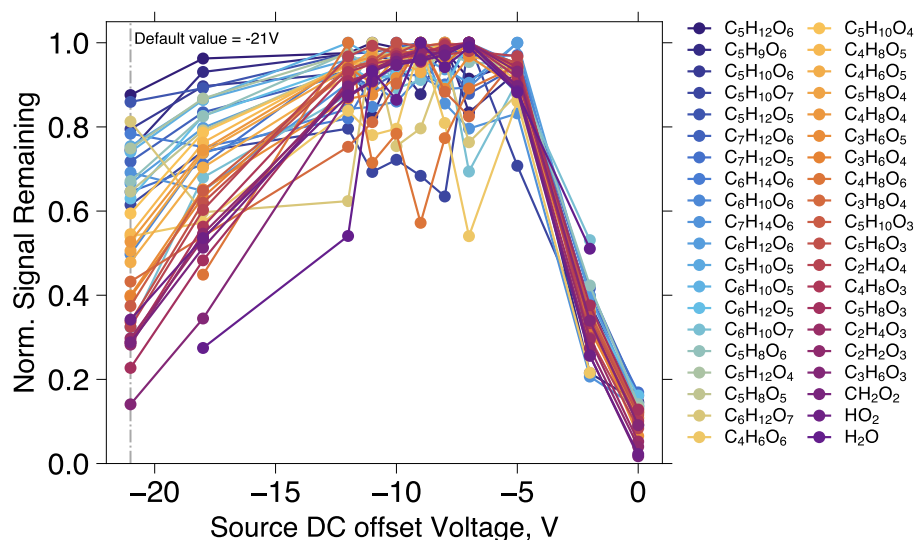


Figure 4. Normalised signal remaining as a function of Source DC offset. For each species, the signal was normalised to its maximum value across the tested voltage range. The Source DC offset adopted in this study is -10 V. Species are coloured by their normalised signal retained at an S-lens RF level of 60 % (Figure 3), from dark indigo (most) to purple (least), so that colours are consistent between the two figures.

3.1.3 Source DC offset

The Source DC offset regulates the potential difference between the ion source and the S-lens, controlling the efficiency of ion extraction and transfer into the ion optics. As shown in Figure 4, making the Source DC offset less negative than its default of -21 V - that is, reducing the potential difference between the ion source and the S-lens - substantially enhances the signal of all detected species across the m/z range of approximately 110-260, with the signal rising steeply between -21 and -12 V, though the magnitude of improvement varies among species. The signal then plateaus between roughly -12 and -5 V and falls sharply as the offset approaches 0 V, where the source-to-S-lens difference becomes too small to extract and transmit the ions efficiently. The lower signal at the most negative offsets is instead consistent with over-acceleration that declusters the weakly bound bromide adducts, an effect most pronounced for the light, low- m/z species. An optimised Source DC offset of -10 V was therefore adopted in this study, yielding a 10-90 % increase in normalised signal intensities relative to the default setting.

3.2 Direct comparison between Br^- -MION2-Orbitrap and Br^- -MION2-API-TOF

3.2.1 Spectra comparison

Figure A5 compares the mass spectra obtained with the Br^- -MION2-Orbitrap and the Br^- -MION2-API-TOF during OH-initiated isoprene oxidation chamber experiments, both before (a) and after (b) optimisation of the Orbitrap system. The optimisation focused on the parameters discussed above (injection time, S-lens RF level and Source DC offset) and substantially

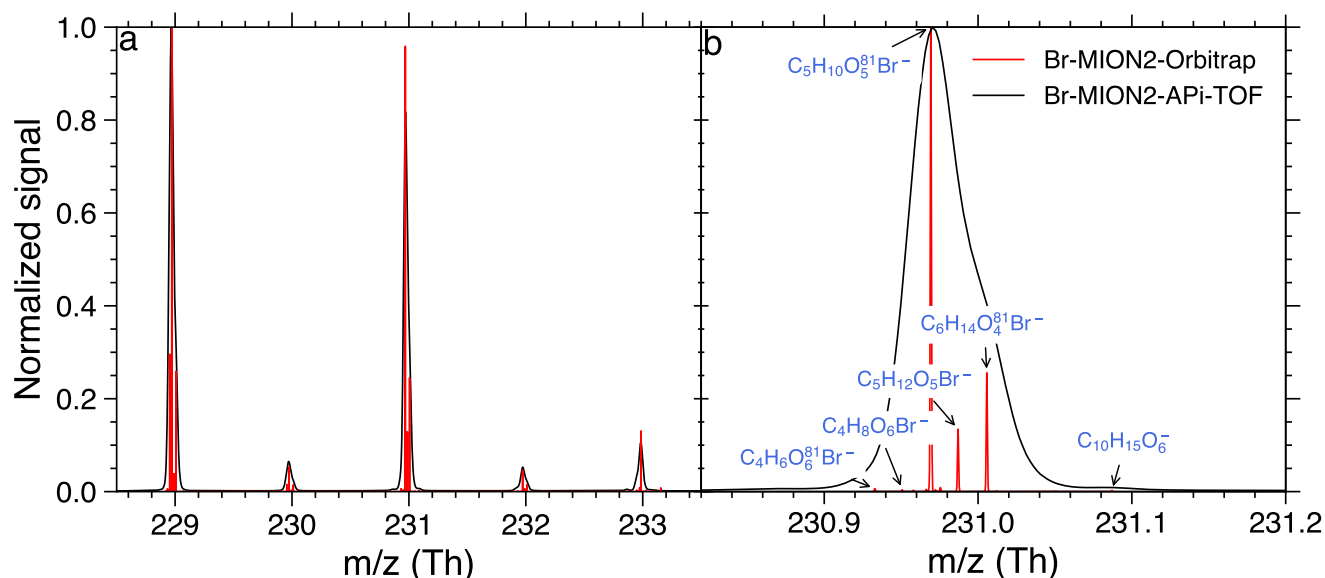


Figure 5. Comparison of mass spectra from the Br^- -MION2-Orbitrap and Br^- -MION2-APi-TOF during OH-initiated isoprene oxidation chamber experiments: (a) the m/z 229–233 range, where many isoprene oxidation products appear, and (b) a zoom at m/z 231. The higher resolving power of the Orbitrap separates the near-isobaric $\text{C}_5\text{H}_{12}\text{O}_5\text{Br}^-$, $\text{C}_5\text{H}_{10}\text{O}_5^{81}\text{Br}^-$, and $\text{C}_6\text{H}_{14}\text{O}_3\text{Br}^-$ (differing by as little as 0.001 in m/z), which the APi-TOF cannot resolve.

improved the sensitivity of the Orbitrap, particularly in the higher mass range ($m/z > 200$). Before optimisation, the two instruments differ noticeably in their peak distributions: the Orbitrap gives markedly weaker signals for high-mass species (above m/z 200) than the APi-TOF. This is evident in the dominant peaks - $\text{CH}_2\text{O}_2\text{Br}^-$, $\text{C}_5\text{H}_{10}\text{O}_3\text{Br}^-$ and $\text{C}_5\text{H}_{10}\text{O}_5\text{Br}^-$ in the Orbitrap spectrum, compared with $\text{C}_6\text{H}_{14}\text{O}_3\text{Br}^-$, $\text{C}_5\text{H}_{10}\text{O}_3\text{Br}^-$ and $\text{CH}_2\text{O}_2\text{Br}^-$ in the APi-TOF spectrum. After optimisation, the two spectra become much more comparable, showing similar product-peak distributions. The main residual difference is that the APi-TOF retains slightly higher intensities for several background contaminants, such as HNO_3Br^- , $\text{C}_3\text{H}_6\text{O}_3\text{Br}^-$ and Br_3^- , most likely reflecting differences in inlet history. Because optimisation maximises the Orbitrap's sensitivity - after which its measurements agree with those of the independently characterised APi-TOF - all Orbitrap data discussed in the following sections were acquired after optimisation unless otherwise noted.

Beyond the overall spectral comparison, we examine specific peaks in the m/z 229–233 range, where many isoprene oxidation products appear (Figure 5a). These results show that the optimised Orbitrap detects these species as effectively as the APi-TOF and, in most cases, resolves them in greater detail owing to its higher mass resolving power. This advantage is decisive where products overlap with near-isobaric interferences. A key example is $\text{C}_5\text{H}_{12}\text{O}_5\text{Br}^-$, an important IP-OOM product whose accurate quantification is essential for elucidating isoprene oxidation mechanisms but is only possible once the ion is separated from its interferences. At m/z 231 (Figure 5b), the Orbitrap achieves exactly this, clearly distinguishing $\text{C}_5\text{H}_{12}\text{O}_5\text{Br}^-$ from both $\text{C}_5\text{H}_{10}\text{O}_5^{81}\text{Br}^-$ and $\text{C}_6\text{H}_{14}\text{O}_3\text{Br}^-$ and resolving mass differences as small as 0.001 in m/z . Such separation is chal-



lensing for the APi-TOF because these species have nearly identical m/z values, and the latter two are more abundant than $C_5H_{12}O_5Br^-$. In such cases, the APi-TOF must rely on isotopic patterns to aid peak identification, which becomes unreliable when the target species is in low abundance and its isotopic peaks are weak, especially in ambient measurements where it may be unclear whether the species is present at all.

Furthermore, the Orbitrap can identify lower-abundance species, such as $C_4H_6O_8^{81}Br^-$ and $C_4H_8O_6Br^-$, that are easily overlooked or misidentified in APi-TOF spectra owing to their low concentrations. Although these additional species do not substantially affect the total IP-OOM quantification, their detection enriches the chemical characterisation of the oxidation products. This capability is particularly important for detecting peroxy radicals, such as $C_5H_9O_6Br^-$ and $C_5H_{11}O_6Br^-$, which are key intermediates in IP-OOM formation yet occur at low concentrations. These comparisons show that the Orbitrap provides comparable or superior performance to the APi-TOF for detecting and characterising isoprene oxidation products using the bromide chemical ionisation method, owing primarily to its higher mass resolving power. The improved resolution facilitates the separation of closely spaced peaks, making both the assignment of dominant signals and the interpretation of isotopologue patterns more reliable.

3.2.2 Species comparison

In addition to the qualitative comparison of mass spectra, we quantitatively compare the species measured by the Br^- -MION2-Orbitrap and Br^- -MION2-APi-TOF. Absolute concentrations are estimated for each species using the H_2SO_4 calibration factor; because this represents the maximum (collision-limited) sensitivity, the resulting concentrations are lower limits (He et al., 2023). The calibrations were determined independently for each instrument as described in the Methods section. Direct calibration of individual products was not feasible owing to the lack of standards or authentic generation methods. These data are shown in Figure A6; species are included if they are detected by both instruments and relevant to isoprene oxidation. A small number of species are excluded because ion-source contamination or unstable behaviour causes each to be detected by only one of the two instruments, precluding a direct comparison. The measurements show strong agreement, with a clear linear correlation spanning almost five orders of magnitude (10^5 to 10^{10} cm^{-3}), a dynamic range typical of atmospheric measurements.

Despite the strong overall correlation, the measurement ratio varies considerably among species, indicating systematic, composition-dependent differences in quantification. Although the figure groups species by carbon number, these differences are most clearly understood in terms of oxygen content and degree of saturation, which we consider in turn. For example, three-oxygen species such as $C_2H_2O_3$, $C_2H_4O_3$, $C_4H_8O_3$, $C_5H_6O_3$, $C_5H_8O_3$, and $C_5H_{10}O_3$ generally cluster around the 4:1 line, where the Br^- -MION2-APi-TOF reports consistently higher concentrations than the Orbitrap. These species also show lower signal at higher S-lens RF levels (Figure 3a), consistent with reduced transmission of light m/z ions and less stable bromide adducts that are more prone to fragmentation or loss in the Orbitrap. Decreasing the S-lens RF level could therefore improve this agreement. Species with more than three oxygen atoms are particularly important, as they often correspond to IP-OOM, which contribute to new particle formation (Shen et al., 2024). For instance, four-oxygen species such as $C_3H_6O_4$, $C_3H_8O_4$, $C_4H_8O_4$, $C_5H_8O_4$, and $C_5H_{10}O_4$ show ratios between 4 and 1, indicating closer agreement. These compounds show moderate signal at higher S-lens RF levels, as shown in Figure 3b.

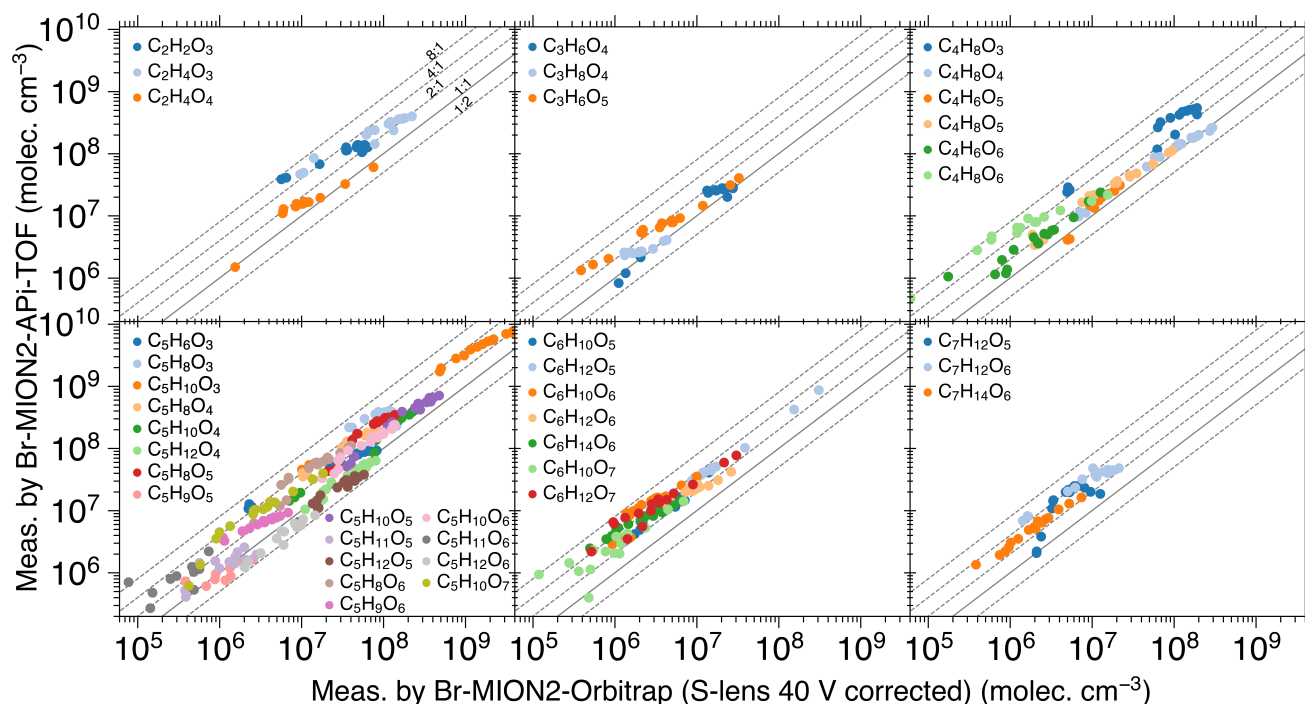


Figure 6. Species-by-species comparison of the concentrations measured by the Br⁻-MION2-Orbitrap and Br⁻-MION2-API-TOF in chamber experiments. The Orbitrap concentrations have been corrected for S-lens transmission using the RF scan in Figure 3. For each species, the ratio of its signal at the 40 % RF level used in this study to its maximum signal in the scan gives its transmission efficiency; every measured concentration was then divided by this ratio to recover the value at peak transmission. Species without a valid 40 % value in the S-lens scan C₅H₁₁O₅ are shown at their uncorrected values. Species are grouped by carbon number (panels, C₂-C₇) and distinguished by colour within each panel. Each point is a chemical formula detected by both instruments, with the Orbitrap-measured concentration on the *x*-axis and the API-TOF-measured concentration on the *y*-axis; diagonal lines mark concentration ratios of 8:1, 4:1, 2:1, 1:1 (solid line), and 1:2. All compounds are quantified using the H₂SO₄ calibration factor, determined independently for each instrument. The two instruments correlate over roughly five orders of magnitude (10⁵ to 10¹⁰ cm⁻³), with the Br⁻-MION2-API-TOF reporting concentrations approximately twice those of the Br⁻-MION2-Orbitrap on average, within the uncertainty of the H₂SO₄ calibration factor.



In addition to oxygen content, the degree of saturation also influences the measurement ratios. Within the $C_5H_xO_4$ series, the ratio decreases systematically as the hydrogen number increases: 2.4, 1.8, and 0.9 for $C_5H_8O_4$, $C_5H_{10}O_4$, and $C_5H_{12}O_4$, respectively. This same saturation trend persists at higher oxygen content across the C_5 series, which dominates the IP-OOM population (Figure A6): the $C_5H_xO_5$ group falls from 2.8 to 1.7 to 0.8 ($C_5H_8O_5$, $C_5H_{10}O_5$, $C_5H_{12}O_5$), and the $C_5H_xO_6$ group from 3.1 to 1.8 to 0.7 ($C_5H_8O_6$, $C_5H_{10}O_6$, $C_5H_{12}O_6$). This consistent decline likely reflects the current Orbitrap tuning favouring the transmission of more stable bromide adducts, which are more prevalent among the saturated species. In summary, the inter-instrument ratios track the single-instrument S-lens RF scan (Figure 3): a species' position relative to the 1:1 line largely follows from its transmission at the 40 % operating point, providing an independent confirmation of the behaviour characterised there.

Building on this diagnostic, we propose a transmission correction for Br^- -MION2-Orbitrap data based on the single-instrument S-lens RF scan. For each species, its signal at the operating RF level (40 % here) is expressed as a fraction of its maximum across the scan, giving a per-species transmission efficiency; dividing the measured concentration by this efficiency recovers the value at peak transmission (Figure 3). The procedure requires only an RF scan under the same reagent-ion chemistry and can be applied to any species detected in it, offering a simple, standard-free way to remove the tuning-dependent transmission bias; here, one species ($C_5H_{11}O_6$) lacks a valid 40 % value and is left uncorrected.

The corrected comparison is shown in Figure 6, and the effect is strongly composition-dependent. The saturated, higher- m/z species are already transmitted close to their maximum at 40 % and change little, whereas the low- m/z , low-oxygen species are improved substantially. The effect is largest for the three-oxygen species, which are the most strongly under-reported in the Orbitrap: their median API-TOF-to-Orbitrap ratio falls from about 4.4 to 3.0, and the lowest- m/z members $C_2H_2O_3$ and $C_2H_4O_3$ improve most, from about 4.4 to 2.7. This substantially reduces the excess under-reporting of the low- m/z species; across the full population, however, the median ratio falls only from about 2.6 to 2.2, leaving a common, transmission-independent offset of roughly a factor of two set by the calibration. We therefore recommend applying this RF-scan correction to Br^- -MION2-Orbitrap data, especially when low- m/z species are of interest and lack direct calibration.

Because both instruments use identical chemical ionisation and inlets, these composition-dependent differences arise in the mass analysers, from ion transmission and bromide-adduct stability under each instrument's tuning, rather than from any inherent limitation of either instrument. Under the tuning used here, the Orbitrap is more sensitive to higher- m/z , more saturated species.

The RF-scan correction is an internal, relative one: it recovers each Orbitrap species to its own peak transmission across the S-lens scan, but it does not establish the instrument's absolute transmission efficiency. That absolute, m/z -dependent transmission curve - the overall efficiency of each analyser as a function of mass at fixed tuning - is missing for both instruments, as we did not measure it here. Published characterisations show it to be pronounced in both types, with the transmission maximum at relatively high m/z for a CI-API-TOF (Heinritzi et al., 2016) and at intermediate m/z for a CI-Orbitrap (Yuan et al., 2025). Because these maxima fall at different m/z , the instruments' relative response varies across the mass range, so a composition-dependent difference beyond the S-lens effect may remain; its magnitude and direction cannot be quantified without instrument-specific absolute transmission calibrations.



Notwithstanding this unquantified residual, the two instruments still agree to within a factor of about two overall: for species with more than three carbon, hydrogen and oxygen atoms, the API-TOF reports concentrations roughly 1.8 times (0.72 to 3.1 across species) those of the Orbitrap, even after the transmission correction. This offset is not a concern for quantifying isoprene oxidation products, as it falls within the typical uncertainty of the H_2SO_4 calibration factor, which can itself vary by up to a factor of two.

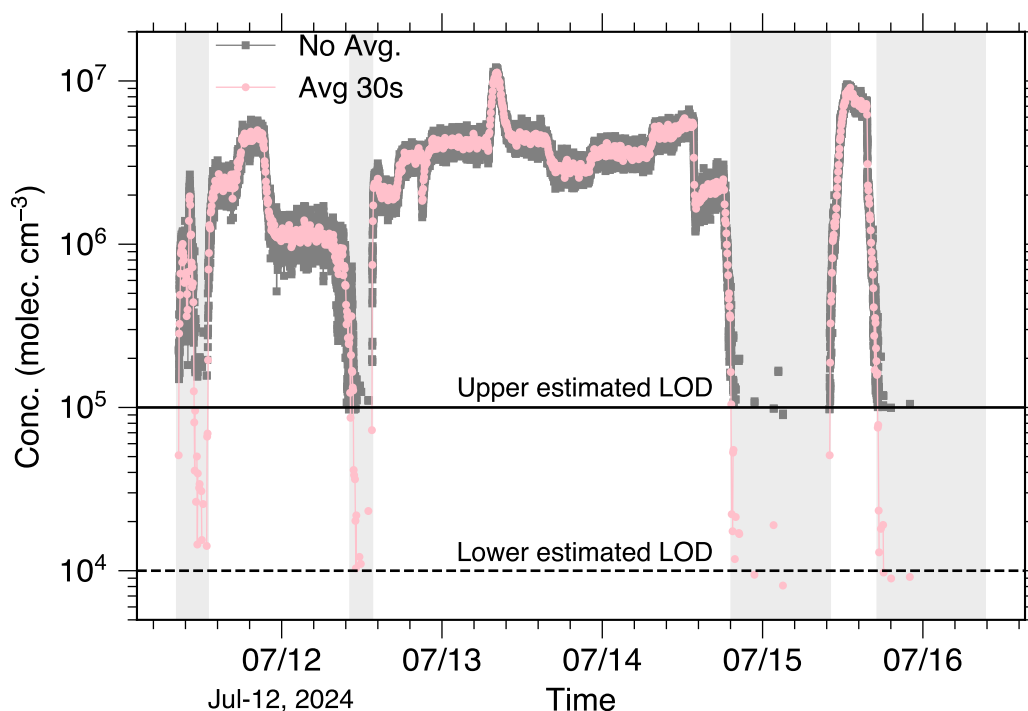


Figure 7. Effect of post-acquisition averaging on the Br^- -MION2-Orbitrap detection limit, illustrated for the time series of $\text{C}_5\text{H}_9\text{O}_6\text{Br}^-$. The same data are processed with averaging disabled (10 s per scan, grey) and with 30 s averaging (pink). The two agree at high concentrations, but in the low-concentration region (shaded) the averaged signal is suppressed by more than an order of magnitude, because the average includes the artificial zeros introduced by the instrument's internal noise threshold, mimicking a non-linear response. The solid line is a conservative (upper-bound) estimate of the detection limit; its value is expected to lie between the solid and dashed lines.

3.3 Br^- -MION2-Orbitrap linear response and detection limits

The detection limit and the apparent low-concentration non-linearity of intensities of the Orbitrap both follow from how the instrument records weak signals, which we discuss here first. Registering a peak requires a certain number of ions to induce a detectable image current in the Orbitrap analyser. The number of ions needed is associated with the level of electronic noise, the duration of the acquired microscans, and the microscan number. Before any user-side post-acquisition data processing,



the instrument Fourier-transforms the image current into a mass spectrum and applies a noise threshold below which no peak intensities are reported; absences of reported peaks are not equivalent to the detection of zero-intensity signals but rather non-detections with an associated intensity anywhere between zero and the threshold.

565 Peak intensities can be classified into three regimes for the convenience of illustration: High-intensity peaks are detected in every scan; weak peaks that drift in and out of the threshold are detected only intermittently; marginal intensity peaks are detected only spuriously in single scans. In the intermittent regime the temporally averaged peak intensities can be biased either high or low depending on how the non-detections are treated: keeping only the scans that exceed the threshold, which ride up on positive noise, might bias the average slightly high, whereas averaging that substitutes non-detections with zero biases it low
 570 (Helsel, 2006). The near-continuous detection of a peak in the intermittent regime, with only spurious non-detections, supports the interpretation of a real ion abundance close to the threshold, especially if a large intensity variability on the involved time scales is not physically feasible. Under these conditions, the average intensity can still be estimated by treating each non-detection as an unknown value between zero and the threshold, rather than as zero. Isolated single-scan detections, i.e., outliers, are the least quantitative. They may be noise spikes rather than real signal. Averaging such an outlier to a long period
 575 without detection, resulting in an average intensity maybe orders of magnitude below the threshold intensity, would require robust physical reasoning to be justified: not only a known and stable instrument behaviour is needed, but also an analyte ion abundance variation exactly as during a required instrument characterization. Both the detection limit and the apparent non-linearity discussed below follow from this post-transform zeroing of sub-threshold peaks.

3.3.1 Detection limits

580 We take the detection limit as the concentration at which a species is quantified continuously rather than only intermittently; because of the sub-threshold zeros it is bounded rather than pinned exactly.

Figure 7 illustrates this for the reported time series of $\text{C}_5\text{H}_9\text{O}_6\text{Br}^-$: temporally averaging the concentration over 30 s (pink) versus using the native per-scan values (grey) gives results that coincide at high concentration but diverge by more than an order of magnitude near the detection limit, where the average is pulled down by the non-detection, substituted by zeros. For
 585 the nitrate CI-Orbitrap, Cai et al. (2022) defined the detection limit from the noise floor (its mean plus three standard deviations) and lowered it to $\sim 5 \times 10^4 \text{ cm}^{-3}$ through spectral averaging (e.g., over 1 hour) at higher AGC target and microscan number; this averaging reduces noise and is distinct from the intensity-dependent underestimation of weak signals. The underestimation they characterised and corrected separately, using the isotopologue peaks as internal references: because an isotope peak (e.g., ^{13}C) has a known abundance relative to its parent, the ratio of measured to expected isotope signal maps the loss of sensitivity
 590 toward low intensity, giving a curve applied to correct signals below a defined sensitivity threshold. As those authors note, this correction improves the reported concentrations but does not affect the detection limit, and it carries its own limitations (discussed below).

We instead exclude the zeroed scans, averaging only over the intervals in which the mass spectrometric signal is reported (the shaded region in Figure 7). This removes the downward bias but biases the estimate upward, and forgoes part of the
 595 noise reduction, so the resulting $\sim 1.3 \times 10^5 \text{ cm}^{-3}$ for the Br^- -MION2-Orbitrap (with the H_2SO_4 calibration factor; solid line



in Figure 7) is a conservative overestimate rather than an unbiased detection limit. The detection limit of a single scan without further averaging is thus bracketed between the two, lying above the dashed (averaged) line but below the solid (non-averaged) line; concentrations reported below the solid line are close to the instrument's intrinsic detection limit and the chosen noise threshold, and may be affected by the non-linearity discussed in the next section.

600 For comparison, the Br^- -MION2-API-TOF used in this study yields a detection limit of approximately 10^5 cm^{-3} for H_2SO_4 , consistent with previous characterisations of the same instrument (He et al., 2023); this value is higher than that of a typical, newer API-TOF because the instrument used here carries an aged microchannel plate (MCP) detector with elevated background noise. Although both detection limits are derived from H_2SO_4 , they are expected to be representative of the target species: in the species comparison (Figure 6), the isoprene oxidation products are detected down to $\sim 10^5 \text{ cm}^{-3}$, and neither instrument
 605 probed lower concentrations. The Orbitrap detection limit is not fixed: it can be lowered by increasing the microscan number (e.g., to 100) and the accumulation time, by tuning the AGC target and the reagent-ion exclusion (Yuan et al., 2025).

3.3.2 Linear response

Above this detection floor, previous studies reported a non-linear response of the nitrate CI-Orbitrap below $\sim 1 \times 10^6 \text{ cm}^{-3}$, attributed it to an inherent limitation of the instrument, and proposed empirical corrections for it (Cai et al., 2022; Riva et al.,
 610 2020). This non-linearity is the same thresholding effect described above, which Riva et al. (2020) also noted: near the detection limit, temporally averaging over the substituted zeros biases the reported signal low (Figure 7), mimicking a non-linear response. The Orbitrap's intrinsic detection principle is, however, linear in the number of ions - there is no physical mechanism that would compress its response at low concentrations. The apparent non-linearity instead falls below the single-scan detection limit, and is revealed only because spectral averaging lowers the detection limit of the averaged spectrum, opening
 615 a concentration window in which the signal is intermittent: detected in some scans and set to zero in others. Averaging a continuous signal simply reduces the random noise by a factor of $\sqrt{N}$ for N scans and leaves the response linear; it is only when a non-continuous signal is averaged over its interspersed zeros that the mean is biased low, mimicking a non-linear response. The non-linearity can therefore be taken as a data-processing artefact rather than an intrinsic limitation of the analyser.

Because the artefact arises from averaging over the substituted zeros, the empirical corrections proposed for it (Cai et al.,
 620 2022; Riva et al., 2020) can only reshape data that are already biased. Low concentrations are better accessed by lowering the detection limit at the instrument (Cai et al., 2022) than by post-processing, so that weak species are genuinely detected in individual scans rather than intermittently thresholded. Removing the high-abundance reagent ions before ion accumulation (Yuan et al., 2025), for example, lowers the single-scan detection limit and, in turn, the artefact's influence on the averaged spectrum. The Br^- -MION2-API-TOF applies no such internal noise gate before recording the data - it stores the raw signal,
 625 noise included - and is therefore never exposed to the zero-substitution artefact in the first place, making it an independent check on the processed Orbitrap data rather than a comparison between two instruments that could share the same bias. Over the concentrations both instruments detect (10^5 to 10^{10} cm^{-3} ; Figure 6), the processed Orbitrap tracks the API-TOF, confirming that its response is genuinely linear across this range and not an artefact of the data processing, consistent with Riva et al. (2020). Below this shared floor, neither instrument constrains the response.

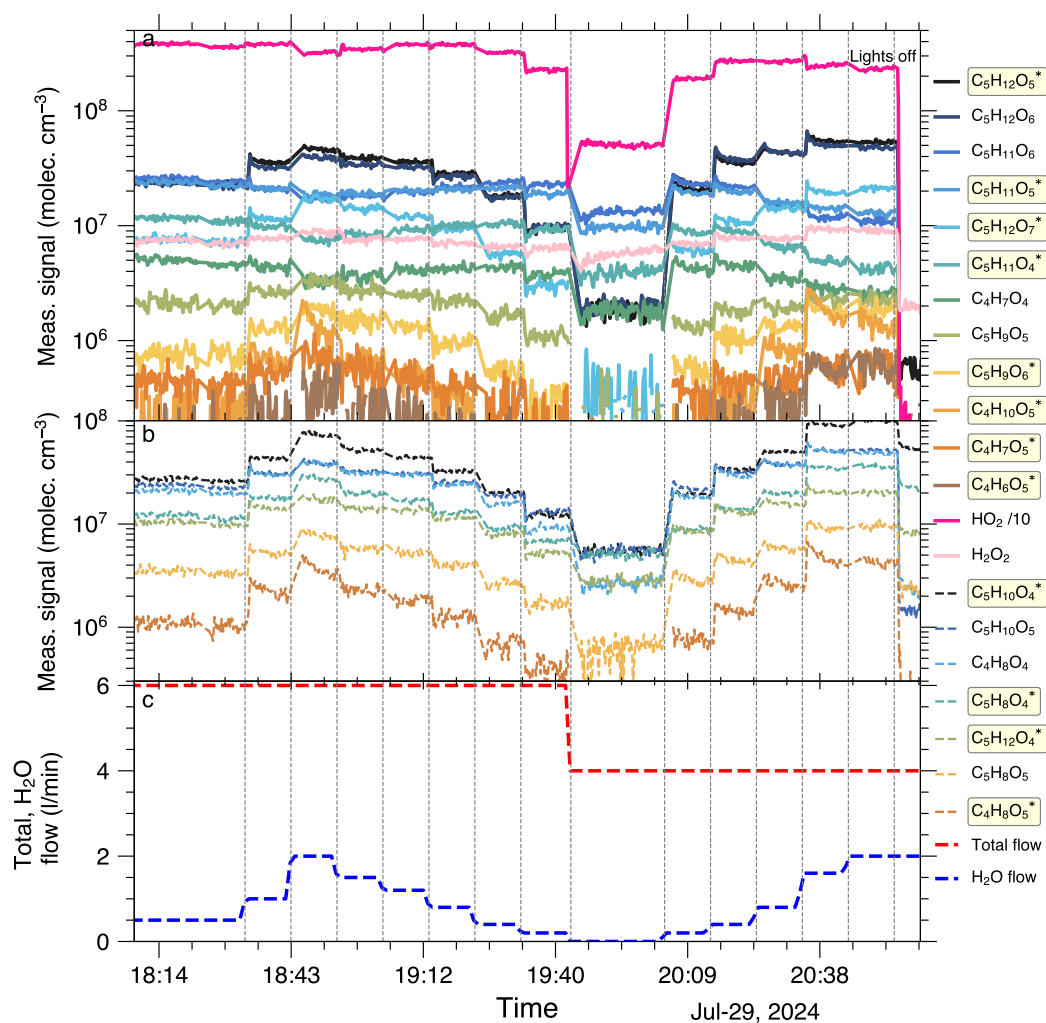


Figure 8. Time series of the products measured during OH-initiated oxidation of 1,2-ISOPOOH in the flow reactor under stepwise-varied OH. 1,2-ISOPOOH was injected at a constant 1.2×10^9 molecules cm^{-3} , while OH was varied by adjusting the H_2O flow through the UV illuminated section; the step-like responses of many products track OH concentration change. Solid lines denote predominantly OH-driven species, dashed lines are species with notable background or wall contributions, and light-yellow boxes with an asterisk mark abundant species not represented in the current Wennberg et al. (2018) mechanism. When the lights are switched off at the end, most signals decrease rapidly, confirming that OH oxidation accounts for the majority of these products.



630 3.4 Application of Br⁻-MION2-Orbitrap for OH oxidation of 1,2-ISOPOOH

Following the characterisation and evaluation of the Br⁻-MION2-Orbitrap, we applied it to investigate the OH-initiated oxidation of 1,2-ISOPOOH in flow reactor experiments. As shown in Figure A7, we compared light-on and light-off periods to distinguish OH-initiated oxidation from background signals, which arise from wall residues and reactions as well as from contamination in the 1,2-ISOPOOH sample. Within this framework, solid-line species are predominantly OH-driven, whereas
 635 dashed-line species combine OH-driven signals with contributions from background or wall reactions.

Figure 8 presents an overview of the 1,2-ISOPOOH flow reactor oxidation experiments under different OH production conditions. The experiments begin with a constant injection of 1,2-ISOPOOH at 1.2×10^9 molecules cm⁻³. OH is produced by H₂O photolysis under the UV lamp, and the OH concentration is stepped by adjusting the H₂O flow. Because this flow (0.1-2 slpm) is small relative to the total flow (4-6 slpm), it sets the OH concentration without appreciably affecting the residence
 640 time (Figure A2); the total flow in Figure 8c itself is changed only once, reduced from 6 to 4 L min⁻¹, partway through the experiment.

The stepwise changes in H₂O flow are mirrored by coordinated, step-like responses of most products, indicating strong OH dependence. This coupling is particularly clear for many highly oxygenated C₅ species, whose signals decrease when H₂O flow is reduced and recover when H₂O flow is increased. In contrast, the RO₂ radicals C₅H₁₁O₄, C₅H₁₁O₅, and C₅H₁₁O₆ show
 645 the opposite trend (Figure A8), their signals decreasing when the H₂O flow is increased. These opposing trends reflect a HO₂ termination process: in this low-NO_x system HO₂ is abundant (Figure 8), and these RO₂ radicals are consumed by HO₂ to form the corresponding hydroperoxides (e.g. C₅H₁₁O_x + HO₂ → C₅H₁₂O_x + O₂). As OH increases, the radicals are therefore drawn down while their hydroperoxide products accumulate, consistent with the C₅H₁₂O_x hydroperoxides being among the most abundant IP-OOM. By contrast, C₅H₉O₅ and C₅H₉O₆ do not decrease with increasing OH in this way (Figure A8),
 650 indicating that their loss is not governed by HO₂ alone. When the lamp is switched off at the end, most signals decrease rapidly, confirming that OH oxidation drives a major fraction of the products, including the dashed-line species; these therefore combine background and OH-oxidation contributions rather than being pure contamination or wall reactions.

Many observed products are represented in the Wennberg isoprene oxidation mechanism (Wennberg et al., 2018), for example C₅H₁₂O₆. However, many abundant species are not included in the current mechanism, namely C₄H₆O₅, C₄H₇O₅,
 655 C₄H₈O₅, C₄H₁₀O₅, C₅H₈O₄, C₅H₁₀O₄, C₅H₁₁O₄, C₅H₁₂O₄, C₅H₁₁O₅, C₅H₁₂O₅, C₅H₉O₆, and C₅H₁₂O₇ (highlighted by light-yellow boxes in Figure 8). Overall, these species carry a strong OH-driven component and together form a major fraction of the total IP-OOM signal. Their formation pathways, however, remain unresolved and may involve photolysis of hydroperoxide groups under the UV irradiation used here. In particular, C₅H₁₂O₅ (not currently represented in the mechanism) and C₅H₁₂O₆ are both formed through OH-initiated oxidation of 1,2-ISOPOOH; together they contribute approximately one quarter of the
 660 total measured IP-OOM signal in the 1,2-ISOPOOH + OH system.



3.5 Evaluation of the MARFORCE model

To interpret the measured products mechanistically and quantitatively, we simulate the experiments with MARFORCE, which resolves the flow reactor's transport alongside the chemistry and so disentangles genuine chemistry from transport and wall losses.

665 The original model advanced transport and chemistry together on a single time step, which is not possible for the large isoprene mechanism; we therefore extended MARFORCE to advance them in separate steps (operator splitting), cutting the computational cost enough to make the mechanism tractable (Sect. 2.3). Because this scheme is new, we evaluate it before applying the model: the numerical scheme against the original coupled solver, and the chemistry against the FOAM box model. Run on the H_2SO_4 calibration scenario, the two schemes agree to better than 0.05 % for H_2SO_4 and 0.02 % for HO_2 , at a
670 fourfold lower computational cost (Figure A3). The short-lived radicals OH and HSO_3 differ more (21-27 %) because their chemical lifetimes (~ 0.028 s for OH) are close to the 0.01 s time step, so advancing chemistry and transport in sequence is less accurate for them; this is a controllable numerical artefact, common to any operator-splitting scheme and shrinking as the step is reduced, rather than a structural difference between the models. It does not affect H_2SO_4 or the slower-evolving oxidation products, and in the 1,2-ISOPOOH system OH is longer-lived than in the SO_2 -rich calibration, so the splitting
675 error is smaller still (full characterisation in Appendix A3). The chemistry, in turn, agrees with the FOAM box model (Wolfe et al., 2016) to within 2 % for all species, with similar temporal profiles and comparable peak concentrations (Figure A9), confirming that the mechanism is implemented consistently. With the numerical scheme and the chemistry both confirmed, any remaining discrepancy with the 1,2-ISOPOOH measurements must originate in the chemical mechanism rather than in the model machinery.

680 3.6 Simulation of 1,2-ISOPOOH oxidation

After evaluation, the MARFORCE model is used to simulate the oxidation of 1,2-ISOPOOH in the flow reactor and to identify priorities for future mechanistic investigations. This comparison is necessarily limited to species present in the Wennberg mechanism, since only these can be simulated; the abundant species identified in the previous section that are absent from the mechanism cannot be included.

685 Because the unfiltered lamp unavoidably photolyses the -OOH-bearing products (Sect. 2.3.2), photolysis is expected to be an essential process in these experiments. The simulations confirm this: without photolysis ($\text{SUN} = 0$), the model fails to reproduce the observed product distribution, with several detected species, such as $\text{C}_4\text{H}_6\text{O}_2$ and $\text{C}_4\text{H}_7\text{O}_3$, not formed at all (Figure 9) and many others, such as $\text{C}_5\text{H}_{12}\text{O}_6$, failing to reach steady state within the experimental timescale, their concentrations still evolving after 4×10^3 s of simulation whereas the experiments reach equilibrium within minutes.

690 We represent this photolysis through the SUN scaling factor described in Sect. 2.3.2, tuned empirically as a sensitivity parameter. As shown in Figure 9, increasing SUN substantially improves the overall agreement: the overpredicted terminal products decrease toward the measurements, missing products are formed, H_2O_2 approaches the observed values, and HO_2 rises. The best overall agreement is obtained at $\text{SUN} = 1 \times 10^4$, where the model reproduces the measured time traces reason-

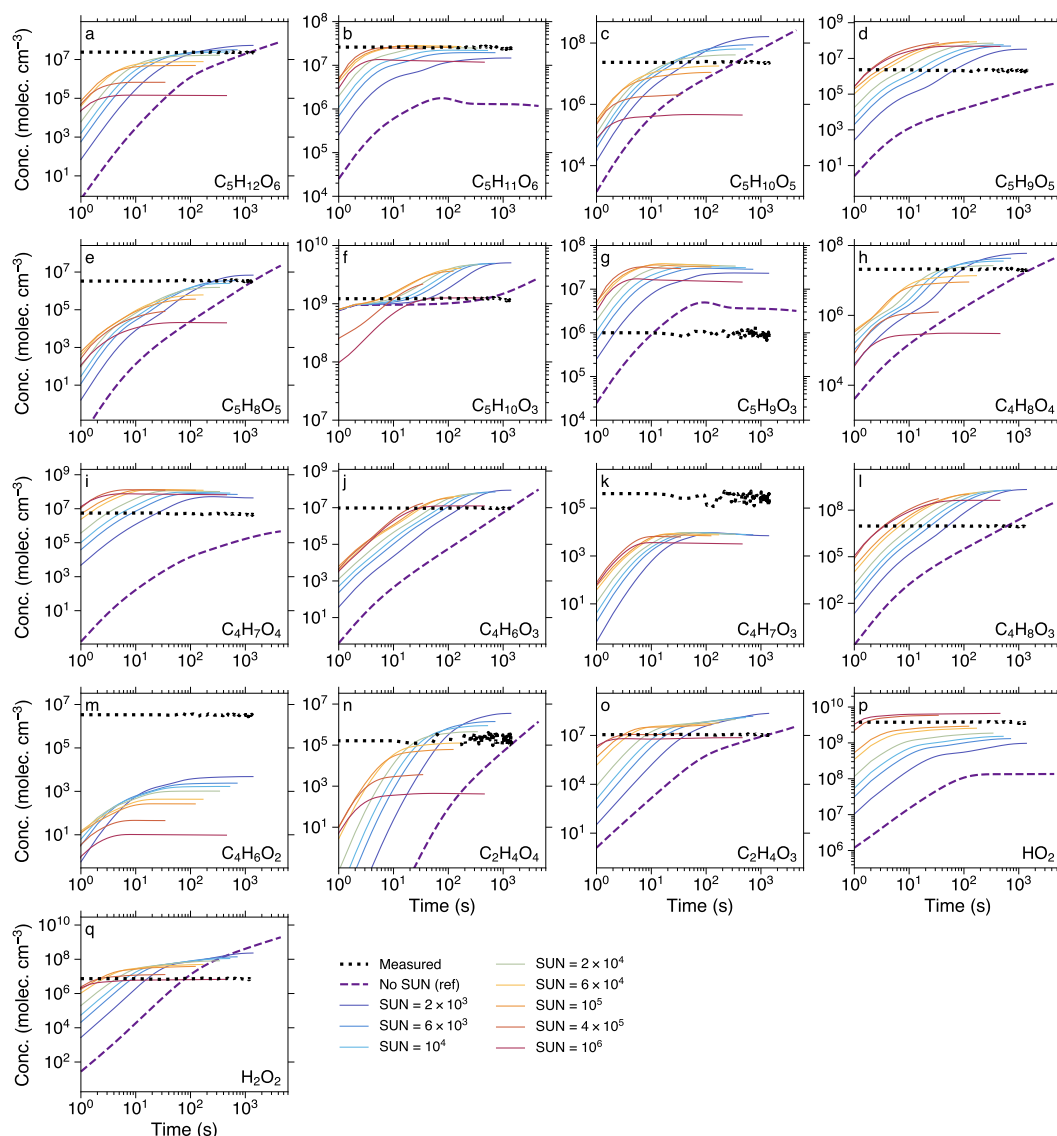


Figure 9. Effect of the photolysis scaling factor SUN on the MARFORCE simulation of the 1,2-ISOPOOH + OH system. The measurements represent steady-state (equilibrium) conditions in the flow reactor, whereas each simulation is initialised from a clean state, with no oxidation products present, and integrated forward until it reaches steady state, where it can be compared with the measurements. MARFORCE-modelled concentrations of key isoprene oxidation products and radicals are compared with Br⁻-MION2-Orbitrap measurements over a range of SUN values; increasing SUN raises HO₂ and lowers the overpredicted terminal products toward the observations, with the best overall agreement at SUN = 1 × 10⁴. SUN is a single dimensionless factor that scales every species' photolysis frequency ($J_i = f_i \times \text{SUN}$) in the Wennberg et al. (2018) mechanism, with SUN = 0 corresponding to no photolysis and higher values to stronger photolysis (see Methods for the parameterisation).



ably well (median simulation-to-measurement ratio of 4.3) and reaches steady state within a few minutes of simulated time,
695 matching the experimental timescale.

At this best fit, the implied photolysis frequency of H_2O_2 is $\sim 0.5 \text{ s}^{-1}$, far above the upper-tropospheric value ($\sim 1 \times 10^{-5} \text{ s}^{-1}$), so in absolute terms the experiments do not reproduce atmospheric photolysis rates. It is nonetheless comparable to the reactor's dominant loss, wall deposition at $\sim 0.3 \text{ s}^{-1}$; the photolysis-to-loss balance that governs product branching is therefore reproduced, confirming the expectation set out in Sect. 2.3.2.

700 This overall agreement masks strong species-to-species variation, with simulation-to-measurement ratios for most species ranging from about 0.5 to about 100. Several key products are reproduced well, with ratios of 0.9 ($\text{C}_5\text{H}_{12}\text{O}_6$), 1.1 ($\text{C}_5\text{H}_{11}\text{O}_6$), and 2.4 ($\text{C}_5\text{H}_{10}\text{O}_5$). Others are systematically overpredicted: $\text{C}_5\text{H}_{10}\text{O}_3$ (1,2-ISOPPOOH) by a factor of ~ 4 , and $\text{C}_5\text{H}_9\text{O}_5$ by more than one order of magnitude. Although $\text{C}_5\text{H}_9\text{O}_5$ appears better reproduced without photolysis, that simulation has not reached steady state, and its concentration is still increasing, so the apparent agreement is transient rather than genuine. Two
705 species, $\text{C}_4\text{H}_6\text{O}_2$ and $\text{C}_4\text{H}_7\text{O}_3$, are instead strongly underpredicted, $\text{C}_4\text{H}_6\text{O}_2$ by more than three orders of magnitude. Both are photolysis products of $\text{C}_5\text{H}_8\text{O}_3$ and are therefore absent from the $\text{SUN} = 0$ simulation, yet they are clearly detected in our measurements, further evidence that photolysis is an important control on the product distribution under the UV irradiation used here.

The overpredictions most likely reflect missing loss pathways or overactive formation in the mechanism, whereas the under-
710 derpredictions involve photolysis products whose formation pathways are present but underestimated by the single photolysis scaling factor, which cannot capture species-dependent behaviour; species-specific rates would be needed for quantitative closure. A further source of bias is the absence of many measured oxidation products from the current mechanism (Figure 8): because a substantial fraction of the measured species are not represented, their formation and interactions with the simulated species likely contribute to the discrepancies in Figure 9.

715 Fully constraining the photolysis rates and quantitatively characterising all species and pathways are left for future work. Here, our focus is on establishing an integrated framework - combining the Br^- -MION2-Orbitrap, flow reactor, chamber, and the MARFORCE model - for characterising isoprene photochemical oxidation. This framework extends naturally also to other molecules of atmospheric interest, including sulfur- and iodine-containing species and both anthropogenic and biogenic organics.

720 4 Conclusions

Isoprene oxygenated organic molecules (IP-OOM) contribute to new particle formation, yet the chemistry that produces them, photochemical oxidation of ISOPPOOH under tropospheric conditions, has remained poorly constrained: resolving it requires both sensitive, high-resolution molecular measurements and a flow reactor model able to separate genuine chemistry from transport and wall losses. In this work we develop both the measurement and modelling capabilities and combine them with
725 controlled flow reactor experiments, into a single framework which pairs the optimised Br^- -MION2-Orbitrap with a substantially extended MARFORCE flow reactor and chamber model to investigate this chemistry.



On the instrument side, we optimise the Br^- -MION2-Orbitrap for isoprene oxidation products by tuning three operating parameters: a short maximum injection time (100 ms here, below the ~ 400 ms onset of losses) to limit ion losses in the C-trap, an S-lens RF level of 20-40 % rather than the 50 % default, and a Source DC offset raised from -21 V to -10 V. The influence of each parameter is species-dependent, changing individual-species signals by 10-90 %. With the Orbitrap instrument optimised, we benchmark it side by side against the widely used Br^- -MION2-API-TOF in isoprene oxidation chamber experiments: for the compared species with more than three carbon, hydrogen and oxygen atoms, the API-TOF reports concentrations about 1.8 times those of the Orbitrap, within the uncertainty of the H_2SO_4 calibration. Additionally, the Orbitrap's mass resolving power ($280\,000$ at $m/z\,200$) resolves isobaric interferences that the API-TOF cannot, sharpening the identification of species such as $\text{C}_5\text{H}_{12}\text{O}_5\text{Br}^-$ and low-abundance RO_2 radicals.

A second, more fundamental result concerns the Orbitrap's apparent non-linearity at low concentrations, previously reported as an intrinsic instrument limitation. We show it is instead a data-processing artefact: the instrument's noise threshold sets sub-threshold scans to zero, and averaging over these zeros biases the signal low near the detection limit, whereas the analyser itself responds linearly in the number of ions. Over 10^5 to $10^{10}\,\text{cm}^{-3}$ the Orbitrap agrees with the gate-free Br^- -MION2-API-TOF; we report a conservative, upper-bound detection limit of $\sim 1.3 \times 10^5\,\text{cm}^{-3}$ and recommend accessing lower concentrations by lowering the detection limit at the instrument (e.g. more microscans, removing reagent ions before accumulation) rather than by an empirical correction.

On the modelling side, we extend MARFORCE from the simple inorganic chemistry for which it was originally designed to comprehensive organic mechanisms of hundreds of species, adding a continuous, spatially distributed OH source and an operator splitting scheme that cuts the computational cost about fourfold and makes such simulations feasible within hours rather than days. A complementary box model mode is also added for chamber simulations. Validated against FOAM (agreement within 2 % for all species) and reproducing the previously established H_2SO_4 transport behaviour, the model is numerically reliable, so that model-measurement differences can be attributed to the chemical mechanism rather than to transport or numerical effects.

Applying this combined framework to the OH oxidation of 1,2-ISOPOOH under UVC illumination, we detect several abundant products not represented in the Wennberg et al. (2018) mechanism, including $\text{C}_5\text{H}_{10}\text{O}_4$, $\text{C}_5\text{H}_{12}\text{O}_4$, $\text{C}_5\text{H}_{12}\text{O}_5$, and $\text{C}_5\text{H}_{12}\text{O}_7$. The framework further identifies photolysis of $-\text{OOH}$ -containing products as a key, previously underappreciated control on the product distribution under the UV irradiation of these experiments: including it brings the simulation to steady state within the experimental timescale and gives a median simulation-to-measurement ratio of 4.3, whereas neglecting it leaves several detected species, such as $\text{C}_4\text{H}_6\text{O}_2$ and $\text{C}_4\text{H}_7\text{O}_3$, unformed in the model. Agreement nonetheless remains species-dependent, with $\text{C}_5\text{H}_{10}\text{O}_3$ overpredicted by ~ 4 and $\text{C}_5\text{H}_9\text{O}_5$ by more than an order of magnitude, pointing to specific gaps that future mechanism development should address.

More broadly, the combined Br^- -MION2-Orbitrap and MARFORCE framework links high-resolution molecular measurements with a process-level model that resolves chemistry and transport together, providing a transferable basis for diagnosing missing chemistry and evaluating isoprene- and other VOC-oxidation mechanisms. Because transport and diffusion are represented explicitly, the framework also offers a complementary route to the wall-loss-free flow reactor approach: rather than



engineering the reactor toward ideal, wall-loss-free behaviour, which can restrict the accessible parameter space, the chemistry can now be studied in a deliberately simple reactor whose wall losses are quantified by the model. The fate of a photolabile product is set not by its photolysis rate alone but by the competition between photolysis and removal (wall deposition in our reactor, the condensation sink in the clean upper troposphere), so it is the ratio of these rates that shapes the product distribution. By quantifying the wall loss, the model recovers this ratio and places it on the same footing as its atmospheric counterpart, so the reactor's fast wall loss becomes a controlled proxy for the atmospheric sink rather than a limitation, letting a simple reactor probe photochemistry otherwise difficult to reach at atmospheric loss rates.

Taken together, our results identify photolysis as the least constrained element of upper tropospheric isoprene oxidation: because the photolysis rates of isoprene oxidation products under the upper tropospheric solar spectrum remain poorly constrained, many of these products are still poorly reproduced by current mechanisms. Closing this gap is a clear priority for understanding isoprene's global impact through upper tropospheric processes. Future work should constrain these photolysis rates under controlled laboratory conditions, incorporate the newly identified products into chemical mechanisms, and extend the Br⁻-MION2-Orbitrap to field measurements of IP-OOMs and their role in new particle formation. Together, these steps would substantially sharpen our quantitative understanding of isoprene photochemistry and its influence on the composition of the upper troposphere.

Code and data availability. The upgraded MARFORCE flow reactor model will be made publicly available upon publication. The processed measurement data and analysis scripts used to produce the figures in this study are available from the corresponding authors upon reasonable request.



780 Appendix A: Calibration of Br^- -MION2-Orbitrap

A1 Br^- -MION2-Orbitrap calibration

Among the detected isoprene oxidation products, $\text{C}_5\text{H}_{10}\text{O}_3$ exhibits the highest concentration (Figure 6). Its dominant isomer, 1,2-ISOPOOH, is the most abundant first-generation product of isoprene oxidation and was used in this study as the precursor for flow reactor experiments. Accurate quantification of 1,2-ISOPOOH by the Br^- -MION2-Orbitrap therefore requires a
 785 reliable calibration factor.

As shown in Figure A10, the derived calibration factor for 1,2-ISOPOOH is 2.5×10^{10} molecules cm^{-3} per normalised signal, approximately twice the H_2SO_4 calibration factor (1.33×10^{10} molecules cm^{-3}) and about five times lower than the HO_2 calibration factor (1.2×10^{11} molecules cm^{-3}). This agrees with the factor of ~ 2 relative to H_2SO_4 assumed for the Br^- -MION2-API-TOF in our earlier work (Shen et al., 2024). That estimate equated the sensitivity of 1,2-ISOPOOH with that of
 790 HOI, on the basis of the similar formation free enthalpies of the 1,2-ISOPOOH $\cdot \text{Br}^-$ cluster (-27.5 kcal mol^{-1} ; Table A1) and the HOI $\cdot \text{Br}^-$ cluster (-26.9 kcal mol^{-1}), with HOI in turn having a calibration factor about twice that of H_2SO_4 . The direct Orbitrap calibration therefore supports this binding-energy-based estimate for 1,2-ISOPOOH. Because instrument-specific parameters such as ion transmission efficiency and declustering conditions can still shift calibration factors between instruments, direct calibration of each analyte-instrument combination remains preferable where standards are available.

795 A2 RH effect on the measurement of isoprene-derived organic species

Relative humidity (RH) was systematically varied from 1 % to 30 % at room temperature under otherwise stable conditions during the 1,2-ISOPOOH + OH oxidation experiments. All detected isoprene oxidation products show a decrease in detection efficiency with increasing RH (Figure A11), consistent with earlier observations for inorganic species in the Br^- -MION2 system (He et al., 2023), where water vapour competes with analyte molecules for clustering with the bromide reagent ion.
 800 Based on the magnitude of the RH response, the organic species fall into two distinct groups.

The first group (Figure A11 a) exhibits a strong RH dependence, with signal intensities reduced by 50-80 % at 30 % RH relative to dry conditions. These species are predominantly C_4 - C_5 compounds with three oxygen atoms ($\text{C}_4\text{H}_6\text{O}_3$, $\text{C}_4\text{H}_8\text{O}_3$, $\text{C}_5\text{H}_6\text{O}_3$, $\text{C}_5\text{H}_8\text{O}_3$, $\text{C}_5\text{H}_{10}\text{O}_3$, and $\text{C}_5\text{H}_{12}\text{O}_3$), likely containing hydroxy, carbonyl, or carboxylic functional groups. The second group (Figure A11 b) shows a more moderate response, with signals decreasing by only 20-40 % at 30 % RH, similar to the
 805 behaviour of H_2SO_4 and HOI reported by He et al. (2023). These species generally contain more oxygen atoms (O_4 - O_6), with the exception of $\text{C}_4\text{H}_6\text{O}_2$, suggesting a greater number of polar functional groups that can stabilise the bromide adduct.

The difference in RH sensitivity between the two groups is qualitatively consistent with the S-lens RF voltage scan (Sect. 3.1). The first-group species all fall into the low-RF category (peak at ≤ 20 %; Figure 3 a), whereas the second-group species peak at higher RF levels (30-50 %; Figure 3 b and c). As discussed in Sect. 3.1, the optimal RF level reflects both m/z and adduct stability, and the two factors are partially confounded here: the more RH-sensitive first group consists of smaller, less oxidised
 810 molecules that are both lower in m/z and expected to form weaker bromide adducts. Nevertheless, the RH effect itself is most naturally attributed to adduct stability rather than m/z , because the signal suppression arises from water molecules competing



with the analyte for clustering with Br^- , a chemical process governed by relative binding affinities, not ion mass. This interpretation is consistent with the findings of He et al. (2023), who showed that more strongly bound species (e.g., H_2SO_4 , I_2) are less susceptible to humidity-induced signal loss.

Interestingly, the within-group RH response is relatively uniform despite considerable variation in RF-derived stability among individual species. This suggests that the relationship between binding affinity and RH sensitivity is not linear but saturating. Below a certain binding strength, RH effects are pronounced; above it, the adduct is sufficiently stable that further increases in binding affinity provide diminishing protection against water-induced signal loss. Overall, these results indicate that RH-dependent signal corrections are necessary for the Br^- -MION2-Orbitrap, with the magnitude of the correction dependent on the adduct stability of each analyte. The empirical RH response curves shown in Figure A11 can be used to apply such corrections within the 1-30 % RH range covered by these experiments.

A3 Validation of the operator-splitting scheme

The updated MARFORCE model was evaluated against the original implementation using an H_2SO_4 calibration scenario. Under identical numerical settings - the same time step (0.01 s) and convergence criterion (10^{-5}) - the updated version achieved a fourfold improvement in computational efficiency over the original design in He et al. (2023). The two versions agreed closely for stable species, differing by less than 0.05% for H_2SO_4 and 0.02% for HO_2 , but diverged more for the short-lived radicals OH (21%) and HSO_3 (27%), as shown in Figure A3.

These differences originate from the operator-splitting scheme itself. In reality, each species is transported and chemically produced or consumed at the same time; operator splitting approximates this by advancing the two processes one after the other within each time step - first solving the chemistry, then applying transport to the updated concentrations. Solving them sequentially rather than simultaneously is accurate only when neither process changes a species' concentration by much during a single step, and whether this holds depends on how the species' chemical lifetime compares with the length of the time step. OH and HSO_3 are highly reactive radicals with chemical loss lifetimes of only ~ 0.028 s (for OH, e.g. through $\text{OH} + \text{SO}_2$) - only about three times the 0.01 s step - so chemistry removes a substantial fraction, roughly a third, of each radical within a single step. Because this large change is imposed while transport is held fixed, and transport is then applied to the already-depleted concentration field, the sequential update departs appreciably from the true evolution in which chemistry and transport act on the radical at the same time. The outcome becomes sensitive to the length and ordering of the sub-steps, producing the 21-27% differences for these radicals. H_2SO_4 , by contrast, is the stable end-product of this chemistry: although it forms rapidly, it has no gas-phase sink, so once produced it is not chemically destroyed but simply accumulates. Its concentration therefore barely changes over a single 0.01 s step, and solving chemistry and transport separately gives essentially the same result as solving them together.

The splitting error is first order in the time step: reducing the step to 10^{-4} s, well below the OH lifetime, brings the two versions into close agreement, confirming that the 21-27% difference is a controllable numerical artefact rather than a structural difference between the models. Driving it to zero, however, requires proportionally more steps and raises the computational cost back toward that of the original solver, so step length and accuracy must be balanced. For this calibration the quantity



of interest is H_2SO_4 , which the 0.01 s step reproduces accurately; this step therefore offers a favourable compromise for the scenarios considered here. In the 1,2-ISOPOOH + OH experiments that are the focus of this study, OH remains a critical species, but there the OH-consuming reactants are present at much lower concentrations than the SO_2 used for calibration, and
 850 OH is supplied continuously along the quartz flow tube rather than titrated away. OH therefore has a longer chemical lifetime, so the splitting error is correspondingly smaller and is not expected to be significant for that system. More generally, this behaviour is not unique to MARFORCE: any operator-splitting scheme produces similar discrepancies for short-lived species, subject to the same trade-off between accuracy and computational cost.

A4 Quantum Chemical Calculations

855 For the clustering calculations, the Spartan '20 program (Wavefunction, Inc.) was used to generate an initial set of conformers of the reactants and the bromide bound clusters. These were first optimised at the B3LYP/6-31+G* level of theory, followed by optimisation and frequency calculations at the $\omega\text{B97X-D/ aug-cc-pVTZ-PP}$ level of theory for conformers within 2 kcal/mol in relative electronic energies of the lowest energy conformer. These calculations were performed using the Gaussian 16 program (Frisch et al., 2016). Pseudopotentials for bromide were taken from the EMSL basis set library (Pritchard et al., 2019; Feller,
 860 1996; Schuchardt et al., 2007; Peterson et al., 2003). Finally, the energies were corrected for the lowest energy conformers at the DLPNO-CCSD(T)/def2-QZVPP level of theory (Riplinger and Neese, 2013; Riplinger et al., 2013; Weigend and Ahlrichs, 2005).

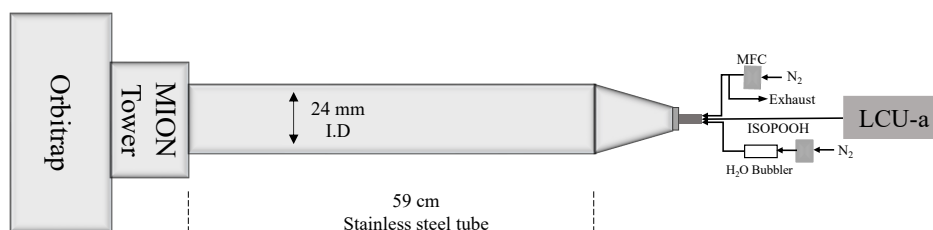


Figure A1. Schematic of the setup used to calibrate the Br^- -MION2-Orbitrap with the 1,2-ISOPOOH sample delivered by the LCU-a unit.

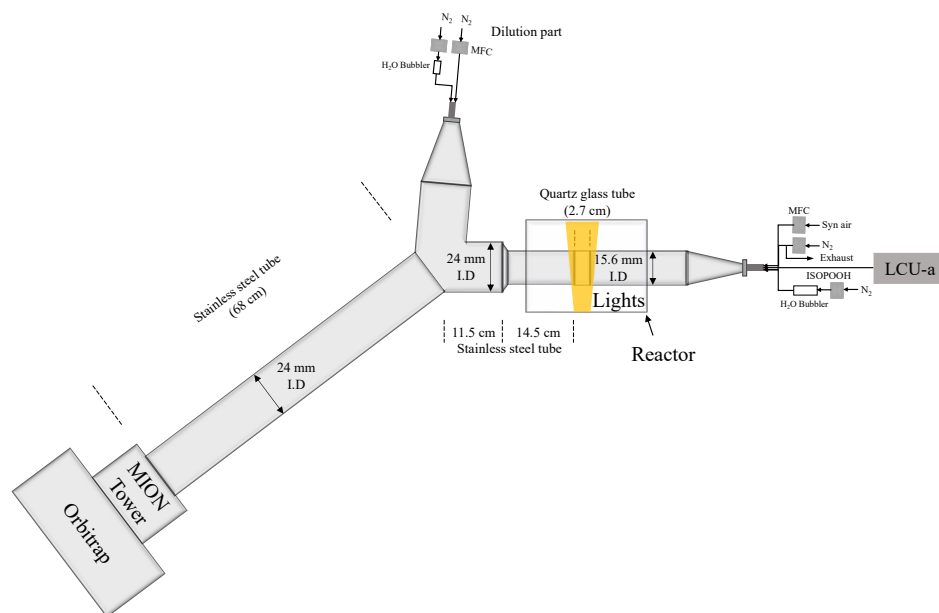


Figure A2. Schematic of the flow reactor setup for the OH-initiated oxidation of 1,2-ISOPOOH: the sample in air passes through a quartz tube irradiated by a mercury UV lamp that generates OH in situ, and the products are then diluted through a Y-piece and sampled by the Br^- -MION2-Orbitrap.

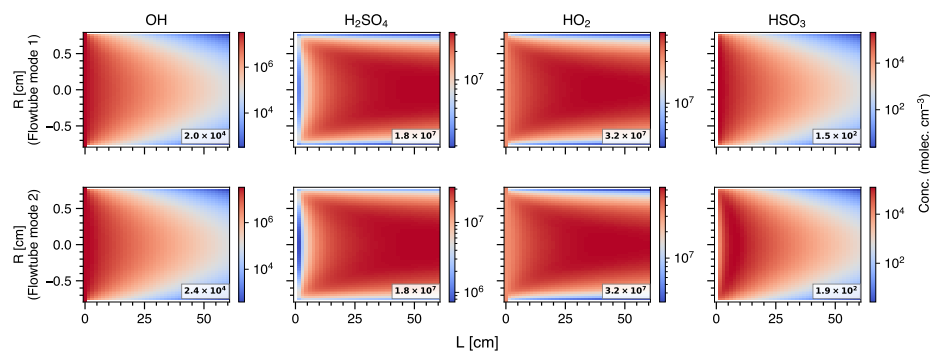


Figure A3. MARFORCE-simulated two-dimensional concentration profiles of OH, H₂SO₄, HO₂, and HSO₃ along the flow tube, shown as a function of axial position (L) and radial position (R) for the two flow-tube modes. The colour scale is logarithmic; the boxed value in each panel gives the final concentration (molec. cm⁻³) at the tube outlet. The profiles illustrate the radial concentration gradients and wall losses that arise from the coupled transport, diffusion, and chemistry resolved by the model.

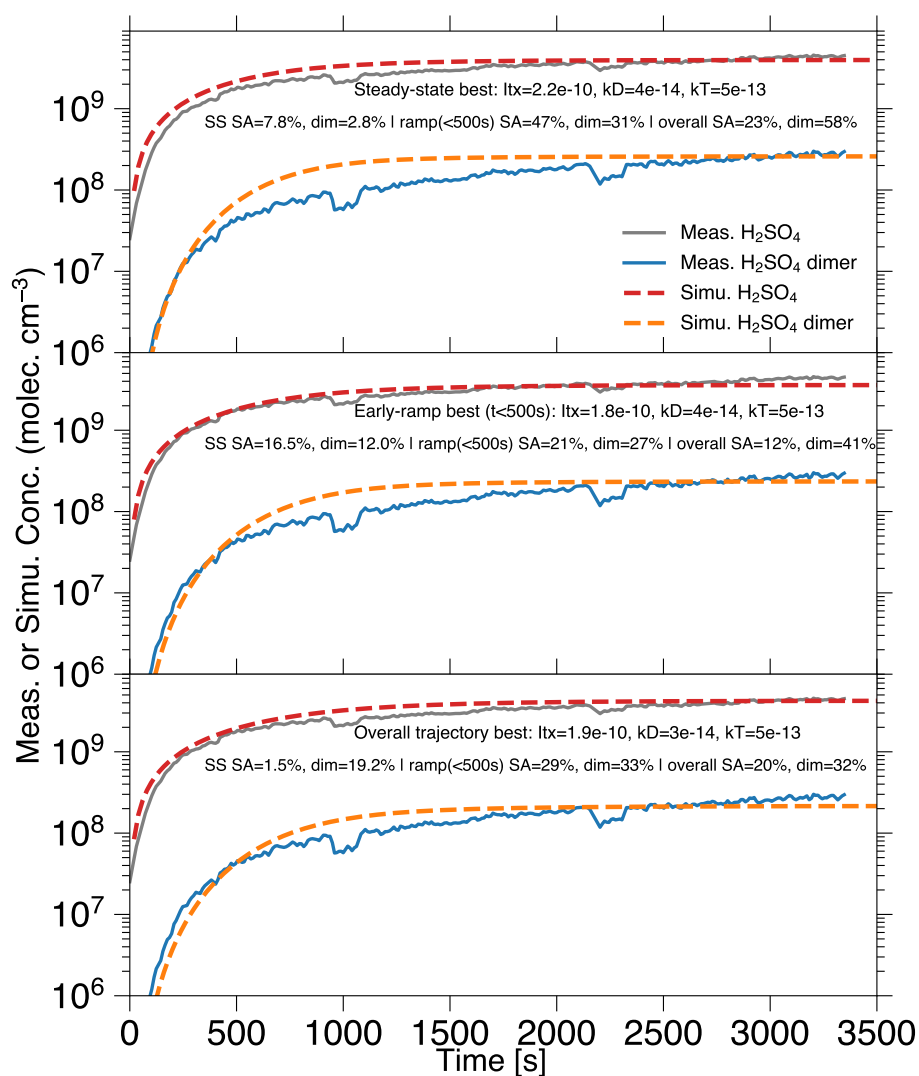


Figure A4. Determination of the OH production rate from the H_2SO_4 formation experiment. MARFORCE-simulated H_2SO_4 monomer and dimer concentrations (from $SO_2 + OH$) are shown as a function of time and compared with the Br^- -MION2-Orbitrap measurements, with the OH production rate adjusted to best reproduce the observations. The agreement in the temporal evolution of both the monomer and dimer, which is governed by transport and diffusion, also confirms that the transport and diffusion scheme in MARFORCE is correctly implemented.

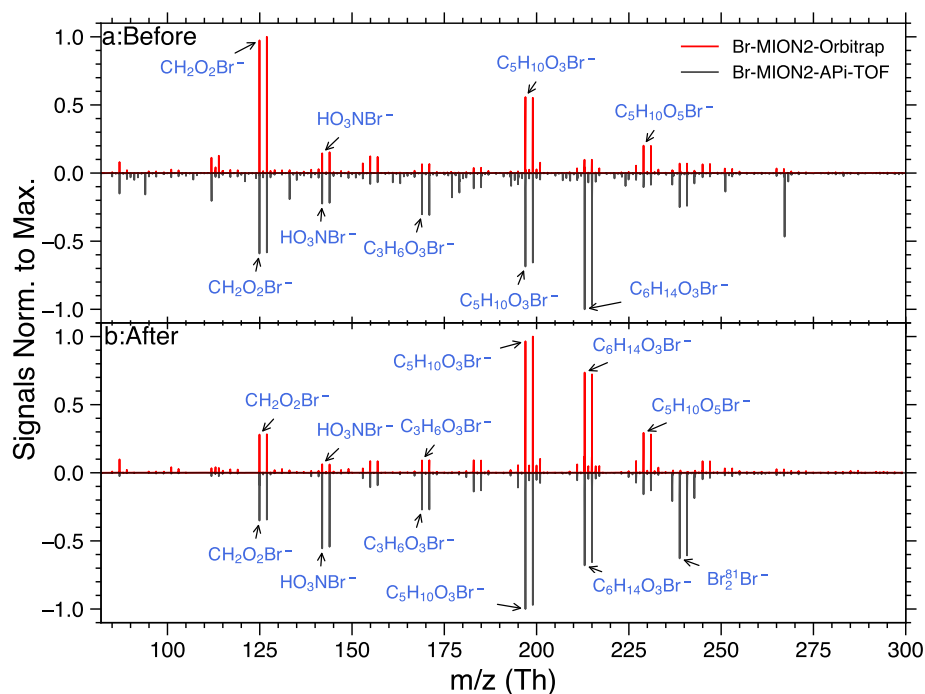


Figure A5. Comparison of mass spectra from the Br^- -MION2-Orbitrap and the Br^- -MION2-APi-TOF during OH-initiated isoprene oxidation chamber experiments, (a) before and (b) after optimisation of the Orbitrap system (displayed mass range m/z 82-300). Before optimisation, the Orbitrap underrepresents high-mass species ($> m/z$ 200) relative to the APi-TOF spectrum; after optimisation, the two show closely matching peak distributions.

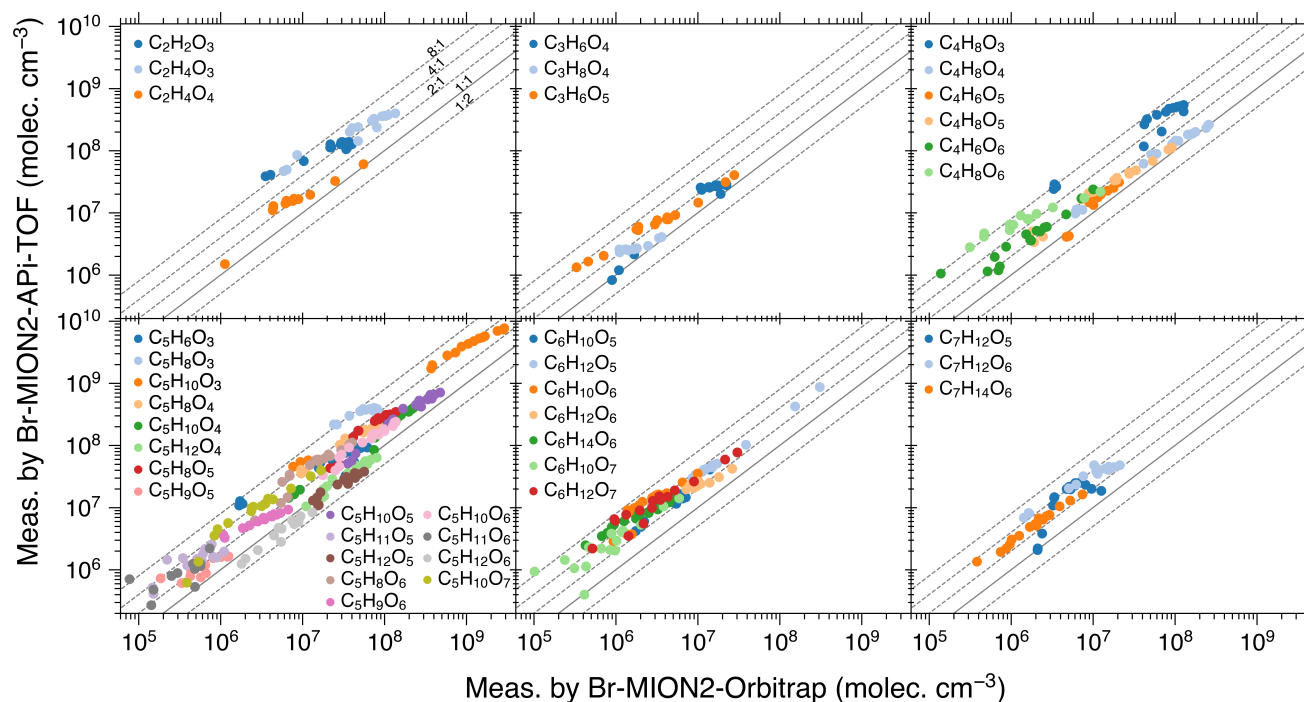


Figure A6. Species-by-species comparison of isoprene oxidation products measured by the Br^- -MION2-Orbitrap and Br^- -MION2-API-TOF in chamber experiments. Species are grouped by carbon number (panels, C_2 - C_7) and distinguished by colour within each panel. Each point is a chemical formula detected by both instruments, with the Orbitrap-measured concentration on the x -axis and the API-TOF-measured concentration on the y -axis; diagonal lines mark concentration ratios of 8:1, 4:1, 2:1, 1:1, and 1:2. All compounds are quantified using the H_2SO_4 calibration factor, determined independently for each instrument. The two instruments correlate over roughly five orders of magnitude (10^5 to 10^{10} cm^{-3}), but before the transmission correction the ratio is composition-dependent, with the low- m/z , low-oxygen species most strongly under-reported by the Orbitrap.

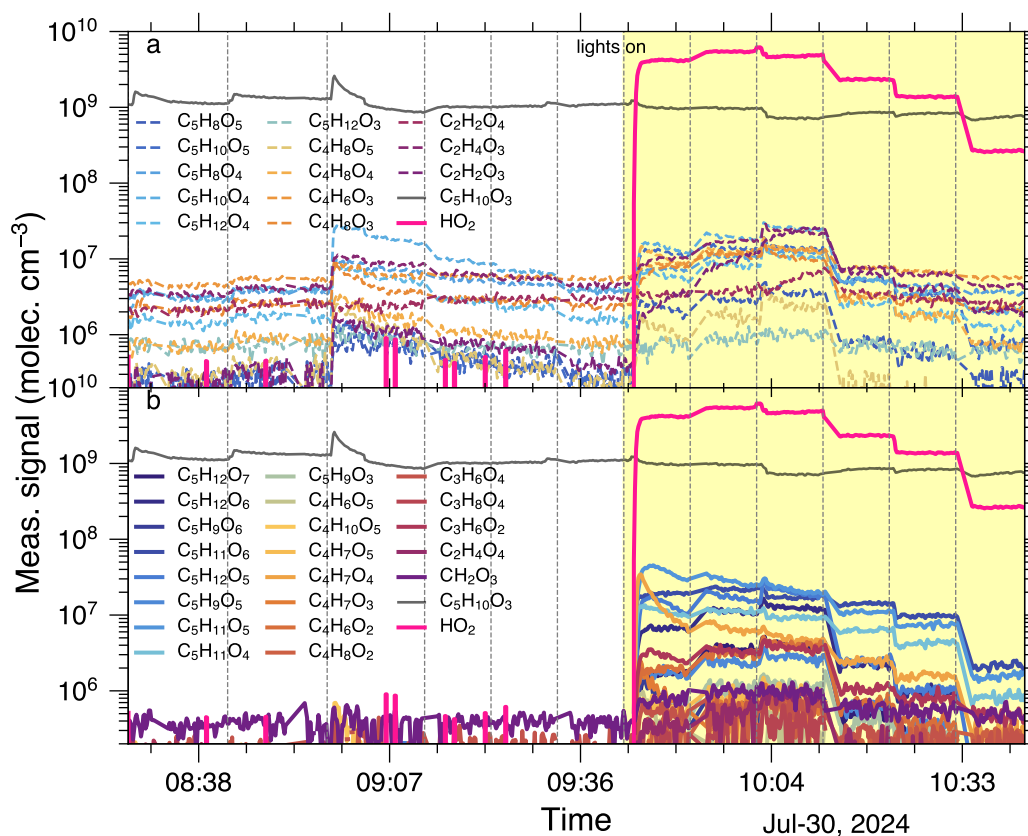
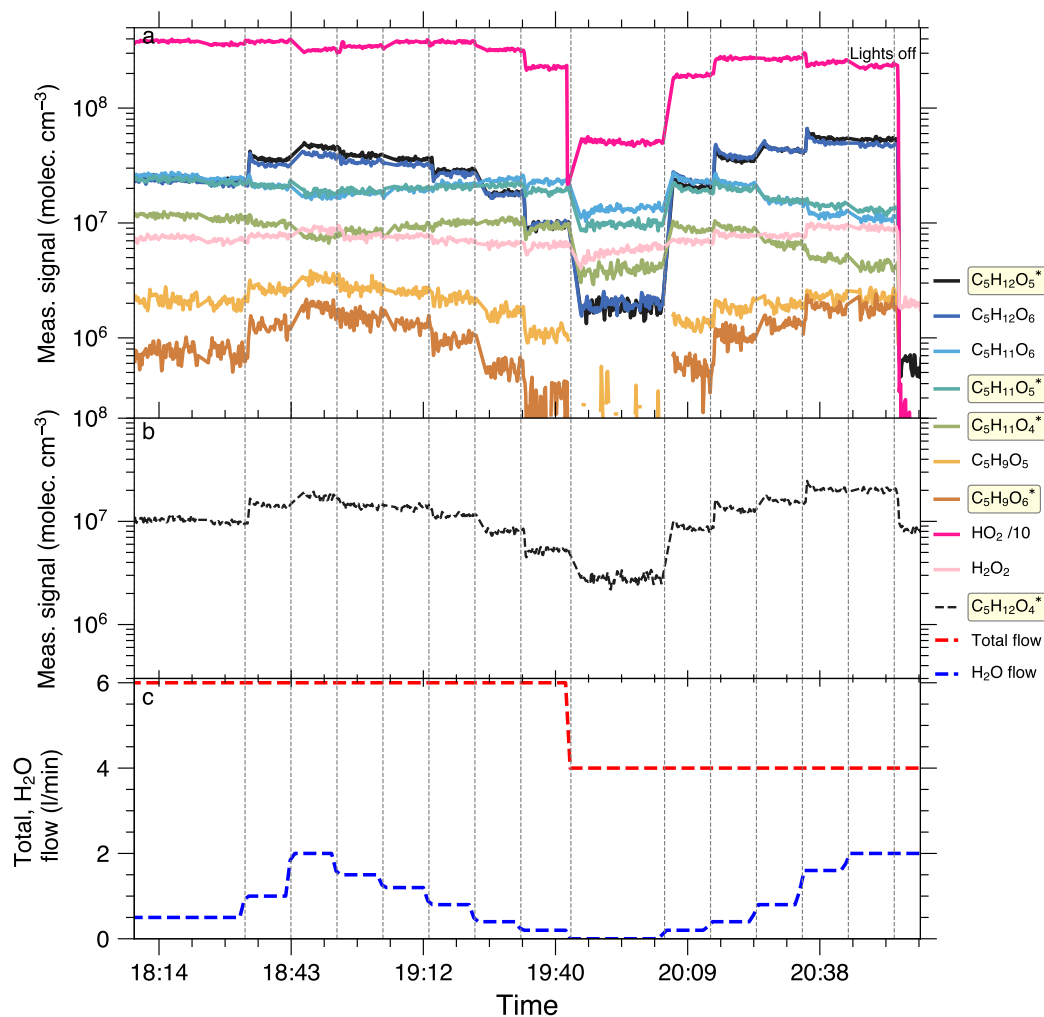


Figure A7. Assessment of 1,2-ISOPOOH sample purity and background from light-on and light-off comparisons. Signals that remain with the lights off (a) indicate background contributions from wall (aqueous-phase) reactions and from impurities in the 1,2-ISOPOOH sample, distinguishing these from the OH-initiated oxidation products that appear with the lights on (b).



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Figure A8. Selected species from the OH-initiated oxidation of 1,2-ISOPOOH of Figure 8, shown separately for clarity. The RO₂ radicals C₅H₁₁O₄, C₅H₁₁O₅, and C₅H₁₁O₆ decline as the H₂O flow (and hence OH) increases, while their C₅H₁₂O_x hydroperoxide products rise; C₅H₉O₅ and C₅H₉O₆ do not follow this pattern. Line styles and light-yellow boxes are as in Figure 8.

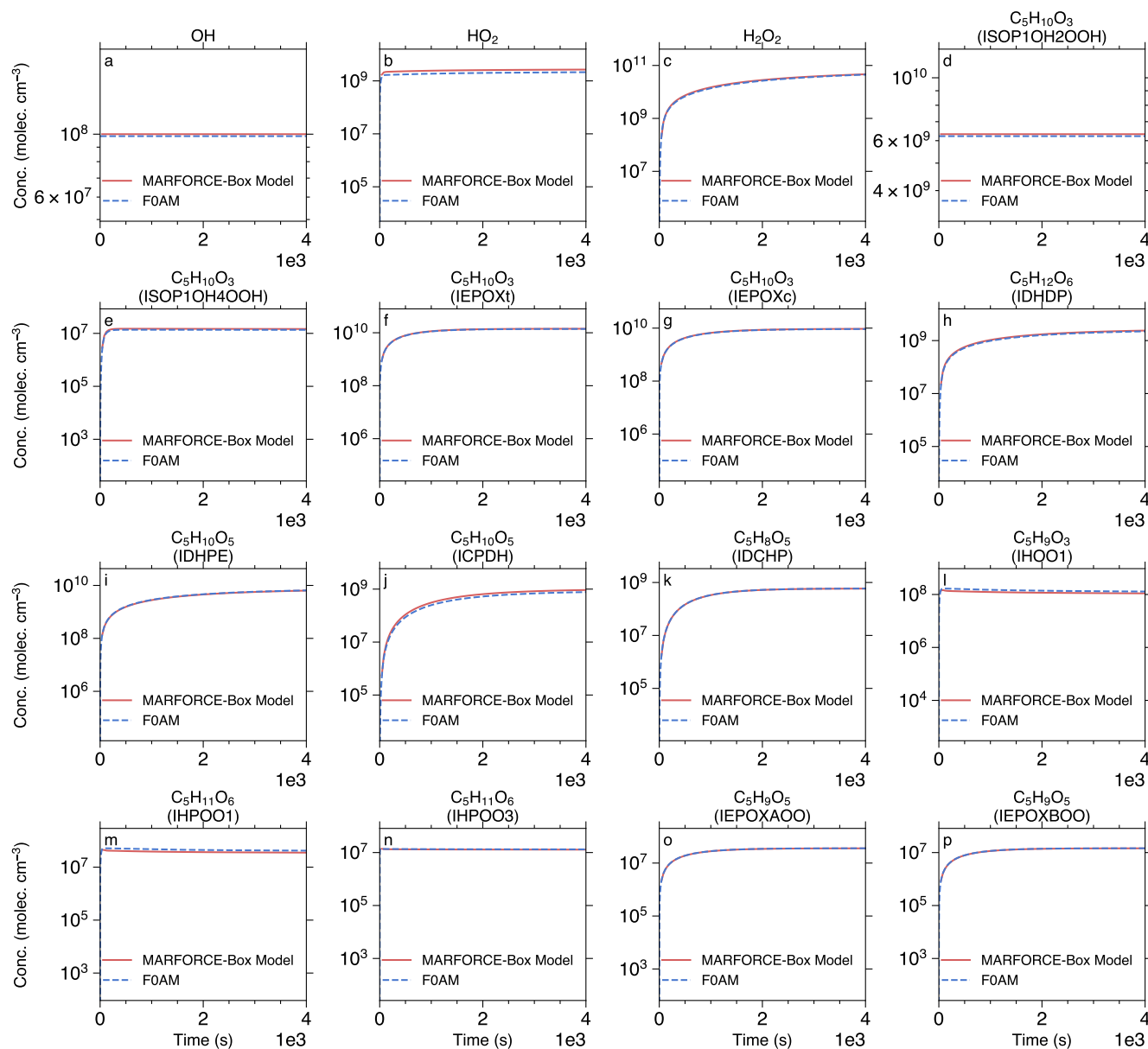


Figure A9. Comparison of key species between the MARFORCE box model and the F0AM box model for the 1,2-ISOPOOH + OH system, using identical initial conditions and the same reaction mechanism. The two models agree to within 2 % for all species, confirming that MARFORCE implements the gas-phase chemistry consistently.

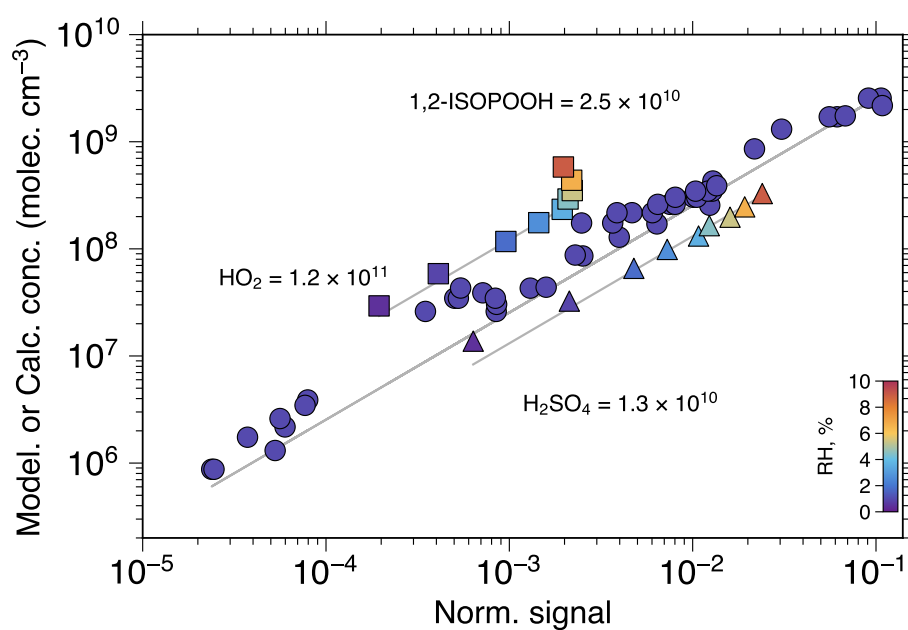


Figure A10. Calibration of the Br⁻-MION2-Orbitrap for 1,2-ISOPPOOH (using the LCU-a calibration unit) and for H₂SO₄ and HO₂ (using the H₂SO₄ calibration setup (He et al., 2023)). For each species, the reference vapour concentration (modelled or calculated) is plotted against the normalised signal, and the slope of the linear fit (solid grey lines) gives the species-specific calibration factor.

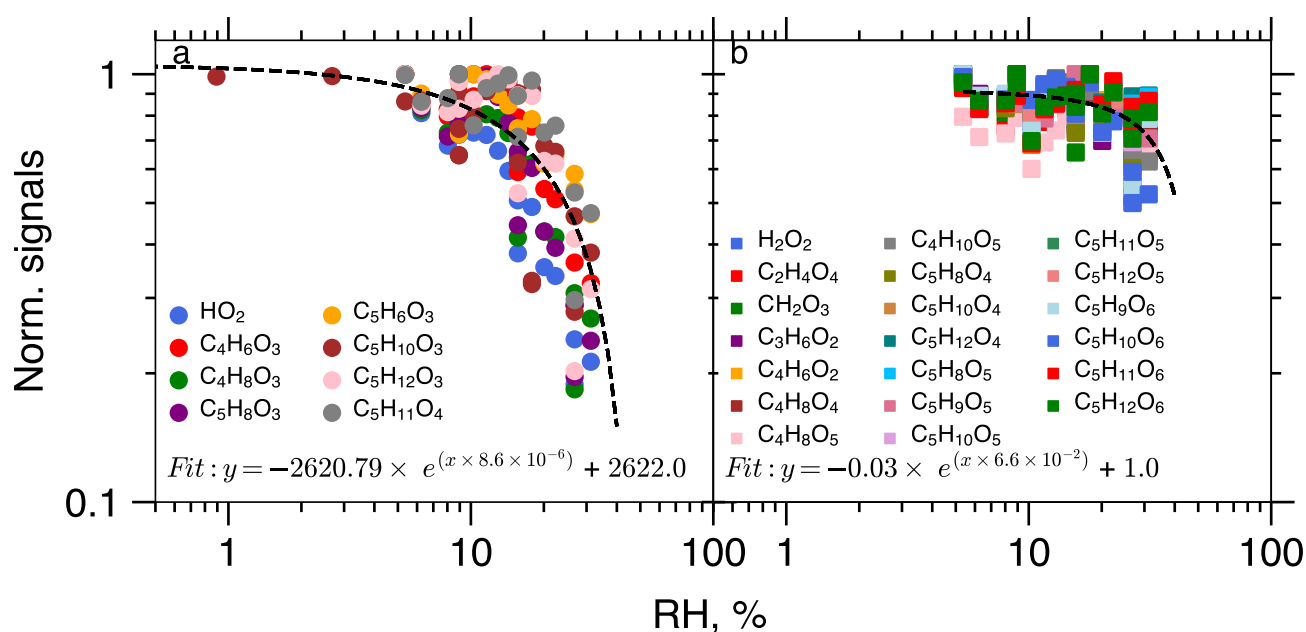


Figure A11. Effect of relative humidity (RH) on the detection efficiency of isoprene oxidation products in the flow-reactor experiments. For each species, the signal relative to dry conditions is shown as a function of RH (1-30 %); detection efficiency decreases with increasing RH as water competes with the analytes for clustering with Br^- . Species are split into two panels by the strength of their RH dependence: (a) a strongly RH-dependent group, with signals reduced by 50-80 % at 30 % RH, and (b) a more weakly dependent group, reduced by 20-40 %. Dashed lines are empirical fits of the RH response for each group, which can be used to apply RH corrections.



Table A1. Binding energies of selected isoprene oxidation products with the bromide anion (Br^-); the last column gives the corresponding species name in the Wennberg et al. (2018) mechanism.

Molecule	formation free enthalpies (kcal/mol)	Name in Wennberg et al.
$\text{C}_5\text{H}_{12}\text{O}_6$	33.5	dihydroxy-dihydroperoxide
$\text{C}_5\text{H}_{11}\text{O}_6$	34.4	ISOP1OH2OOH3OH4OO
$\text{C}_5\text{H}_{10}\text{O}_5$	33.3	dihydroxy-hydroperoxy-epoxide
$\text{C}_5\text{H}_{10}\text{O}_3$	27.5	ISOP1OH2OOH
$\text{C}_5\text{H}_8\text{O}_3_{\text{a}}$	24.6	hydroperoxy-carbonyl-isoprene beta-HPALD
$\text{C}_5\text{H}_8\text{O}_3_{\text{b}}$	24.1	hydroperoxy-carbonyl-isoprene delta-HPALD
$\text{C}_4\text{H}_8\text{O}_3_{\text{a}}$	25.8	DHMP
$\text{C}_4\text{H}_8\text{O}_3_{\text{b}}$	26.1	DHBO
HO_2	23.1	Hydroperoxyl
H_2O	13.2	Water

Author contributions. X.-C.H. and J.S. conceptualised the study. J.S. and X.-C.H. carried out the measurements and performed the data analysis with help from J.Z. and H.F. J.S., X.-C.H. and Y.L. wrote the manuscript with input from A.S., N.V., and Z.A. J.S. and X.-C.H. developed and ran the MARFORCE model simulations with input from P.Z. S.I. performed the quantum chemical calculations. Y.L., Z.A. and F.K. synthesised the 1,2-ISOPOOH sample. N.V. conducted 1,2-ISOPOOH quantification using nuclear magnetic resonance (NMR) spectroscopy. P.J., J.M., and A.S. supported the MION2 inlet and instrument operation. All authors discussed the results and commented on the manuscript.

Competing interests. Aleksei Shcherbinin works for Ultrace Trace Systems Oy, Ltd., Finland. Paxton Juuti and Jyri Mikkilä worked for Karsa, Ltd., Finland, before.

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