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Development and Characterization of the Airborne Chemical Ionization Mass Spectrometer FunMass-C for Atmospheric Trace Gas Measurements

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Contents

1	Introduction	1
1.1	Sulfur Chemistry and Climate	1
1.2	IAGOS-CARIBIC	3
1.3	Mass Spectrometry for Atmospheric Monitoring	6
1.3.1	Mass Analyzer	7
1.3.2	Ionization Methods	8
1.4	Motivation	11
2	Atmospheric Trace Gases	13
2.1	Hydrogen Cyanide	13
2.2	Sulfur Dioxide	15
3	Development of FunMass-C	25
3.1	Aspects of Key Components	25
3.1.1	Inlet	28
3.1.2	Scrubber	29
3.1.3	Vacuum Ultraviolet Lamp as Ion Source	39
3.1.4	Ion Molecule Reaction Zone	42
3.1.5	Time-of-Flight Mass Spectrometer	57
3.2	Chemical ionization within FunMass	66
3.2.1	Reagent Ion Precursor	68

4	Characterization and Calibration of FunMass-C	75
4.1	Calibration Rack	75
4.2	Insides of Detectable Species using CF_3O^-	82
4.3	Sensitivity	84
4.3.1	Theory	84
4.3.2	FunMass-C Calibration	87
4.4	CF_3OOCF_3 Dependence	94
4.5	Benzene Dependence	95
4.6	IS Flow Dependence	97
4.7	IMR Pressure Dependence	101
4.8	Total IMR Flow Dependence	103
4.9	IMR Temperature Dependence	108
4.10	Sensitivity Dependence on other Trace Gases	112
4.10.1	Water Vapor	112
4.10.2	Ozone	118
4.10.3	Isobaric Interference	121
4.11	Sensitivity Dependence on MCP Voltage	128
4.12	Computational Investigation of the CF_3O^- Ion Chemistry	133
4.13	Positive Mode	136
4.13.1	C_6H_6^+ - CIMS in FunMass	136
4.13.2	Calibration of DMS and NH_3	138
5	DMS oxidation at SAPHIR-STAR	142
5.1	Theory	142
5.2	SAPHIR-STAR	149
5.3	Experimental Details	151
5.3.1	The 2023 Campaign	151
5.3.2	The 2024 Campaign	154
5.4	FunMass at SAPHIR-STAR	156

CONTENTS

5.4.1	Setup	156
5.4.2	SO ₂ Calibration	158
5.5	Results	159
5.5.1	Dry Conditions	161
5.5.2	Humidification	178
5.5.3	NO Addition	190
5.5.4	Estimation of the HPMTF Calibration Factor for FunMass	199
6	Conclusions and Outlook	208
6.1	FunMass	208
6.2	DMS Oxidation	211
	Appendix	216
S1	Further Details of the Inlet Motor	216
S2	Further Details of the Scrubber Valve	218
S3	Further Details of the IMR	219
S4	Further Details of Characterization and Calibration of FunMass-C	224
S5	Further Details of IMR Ion Chemistry	225
S6	Further Details on DMS oxidation	226
	Bibliography	230

CONTENTS

List of Figures

1.1	Schematic of the relevant processes that govern the stratospheric aerosol life cycle and distribution. The large blue arrows indicate the large-scale circulation, while the red arrows indicate transport processes. The black arrows indicate chemical conversions between compounds. The different chemical species are marked as either gas phase (grey triangle) or aqueous phase (blue drop). The blue thin arrows represent sedimentation of aerosol from the stratosphere to the troposphere. Adapted from Kremser et al. (2016).	2
1.2	Annual mean top of the atmosphere radiative forcing due to aerosol– radiation interactions (RF _{atm} , in W m ⁻²) due to different anthropogenic aerosol types, for the 1750–2010 period. Hatched whisker boxes show median (line), 5th to 95th percentile ranges (box) and min/max values (whiskers) from AeroCom II models (Myhre et al., 2013) corrected for the 1750–2010 period. Solid colored boxes show the AR5 best estimates and 90 % uncertainty ranges. BC FF is for black carbon from fossil fuel and biofuel, POA FF is for primary organic aerosol from fossil fuel and biofuel, BB is for biomass burning aerosols and SOA is for secondary organic aerosols. Adapted from Boucher et al. (2013). .	4
1.3	Flight routes of CARIBIC Phase 2 (IAGOS-CARBIC, 2025).	5

2.1	Time-altitude section of monthly mean HCN mixing ratios from ACE-FTS [unit: ppbv] averaged between 15°S and 15°N latitude for 2005–2019. Gray solid dots represent vertical velocity estimated based on Mote et al. (1996) with the tape recorder head placed in October each year. Black solid dots indicate tape recorder signal starting in February 2016 (see text for details). Red solid contours are added to mark high HCN mixing ratios (0.25, 0.27, and 0.29 ppbv). Monthly mean tropopause height obtained from the NCEP/NCAR reanalysis (unit: km) is shown as a thick gray solid line. ACE-FTS, Atmospheric Chemistry Experiment Fourier Transform Spectrometer; HCN, hydrogen cyanide. Source: (Park et al., 2021).	14
2.2	Atmospheric sulfur budget from SOCOL-AERv2 under volcanically quiescent conditions for the year 2000. The figure is produced using output diagnostics that track sulfur fluxes and burdens within the planetary boundary layer (PBL), free troposphere, and stratosphere. Solid arrows show net fluxes and dashed arrows show one-way fluxes, all in gigagrams of sulfur per year (Gg S yr ⁻¹). Simulated burdens of sulfur species are given within the boxes, in units of gigagrams of sulfur (Gg S). Italicized numbers represent fluxes that are derived by balancing other fluxes, assuming steady state of the upper layers. For example, net cross-tropopause fluxes are calculated by balancing the stratospheric chemical fluxes and net cross-PBL fluxes are calculated by balancing the free tropospheric chemical fluxes. Upward OCS and sulfate aerosol cross-tropopause fluxes are calculated based on the residual meridional and vertical air velocities (v^* and w^*) and concentrations at the tropopause. Black numbers: SOCOL-AERv2 results. Red numbers: (a) SAGE-3 λ stratospheric aerosol burden (b) DMS emissions estimated by (Lana et al., 2011) (c) dry deposition fluxes from NCAR-CAM3.5 model (Lamarque et al., 2012) for the year 2000, which participated in ACCMIP (d) multimodel mean wet deposition from ACCMIP models for the year 2000 (Lamarque et al., 2012). Source: (Feinberg et al., 2019)	16

LIST OF FIGURES

2.3	Chemical mechanistic representation of (a) Gas-Phase Hydrolysis of SO_3 , (b) Water-Assisted Gas-Phase Hydrolysis of SO_3 , and (c) Molecule-Assisted Gas-Phase Hydrolysis of SO_3 (Torrent-Sucarrat et al., 2012). HY can be e.g., HCOOH , HO radical, or H_2O . X represents the corresponding bases of these species.	17
2.4	Effective Henry's law constant for SO_2 as a function of solution pH at 298 K (Seinfeld and Pandis, 2016.).	20
2.5	Concentrations of S(IV) species expressed as S(IV) mole fractions. These fractions are independent of the gas-phase SO_2 concentration (Seinfeld and Pandis, 2016.).	20
3.1	CAD sketch of FunMass-C. Source: Jochen Barthel.	26
3.2	Components of FunMass. Different colours indicate work done by different institutes: ICE-4 (blue) and TOFwerk (yellow). The complete structure and the housings indicated by the grey rectangles have been constructed and built by ITE.	27
3.3	Gas flowchart of FunMass-C deployed on IAGOS-CARIBIC. Source: Fred Strohm.	27
3.4	Inlet valve of FunMass-C. Source: Jochen Barthel.	28
3.5	Histogram (absolute counts of data points) of water vapor mixing ratio in ppm in the CARIBIC phase 2 data sets (10 s average; only data points above 5000 m) with bin size of 20 ppm (sky blue). The dashed red lines represent the three quartiles (18.5, 38.6, and 85.3 ppm). The minimum and maximum mixing ratios are 0 (below detection limit) and 10195.4 ppm (Zahn et al., 2024).	30
3.6	Histogram (absolute counts of data points) of ozone mixing ratio in ppb in the CARIBIC phase 2 data sets (10 s average; only data points above 5000 m) with bin size of 11 ppb (sky blue). The dashed red lines represent the three quartiles (57.49, 89.29, and 221.76 ppb). The minimum and maximum mixing ratios are 1.4 and 1138.75 ppb (Zahn et al., 2024).	30

3.7	Cross-section of the homemode scrubber valve in closed position (direct sampling of ambient air). The main block (beige) and the movable inset (turquoise) are made of PTFE and PFA, respectively. The PFA inset is moved by a pneumatic solenoid (light gray) from Festo (Model: short-stroke cylinder AEVC-16-10-A-P). Additionally, there are two 1/8" threads (in dark grey) to add a dilution or humidification flow (before PFA inset) and the calibration flow (after PFA inset), respectively. Source: Jochen Barthel.	31
3.8	The two positions of the scrubber valve in the xy-plane. Source: Jochen Barthel.	32
3.9	PFA inset with drilled holes to minimize flow distortion. Source: Jochen Barthel.	33
3.10	Relative decrease of the reagent ion due to the scrubber in % as a proxy of impurities emitted from the scrubber material.	34
3.11	Removing efficiency of water vapor of various materials. Upper panel: Total amount of water vapor from the calibration in ppm is represented by total light blue column (Scrubber off (total)). Residual water vapor going through the scrubber is colored hatched light blue. Lower panel: Baseline shift of water vapor signal in ppm due to the scrubber.	35
3.12	Removing efficiency of SO ₂ by various materials. Upper panel: Total amount of SO ₂ from the calibration in ppt is represented by the total light blue column (Scrubber off (total)). Residual or added SO ₂ going through the scrubber is colored hatched light blue or orange, respectively. Lower panel: Baseline shift of SO ₂ signal in ppt due to the scrubber.	37
3.13	Removing efficiency of HCN by various materials. Upper panel: Total amount of HCN from the calibration in ppt is represented by the total light blue column (Scrubber off (total)). Residual HCN going through the scrubber is colored hatched light blue. Lower panel: Baseline shift of HCN signal in ppt due to the scrubber.	37
3.14	Krypton VUV lamp Type PKS 106 from Heraeus (Lab-Club, 2025).	40
3.15	Customized mounting for the VUV lamp. Source: Jochen Barthel.	41

3.16 VUV spectrum of a Krypton lamp similar to the one used in FunMass-C, showing the two atomic line emissions at 116.5 nm (10.6 eV) and 123.6 nm (10 eV) (Northway et al., 2007). Note that the commercially available lamps are likely much weaker in output.	42
3.17 A schematic of the IMR (sample airflow from right to left). At the inlet, the scrubber valve (beige) with its inset (turquoise) is visible. The main IMR part is a stainless steel mixing tube (darkblue; 50 mm diameter) with a PTFE inset (beige). On each side of the mixing tube are G 1/8 threads to mount short 6 mm stainless steel tubes (darkblue) to supply VUV light (violet) and a little purge flow to keep the VUV windows (pink) in front of the lamp clean. The VUV beams from the lamps are reflected into themselves by two VUV mirrors (Edmund Optics; yellow) in order to enhance ion generation. A smaller aluminium cylinder (orange) is attached to the mixing tube in order to focus the airflow to the ToF inlet. A stainless steel plate (blue) with a small orifice (0.4 - 0.5 mm) is put in front of the ToF. It is isolated by a ceramic plate (red). The mixing tube is mounted in a 140 mm × 105 mm × 112 mm (L × W × H) aluminium box.	43
3.18 The stainless steel mixing tube with a inner diameter of 50 mm and two G 1/8 threads to plug in the ion source. Source: Jochen Barthel	44
3.19 IMR3 inset made of PTFE. Source: Jochen Barthel.	47
3.20 Technical drawing of the IMR3 inset made of PTFE. Source: Jochen Barthel.	48
3.21 Fluid dynamics CFX simulation inside the IMR3 version using ANSYS 2022 R1. The color code represents the velocity of the air in m/s. Source: Simon Heger (Josip Heger und Simon Heger GbR).	50
3.22 Fluid dynamics CFX simulation inside the IMR4 version using ANSYS 2022 R1. The color code represents the velocity of the air in m/s. Source: Simon Heger (Josip Heger und Simon Heger GbR).	50

3.23 Fluid dynamics CFX simulation inside the IMR4 version using ANSYS 2022 R1. The color code represents the N ₂ mass fraction introduced via the ion source. If both air flows (air inlet and ion source) are ideally mixed, the N ₂ mass fraction should be $2.982 \cdot 10^{-1}$. Source: Simon Heger (Josip Heger und Simon Heger GbR).	51
3.24 Cross-section of the IMR4. The airflow enters the system from the right side, first passing through the scrubber valve (see 3.7). It then enters the IMR, where the IMR inset is divided into three parts to facilitate the manufacturing process. The entire inset is made of SilcoNert2000®-coated aluminum. A portion of the airflow continues into the ToF through a nozzle, also made of SilcoNert2000®-coated aluminum. Perpendicular to the airflow, on both sides, VUV lamps (violet) illuminate channels flushed with a dedicated gas mixture. Source: Jochen Barthel.	52
3.25 The stainless steel mixing tube of IMR4. Source: Jochen Barthel	53
3.26 First part of the IMR4 made of SilcoNert2000®-coated aluminum. Source: Jochen Barthel.	53
3.27 Technical drawing of the first part of the IMR4 version made of SilcoNert2000®-coated aluminum with focus on the oblong hole. Source: Jochen Barthel.	54
3.28 Second part of the IMR4 made of SilcoNert2000®-coated aluminum. Source: Jochen Barthel.	54
3.29 Third part of the IMR4 made of SilcoNert2000®-coated aluminum. Source: Jochen Barthel.	55
3.30 Front plate of the mixing tube and second cylinder of the ion source made of SilcoNert2000®-coated aluminum for the IMR4. Source: Jochen Barthel.	55

3.31	Schematic of the ion source for the IMR4. Each VUV lamp (violet) has its own reagent ion mixture supply line, along with a separate nitrogen supply line to keep the windows (pink) clean. Upon entering the ion source tube, the reagent ion mixture flow and the VUV beam are oriented perpendicular to the IMR4 flow, preventing VUV light from entering the IMR4. To enhance ionization, the VUV beam is reflected by a VUV mirror (yellow), effectively doubling the beam path length. The ionized reagent ion flow then enters the IMR4 through the oblong holes. The inner wall of the IMR is illustrated in green to be better distinguished to the IS. Source: Jochen Barthel.	56
3.32	The dependence of the flow into the ToF (black) in SCCM, BSQ pressure (blue) in mbar, ToF pressure (orange) in mbar, and Turbo power consumption (red) in W on the IMR pressure in mbar for the IMR3 setup with the stainless steel ToF orifice	58
3.33	Schematic of the ion transfer stages and CToF analyzer	59
3.34	The minimum ToF pressure in hPa required to minimize collisions as function of the mean free path in m at 300 K for different kinetic diameters (265 pm (black), 360 pm (blue), and 590 pm (orange)). The red dashed line represents the minimum mean free path needed in FunMass.	62
3.35	SIS (in mV · ns) as function of the m/z (in Th). The SIS was determined five times within 7 hours under dry conditions and the MCP voltage was set to 2150 V. Average SIS: 1.3 - 1.32 mV · ns.	64
3.36	SIS (in mV · ns) over time and for various humidity levels. The SIS under dry condition is represented by black circles and under humidified conditions by orange circles. The blue circles present the water vapor mixing ratios (in ppm). The MCP voltages were turned on between 10:30 and 10:35 UTC. . .	65

3.37	Standard Gibbs free energy change of cluster formation, $\Delta_r G_0$ in kJ/mol, between neutral SO_2 and various ions (F^- , Cl^- , Br^- , I^- , O^- , and NO_3^-) in the gas phase. Note: The $[\text{SO}_2 \cdot \text{O}]^-$ cluster is formed through the reaction of SO_2 with CO_3^- . Data adapted from (Fehsenfeld and Ferguson, 1974; Keesee et al., 1980; Banic and Iribarne, 1985; Caldwell and Kebarle, 1985; Larson and McMahon, 1985).	67
3.38	Absorption cross section [$\text{cm}^2 \cdot \text{molecule}^{-1}$] in logarithmic scale within the wavelength range of 5 - 275 nm for the molecules CF_3OOCF_3 (black), CF_3CF_5 (red), SF_6 (green), and C_6H_6 (blue) (Blechschmidt et al., 1972; Chim et al., 2003; Meller and Moortgat, 1995; Ravishankara et al., 1993; Yoshino et al., 1973). The purple dashed lines indicate the two emission lines of the Kr VUV lamp (116.5 and 123.6 nm).	69
3.39	Spectrum of FunMass using BTP and benzene as precursor. The main signals are CF_3O^- (85 Th), $[\text{CF}_3\text{O} \cdot \text{H}_2\text{O}]^-$ (103 Th), $[\text{CF}_3\text{O} \cdot \text{HF}]^-$ (105 Th). The three larger impurity peaks can be assigned to HCl ($[\text{HF} \cdot \text{Cl}]^-$; 55 and 57 Th) and HCOOH ($[\text{HF} \cdot \text{HCOO}]^-$; 65 Th)	70
4.1	Funmass calibration rack. Source: Sarah Honold and Wilhelm Steffes.	76
4.2	Water vapor mixing ratio in ppm for various synthetic airflows in SCCM through the gas scrubber bottle containing liquid HPLC grade water. The main gas flow was set to 700 SCCM.	78
4.3	Ozone mixing ratio in ppb for varying pure oxygen flow in SCCM mixed into 200 SCCM nitrogen flow on three consecutive days (first day (black), second day (blue), and third day (orange)). The main gas flow was set to 2 SLM. . .	79
4.4	The emerging pressure gradient in hPa against the flow through the PTFE critical orifice in SCCM for various main airflows (1 SLM (black), 3 SLM (blue), and 5 SLM (orange) in the calibration rack.	81

LIST OF FIGURES

4.5	Relative proportion of the various clusters formed inside the IMR by 1.8 ppb HCN, 2.6 ppb HCl, and 1.2 ppb SO ₂ under dry conditions. X represents CN, Cl, and SO ₂ , respectively.	83
4.6	Raw signal of superoxide anion (orange) and its water cluster (black) in cps over time (s), with nitrogen (white-shaded) and synthetic air (gray-shaded) as carrier flows in the main airflow.	85
4.7	Calibration series for HCN (black), SO ₂ (orange), HCOOH (blue), and CH ₃ COOH (green) under dry and ozone-free conditions.	88
4.8	Calibration series of water vapor under ideal conditions. The calculated LOD(2 σ , 10 s) is 0.06 ppm.	89
4.9	Overlapping Allan deviation calculated from continuous calibration measurements of 922 ppt SO ₂ and 1017 ppt HCN over 1 hour at a 1.5 Hz sampling frequency.	91
4.10	The decay of the normalized signal (in ncps) after the calibration of 1.8 ppb HCN (black), 1.1 ppb SO ₂ (orange), 2.9 ppb HCOOH (green), and 2.8 ppb CH ₃ COOH (green). Dashed lines show the exponential fit, described in Equation 4.7, to the decays.	93
4.11	Relative sensitivity, which is the sensitivity normalized to the response at 0.2 SCCM of a 190 ppm CF ₃ OOCF ₃ /N ₂ mixture, shown for various CF ₃ OOCF ₃ mixture flow rates (in SCCM) added to 200 SCCM N ₂ (5.0). In orange the fluoride cluster of SO ₂ and in green the CF ₃ O ⁻ cluster of HCN are shown. . .	95
4.12	Relative sensitivity, which is the sensitivity normalized to the response at 3.5 SCCM of 0.7 % benzene mixed in N ₂ (5.0), shown for various benzene mixture flow rates (in SCCM) added to 200 SCCM N ₂ (5.0). In orange the relative sensitivity of the fluoride cluster of SO ₂ , in black the relative sensitivity of the CF ₃ O ⁻ cluster of HCN, and in blue the raw signal of CF ₃ O ⁻ in cps as a proxy for the TIC are shown.	96

4.13	Relative sensitivity, which is the sensitivity normalized to the response at 200 SCCM of the IS carrier flow (N ₂ 5.0 grade), shown for various IS carrier flow rates (in SCCM). In orange the relative sensitivity of the fluoride cluster of SO ₂ , in black the relative sensitivity of the CF ₃ O ⁻ cluster of HCN, and in blue the raw signal of CF ₃ O ⁻ in cps as a proxy for the TIC are shown.	98
4.14	Relative sensitivity, which is the sensitivity normalized to the response at 20 SCCM of the IS lamp flow (N ₂ 5.0 grade), shown for various IS lamp flow rates (in SCCM). In orange the relative sensitivity of the fluoride cluster of SO ₂ , in black the relative sensitivity of the CF ₃ O ⁻ cluster of HCN, and in blue the raw signal of CF ₃ O ⁻ in cps as a proxy for the TIC are shown.	100
4.15	Relative sensitivity, which is the sensitivity normalized to the response at 35 mbar, shown for various IMR pressures (in mbar). In orange the relative sensitivity the fluoride cluster of SO ₂ , and in black the relative sensitivity of the CF ₃ O ⁻ cluster of HCN. All the flows kept constant while varying the IMR pressure.	101
4.16	Relative proportion of the various clusters formed inside the IMR by adding 1.8 ppb HCN for different IMR pressures (in mbar).	102
4.17	Signal to noise ratio (1 σ , 10s) for various IMR pressures while adding 109 ppt HCN or 103 ppt SO ₂ , respectively. In orange the signal to noise ratio of the fluoride cluster of SO ₂ , and in black the signal to noise ratio of the CF ₃ O ⁻ cluster of HCN	103
4.18	Residence time inside the IMR (only for the mixing tube) in ms for various total IMR flows in SCCM. For the calculation of the residence time, ideal cylinders were assumed as well as a IMR pressure and temperature of 35 mbar and 303 K, respectively.	104

LIST OF FIGURES

4.19	Relative sensitivity, which is the sensitivity normalized to the response at a total IMR flow of 665 SCCM (HCN) and 685 SCCM (SO ₂) respectively, shown for various total IMR flows (in SCCM). In orange the relative sensitivity the fluoride cluster of SO ₂ , and in black the relative sensitivity of the CF ₃ O ⁻ cluster of HCN	105
4.20	Relative proportion of the various clusters formed inside the IMR by adding 0.95 - 1.0 ppb HCN (IMR mixing ratio) for different total IMR flows (in SCCM).106	
4.21	Signal to noise ratio (1 σ , 10s) for various total IMR flows while adding 61-84 ppt HCN or 46-79 ppt SO ₂ (IMR mixing ratios), respectively. In orange the signal to noise ratio of the fluoride cluster of SO ₂ , and in black the signal to noise ratio of the CF ₃ O ⁻ cluster of HCN is shown.	107
4.22	Relative sensitivities of HCN (black), SO ₂ (orange), and HCOOH (blue), normalized to the response at 303 K, as function of IMR temperature (in K). The dashed lines represent an exponential fit with the function $f(T) = a \cdot e^{-b \cdot (T-303)}$.108	
4.23	The logarithm of the relative sensitivities of HCN (black), SO ₂ (orange), and HCOOH (blue), normalized to the response at 303 K, as function of the inverse temperature (in 1/K). The dashed lines represent a linear fit.	110
4.24	Relative sensitivities of HCN (black), SO ₂ (orange triangles (2023) and circles (2025)), and HCOOH (blue), normalized to the response at 0 ppm water vapor as function of water vapor content (in ppm).	113
4.25	Relative proportion of the major clusters formed inside the IMR by adding 4.0 - 4.8 ppb HCOOH under various water vapor mixing ratios (in ppm).	115
4.26	LOD(2 σ , 10s) of HCN(black), SO ₂ (orange), and HCOOH (blue) at various water vapor mixing ratios (in ppm). The circles and triangles represent LOD calculated using the sensitivities under dry condition and water vapor-corrected sensitivities, respectively.	116
4.27	Relative sensitivities of HCN (black), SO ₂ (orange), and HCOOH (blue), normalized to the response at 20 ppb ozone as function of ozone mixing ratios (in ppb) for dry conditions.	118

LIST OF FIGURES

4.28	LOD(2σ , 10s) of HCN(black), SO ₂ (orange), and HCOOH (blue) at various ozone mixing ratios (in ppb). The circles and triangles represent LOD calculated using the sensitivities under ozone-free conditions and ozone-corrected sensitivities, respectively.	120
4.29	SO ₂ equivalent signal resulting from the addition of 4.0 – 4.8 ppb HCOOH under varying water vapor mixing ratios. The black circles represent the calculated SO ₂ equivalent using the sensitivity determined under dry conditions, while the orange circles show the values corrected for water vapor effects using the SO ₂ sensitivity derived under humid conditions.	123
4.30	SO ₂ equivalent signal resulting from the HCOOH addition at a water vapor mixing ratio of 600 ppm.	124
4.31	SO ₂ equivalent in ppt per 1 ppt HCOOH for various water vapor mixing ratios (in ppm). The black circle values are derived by adding 4 - 4.8 ppb HCOOH, while the orange circles are determined by a calibration row varying the HCOOH mixing ratios between 0 - 2.2 ppb.	125
4.32	HCN equivalent in ppt per 1 ppt SO ₂ for various ozone mixing ratios (in ppb).	127
4.33	HCN equivalent in ppt per 1 ppt SO ₂ for various water vapor mixing ratios (in ppm). The black circles represent the calculated HCN equivalent using the sensitivity determined under dry conditions, while the orange circles show the values corrected for water vapor effects using the sensitivity derived under humid conditions.	129
4.34	Relative sensitivity of SO ₂ , which is the sensitivity normalized to the response at 1.37 mV · ns for various SIS (in mV · ns).	130
4.35	The background-corrected normalized signal of the fluoride cluster of SO ₂ in ncps as function of SO ₂ mixing ratio in ppt. The black circles and orange circle represent calibrations using a SIS of 1.37 mV · ns and 0.95 mV · ns (at MCP voltages of 2150 and 2000 V), respectively.	132

4.36	Calculated relative energies for complexes formed between CF_3O^- and various interacting acids (HX). All energies are presented in kcal/mol, based on Coupled Cluster level of theory DLPNO-CCSD(T)/cc-pVQZ // B3LYP/def2-TZVP. “§” indicates bonding via fluorine atoms.	134
4.37	Reagent ion spectrum of FunMass in the positive mode with C_6H_6^+ as a reagent ion	137
4.38	Calibration using C_6H_6^+ - CIMS for DMS. The C_6H_6^+ cluster and the H^+ cluster of DMS (140 Th and 63 Th, respectively) are presented in black and orange, respectively.	139
4.39	Calibration using C_6H_6^+ - CIMS for NH_3 . The C_6H_6^+ cluster and the H^+ cluster of NH_3 (95 and 18 Th, respectively) are presented in black and orange, respectively.	140
5.1	Chemical mechanism for the gas-phase OH-oxidation of dimethyl sulfide. Simplified chemical mechanism for the production of carbonyl sulfide (OCS) in the gas-phase OH-oxidation of dimethyl sulfide and methanethiol. The mechanism shown here combines the work of Barnes et al. (1994) and the hydroperoxymethyl thioformate (HPMTF)-derived OCS production pathway proposed in Jernigan et al. (2022b). Source: Jernigan et al. (2022b)	145
5.2	Probability distribution of the estimated k_{isom} adapted from Ye et al. (2021). The dotted lines are retrieved using the data of Wu et al. (2015) (293 K), Berndt et al. (2019) (295 K), Veres et al. (2020) (298 K), Jernigan et al. (2022a) (298 K), Ye et al. (2021) (298 K), and Assaf et al. (2023) (298 K). The gray area represents the uncertainty range in Berndt et al. (2019).	148
5.3	Photograph of the SAPHIR-STAR chamber. Source: Sören Zorn.	149
5.4	Schematic of the SAPHIR-STAR chamber during the DMS oxidation experiments in 2023.	151
5.5	Setup of FunMass during the DMS oxidation experiment at SAPHIR-STAR in 2023 and 2024.	156

5.6	Comparison of the SO ₂ calibration using the 2 m PTFE tube (6 mm) and the other using the 53 cm SilcoNert2000®-coated SS tube (6 mm) connected to the 4 cm PFA tube (6 mm) via a PTFE 3-way valve.	159
5.7	The relative sensitivity of the SO ₂ calibration using its fluoride cluster as a function of the [H ₂ O ₂ · CF ₃ O] ⁻ to [CF ₃ O] ⁻ ratio in %.	160
5.8	DMS oxidation under dry conditions in 2023. (a) UV-C lamp opening (black; in %) and DMS concentration injected (orange; in ppb). (b) Temperature (black; in °C) and relative humidity (orange; in %). (c) Time series of H ₂ O ₂ (black; in ppb), O ₃ (orange; in ppb), and HO ₂ measured by the Br ⁻ mode of the MION (blue; in ncps). (d) SO ₂ measured by FunMass (black; in ppt) , H ₂ SO ₄ (orange; in ncps), and MSA (blue; in ncps) measured by the NO ₃ ⁻ mode of the MION. (e) Normalized signals (in ncps) of HPMTF (black), thioperformic acid (TPA; orange), and thioformic anhydride (TFA; blue) using the Br ⁻ mode of the MION.	162
5.9	Time series of the normalized HPMTF signals measured by NO ₃ ⁻ mode MION (black; 100 · ncps), I ⁻ HToF (orange; 2 · ncps), Br ⁻ mode MION (blue; 0.5 · ncps), and CF ₃ O ⁻ FunMass (green; 1 · ncps) during the DMS oxidation campaign in 2023 under dry conditions.	165
5.10	DMS oxidation under dry conditions in 2024. (a) UV-C lamp opening (black; in %) and the DMS consumption (orange; in ppb). (b) Temperature (black; in °C) and relative humidity (orange; in %). (c) Time series of H ₂ O ₂ (black; in ppb), O ₃ (orange; in ppb), and CO (blue; in ncps). (d) SO ₂ (black; in ppt) and its sensitivity (orange, ncps · ppt ⁻¹). (e) Normalized signal (in ncps) of HPMTF (black, FunMass), HO ₂ multiplied by 0.5 (blue; MION), H ₂ SO ₄ (green; MION), and MSA 8 · 10 ⁻² (red; MION). (f) OCS (black; in ppt) and the yield of SO ₂ (orange; in %S) and OCS (blue; in 10 · %S).	166
5.11	Estimated steady state OH concentration [OH] _{ss} in molecules · cm ⁻³ for various UV-C lamp opening positions in %.	168

5.12	The relative signal change in % of HPMTF (black) and SO ₂ (orange) for several UV-C lamp shielding changes under dry conditions.	171
5.13	The logarithmic normalized signal of HPMTF (black) and SO ₂ (orange) as a function of time since the lamp was turned off in seconds under dry conditions.	174
5.14	Time series of the normalized signals of HPMTF (black) and TFo (orange) in ncps under dry conditions.	176
5.15	Correlation between the baseline-corrected normalized signal of 81 Th in ncps against the baseline-corrected normalized signal of 61 Th in ncps under dry conditions. Dashed line represents the linear fit ($y = mx$).	177
5.16	DMS oxidation under humid conditions in October 2024. (a) UV-C lamp opening (black; in %) and DMS consumption (orange; in ppb). (b) Temperature (black; in °C) and relative humidity (orange; in %). (c) Time series of H ₂ O ₂ (black; in ppb, FunMass), O ₃ (orange; in ppb), and CO (blue; in ncps). (d) SO ₂ (black; in ppt; HCOOH-corrected) and its sensitivity (in orange, ncps · ppt ⁻¹), both measured by FunMass. (e) Normalized signal (in ncps) of HPMTF (black, FunMass), of H ₂ SO ₄ (green, MION), and MSA multiplied by 0.8 (red, MION). (f) OCS (black; in ppt) and the yield of SO ₂ (in %S) and OCS (in 10 · %S).	179
5.17	The relative signal change in % of HPMTF (black) and SO ₂ (orange) for several UV-C lamp shielding changes under humid conditions.	181
5.18	The logarithmic normalized signal of HPMTF (black) and SO ₂ (orange) as function of the time since the lamp was turned off in seconds under humid conditions (RH = 30 %).	182
5.19	The time series of the SO ₂ wall loss rates k_{wall} in s ⁻¹ for the several conditions: dry + OH (black), humid + OH (orange), dry + OH + NO (blue), and dry + NO ₃ (green).	185

5.20	DMS oxidation under humid conditions in November 2024. (a) UV-C lamp opening (black; in %) and DMS consumption (orange; in ppb). (b) Temperature (black; in °C) and relative humidity (orange; in %). (c) Time series of H ₂ O ₂ (black; in ppb, FunMass), O ₃ (orange; in ppb), and CO (blue; in ncps). (d) SO ₂ (black; in ppt; HCOOH-corrected) and its sensitivity (in orange, ncps · ppt ⁻¹), both measured by FunMass. (e) Normalized signal (in ncps) of HPMTF (black, FunMass), of H ₂ SO ₄ (green, MION), and MSA multiplied by 0.8 (red, MION). (f) OCS (black; in ppt) and the yield of SO ₂ (in %S) and OCS (in 10 · %S).	186
5.21	The normalized signal of HPMTF using the MION NO ₃ ⁻ mode (in black; 40 · ncps), HTof I ⁻ mode (in orange; ncps), MION Br ⁻ mode (in blue; ncps), and FunMass CF ₃ O ⁻ (in green; 3 · ncps) during the DMS oxidation campaign in 2023 for various relative humidity levels set (0, 20, 40, and 60 %) . Additionally, the relative humidity in the chamber (in %) is shown in red.	187
5.22	The relative sensitivity of HPMTF using the FunMass CF ₃ O ⁻ - CIMS for the chamber experiment in 2023 (black) and the water vapor addition to the inlet flow of FunMass in 2024 as function of the normalized water vapor signal in ncps.	189
5.23	DMS oxidation adding NO in 2023. (a) UV-C lamp opening (black; in %), UV-A lamp opening (orange; in %), NO injection aimed (blue; in ppb), NO monitor (green; in 10 · ppb), and NO _x monitor (red; in ppb). (b) Temperature (black; in °C) and relative humidity (orange; in %). (c) Time series of H ₂ O ₂ (black; in ppb), O ₃ (orange; in ppb), and HO ₂ measured by the Br ⁻ mode of the MION (blue; in ncps). (d) SO ₂ measured by FunMass (black; in ppt) , H ₂ SO ₄ (orange; in ncps), and MSA (blue; in ncps) measured by the NO ₃ ⁻ mode of the MION. (e) Normalized signals (in ncps) of HPMTF (black), thioperformic acid (TPA; orange), and thioformic anhydride (TFA; blue) using the I ⁻ - CIMS. . .	192

5.24	Time series of the normalized HPMTF signals measured by NO_3^- mode MION (black; $100 \cdot \text{ncps}$), I^- HToF (orange, $4 \cdot \text{ncps}$), Br^- mode MION (blue, $0.2 \cdot \text{ncps}$), and CF_3O^- FunMass (green; $1 \cdot \text{ncps}$) during the DMS oxidation campaign in 2023 for various NO injections (0, 5, 10, and 20 ppb). Additionally, the NO in the chamber (in ppb) is shown in red.	195
5.25	DMS oxidation adding NO in 2024. (a) UV-C lamp opening (black; in %), UV-A lamp opening (orange; in %), NO injection aimed (blue; in ppb), and NO_x monitor (green; in ppb).. (b) Temperature (black; in $^\circ\text{C}$) and relative humidity (orange; in %). (c) Time series of H_2O_2 (black; in ppb), O_3 (orange; in ppb), and CO (blue; in ncps). (d) SO_2 (black; in ppt) and its sensitivity (orange, $\text{ncps} \cdot \text{ppt}^{-1}$). (e) Normalized signal (in ncps) of HPMTF (black, FunMass), H_2SO_4 (blue; MION), and MSA multiplied by $3 \cdot 10^{-2}$ (green; MION), and the DMS consumption (orange; in ppb). (f) OCS (black; in ppt) and the yield of SO_2 (orange; in %S) and OCS (blue; in $10 \cdot \%S$).	197
5.26	Normalized signal of HPMTF in ncps using FunMass under varying NO additions (5, 10, and 20 ppb) and 150 ppb O_3	198
5.27	Estimated HPMTF sensitivity in $\text{ncps} \cdot \text{ppt}^{-1}$ as function of f_{isom} calculated using three different $k_{\text{HPMTF}+\text{OH}}$ ($0.24 \cdot 10^{-11} \text{ cm}^3\text{molecules}^{-1}\text{s}^{-1}$ in black, $1.4 \cdot 10^{-11} \text{ cm}^3\text{molecules}^{-1}\text{s}^{-1}$ in orange, and $2.4 \cdot 10^{-11} \text{ cm}^3\text{molecules}^{-1}\text{s}^{-1}$ in blue) according to Jernigan et al. (2022a). The shades represents the experimental error using the average of the three steady states.	202
5.28	Estimation of f_{isom} as a function of the $[\text{H}_2\text{O}_2]_{\text{SS}}$ for several isomerization rate constants (0.04 s^{-1} in black (Assaf et al., 2023; Veres et al., 2020), 0.1 s^{-1} in orange (Jernigan et al., 2022a; Ye et al., 2021), and 2.1 s^{-1} in blue (Wu et al., 2015)) using $k_{\text{HO}_2+\text{OH}} = 1.3 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$	205
5.29	Estimation of HPMTF mixing ratio (in ppt) under dry conditions for f_{isom} (0.15 in black, 0.4 in orange, and 0.8 in blue) The lower and upper limit represents $k_{\text{HPMTF}+\text{OH}} = 1.4$ and $2.4 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, respectively.	206

LIST OF FIGURES

S1.1 External linear actuator from Nanotec (Nema 6 model LSA141S03-A-TDBA-102 (Nanotec [®] , 2025).	217
S1.2 Amplified Piezo Actuator APA600M from CEDRAT TECHNOLOGIES (CEDRAT, 2025).	217
S1.3 Voltage supplied to piezo actuator in V against flow to IMR in SCCM. Source: Sarah Honold.	218
S2.1 Festo AEVC-16-10-A-P short-stroke cylinder used for the scrubber valve of FunMass-C (FESTO, 2025).	218
S3.1 IMR1 inset made of PTFE. Source: Jochen Barthel.	219
S3.2 The main reagent ion CF_3O^- (85 Th; black) and the background-corrected and to CF_3O^- normalized SO_2 signal (83 Th; orange), both normalized to their respective signals at 20 mm, as a function of the tube ending distance from the IMR1. The position 0 mm corresponds to the tube ending at the edge of the cone wall, with negative values indicating movement toward the cone wall. During the calibration 344 ppt SO_2 was introduced to FunMass.	221
S3.3 Technical drawing of the IMR2 inset made of PTFE. Source: Jochen Barthel.	222
S4.1 Gravimetric analysis of the permeation tubes	224
S6.1 The relative sensitivity of HPMTF using the MION NO_3^- mode (in black), MION Br^- mode (in orange), HToF I^- mode (in blue), and FunMass CF_3O^- (in green) as function of the relative humidity in the chamber (in %)	226
S6.2 The normalized background signal of HPMTF using the MION NO_3^- mode (in black; $40 \cdot \text{ncps}$), MION Br^- mode (in orange; ncps), HToF I^- mode (in blue; ncps), and FunMass CF_3O^- (in green; $3 \cdot \text{ncps}$). Additionally, the relative humidity (in %) in the chamber is shown in red.	227

S6.3	Gas-phase DMS + OH oxidation mechanism. Measured closed-shell products are shown in bold. Reactions in black are taken from MCM (Master Chemical Mechanism); reactions in red, related to hydroperoxymethyl thioformate (HPMTF, HOOCH ₂ SCHO) chemistry, are taken from Wu et al. (2015). Products that do not contain sulfur are not shown. The CH ₃ SO ₂ radical (marked in blue) represents a link between addition and abstraction pathway products. Note that several products are shown multiple times.	228
S6.4	Normalized signal of HONO (black) and HNO ₃ (orange) in ncps for the NO addition experiment in 2024. The shaded areas corresponds to measurement uncertainty (approx. 17%)	228
S6.5	Estimation of HPMTF mixing ratio (in ppt) under dry condition for f_{isom} (0.15 in black, 0.4 in orange, and 0.8 in blue) The lower and upper limit represents $k_{\text{HPMTF}+\text{OH}} = 1.4$ and $2.4 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, respectively. A wall loss rate of $1.0 \cdot 10^{-4} \text{ s}^{-1}$ was applied instead of the $0 \cdot 10^{-4} \text{ s}^{-1}$	229

List of Tables

3.1	Tested scrubber materials and their cleaning procedure	34
3.2	Summary of the applications of reagent ions for measuring trace species. Adapted from (Zhang et al., 2023).	66
4.1	Calibration characteristics of FunMass-C.	87
4.2	Reaction enthalpies determined using DFT calculation (B3LYP / def2-TZVP) in kcal/mol for the four reactions at 300 K. Source: Jan Meissner (Heinrichs- Heine University (HHU) in Düsseldorf).	111
5.1	Summary of the four DMS oxidation experiments in 2023	152
5.2	Summary of the CIMS used during the DMS oxidation experiments in 2023. .	153
5.3	Summary of the three DMS oxidation experiments in 2024	156
5.4	Summary of the parameters used to determine the HPMTF calibration factor.	201
S5.1	Calculated relative energies for complexes formed between CF_3O^- and various interacting molecules (X). All energies are presented in kcal/mol, based on Coupled Cluster level of theory DLPNO-CCSD(T)/cc-pVQZ // B3LYP/def2- TZVP. “§” indicates bonding via fluorine atoms.	225

LIST OF TABLES

List of Abbreviations

3D CTM Three-dimensional Chemical Transport Model.

AA Anion Abstraction.

ACCMIP Atmospheric Chemistry and Climate Model Intercomparison Project.

ACE-FTS Atmospheric Chemistry Experiment Fourier Transform Spectrometer.

ADQ1600 Analog-to-digital converter used by ToFwerk mass spectrometers.

AeroCom II Aerosol Comparisons between Observations and Models Phase II.

AIM Atmospheric Ionization Mass Spectrometer.

API-ToF Atmospheric Pressure Interface Time-of-Flight.

AR5 Fifth Assessment Report (IPCC).

ASM Asian Summer Monsoon.

BB Biomass Burning (Aerosols).

BC FF Black Carbon from Fossil Fuel and Biofuel.

BSQ Big Segmented Quadrupole.

BTP Bis(trifluoromethyl)peroxide.

C₆H₆⁺ Benzene Cation (reagent ion).

CAD Computer-Aided Design.

CARIBIC Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container (part of IAGOS infrastructure).

CD Corona Discharge.

CEDRAT CEDRAT TECHNOLOGIES (manufacturer of Amplified Piezo Actuator).

CFX Computational Fluid Dynamics.

CH₃CN Acetonitrile.

CH₃COOH Acetic Acid.

CH₃OOH Methyl Hydroperoxide.

CI Chemical Ionization.

CIMS Chemical Ionization Mass Spectrometry / Spectrometer.

Cl Chlorine Radical.

Cl₂ Chlorine.

Cl₂⁻ Dichloride Anion.

Cl⁻ Chloride Ion.

ClONO₂ Chlorine Nitrate.

CO Carbon Monoxide.

CO₂ Carbon Dioxide.

CO₃⁻ Carbonate Ion.

cps Counts Per Second.

CSTR Continuously Stirred Tank Reactor.

CT Charge Transfer.

CTOF Compact Time-of-Flight.

DEC Dissociative Electron Capture.

DFT Density Functional Theory.

DIAL Differential Absorption Lidar.

DLPNO-CCSD(T)/cc-pVQZ // B3LYP/def2-TZVP Coupled Cluster with Density Fitting and Perturbative Triples Correction using a Quadruple-Zeta Basis Set // Becke, 3-parameter, Lee–Yang–Parr functional with a triple-zeta valence plus polarization basis set (Computational Chemistry methods).

DLT-100 Delta Laser Technology-100.

dm-drogerie markt GmbH + Co. KG Ebelin German drugstore chain's brand of cosmetic materials.

DMS Dimethyl Sulfide.

DMSO Dimethyl Sulfoxide.

DMSO₂ Dimethyl Sulfone.

EA Electrophilic Addition.

EC Electron Capture.

ECC Electrochemical Concentration Cell.

EGU European Geosciences Union.

EI Electron Ionization.

EP Electron Providing Substance.

ESA European Space Agency.

ET Electron Transfer.

F Total Chamber Flow Rate.

f_{isom} Branching ratio between the isomerization pathway and the bimolecular reaction of MTMP.

F⁻ Fluoride Ion.

f_{abs} Branching ratio between abstraction and addition pathways in OH-initiated DMS oxidation.

FESTO Festo GmbH (manufacturer of pneumatic solenoid).

FIGAERO-CIMS Filter Inlet for Gases and AEROsols – Chemical Ionization Mass Spectrometer.

FISH Fast In situ Hygrometer.

FTIR Fourier Transform Infrared Spectroscopy.

FunMass-C FunMass IAGOS-CARIBIC version (CToF).

FunMass-L FunMass Laboratory version (HToF).

GC-MS Gas Chromatography – Mass Spectrometry.

Gg S Gigagrams of Sulfur.

Gg S yr⁻¹ Gigagrams of Sulfur per year.

H₂O Water.

H₂O₂ Hydrogen Peroxide.

H₂S Hydrogen Sulfide.

H₂SO₄ Sulfuric Acid.

HBr Hydrogen Bromide.

HCl Hydrogen Chloride.

HCN Hydrogen Cyanide.

HCOOH Formic Acid.

HF Hydrogen Fluoride.

HO₂ Hydroperoxy Radical.

HONO Nitrous Acid.

hPa Hectopascal.

HPLC High-Performance Liquid Chromatography.

HPMTF Hydroperoxymethyl Thioformate.

HToF High-Resolution Time-of-Flight.

I⁻ Iodide Ion.

IAGOS In-Service Aircraft for a Global Observing System.

IAGOS-CARIBIC Integrated project, formerly independent CARIBIC, now part of IAGOS.

IAGOS-Core A component of IAGOS that uses compact, automated instruments on multiple aircraft.

IASI Infrared Atmospheric Sounding Interferometer.

ICE Institute of Climate and Energy Systems.

IEK Institute for Energy and Climate Research.

IFS Integrated Flight System.

IMK Institute of Meteorology and Climate Research.

IMR Ion Molecule Reaction Zone.

In-situ In place, on-site measurement.

IP Ionization Potential.

IPF Ion-Pair Formation.

IS Ion Source.

ITE Institute of Technology and Engineering.

JPAC Jülich Plant-Atmosphere Chamber facility.

JPL Jet Propulsion Laboratory.

k_{dil} Dilution Rate.

k_{HPMTF+OH} Rate coefficient for the reaction of HPMTF with OH radicals.

k_{isom} Isomerization Rate Constant.

k_{OH} Bimolecular rate constant for the reaction between DMS and OH.

k_{wall} Wall Loss Rate.

KIT Karlsruhe Institute of Technology.

LC-MS Liquid Chromatography – Mass Spectrometry.

LIF Laser-Induced Fluorescence.

LOD Limit of Detection.

LSR Lower Stratosphere.

m/q Mass-to-charge ratio.

MBL Marine Boundary Layer.

MCM v3.3.1 Master Chemical Mechanism version 3.3.1.

MCP Microchannel Plate (detector).

MFC Mass Flow Controller.

MFM Mass Flow Meter.

Mg_x(OH)_y(CO₃)_z Magnesium Hydroxide Carbonate.

MgCO₃ Magnesium Carbonate.

MgF₂ Magnesium Fluoride.

MICA Mid-Infrared Cavity enhanced Absorption spectrometer.

MION Multi-scheme chemical ionization inlet.

MIPAS Michelson Interferometer for Passive Atmospheric Sounding.

MPI-C Max Planck Institute for Chemistry.

MS Mass Spectrometry / Spectrometer.

MSA Methane Sulfonic Acid.

MSIA Methanesulfinic Acid.

MTF Methylthioformate.

MTMP Methylthiomethyl Peroxy Radical.

N₂ Nitrogen.

N₂O₅ Dinitrogen Pentoxide.

NA Nucleophilic Addition.

NASA National Aeronautics and Space Administration.

NATEC Natec Sensors GmbH.

NBP Net Biome Production.

NCEP/NCAR National Centers for Environmental Prediction / National Center for Atmospheric Research.

ncps Normalized Counts Per Second.

NH₃ Ammonia.

NH₄⁺ Ammonium Ion.

NICI Negative Ion Chemical Ionization.

NO Nitric Oxide.

NO₃ Nitrate Radical.

NO₃⁻ Nitrate Ion.

NO_x Nitrogen Oxides.

NTC Negative Temperature Coefficient (thermistor).

O₂ Oxygen.

O₂⁻ Superoxide Anion.

O₃ Ozone.

O⁻ Oxygen Anion.

OCS Carbonyl Sulfide.

OH Hydroxyl Radical.

OH⁻ Hydroxyl Anion.

OMI Ozone Monitoring Instrument.

PBL Planetary Boundary Layer.

PICI Positive Ion Chemical Ionization.

PID Proportional-Integral-Derivative (controller).

Po Polonium.

POA FF Primary Organic Aerosol from Fossil Fuel and Biofuel.

ppb Parts per billion.

ppbv Parts per billion by volume.

ppm Parts per million.

ppmv Parts per million by volume.

ppt Parts per trillion.

PT Proton Transfer.

PT100 Platinum Resistance Thermometer 100.

PTFE Polytetrafluoroethylene.

PTR-MS Proton-Transfer-Reaction Mass Spectrometry.

RFari Radiative Forcing due to Aerosol–Radiation Interactions.

RH Relative Humidity.

RO₂ Peroxy Radicals.

ROOH Organic Hydroperoxides.

S(IV) Sulfur in oxidation state +4.

S(VI) Sulfur in oxidation state +6.

SAPHIR-STAR Simulation of Atmospheric PHotochemistry In a large Reaction chamber
– Stirred Atmospheric flow Reactor.

SCCM Standard Cubic Centimeters per Minute.

SF₅⁻ Sulfur Pentafluoride Anion.

SF₆ Sulfur Hexafluoride.

SF₆⁻ Sulfur Hexafluoride Anion.

SIS Single Ion Signal.

SLM Standard Liters per Minute.

SO₂ Sulfur Dioxide.

SO₃ Sulfur Trioxide.

SO_x Sulfur Oxides.

SOA Secondary Organic Aerosols.

SOCOL-AERv2 Solar Climate Ozone Links – Aerosol version 2 (model).

SS Stainless Steel.

SSQ Small Segmented Quadrupole.

T Temperature.

TFA Thioformic Anhydride.

TFo Thioformic Acid.

Tg(S) yr⁻¹ Teragrams of Sulfur per year.

Th Thomson (unit for mass-to-charge ratio).

TIC Total Ion Count.

TME Tetramethylethene.

TMSPF Trifluoromethoxy Sulfur Pentafluoride.

ToF Time-of-Flight (Mass Spectrometer).

ToF-CIMS Time-of-Flight Chemical Ionization Mass Spectrometer.

TPA Thioperformic Acid.

TPI Thermal Process Intensification.

TROPOMI Tropospheric Monitoring Instrument.

UTLS Upper Troposphere and Lower Stratosphere.

UV Ultraviolet.

UV-A Ultraviolet A.

UV-C Ultraviolet C.

VOC Volatile Organic Compound.

VUV Vacuum Ultraviolet.

VUV-IS Vacuum Ultraviolet Ion Source.

ZE-1 Central Institute of Engineering, Electronics and Analytics: Engineering.

ZE-2 Central Institute of Engineering, Electronics and Analytics: Electronic Systems.

Abstract

This dissertation focuses on the further development and comprehensive characterization of the state-of-the-art airborne chemical ionization mass spectrometer FunMass-C. FunMass-C was specifically developed for the regular in-situ measurement of various trace gases in the upper troposphere and lower stratosphere (UTLS). These include sulfur dioxide (SO_2), hydrogen cyanide (HCN), other inorganic and organic acids, and hydroperoxides. Starting in 2026, FunMass-C will be deployed on a Lufthansa Airbus A350 as part of the IAGOS-CARIBIC infrastructure to provide global, high-resolution atmospheric data.

The work describes the new development and optimization of central FunMass-C components, including the Ion-Molecule Reaction (IMR) zone and the ion source (IS), which is based on vacuum UV lamps. Trifluoromethoxide (CF_3O^-) is primarily used as the reagent ion for chemical ionization.

Some materials were tested as scrubbers to selectively remove SO_2 and HCN from the sample air, while keeping other conditions, especially water vapor content, as constant as possible.

The positive ionization mode with benzene (C_6H_6^+) as the reagent ion also enabled the detection of dimethyl sulfide (DMS) and ammonia (NH_3).

FunMass-C achieves high sensitivity in the order of 10^{-5} ncps $\cdot$ ppt $^{-1}$ and low detection limits (LOD(2σ , 10 s) of 2 to 9 ppt) for most target species (SO_2 , HCN, formic acid (HCOOH), acetic acid (CH_3COOH), and hydrogen chloride (HCl)). For DMS in the positive mode, an LOD(2σ , 10 s) of 0.6 ppt was achieved. The influence of water vapor and ozone on sensitivity and LODs was studied in detail. Water vapor and ozone mainly lead to a decrease in sensitivity and an increase in signal noise. Isobaric interferences, such as that of HCOOH on the SO_2

signal or SO₂ on the HCN signal, were quantified. These interferences can significantly affect measurement accuracy and require corresponding corrections, especially with increased humidity or ozone concentration.

Theoretical calculations of the ion chemistry of CF₃O⁻ showed that weak acids preferentially form CF₃O⁻ clusters, while strong acids lead to the protonation of CF₃O⁻ and subsequent catalytic decomposition of CF₃OH, with their fluoride clusters being detected. The decomposition of CF₃OH can significantly be catalytically accelerated by water vapor and acids. This will help to better understand ion reactions inside the IMR, which allows to predict potential by-products and isobaric interferences.

DMS oxidation experiments were a further focus of the work, conducted in the SAPHIR-STAR simulation chamber in 2023 and 2024. The oxidation of DMS was investigated under dry, humid, and NO_x-influenced conditions. Hydroperoxymethylthioformate (HPMTF), an important intermediate, was successfully detected using various CIMS techniques (NO₃⁻, Br₃⁻, I₃⁻ and CF₃O⁻). The yields of SO₂ and carbonyl sulfide (OCS) were determined under dry conditions, with values of 28–40 % S for SO₂ and 3–5 % S for OCS.

It was shown that increased humidity can increase the sensitivity of HPMTF up to a factor of 3 for CF₃O⁻. The NO_x experiments indicate that the NO₃⁻ and Br⁻ modes of the Multi-scheme chemical ionization atmospheric-pressure-interface long-time-of-flight mass spectrometer (MION API-LTOF) are strongly negatively affected by the addition of NO, therefore HPMTF measurement data from MION API-LTOF during NO addition cannot be used. An isobaric interference of N₂O₅ on HPMTF for the CF₃O⁻-CIMS (FunMass-C) was ruled out. A first estimate of the HPMTF calibration factor for FunMass was derived, which is in the same order of magnitude (10⁻⁶ ncps · ppt⁻¹) as that for H₂O₂.

Zusammenfassung

Diese Dissertation befasst sich mit der Weiterentwicklung und umfassenden Charakterisierung des hochmodernen flugzeuggetragenen chemischen Ionisations-Massenspektrometers FunMass-C. Das Gerät wurde speziell für die regelmäßige in-situ-Messung verschiedener Spurengase, einschließlich Schwefeldioxid (SO_2), Cyanwasserstoff (HCN), andere anorganischer und organischer Säuren sowie Hydroperoxide, in der oberen Troposphäre und unteren Stratosphäre (UTLS) entwickelt. FunMass-C wird ab 2026 im Rahmen der IAGOS-CARIBIC-Infrastruktur auf einem Lufthansa Airbus A350 eingesetzt, um globale, hochauflösende atmosphärische Daten zu liefern.

Die Arbeit beschreibt die Neuentwicklung und Optimierung zentraler Komponenten von FunMass-C, darunter die Ionen-Molekül-Reaktionszone (IMR) und die Ionenquelle, die auf Vakuum-UV-Lampen basiert. Für die chemische Ionisation wird hauptsächlich Trifluormethoxid (CF_3O^-) als Reagenz-Ion verwendet.

Zudem wurde einige Materialien als Scrubber getestet, um SO_2 und HCN selektiv aus der Probenluft zu entfernen, während andere Bedingungen, insbesondere der Wasserdampfgehalt, möglichst konstant bleiben.

Der positive Ionisationsmodus mit Benzol (C_6H_6^+) als Reagenz-Ion ermöglichte zudem den Nachweis von Dimethylsulfid (DMS) und Ammoniak (NH_3).

FunMass-C erreicht eine hohe Sensitivität in der Größenordnung von 10^{-5} ncps $\cdot$ ppt $^{-1}$ und niedrige Nachweisgrenzen, LOD(2σ , 10 s) von 2 bis 9 ppt für die meisten Zielspezies (SO_2 , HCN, Ameisensäure (HCOOH), Essigsäure (CH_3COOH) und Chlorwasserstoff (HCl)). Für DMS wurde im positiven Modus LOD(2σ , 10 s) von 0,6 ppt erreicht. Des Weiteren wurde der Einfluss von Wasserdampf und Ozon auf die Sensitivität und LODs detailliert untersucht.

Wasserdampf und Ozon führen hauptsächlich zu einer Verringerung der Sensitivität und zu einer Erhöhung des Signalrauschens. Isobare Interferenzen, wie die von HCOOH auf das SO₂-Signal oder von SO₂ auf das HCN-Signal, wurden quantifiziert. Diese Interferenzen können die Messgenauigkeit erheblich beeinflussen und erfordern entsprechende Korrekturen, insbesondere bei erhöhter Feuchtigkeit oder Ozonkonzentration.

Theoretische Berechnungen der Ionenchemie von CF₃O⁻ zeigten, dass schwache Säuren bevorzugt CF₃O⁻-Cluster bilden, während starke Säuren zur Protonierung von CF₃O⁻ und der anschließend Zersetzung von CF₃OH führen, wobei dahingehend deren Fluorid-Cluster nachgewiesen werden. Der Zetzungsprozess von CF₃OH kann durch Wasserdampf und Säuren katalytisch beschleunigt werden. Diese Ergebnisse helfen, die Ionenchemie besser zu verstehen und zudem potentielle Nebenprodukte und isobare Interferenzen vorherzusagen.

Ein weiterer Schwerpunkt der Arbeit waren die DMS-Oxidationsexperimente, die in den Jahren 2023 und 2024 in der SAPHIR-STAR-Simulationskammer durchgeführt wurden

Die Oxidation von DMS wurde unter trockenen, feuchten und NO_x-beeinflussten Bedingungen untersucht. Hydroperoxymethylthioformiat (HPMTF), ein wichtiges Zwischenprodukt, konnte erfolgreich mit verschiedenen CIMS-Techniken (NO₃⁻, Br⁻, I⁻ und CF₃O⁻) nachgewiesen werden. Die Ausbeuten von SO₂ und Carbonylsulfid (OCS) wurden unter trockenen Bedingungen bestimmt, mit Werten von 28–40 % S für SO₂ und 3–5 % S für OCS

Es konnte gezeigt werden, dass erhöhte Luftfeuchtigkeit die Sensitivity von HPMTF bis zu einem Faktor 3 für CF₃O⁻ erhöhen kann. Die NO_x-Experimente weisen daraufhin, dass der NO₃⁻ und Br⁻ Modus des Mehrschema chemische Ionisations Atmosphärendruck-Interface Langzeit-Flugzeit-Massenspektrometers (MION API-LTOF) stark negativ durch die Zugabe von NO beeinflusst wird und daher die HPMTF Messdaten des MION API-LTOFs während der NO-Zugabe nicht verwendet werden können. Außerdem wurden eine isobare Interferenz von N₂O₅ auf HPMTF für das CF₃O⁻ - CIMS (FunMass-C) ausgeschlossen. Es wurde eine erste Abschätzung des HPMTF-Kalibrierfaktors für FunMass abgeleitet, die in der gleichen Größenordnung (10⁻⁶ ncps · ppt⁻¹) wie der für H₂O₂ liegt.

Chapter 1

Introduction

1.1 Sulfur Chemistry and Climate

Sulfur chemistry plays a critical role in atmospheric composition, aerosol formation, and climate regulation. The key emitted sulfur species are dimethyl sulfide (DMS), carbonyl sulfide (OCS), and sulfur dioxide (SO_2). They are emitted naturally (e.g., DMS emissions by phytoplanktons or emitted SO_2 due to volcanic eruptions) and partially anthropogenically (e.g., SO_2 emission of industry) as shown in figure 1.1. The tropospheric and stratospheric oxidation of the sulfur species ends ultimately in sulfuric acid (H_2SO_4 or dissolved sulfate. H_2SO_4 is an important molecule for aerosol formation. In the troposphere, aerosols can affect human health and the air quality, especially in larger cities. Moreover, they can provide surfaces and hence, influence the tropospheric chemistry (heterogeneous chemistry). However, sulfate aerosols have a more important role for the climate in the stratosphere. Junge et al. (1961) found a global aerosol layer, mainly composed of aqueous sulfuric acid, in the lower stratosphere (approximately 15–25 km in altitude). This region plays a key role in Earth’s radiation budget as sulfate aerosols are reflective and effectively scatter incoming shortwave radiation back to space, leading to net cooling of the Earth’s surface (Kremser et al., 2016). Volcanic eruptions like the Pinatubo in 1991 can influence the climate globally, particular having a cooling effect, due to the perturbation of the stratospheric aerosol layer (Thompson et al., 2009; Canty et al., 2013; Wunderlich and Mitchell, 2017). But also the non-volcanic

1.1. SULFUR CHEMISTRY AND CLIMATE

time periods, the (background) stratospheric aerosol layer is crucial for the global radiative budget. Moreover, heterogeneous chemistry on the stratospheric aerosol can also have a significant effect on the ozone (Solomon, 1999).

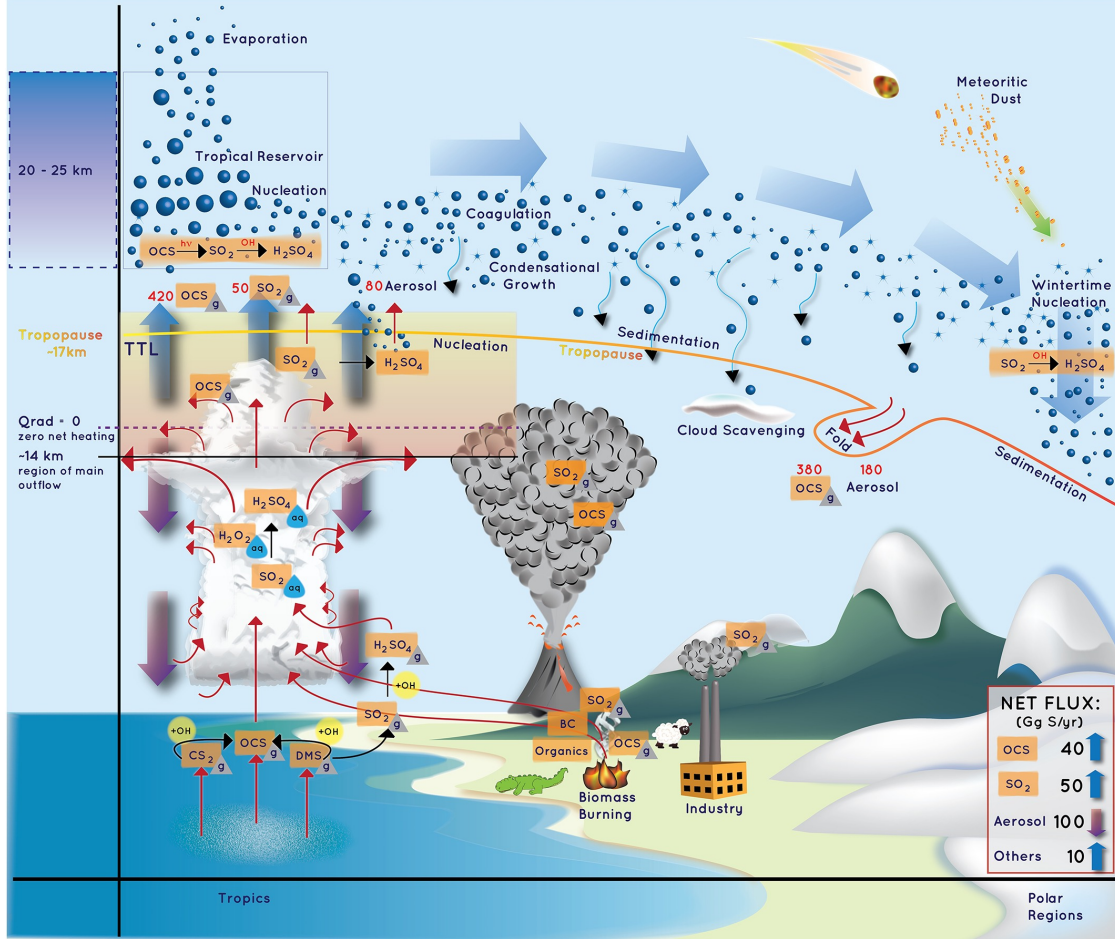


Figure 1.1: Schematic of the relevant processes that govern the stratospheric aerosol life cycle and distribution. The large blue arrows indicate the large-scale circulation, while the red arrows indicate transport processes. The black arrows indicate chemical conversions between compounds. The different chemical species are marked as either gas phase (grey triangle) or aqueous phase (blue drop). The blue thin arrows represent sedimentation of aerosol from the stratosphere to the troposphere. Adapted from Kremser et al. (2016).

Figure 1.2 shows the large uncertainties in the radiative effect of (sulfate) aerosols (Boucher et al., 2013). Moreover, large uncertainties remain with respect to the contribution from anthropogenic sulfur dioxide emissions (Kremser et al., 2016). Stratospheric aerosol can also contain small amounts of non-sulfate matter such as black carbon and organics. The impact of non-sulfate materials on stratospheric aerosol formation is not well understood, but is

considered to be small. However, their contribution can increase due to enhancing wildfires (e.g. Australian and Canadian wildfires) (Boer et al., 2020; Khaykin et al., 2020; Kloss et al., 2021).

Besides the well-established satellite measurements of stratospheric aerosol and its precursor molecules (e.g., SO_2), non-regularly in-situ measurements of the precursor in the upper troposphere and lower stratosphere (UTLS) are carried out. Especially, SO_2 as the direct precursor of H_2SO_4 and HCN as a typical biomass burning tracer are interesting molecules for investigation. IAGOS-CARIBIC provides a platform for regular and global flights in the UTLS (more details in Section 1.2).

1.2 IAGOS-CARIBIC

The IAGOS-CARIBIC (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container), which utilizes commercial passenger aircraft to conduct atmospheric measurements, is part of the European research infrastructure IAGOS (In-Service Aircraft for a Global Observing System). Using long-haul passenger aircraft is much more cost effective than research aircraft and allows regular measurements and high global coverage (Brenninkmeijer et al., 1999).

The goal of IAGOS-CARIBIC is to improve the understanding of the processes in the global atmosphere, focusing on the upper troposphere and lower stratosphere (UTLS). The UTLS plays a major role in radiative forcing, chemistry, and dynamical coupling (Shepherd, 2007). Furthermore, the UTLS is an important region in the Earth atmosphere due to its large climate sensitivity. Riese et al. (2012) showed that variations in the structure and chemical composition (e.g. changes in water vapor) can cause relatively large effects on the radiative forcings of the atmosphere. Therefore, a crucial task is to better understand the UTLS and its processes to improve climate predictions.

The CARIBIC project was started in 1997. In this first phase (CARIBIC phase 1), a Boeing 767ER from LTU airlines was used to deploy a “strongly modified LD4 air freight container with six instruments (including a large air sampler)” (IAGOS-CARIBIC, 2025).

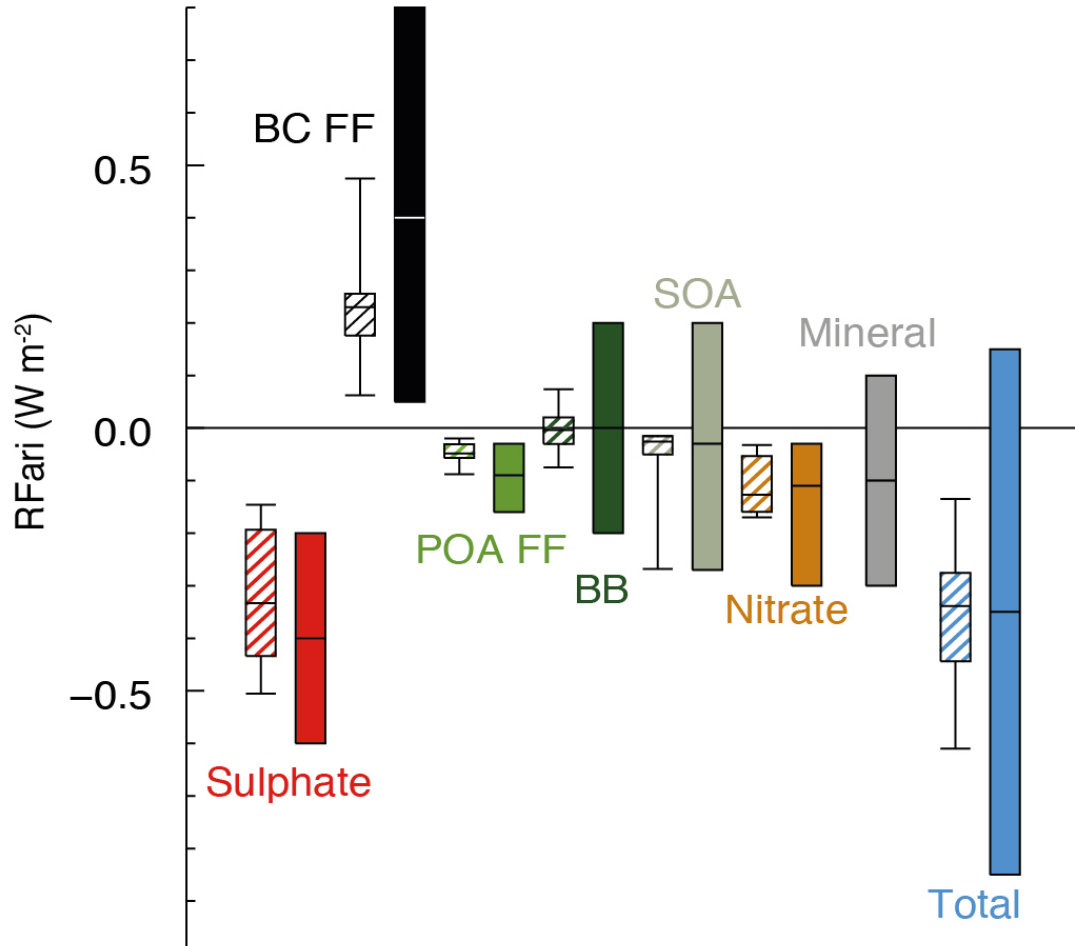


Figure 1.2: Annual mean top of the atmosphere radiative forcing due to aerosol– radiation interactions (RF_{ari} , in $W m^{-2}$) due to different anthropogenic aerosol types, for the 1750–2010 period. Hatched whisker boxes show median (line), 5th to 95th percentile ranges (box) and min/max values (whiskers) from AeroCom II models (Myhre et al., 2013) corrected for the 1750–2010 period. Solid colored boxes show the AR5 best estimates and 90 % uncertainty ranges. BC FF is for black carbon from fossil fuel and biofuel, POA FF is for primary organic aerosol from fossil fuel and biofuel, BB is for biomass burning aerosols and SOA is for secondary organic aerosols. Adapted from Boucher et al. (2013).

Since LTU had financial problems, CARIBIC phase 1 was stopped in April 2002. During this time period, the modified Boeing-767ER flew almost 100 international flights with home bases in Frankfurt on the Main and Düsseldorf (IAGOS-CARBIC, 2025).

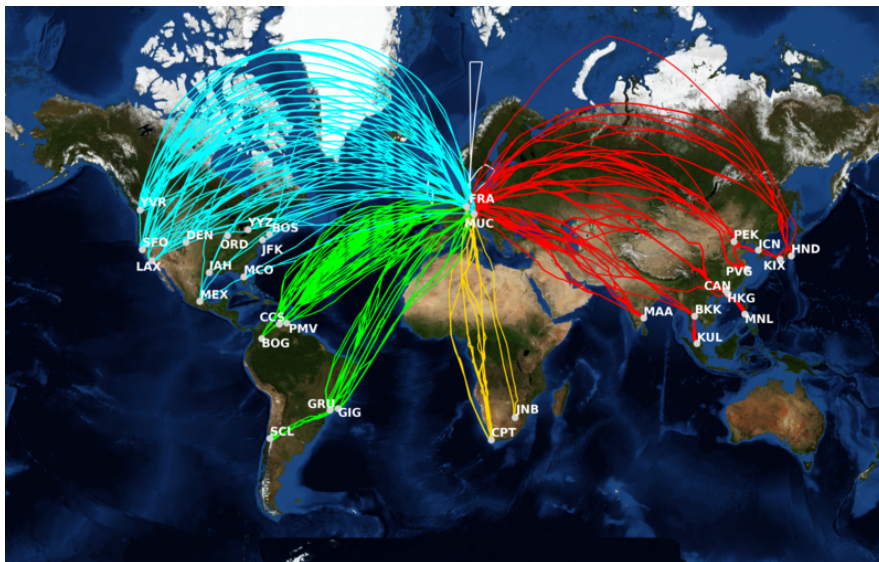


Figure 1.3: Flight routes of CARIBIC Phase 2 (IAGOS-CARBIC, 2025).

CARIBIC phase 2 was operational since December in 2004. In the second phase, a modified LD11 airfreight container was used and additionally, the final amount of instruments increased from 6 to 19 instruments in 9 racks. Instead of LTU, the CARIBIC consortium was cooperating with Lufthansa airlines. Thus, the newly designed container was deployed on an Airbus A340-600. Due to the Corona pandemic, CARIBIC phase 2 was stopped in 2020, since Lufthansa phased-out the A340-600. In the second phase, the A340-600 almost flew 500 times with an global coverage (more than 30 destinations in the northern and southern hemisphere) as shown in Figure 1.3 . The home bases were still in Germany, but this time in Munich and Frankfurt (IAGOS-CARBIC, 2025).

CARIBIC phase 3 will start at the end of 2025 or beginning 2026 and the modified LD6 airfreight container will be deployed on an Airbus A350-900 by Lufthansa airlines (IAGOS-CARBIC, 2025).

The Max Planck Institute for Chemistry (MPI-C) in Mainz was leading the project, until 2015, when the Karlsruhe Institute of Technology (KIT), the Institute of Meteorology and

Climate Research (IMK), took over the lead (IAGOS-CARBIC, 2025). In 2014, the European Research Infrastructure IAGOS, which is the successor of MOZAIC (Measurement of Ozone and Water Vapor on Airbus In-service Aircraft) was built to harmonize various atmospheric programs under an unified framework, incorporating CARIBIC as one of two key elements (Petzold et al., 2015), which are now called IAGOS-Core and IAGOS-CARIBIC. IAGOS-Core uses compact, automated instruments permanently installed on ten passenger aircraft (until end of 2023) to measure atmospheric parameters like greenhouse gases (e.g. carbon dioxide, carbon monoxide, methane, and water vapor), ozone, nitrogen oxides (NO_x or NO_y), number density of cloud particles, aerosol number density and size distribution. The use of these instruments on several commercial airplanes provides frequent, global data for long-term atmospheric monitoring, prioritizing consistency and large-scale spatial and temporal coverage over detailed or specialized measurements. This approach is ideal for detecting trends in basic atmospheric composition over time and to get the climatology (IAGOS, 2025). On the other hand, there is IAGOS-CARIBIC, which uses only one airplane with more and more specialized instruments at the same time. It can measure various parameters like greenhouse gases (e.g., carbon dioxide, methane, water vapor, etc.), (ultra) trace gases (e.g., ozone, carbon monoxide, halocarbons, nitrogen oxides, acetone, methanol, acetonitrile, volatile organic compounds (VOCs), and nitrous acid), aerosol number density and size distribution, aerosol composition, isotopes, and even trace metals. IAGOS-CARIBIC provides less frequent but more detailed data compared to IAGOS-Core, which makes the datasets ideal for studying atmospheric processes, chemistry, and phenomena in specific regions in more depth (IAGOS-CARBIC, 2025). Both projects can be seen in complementary roles in atmospheric monitoring using commercial aircraft.

1.3 Mass Spectrometry for Atmospheric Monitoring

Mass spectrometry (MS) is a powerful tool to detect species qualitatively and quantitatively with high sensitivity. For detection, it measures the mass-to-charge ratio (m/q) of ions (Unit: Thomson (Th)). It can help to identify and often also quantify compounds. Moreover, it

can be used to determine structural information about a substance. In general, it consists of four key components: Ionization source, transfer stage, mass analyzer, and the detector. Depending on the needs (low limit of detection (LOD), purity, etc.) it can also be coupled with chromatography (Gas chromatography (GC-MS) or liquid chromatography mass spectrometer (LC-MS)) for more comprehensive analyses.

1.3.1 Mass Analyzer

The two major analyzers frequently employed in atmospheric sciences are quadrupole and time-of-flight mass spectrometry. Quadrupoles filter ions by oscillating electric fields. This feature allows to tune mass filtering (scan for a specific m/q) and provides high selectivity. They have a wide dynamic range, which makes them suitable for quantitative analysis of analytes across a wide range of concentrations. Moreover, quadrupoles are usually less expensive compared to ToF systems. Advantages for airborne applications are that quadrupoles are typically more compact and have a smaller power requirement than ToFs. Quadrupoles are fast scanning one particular mass-to-charge ratio or steadily hopping between relevant m/q thereby sacrificing time resolution. However, in atmospheric science, it is advantageous to measure a larger number of mass-to-charge ratios simultaneously. This can only be achieved at the cost of time resolution, which is not practical for airborne measurements. Unlike quadrupoles that often focus on a specific small m/q range, ToFs collect a full spectrum of ions (in a certain larger m/q range, which can be customized) within seconds. This is useful for untargeted analyses like environmental screening or for measurements, where measuring various m/q ratios with a high time resolution is crucial, like e.g. for airborne measurements. Furthermore, ToFs provide significantly higher mass resolutions compared to quadrupoles. High mass resolution helps to better distinguish compounds with the same nominal mass (isobaric species). ToFs also usually have a higher mass accuracy (<1 parts-per-million (ppm)), which can be crucial to differentiate between compounds with isobaric masses. However, ToFs are lacking in sensitivity compared to quadrupoles, which are also better suited for absolute quantification. ToFs are useful for measurements requiring both high temporal and mass resolution, as well as for untargeted analyses where a wide range of m/q ratios is advantageous

(e.g., >300 m/q). Quadrupoles, in contrast, are more cost-effective and ideal for routine, targeted quantitative workflows.

1.3.2 Ionization Methods

In mass spectrometry, various ionization techniques are used to convert neutral molecules into ions which can only be detected. These ionization techniques are broadly categorized in soft or hard. Soft ionization methods are characterized by low fragmentation. Thus, the molecular ion structure is usually preserved, which can be often an advantage. However, these techniques also provide limited structural information. A typical soft ionization method is e.g., chemical ionization (CI). On the other hand, hard ionization methods tend to produce an extensive fragmentation pattern. The molecular ion will be destroyed. That can be advantageous if the amount of different molecules in a sample is small and the structural information of the molecule is important. A typical hard method is electron ionization (EI) (Milne et al., 1974; Hanan Awad and El-Aneed, 2015). In atmospheric research, EI is not commonly used since it ionizes most of atmospheric constituents. For atmospheric trace gas measurements, where various substances are probed simultaneously, a soft ionization method is beneficial to avoid fragmentation and unwanted ionization. In the last decades, chemical ionization got more used in atmospheric science.

1.3.2.1 Chemical Ionization Mass Spectrometry

Chemical Ionization Mass Spectrometry (CIMS) is a versatile technique to measure atmospheric (ultra) trace gases (sub-ppb level) in-situ due to its high sensitivity (higher ppb to ppt level) with high selectivity and fast time response (Huey et al., 1995a; Bertram et al., 2011; Crounse et al., 2006). Especially the latter is a notable advantage of CIMS. The fast time response (often less than one second) allows for high-temporal-resolution observations. This feature is beneficial for airborne measurements, where capturing fast-changing atmospheric conditions is essential (Le Breton et al., 2012; Veres et al., 2020). Traditionally, CIMS were coupled with a quadrupole (Huey et al., 1995a). In the last decades, the coupling of chemical ionization with time-of-flight mass spectrometer (ToF-MS) was developed

and improved, which allows to measure tens or even hundreds of compounds simultaneously (Robinson et al., 2022). As a first step of chemical ionization (CI), a reagent ion is formed by ionizing a reagent gas (e.g. water vapor, ammonia, methyl iodide, acetic acid, nitric acid or bis(trifluoromethyl)peroxide (BTP)) utilizing a radioactive source (e.g. ^{210}Po ; see Equation 1.1) (Lee et al., 2014, 2020), vacuum ultraviolet light (Ji et al., 2020) as shown in Equation 1.2, x-ray lamps (Rissanen et al., 2019), dielectric barrier (Albrecht, 2014; Pape and Schmitz, 2024) or corona discharge (CD) (Kürten et al., 2011). Depending on the reagent gas and ionization method used, both positive and negative ions can be formed:



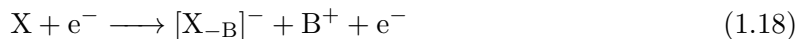
In positive ion chemical ionization (PICI), positive ions (R^+ or $[\text{RH}]^+$) will be formed by

ionizing the reagent gas (e.g. water vapor, ammonia, oxygen, or benzene). There are four typical reaction channels, which an analyte molecule (X) can undergo: proton transfer (PT; see Equation 1.9), electrophilic addition (EA; see Equation 1.10), anion abstraction (AA; see Equation 1.11), and charge transfer (CT; see Equation 1.12) (A and B in Equation 1.9 - 1.18 indicate functional group) (Zhang et al., 2023).



Instead of positive primary ions, negative reagent ions (R^-) can also be formed (NO_3^- , CF_3O^- , CH_3COO^- , CO_3^- , SF_6^- , I^- , Br^- , and O_2^-). That is called negative ion chemical ionization (NICI). The reagent pathways are fairly the same as for the PICI. The proton transfer reagent is replaced by the proton abstraction (PA; see Equation 1.13) and instead of an electrophilic addition, there is a nucleophilic addition (NA; see Equation 1.14). Moreover, negative charge can also be transferred to the analyte molecule X, called electron capture (EC; see Equation 1.15). The latter can be separated in resonance electron capture (REC; see Equation 1.16), electron transfer (ET; see Equation 1.16), dissociative electron capture (DEC; see Equation 1.17), and ion-pair formation (IPF; see Equation 1.18). The reactions are described in the equations 13-18 (Zhang et al., 2023).





1.4 Motivation

This work deals with the development and characterization of state of the art airborne CIMS instrument (FunMass-C), which will be capable to measure various of ultra trace gases including SO_2 , inorganic acids (e.g., HCN and hydrogen chloride; HCl), organic acids such as e.g., formic acid (HCOOH) and acetic acid (CH_3COOH), and hydroperoxides (e.g. H_2O_2) with LODs lower than 10 ppt. FunMass will be part of the IAGOS-CARIBIC container deployed on a Lufthansa A350. It is aimed to provide frequently in-situ data of various ultra trace gases focusing on SO_2 and HCN with a global coverage starting from 2026.

In Chapter 2, the importance and background information of HCN and SO_2 will be presented as they are the two main species measured by FunMass-C. In Chapter 3, the development of the customized ion-molecule reaction zone (IMR), its characterization, and the CF_3O^- ion chemistry is described. Lastly, the results of two DMS oxidation experiments carried out in SAPHIR-STAR in 2023 and 2024, where a predecessor version of FunMass-C was participating, is evaluated in Chapter 5.

1.4. MOTIVATION

Chapter 2

Atmospheric Trace Gases

This chapter deals with the introduction and theory for the two main species (HCN and SO₂) measured by FunMass-C during IAGOS-CARIBIC flights.

2.1 Hydrogen Cyanide

Hydrogen cyanide (HCN) is the most abundant cyanides in the atmosphere (Singh et al., 2003). HCN is primarily emitted to the atmosphere via biomass burning, combustion processes (industrial activities), and biofuel use, while biomass burning is determined to be by far the major source (Li et al., 2000, 2003; Singh et al., 2003; Kleinböhl et al., 2006; Li et al., 2009; Simpson et al., 2011). In the troposphere, HCN is mainly taken up by the oceans, and Cicerone and Zellner (1983) have shown that the oxidation by OH radicals is non-negligible in the troposphere, but its contribution to HCN removal is still uncertain. These tropospheric sources and sinks lead to an estimated tropospheric lifetime of about 5 months (Li et al., 2000, 2003; Singh et al., 2003). Stratospheric HCN is removed photochemically, resulting in a stratospheric lifetime of 3-5 years (Cicerone and Zellner, 1983; Li et al., 2000, 2003). HCN can contribute to the nitrogen cycle and reactive nitrogen; NO_x (Li et al., 2000, 2003, 2009). Understanding its distribution in the UTLS provides valuable insights into global biomass burning patterns, interhemispheric transport, stratosphere-troposphere exchange mechanisms, and in the HCN tape recorder as shown in Figure 2.1 (Randel et al.,

2010; Park et al., 2013; Glatthor et al., 2015b; Pumphrey et al., 2018).

Various observational studies were carried out to investigate the global and regional distribution of HCN using satellite-based remote sensing (e.g., Atmospheric Chemistry Experiment - Fourier Transform Spectrometer (ACE-FTS), Microwave Limb Sounder (MLS), and Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on the satellite ENVISAT), ground-based remote-sensing (e.g., Fourier Transform Infrared (FTIR) Spectroscopy), airborne in-situ measurements (e.g. CIMS) and balloon-borne measurements (Boone et al., 2005; Kleinböhl et al., 2006; Li et al., 2009; Sheese et al., 2017; Pumphrey et al., 2018; De Mazière et al., 2018; Bernath et al., 2021; Li, 2021; Park et al., 2021; Bruno et al., 2023). These observations were accompanied by modeling studies using atmospheric chemical transport models (CTMs) like TOMCAT 3-D CTM to better understand processes causing variability and distribution of HCN in the atmosphere (Chipperfield, 2006; Chipperfield et al., 1993, 2018; Pope et al., 2020; Bruno et al., 2023).

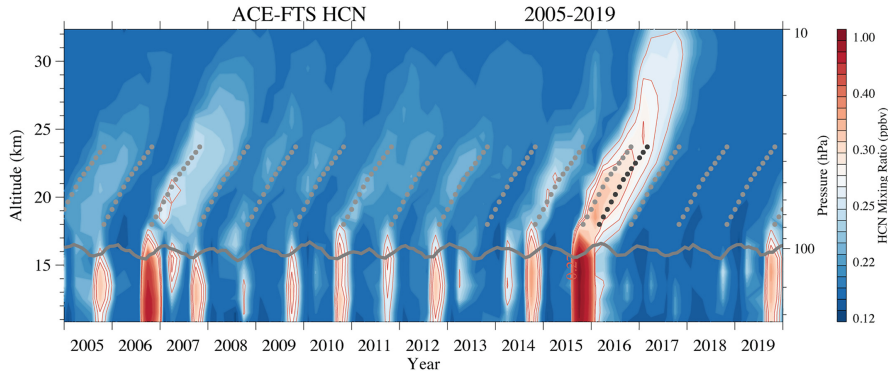


Figure 2.1: Time-altitude section of monthly mean HCN mixing ratios from ACE-FTS [unit: ppbv] averaged between 15°S and 15°N latitude for 2005–2019. Gray solid dots represent vertical velocity estimated based on Mote et al. (1996) with the tape recorder head placed in October each year. Black solid dots indicate tape recorder signal starting in February 2016 (see text for details). Red solid contours are added to mark high HCN mixing ratios (0.25, 0.27, and 0.29 ppbv). Monthly mean tropopause height obtained from the NCEP/NCAR reanalysis (unit: km) is shown as a thick gray solid line. ACE-FTS, Atmospheric Chemistry Experiment Fourier Transform Spectrometer; HCN, hydrogen cyanide. Source: (Park et al., 2021).

However, there are still significant uncertainties in the rate constants of the oxidation by OH and the uptake of HCN by the oceans as well as the stratospheric degradation leading to open questions in the understanding of the atmospheric HCN budget and its variability. Moreover, the impact of climate change on biomass burning frequency and intensity and its feedback behavior will likely be important for future trends in HCN emissions and their implications for UTLS composition, warranting detailed monitoring of HCN across the UTLS.

In this work, only the optimization of the HCN measurement using FunMass is discussed.

2.2 Sulfur Dioxide

Sulfur dioxide (SO_2) is a highly reactive gas with a significant role in atmospheric chemistry, aerosol formation (Seinfeld and Pandis, 2016.), human health via sulfate aerosol inhalation (Lelieveld et al., 2015), and ecosystem health via sulfate aerosol deposition (Vet et al., 2014). SO_2 is the major precursor for stratospheric aerosols (SAs), which mainly consist of sulfate aerosols. Both natural (e.g., volcanoes and biomass burning; BB) and anthropogenic emissions (e.g., fossil fuel; FF) contribute to the presence of SO_2 in the atmosphere (Dentener et al., 2006; Lamarque et al., 2010). Lee et al. (2011) estimated SO_2 emissions from inverse modeling using in situ and global, spaceborne (SCIAMACHY and OMI) observations. According to their analysis, fossil fuel combustion and industry emit $56.3 \text{ Tg(S) yr}^{-1}$, which is in good agreement with the $54.2 \text{ Tg(S) yr}^{-1}$ from Hoesly et al. (2018) derived by using emission inventories, emission factors, and activity and driver data. However, it should be noted that nowadays, these emissions mainly take place in developing countries due to the missing desulfurization at power plants. Natural direct emissions due to volcanoes or biomass burning are estimated to be $6.6\text{-}21.9 \text{ Tg(S) yr}^{-1}$ (Lee et al., 2011; Mills et al., 2016; Carn et al., 2017) or $1\text{-}1.3 \text{ Tg(S) yr}^{-1}$ (Lee et al., 2011; van Marle et al., 2017), respectively. As shown in Figure 2.2, SO_2 is also formed naturally in the atmosphere by gas-phase oxidation of other sulfur-containing species (e.g., carbonyl sulfide (OCS), dimethyl sulfide (DMS), hydrogen sulfide (H_2S)) (Seinfeld and Pandis, 2016.). The DMS oxidation will be discussed in more detail in Chapter 5. Besides direct injection due to large volcanic eruptions (Bernath and Bhusal,

2.2. SULFUR DIOXIDE

2025) and tropical convection (Kremser et al., 2016) like e.g. the Asian Summer Monsoon (ASM) (Randel et al., 2010), UV photolysis of OCS is a major SO_2 source in the stratosphere (Crutzen, 1976; Brühl et al., 2012; Höpfner et al., 2015) (cf. figure 2.2). The tropospheric lifetime of SO_2 is between a few hours and two weeks (average: 2 d) (Lelieveld et al., 1997; Beirle et al., 2014; Fung et al., 2022).

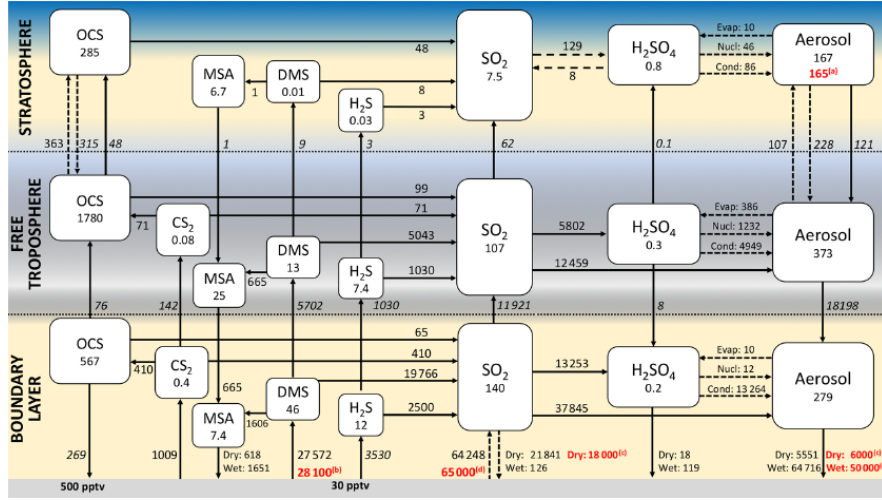
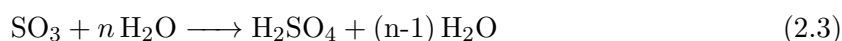
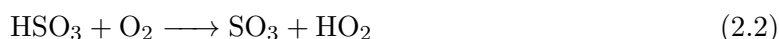
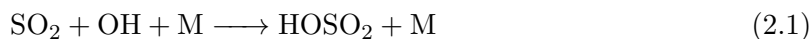


Figure 2.2: Atmospheric sulfur budget from SOCOL-AERv2 under volcanically quiescent conditions for the year 2000. The figure is produced using output diagnostics that track sulfur fluxes and burdens within the planetary boundary layer (PBL), free troposphere, and stratosphere. Solid arrows show net fluxes and dashed arrows show one-way fluxes, all in gigagrams of sulfur per year (Gg S yr^{-1}). Simulated burdens of sulfur species are given within the boxes, in units of gigagrams of sulfur (Gg S). Italicized numbers represent fluxes that are derived by balancing other fluxes, assuming steady state of the upper layers. For example, net cross-tropopause fluxes are calculated by balancing the stratospheric chemical fluxes and net cross-PBL fluxes are calculated by balancing the free tropospheric chemical fluxes. Upward OCS and sulfate aerosol cross-tropopause fluxes are calculated based on the residual meridional and vertical air velocities (v^* and w^*) and concentrations at the tropopause. Black numbers: SOCOL-AERv2 results. Red numbers: (a) SAGE-3 λ stratospheric aerosol burden (b) DMS emissions estimated by (Lana et al., 2011) (c) dry deposition fluxes from NCAR-CAM3.5 model (Lamarque et al., 2012) for the year 2000, which participated in ACCMIP (d) multimodel mean wet deposition from ACCMIP models for the year 2000 (Lamarque et al., 2012). Source: (Feinberg et al., 2019)

Once released to the atmosphere, SO_2 is oxidized either in the gas phase or in droplets as well as in liquid aerosol (Beilke and Gravenhorst, 1978; Cox et al., 1979; Liu et al., 2020). In the gas phase, it is a well-known multi-step reaction. This multi-step reaction is mainly initiated by the OH radical (see reaction 2.1). However, especially in forested regions, stabilized

Criegee intermediates can also act as an initiator radical (Mauldin et al., 2012; Huang et al., 2015; Manonmani et al., 2023).



It is well-known, that reaction 2.1 and 2.3 are rate-limiting and especially, the reaction 2.3 needs a high water vapor concentration (Carmona-García et al., 2021).

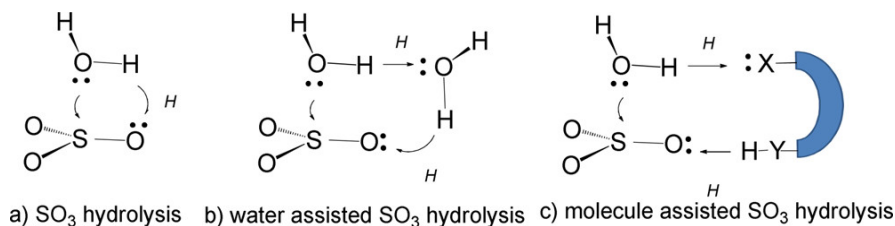


Figure 2.3: Chemical mechanistic representation of (a) Gas-Phase Hydrolysis of SO_3 , (b) Water-Assisted Gas-Phase Hydrolysis of SO_3 , and (c) Molecule-Assisted Gas-Phase Hydrolysis of SO_3 (Torrent-Sucarrat et al., 2012). HY can be e.g., HCOOH , HO radical, or H_2O . X represents the corresponding bases of these species.

In theoretical studies, it could be demonstrated that the hydrolysis of SO_3 needs the presence of at least two water molecules, one of them acting as a catalyst (cf. 2.3 b)). Moreover, Torrent-Sucarrat et al. (2012) could also show, that replacing the catalytic water molecule by a sulfuric acid molecule (or one of its hydrates) can have a catalytic effect of $3\text{-}11 \text{ kcal} \cdot \text{mol}^{-1}$ (see 2.3 c)). This replacement results in the production of either a bare sulfuric acid dimer or a sulfuric acid dimer complexed with a water molecule. These findings of sulfuric acid as autocatalyst in the formation of sulfuric acid can be important in the Earth's stratosphere, where water vapor mixing ratios are low, in the heterogenous formation of sulfuric acid and in the formation of aerosols (Torrent-Sucarrat et al., 2012). Instead of a water molecule or sulfuric acid, other molecules like e.g., formic acid and hydroperoxy radicals

2.2. SULFUR DIOXIDE

can act as catalysts (Gonzalez et al., 2010; Hazra and Sinha, 2011). This can also have a large atmospheric relevance for sulfuric acid formation in regions, where species like for instance formic acid are more abundant. The gas phase oxidation of SO_2 was studied extensively over the last decades, but there still remain major open questions for the full understanding of the mechanism.

Besides the gas phase oxidation, SO_2 also can be oxidized heterogeneously in the liquid phase (water droplets) or on surfaces (e.g. ice). SO_2 dissolves in water well. However, the solubility depends on temperature, pressure and the pH of the solution. Dissolving anhydrides of acids is more complex than non-acids, since the corresponding acid is formed due to hydrolysis. For SO_2 several reactions have to be taken into account:



For reaction 2.4, the Henry's law constant can be described as:

$$H_{\text{SO}_2} = \frac{[\text{SO}_2 \cdot \text{H}_2\text{O}]}{p_{\text{SO}_2}} \quad (2.7)$$

For the other two chemical reactions 2.5 and 2.6, the equilibrium constants can be defined as follows:

$$K_{1,\text{SO}_2} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{SO}_2 \cdot \text{H}_2\text{O}]} \quad (2.8)$$

$$K_{2,\text{SO}_2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} \quad (2.9)$$

The total dissolved sulfur in the oxidation state 4 (S(IV)) is calculated as:

$$[\text{S(IV)}] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] \quad (2.10)$$

Using equation 2.7 - 2.9, the equation 2.10 can be written as:

$$[\text{S(IV)}] = H_{\text{SO}_2} p_{\text{SO}_2} \left[1 + \frac{K_{1,\text{SO}_2}}{[\text{H}^+]} + \frac{K_{1,\text{SO}_2} K_{2,\text{SO}_2}}{[\text{H}^+]^2} \right] \quad (2.11)$$

Thus, the effective Henry's law constant of SO_2 ($H_{\text{S(IV)}}^*$) can be defined as:

$$H_{\text{S(IV)}}^* = H_{\text{SO}_2} \left[1 + \frac{K_{1,\text{SO}_2}}{[\text{H}^+]} + \frac{K_{1,\text{SO}_2} K_{2,\text{SO}_2}}{[\text{H}^+]^2} \right] \quad (2.12)$$

Hence, the amount of dissolved $[\text{S(IV)}]$ depends on temperature, since the equilibria 2.4 - 2.6 are temperature-dependent, on the pH (see $[\text{H}^+]$ dependence of $H_{\text{S(IV)}}^*$), and on the partial pressure of SO_2 , p_{SO_2} (Seinfeld and Pandis, 2016.). The pH dependency of $H_{\text{S(IV)}}^*$ is also illustrated in Figure 2.4. It can be observed that the more alkaline the solution/droplet is the higher $H_{\text{S(IV)}}^*$, thus, the more SO_2 can be dissolved in the liquid phase. However, it is important to note that $H_{\text{S(IV)}}^*$ is always greater than $H_{\text{S(IV)}}$. Consequentially, the hydrolysis of SO_2 increases the solubility of SO_2 in water.

Regarding chemical mechanisms, more precisely SO_2 oxidation in the aqueous phase, it is important in which form the sulfur is present. The fraction of S(IV) which is $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , and SO_3^{2-} depending on the pH is given in Figure 2.5. Between pH 3 to 6, most of the S(IV) is bisulfite (HSO_3^-). However, for analyzing heterogeneous oxidation of SO_2 knowing the pH of the cloud (2-7) or aerosol (e.g., sulfate aerosols: -1-5) droplet is crucial (Pye et al., 2020).

There are several pathways for heterogeneous transformation of S(IV) to S(VI) including reactions with O_3 , H_2O_2 , O_2 (catalyzed by Mn(II) and Fe(III)), OH, SO_5^- , HSO_5^- , SO_4^- , peroxyacetyl nitrate (PAN), CH_3OOH , $\text{CH}_3\text{C}(\text{O})\text{OOH}$, HO_2 , NO_3 , NO_2 , HCHO, Cl_2^- . In the following, only a few of these reactions will be explained briefly since the literature on the chemical reaction kinetics of aqueous sulfur chemistry is large and also not fully understood

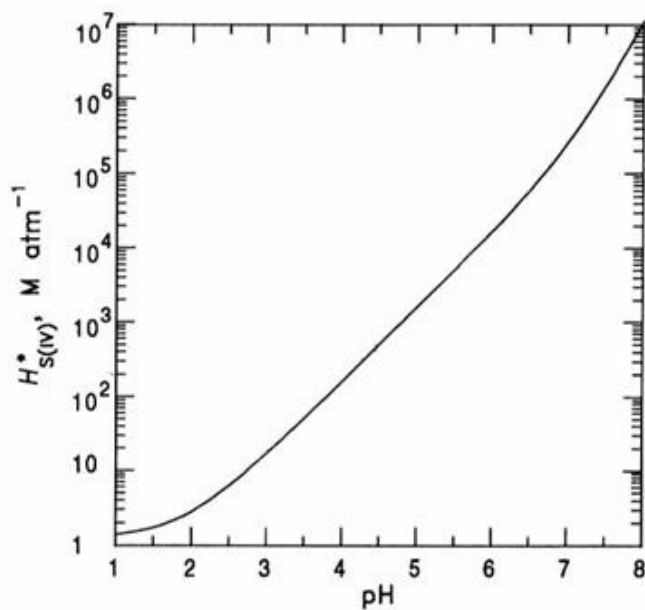


Figure 2.4: Effective Henry's law constant for SO_2 as a function of solution pH at 298 K (Seinfeld and Pandis, 2016.).

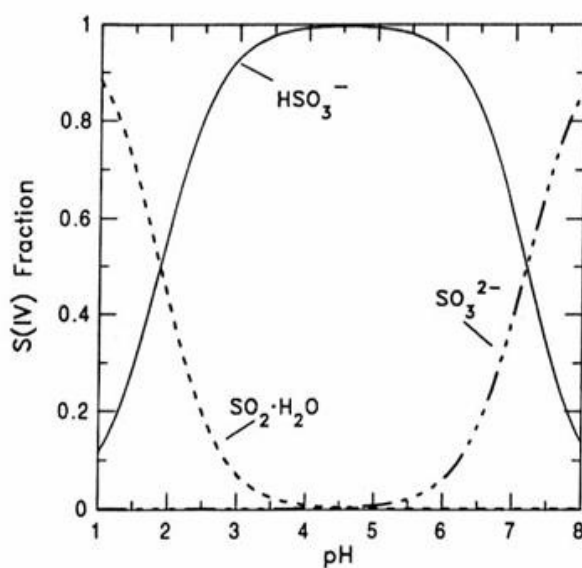
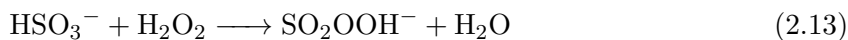


Figure 2.5: Concentrations of S(IV) species expressed as S(IV) mole fractions. These fractions are independent of the gas-phase SO_2 concentration (Seinfeld and Pandis, 2016.).

(Seinfeld and Pandis, 2016.).

While the oxidation of SO_2 by O_3 is very slow in the gas phase, S(IV) reacts rapidly with O_3 in the aqueous phase. O_3 can react with all three forms of dissolved SO_2 . However, SO_3^{2-} is oxidized several orders of magnitude faster by O_3 ($k = 1.5 \pm 0.6 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$) than $\text{SO}_2 \cdot \text{H}_2\text{O}$ and HSO_3^- ($k = 2.4 \pm 1.1 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k = 3.7 \pm 0.7 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively). Mechanistically, O_3 is thought to undergo a nucleophilic attack by the sulfur species. This explains the increased reactivity of SO_3^{2-} compared to the other two forms. As the form of S(IV) present is pH-dependent (cf. Figure 2.5) and the rate constants vary between the three dissolved forms, the overall reaction rate of the oxidation of S(IV) by O_3 increases with increasing pH. This results in a self-limiting nature, since sulfate is produced by this reaction, which lowers the pH and thus, decreases the overall reaction rate (Kerr et al., 1985). Another important oxidant of S(IV) is H_2O_2 . It is very soluble in water (the solubility of H_2O_2 is thousands of times higher than of O_3). That leads to much more H_2O_2 in the aqueous phase compared to O_3 under typical atmospheric conditions (Seinfeld and Pandis, 2016.). It is a two-step oxidation process:



The first step 2.13 is a nucleophilic substitution by H_2O_2 on HSO_3^- . The resulting peroxydisulfuric acid (SO_2OOH^-) is converted to H_2SO_4 via protonation. Thus, the more acidic the aqueous phase is, the faster the second reaction 2.14 will be (McArdle and Hoffmann, 1983). The reaction rate of the first step 2.13 is $k = 7.5 \pm 1.16 \cdot 10^7 \text{ M}^{-1}$. The overall reaction is nearly pH independent, since the pH dependency of S(IV) solubility increases with increasing pH (see figure 2.4) and the reaction rate decreases with increasing pH thereby cancelling each other (Seinfeld and Pandis, 2016.). Typically, the oxidation by H_2O_2 is much faster than by O_3 . But there are occasions, where the O_3 can be the dominant oxidant. Li et al. (2020) showed a shift of the dominant oxidant from H_2O_2 to O_3 due to increasing

O_3 concentration and an increasing trend of pH. Lastly, the oxidation by oxygen (O_2) in the aqueous phase is slow to negligible (Tsunogai, 1971; Huss et al., 1978; Robbin, 1984). However, small amounts of Fe(III) and Mn(II) can catalyze this reaction. Depending on the pH, the oxidation by O_2 catalyzed by trace metals, which are present in aerosols and clouds (Aerosols: Fe(III) = 100-1000 μM and Mn(II) = 0.1-100 μM ; and clouds: Fe(III) = 0.1-100 μM and Mn(II) = 0.1-10 μM), can be in the same order of magnitude as the oxidation by O_3 . This is especially the case at higher pH (Robbin, 1984). Interestingly, these trace metals do not seem to catalyze the oxidation by O_3 (Robbin, 1984; Lagrange et al., 1994). Besides the gas phase and heterogeneous chemistry, dry and wet deposition as well as photolysis (in the stratosphere) can be sinks of SO_2 . The high reactivity of SO_2 leads to very small mixing ratios in the UTLS. The background mixing ratios are between 1 - 100 ppt depending on the region in the UTLS (Höpfner et al., 2015). This requires very sensitive measurement techniques like CIMS or a laser-induced fluorescence instrument (LIF) with LOD(2σ , 2s) below 10 ppt for aircraft measurements (Allen et al., 2021; Rollins et al., 2016; Rickly et al., 2021).

Another observational technique to measure SO_2 in the UTLS is remote sensing (mainly satellite-borne). The typical instruments are/were for instance the MIPAS onboard the European Space Agency’s (ESA) Envisat satellite (ended 2012), the MLS onboard National Aeronautics and Space Administration’s (NASA) Aura satellite, ACE-FTS onboard the Canadian SCISAT satellite, the Tropospheric Monitoring Instrument (TROPOMI) onboard the Sentinel-5 Precursor satellite, the Ozone Monitoring Instrument (OMI) mounted on NASA’s Aura satellite, and the Infrared Atmospheric Sounding Interferometer (IASI) mounted on the MetOp series of satellites. These instruments provide a broad spatial coverage with the ability to capture large-scale distributions over extended periods. Especially, studying the evolution of volcanic plumes or long-range transport, these methods are advantageous (Carn et al., 2016; Kloss et al., 2021; Sellitto et al., 2024). The disadvantage is the lower temporal and vertical resolution and accuracy in comparison to the airborne in-situ measurements, like CIMS, providing high-resolution, localized data, suited for analyzing small-scale processes, variability, and vertical profiles. Another disadvantage of remote sensing techniques is that they can be severely affected by clouds and aerosols (Fischer et al., 2008, e.g.).

Also balloon-borne measurements using electrochemical concentration cell (ECC) En-Sci ozonesondes were carried out to measure SO_2 in the atmosphere for events with enhanced SO_2 mixing ratios (e.g., volcanic eruptions). The dual-sonde approach uses two ozonesondes simultaneously. While one sonde measures the SO_2 -free air (SO_2 is removed by a handmade scrubber placed at the pump inlet of the ozonesonde) and the other one the unfiltered air containing both SO_2 and O_3 . The SO_2 mixing ratios are then determined from the difference between the two sonde measurements (Morris et al., 2010). The dual-sonde approach only works well when the O_3 is greater than the SO_2 concentration. For the opposite conditions (more SO_2 than O_3 in the air) this technique saturates. Moreover, it has large uncertainties in the UTLS. Therefore, Yoon et al. (2022) have developed a novel technique to measure SO_2 using only one ECC En-Sci ozonesonde using a O_3 scrubber and a sample dryer before the inlet. This new approach is advantageous compared to the dual-sonde method, since it is independent of the O_3 concentration, faster in the response and recuperation after being exposed to larger SO_2 plumes, and reduced uncertainty (only one instrument used). Furthermore, it can have lower detection limits in the sub-ppbv level. Balloon-borne observations allow a high vertical resolution, and are cost-effective. Like the aircraft in-situ measurements, the spatial coverage is even more limited. In addition, the sensitivity and LOD are significantly worse compared to the other methods making it only suitable for events with enhanced SO_2 concentration in the atmosphere.

2.2. *SULFUR DIOXIDE*

Chapter 3

Development of FunMass-C

In this chapter, the development and optimization of FunMass-C for deployment in the IAGOS-CARIBIC container will be described. FunMass-C is a redesign of the FunMass instrument, which has flown on the high-altitude research aircraft M55-Geophysica during the StratoClim aircraft field campaign in 2017 (Albrecht, 2014; Khattatov, 2019; Li, 2021).

3.1 Aspects of Key Components

FunMass-C is a time-of-flight chemical ionization mass spectrometer (ToF-CIMS) illustrated in Figure 3.1. Its size is $60\text{ cm} \times 59\text{ cm} \times 85\text{ cm}$ ($L \times W \times H$) and it weighs about 170 kg. It can be mainly divided into the inlet, scrubber (valve), ion source (IS), ion-molecule-reaction zone (IMR), and ToF analyzer. FunMass(-C) was designed by the Institute of Climate and Energy Systems: Stratosphere (ICE-4) (former: Institute for Energy and Climate Research: Stratosphere (IEK-7)). In addition, most of the smaller components, such as IMR, gas deck, scrubber valve, and the inlet block, were constructed and manufactured by the internal workshop of the institute, and most of the electronic elements (e.g., main power supply) were designed and built by the electronics group of ICE-4. The mechanical components like the frame and housings of e.g., main power supply and ToF were manufactured by the Institute of Technology and Engineering (ITE) (former: Central Institute of Engineering, Electronics and Analytics: Engineering (ZEA-1)). An interface card (in the IFS) was manufactured by

3.1. ASPECTS OF KEY COMPONENTS

the Central Institute of Engineering, Electronics and Analytics: Electronic Systems (ZEA-2) (now: “Integrated Computing Architectures” institute division at the Peter Grünberg Institute (PGI-4)). The ToF analyzer including the customized transfer stage and ion optics was delivered by TOFwerk AG, Thun, Switzerland.

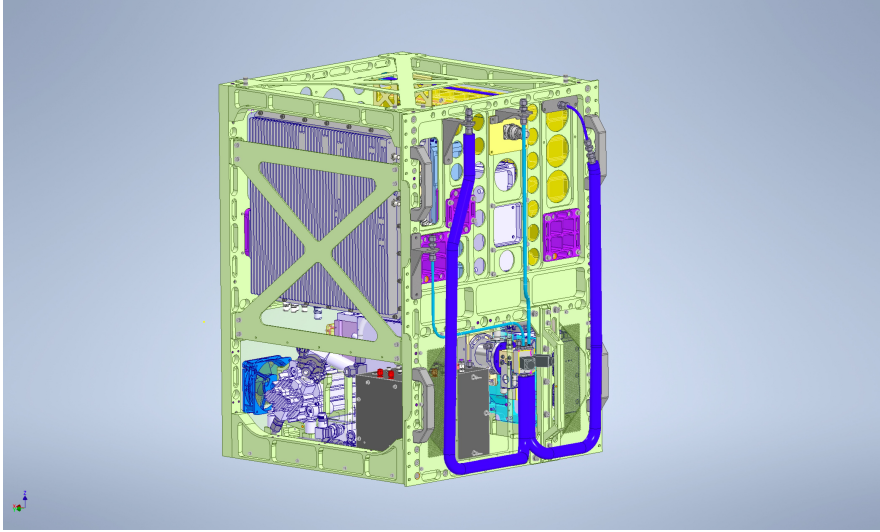


Figure 3.1: CAD sketch of FunMass-C. Source: Jochen Barthel.

Figure 3.3 shows the gas flowchart of FunMass-C. In general, the sample of analyte air goes through the inlet, and the scrubber valve directly to the IMR, which is pumped to a lower pressure (typically between 30-60 mbar) compared to the sample line (approx. ambient pressure) by a fore pump. Most of the sampled air goes via the fore pump to the exhaust. Only a small proportion goes to ToF via a small orifice (between 0.3 - 0.5 mm). The ToF and its transfer stage are pumped by 4-stage Turbo pump (SF270, Pfeiffer Vacuum GmbH), which is on the other hand also pumped by a secondary fore pump.

In the following subsections, each of the major modified components compared to the work of Li (2021) (Air inlet, Scrubber, IS and IS supply, and IMR) will be described in more detail starting with the air inlet. Moreover, the (calibration) gas supply system (Gasdeck) and the fore pumps are updated (still ongoing). Details about the unmodified components can be found in the work of Khattatov (2019) and Li (2021).

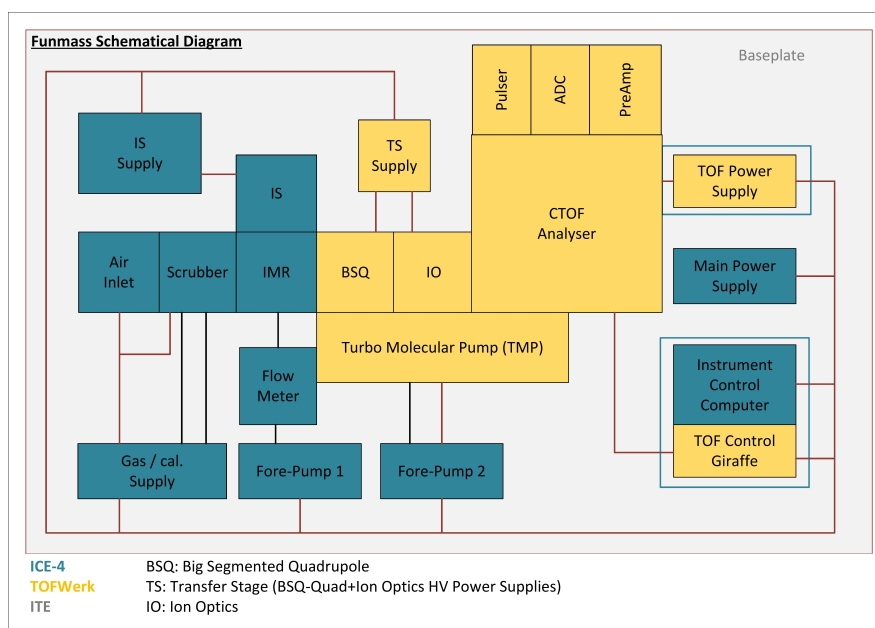


Figure 3.2: Components of FunMass. Different colours indicate work done by different institutes: ICE-4 (blue) and TOFWerk (yellow). The complete structure and the housings indicated by the grey rectangles have been constructed and built by ITE.

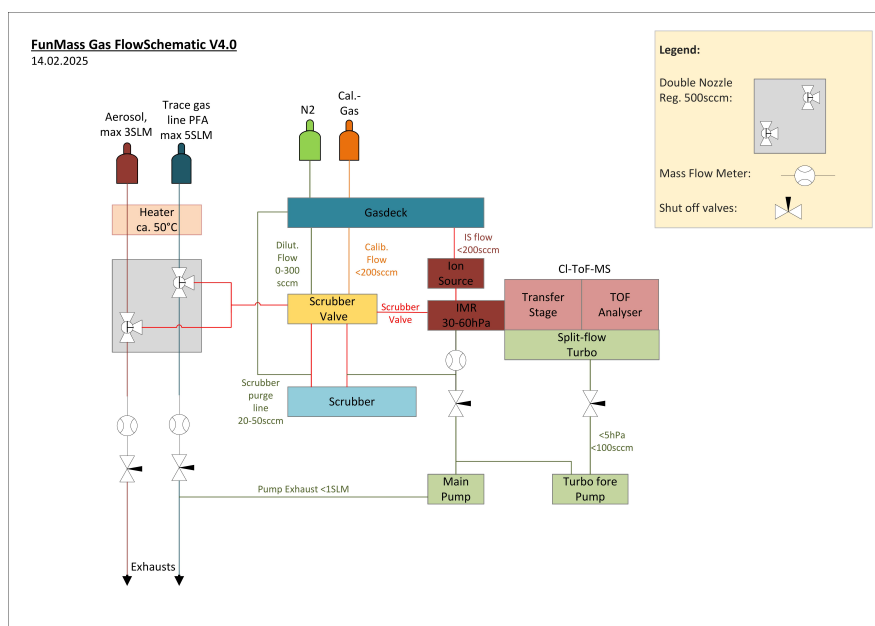


Figure 3.3: Gas flowchart of FunMass-C deployed on IAGOS-CARIBIC. Source: Fred Stroh.

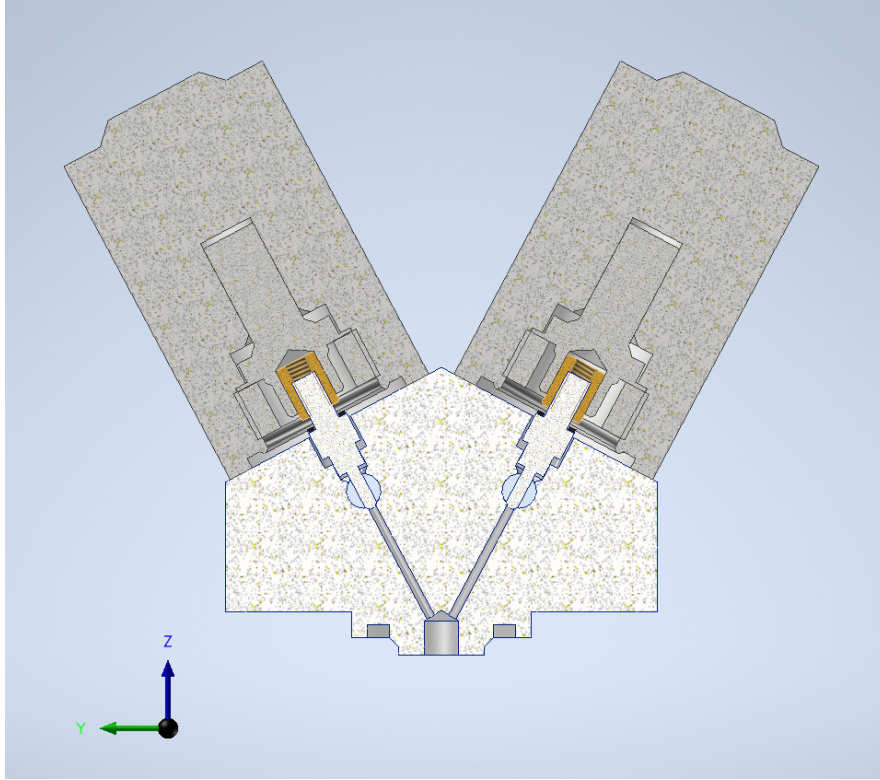


Figure 3.4: Inlet valve of FunMass-C. Source: Jochen Barthel.

3.1.1 Inlet

Deployed on the CARIBIC container, FunMass-C can sample air from both the trace gas line and the aerosol line, both represented by blue tubes in Figure 3.1. The system utilizes the pressure difference between the sample line (high pressure) and the IMR (low pressure) to draw air into the IMR.

The sampled airflows through a three-way block made of SilcoNert2000®-coated (SilcoTekGmbH, 2025) aluminum with 1/8" threads shown in Figure 3.4). A small PFA pin operated by a normally-closed linear action solenoid moves vertically to open an orifice leading to the IMR. Depending on the pin's position, the flow inside the IMR increases or decreases.

The solenoid ensures the valve closes immediately in the event of a power outage, a requirement for certification of deployment on the CARIBIC container. The solenoid valve is PID-regulated based on the target pressure in the IMR (e.g., 35 mbar). A customized aperture is installed in front of the fore pump to restrict the flow to a specific value (e.g., 500

SCCM) at the target pressure. In the lab version, a regulating valve was used instead of this aperture (see Appendix S1).

3.1.2 Scrubber

During field campaigns, regular blank measurements are necessary to establish the baseline of a species under the given specific conditions. This is particularly important when using ToF instruments with low mass resolution due to isobaric interferences from substances with the same nominal mass. Zero synthetic air may be used to obtain the blank. However, it does not accurately represent the real background, leading to greater uncertainties. To address this, a scrubber is used to selectively remove specific substances while preserving other ambient conditions. A scrubber operates on the principle of periodically (e.g., every 20 minutes) diverting the sampled air through an alternative path containing a specialized material designed to selectively remove the target substances while leaving others unaffected. Calibrations will also be performed while scrubbing the sampled air.

For CARIBIC, FunMass-C will primarily focus on measuring SO_2 and HCN. Therefore, the scrubber material must completely remove these two species. Another key consideration is that, during a flight sequence, the UTLS is typically probed, which exhibits large gradients in water vapor and ozone. In CIMS measurements, water vapor and ozone, which can be abundant in large quantities in the UTLS as shown in Figures 3.5 and 3.6, are the two major trace gases that can influence sensitivity and baseline stability. Ideally, these species should remain in the sampled air to avoid affecting measurements. However, due to its high reactivity, ozone is almost impossible to preserve and will always be at least partially removed. In contrast, water vapor can feasibly be retained in the sample air (Allen et al., 2021).

This subsection describes the custom-built scrubber valve and the investigation of an optimal scrubber material—one that effectively removes SO_2 and HCN while preserving water vapor content.

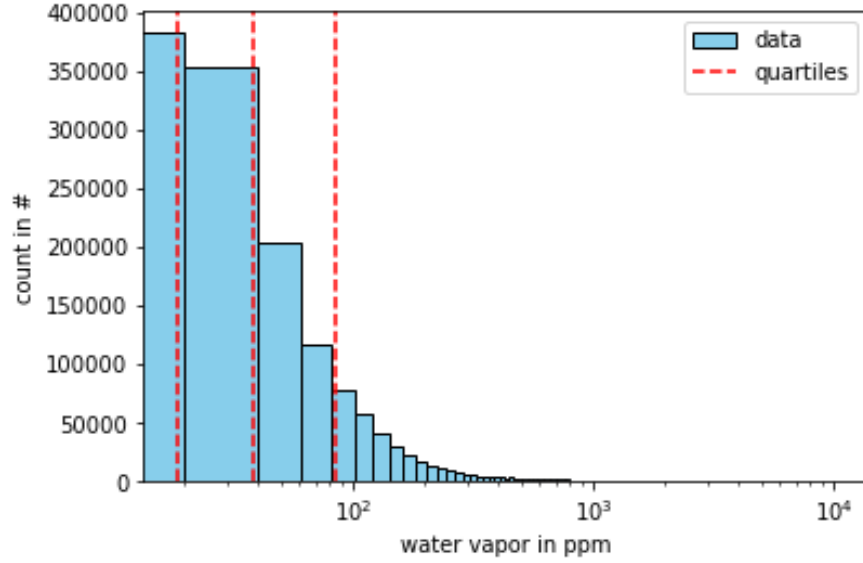


Figure 3.5: Histogram (absolute counts of data points) of water vapor mixing ratio in ppm in the CARIBIC phase 2 data sets (10 s average; only data points above 5000 m) with bin size of 20 ppm (sky blue). The dashed red lines represent the three quartiles (18.5, 38.6, and 85.3 ppm). The minimum and maximum mixing ratios are 0 (below detection limit) and 10195.4 ppm (Zahn et al., 2024).

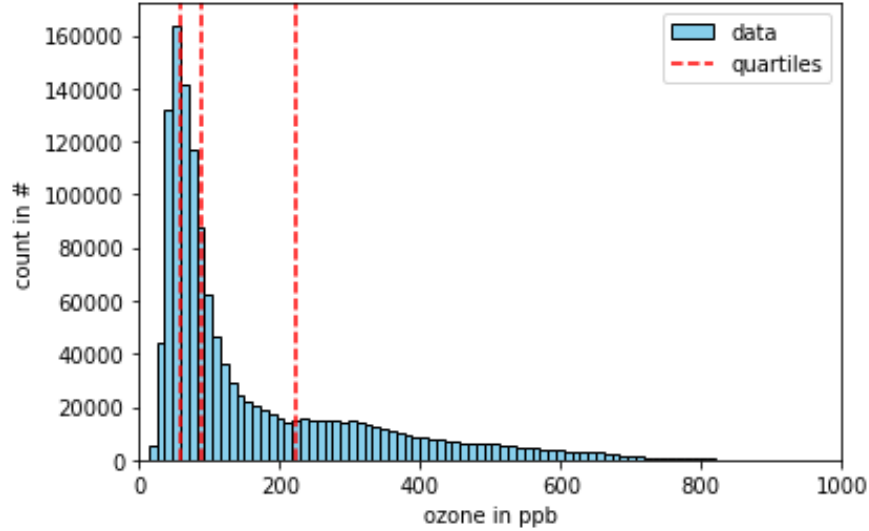


Figure 3.6: Histogram (absolute counts of data points) of ozone mixing ratio in ppb in the CARIBIC phase 2 data sets (10 s average; only data points above 5000 m) with bin size of 11 ppb (sky blue). The dashed red lines represent the three quartiles (57.49, 89.29, and 221.76 ppb). The minimum and maximum mixing ratios are 1.4 and 1138.75 ppb (Zahn et al., 2024).

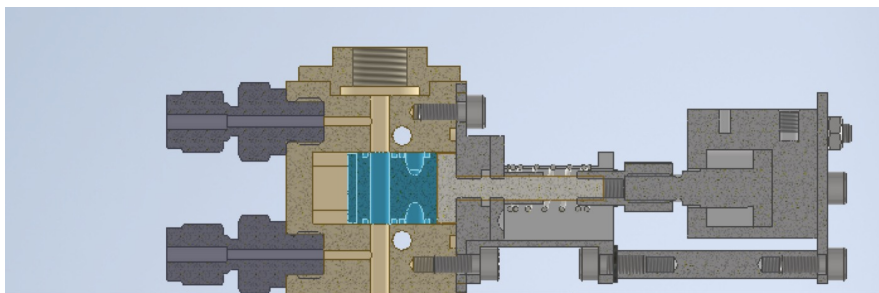


Figure 3.7: Cross-section of the homemode scrubber valve in closed position (direct sampling of ambient air). The main block (beige) and the movable inset (turquoise) are made of PTFE and PFA, respectively. The PFA inset is moved by a pneumatic solenoid (light gray) from Festo (Model: short-stroke cylinder AEVC-16-10-A-P). Additionally, there are two 1/8" threads (in dark grey) to add a dilution or humidification flow (before PFA inset) and the calibration flow (after PFA inset), respectively. Source: Jochen Barthel.

3.1.2.1 Scrubber Valve

A dedicated valve (hereafter referred to as the scrubber valve) is required to switch between two states: direct ambient air sampling without disturbance of the airflow and ambient air filtered through the scrubber. Measuring reactive trace gases necessitates the use of inert materials, such as PFA, PTFE, or SilcoNert2000®. To meet these requirements, the scrubber valve was custom-built by the institute's internal workshop, since commercial valves cause major flow obstructions or switch too slowly.

As shown in Figure 3.7, the scrubber valve consists of a PTFE block (beige) with a 4 mm bore and a 6 mm G-threaded inlet. At the center of the block, a movable PFA inset (turquoise) allows switching between the two sampling states: pure ambient air or air passed through the scrubber as illustrated in Figure 3.8. The PFA inset is actuated by a Festo AEVC-16-10-A-P short-stroke cylinder (see further details in S2). Additionally, the valve features two 1/8" threaded ports, enabling dilution or humidification (before the PFA inset) and calibration of target species (after the PFA inset).

Initially, the scrubber valve was operated manually due to the lack of a suitable solenoid. However, it was observed that slow switching between the two states caused a flow interruption, leading to pressure distortions. Rebalancing to a stable state took anywhere from 10 to 30 minutes, depending on the switching speed.

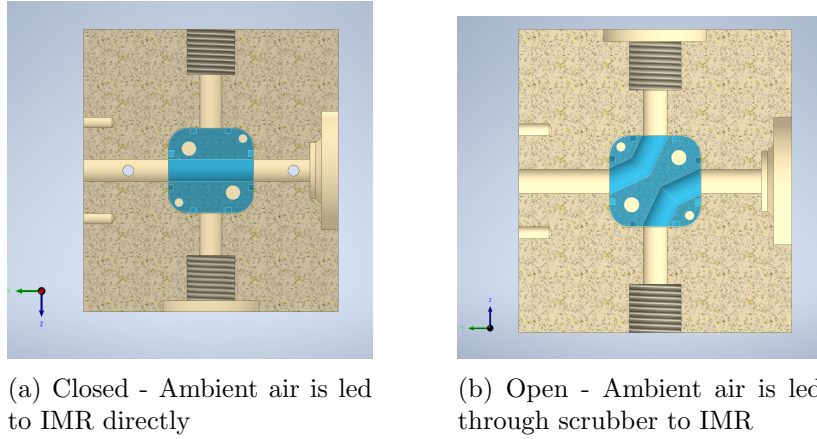


Figure 3.8: The two positions of the scrubber valve in the xy-plane. Source: Jochen Barthel.

An automated solution was planned from the outset, but several factors had to be considered beyond just power consumption, size, and maximum force—notably, the switching speed. Airborne instruments are constrained by limited power and space, so an ideal motor would consume only a few watts, fit within a 3 cm footprint in all directions, and generate sufficient force to fully actuate the inset.

The Nanotec Nema 6 (model LSA141S03-A-TDBA-102 with controller CL3-E-1-0F), described in Subsection 3.1.1, was a promising option in terms of power efficiency, size, and force output. However, its maximum speed was too slow to serve as an effective solution for the scrubber valve.

As an alternative, electromagnetic solenoids were considered, but they were too large, costly, and often required excessive power for the necessary force.

Ultimately, a pneumatic valve system, utilizing the Festo AEVC-16-10-A-P short-stroke cylinder, in combination with 3-way valve (power consumption 12 W) was chosen (more details are shown in the Appendix S2). Even with fast switching, a flow distortion persists, requiring a few minutes for rebalancing. To mitigate this, two small holes were drilled in the middle between the inlet holes of each state illustrated in Figure S2.1. These holes help maintain a more stable flow inside the IMR, minimizing distortion.

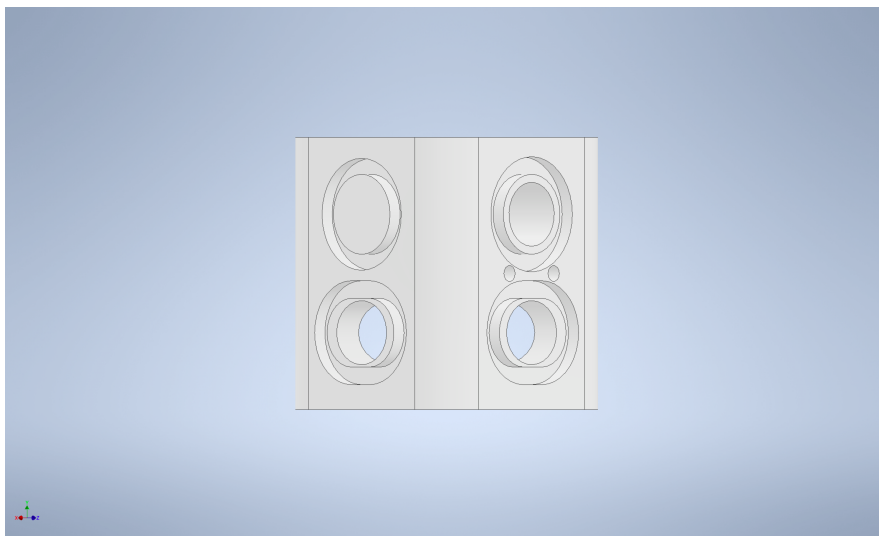


Figure 3.9: PFA inset with drilled holes to minimize flow distortion. Source: Jochen Barthel.

3.1.2.2 Scrubber Material

As already described in Subsection 3.1.2, material is needed which removes SO_2 and HCN but retains the water vapor content (water vapor influences the sensitivity much more than ozone see, which will be discussed in Chapter 4). A proper blank measurement is crucial in order to get the baseline value of SO_2 and HCN . A missing or incorrect baseline value of species under specific conditions can introduce large systematic errors/uncertainties in the actual mixing ratios.

Various materials were tested, some of which are listed in Table 3.1. The table also details the cleaning procedure for each scrubber. In general, each material was heated (when possible) and flushed with N_2 (5.0 grade) for an appropriate duration. Additionally, the materials were subjected to vacuum treatment to further purify them. Some materials required prior cleaning with distilled water and/or acetone.

The tested materials included household-grade stainless steel wool, a nylon filter, commercially available cosmetic cotton pads (dm-drogerie markt GmbH + Co. KG Ebelin), ultra-fine steel wool, dry and humidified magnesium hydroxide carbonate (Merck), 0.5 nm and 1 nm molecular sieves (Merck), superhydrophobic magnesium carbonate (Merck), and steel wool.

In initial trials, activated charcoal and Ascarite (both from Merck) were also tested but

3.1. ASPECTS OF KEY COMPONENTS

Table 3.1: Tested scrubber materials and their cleaning procedure

Material	Cleaning procedure
Stainless steel wool	Cleaned using distill. water and dried. Flushed with N ₂ while heating at 109°C at < 15 mbar for 3 days.
Ultrafine steel wool	Flushed with N ₂ while heating at 103 °C at < 15 mbar for 24 hours
Steel wool	Washed with highly pure water and acetone. Afterwards flushed with N ₂ while heating at 350 °C for > 36 hours
Nylon Filter	Flushed with N ₂ for 2 days
Cotton pads	Flushed < 15 mbar for several days
Mg _x (OH) _y (CO ₃) _z - dry	Flushed with N ₂ for 24 hours at < 15 mbar
Mg _x (OH) _y (CO ₃) _z - humid	Flushed with humidified synthetic air (1000 ppm) for 5 days
Superhydrophobic MgCO ₃	Flushed with N ₂ until dry
0.5 nm mole sieve	Flushed with N ₂ while heating at 70 °C at < 15 mbar for 24 hours
1 nm mole sieve	Flushed with N ₂ while heating at 70 °C at < 15 mbar for 24 hours

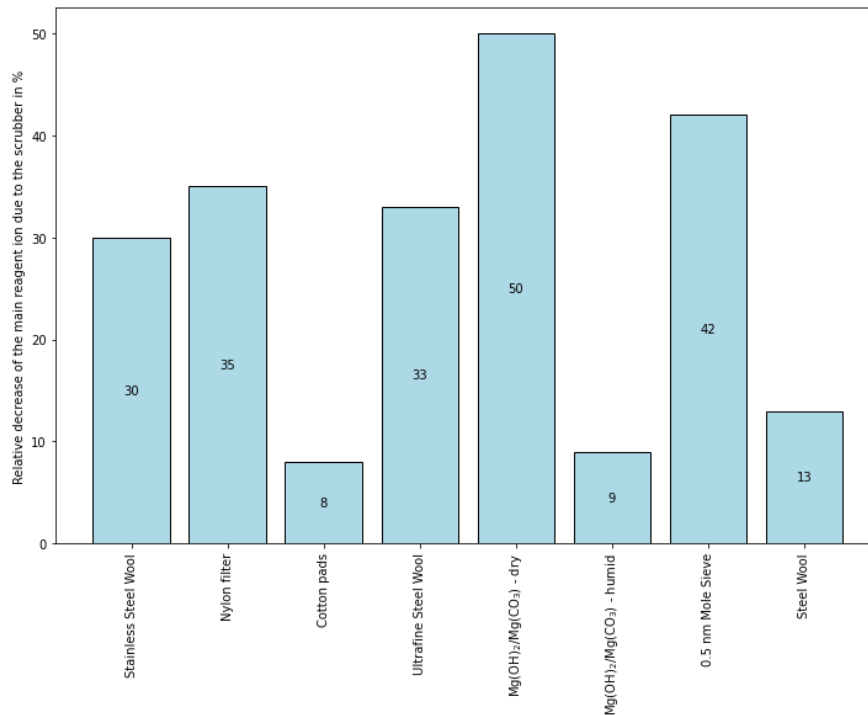


Figure 3.10: Relative decrease of the reagent ion due to the scrubber in % as a proxy of impurities emitted from the scrubber material.

ultimately discarded. Activated charcoal, even after cleaning, contained excessive impurities, while Ascarite exhibited an undesirably high water vapor absorption capacity.

Figure 3.10 shows the percentage decrease of the main reagent ion due to the scrubber when using dry synthetic air. This decrease serves as a proxy for detectable impurities outgassing from the scrubber material. Most materials exhibit significant impurity levels, with a relative decrease of more than 15 %.

In terms of purity, cotton pads, humidified $\text{Mg}(\text{OH})_2\text{Mg}(\text{CO}_3)$, and extensively cleaned steel wool appear to be the best options. In contrast, the 0.5 nm molecular sieve and, especially, dry $\text{Mg}(\text{OH})_2\text{Mg}(\text{CO}_3)$ show the highest impurity levels.

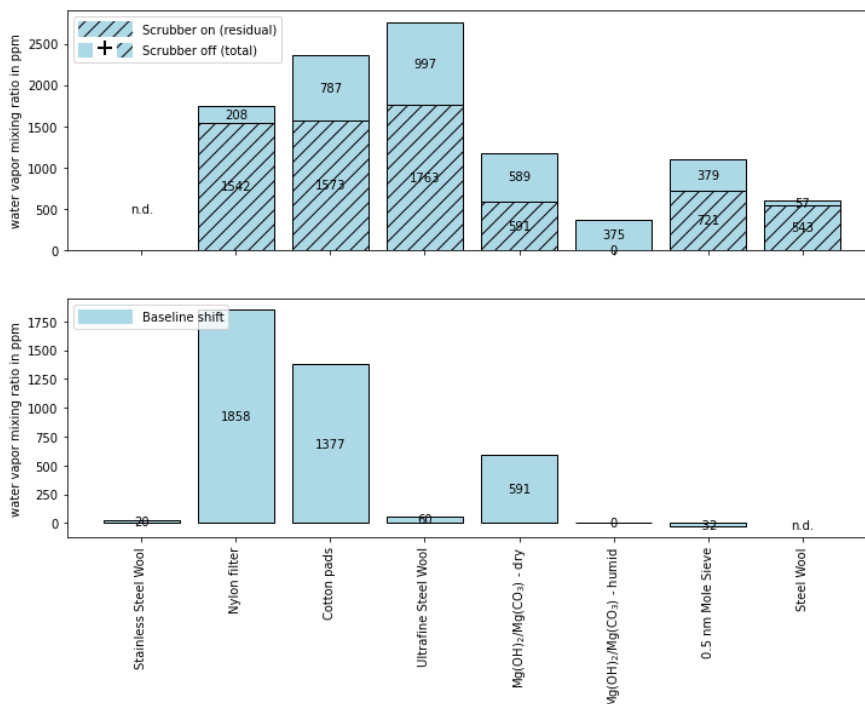


Figure 3.11: Removing efficiency of water vapor of various materials. Upper panel: Total amount of water vapor from the calibration in ppm is represented by total light blue column (Scrubber off (total)). Residual water vapor going through the scrubber is colored hatched light blue. Lower panel: Baseline shift of water vapor signal in ppm due to the scrubber.

Some of the reagent ion depletion could be attributed to water vapor, a manageable impurity as it can be reduced by drying the material. The influence of water vapor was assessed using the reagent ion water cluster, which was simultaneously calibrated with an LGR water vapor isotopes analyzer from Los Gatos. Figure 3.11 illustrates the water vapor behavior

3.1. ASPECTS OF KEY COMPONENTS

of various tested scrubber materials. The upper panel shows the scrubber efficiency for water vapor preservation in ppm. Hatched light blue indicates the residual water vapor detected after passing humidified air through the scrubber, representing its preservation efficiency. The total water vapor content in the synthetic airflow is the sum of the non-hatched and hatched light blue areas. The lower panel shows the baseline shift of the water vapor signal (in ppm) when dry synthetic air passes through the scrubber, indicating the introduction of additional water vapor into the airflow. The nylon filter, cotton pads, and dry $\text{Mg}(\text{OH})_2\text{Mg}(\text{CO}_3)$ introduce additional water vapor into an airflow with a water vapor content of 500 - 2000 ppm, as they are only flushed with N_2 . This issue is mitigated with an improved cleaning procedure, such as longer treatment times, higher temperatures, or lower pressures. However, since these materials continue to release water vapor, it indicates their capacity to absorb moisture to some extent, making them unsuitable for the intended application. Notably, for the nylon filter, the baseline shift and the remaining water vapor after passing through the scrubber do not align. This discrepancy is likely due to a time gap of more than eight hours between the baseline shift and water vapor removal efficiency tests, suggesting that the filter could have undergone further purification.

All other tested materials release minimal water vapor (below 60 ppm). Notably, the 0.5 nm molecular sieve actively dries the synthetic airflow.

It is important to note that "humidified" $\text{Mg}(\text{OH})_2\text{Mg}(\text{CO}_3)$ does not mean it is soaked with water; rather, its crystal structure has changed. As a result, it does not desorb water vapor, as evidenced by the absence of a baseline shift.

Most materials retain at least part of the water vapor content (more than 50 %). Steel wool appears to be the best material to keep the water vapor content constant, absorbing only 9.5 % of the water vapor. On the other hand, humidified $\text{Mg}(\text{OH})_2\text{Mg}(\text{CO}_3)$ absorbs the entire amount.

Ideally, a material's water vapor absorption should not exceed 10 %.

Although extensively cleaned steel wool is the only material that could be seriously considered, all tested materials were evaluated for their efficiency in removing SO_2 and HCN.

Figures 3.12 and 3.13 illustrate the SO_2 and HCN behavior of the various scrubber ma-

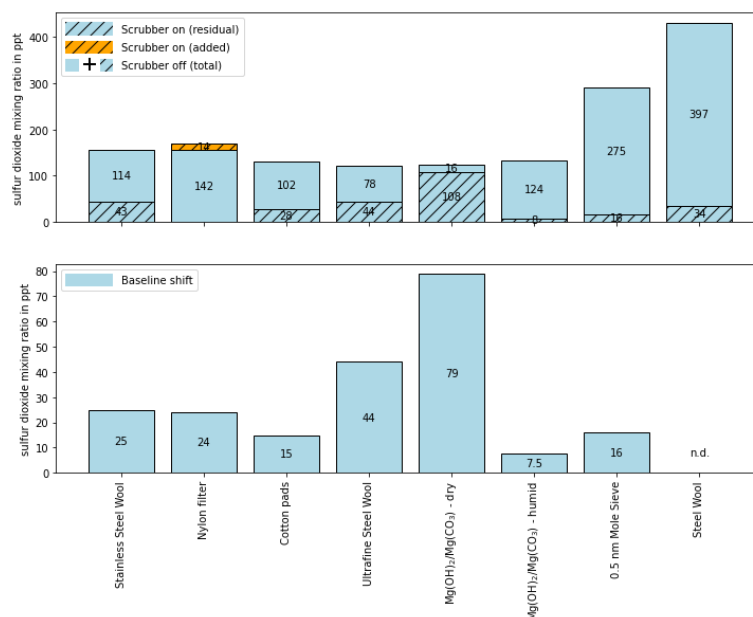


Figure 3.12: Removing efficiency of SO₂ by various materials. Upper panel: Total amount of SO₂ from the calibration in ppt is represented by the total light blue column (Scrubber off (total)). Residual or added SO₂ going through the scrubber is colored hatched light blue or orange, respectively. Lower panel: Baseline shift of SO₂ signal in ppt due to the scrubber.

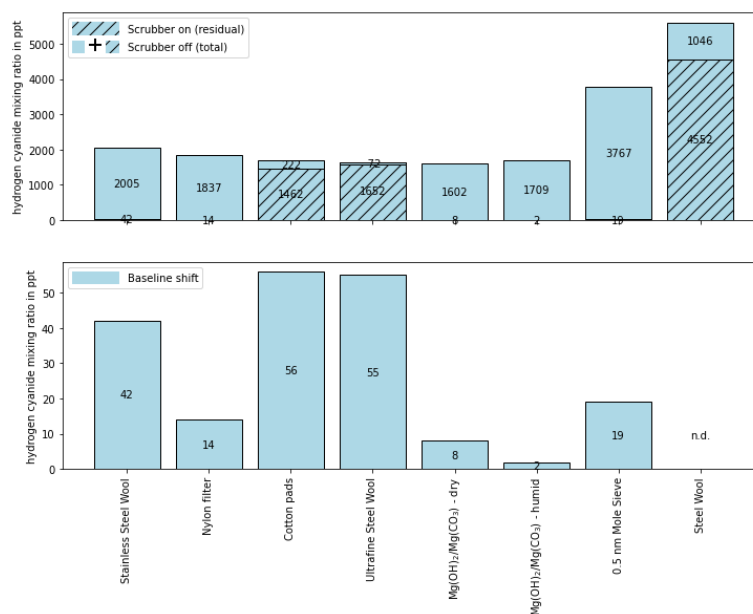


Figure 3.13: Removing efficiency of HCN by various materials. Upper panel: Total amount of HCN from the calibration in ppt is represented by the total light blue column (Scrubber off (total)). Residual HCN going through the scrubber is colored hatched light blue. Lower panel: Baseline shift of HCN signal in ppt due to the scrubber.

3.1. ASPECTS OF KEY COMPONENTS

terials. The upper panel shows the scrubber efficiency for removing each species (in ppt). Hatched light blue represents the residual SO_2 or HCN detected after passing calibration mix through the scrubber, indicating its removal efficiency. In contrast, hatched orange signifies cases where the scrubber introduced additional SO_2 into the flow. The total SO_2 or HCN content in the synthetic airflow is the sum of the non-hatched and hatched light blue areas. Ideally, a material shows no residual SO_2 or HCN (no hatched bar). The lower panel displays the baseline shift of the SO_2 or HCN signal (in ppt) when dry synthetic air passes through the scrubber, indicating the introduction of additional SO_2 or HCN into the airflow.

With the exception of the nylon filter and dry $\text{Mg}(\text{OH})_2\text{Mg}(\text{CO}_3)$, all tested materials quantitatively remove SO_2 as shown in the upper panel of Figure 3.12. However, all materials also cause an increase in the baseline SO_2 signal illustrated in the lower panel of Figure 3.12, resulting in residual SO_2 detection while SO_2 -containing airflows through the scrubber.

This baseline shift may be caused by the release of SO_2 from the scrubber material, the release of a substance that introduces an isobaric interference, or a sensitivity change due to altered conditions in the IMR, leading to enhanced detection. A baseline shift exceeding 10 ppt SO_2 is problematic, as background SO_2 mixing ratios typically range from 1 to 100 ppt. If a material fails to completely remove SO_2 or releases tens of ppt of SO_2 , it can introduce significant errors in background SO_2 measurements, with deviations of at least 10 %.

The same issue applies to HCN, though at higher mixing ratios, as HCN is generally more abundant than SO_2 (see Subsection 2.1). For example, while the 0.5 nm molecular sieve quantitatively removes both SO_2 and HCN, it introduces a baseline shift of 16 ppt for SO_2 and 19 ppt for HCN. In the case of SO_2 , this results in an underestimation of 16 ppt, which, under UTLS background conditions, leads to a systematic error ranging from 16 % to over 200 %.

Considering both removal efficiency and baseline shift, the most viable scrubber materials are the 0.5 nm molecular sieve and humidified $\text{Mg}(\text{OH})_2\text{Mg}(\text{CO}_3)$. However, none of the tested materials fully meet all requirements—purity, water vapor retention, and effective SO_2 and HCN removal without introducing a baseline shift.

Some improvements were implemented to enhance purity. For example, materials like

$\text{Mg}(\text{OH})_2\text{Mg}(\text{CO}_3)$ and molecular sieves were heated and flushed for extended periods under low-pressure conditions, significantly improving both purity and baseline stability. Additionally, heating the scrubber can help retain water vapor, but this negatively impacts SO_2 and HCN removal efficiency.

As a compromise, the purest material with the highest SO_2 and HCN removal efficiency, while maximizing water vapor retention, is selected.

However, Allen et al. (2021) described a procedure to meet these requirements, especially as they also used CF_3O^- as a reagent ion (see Section 3.2). Unfortunately, this scrubber variant will be tried after submission of this work and hence, can not be shown.

3.1.3 Vacuum Ultraviolet Lamp as Ion Source

This section provides a more detailed description of the ion source. As mentioned in the introduction, various methods are used to generate the ions required for chemical ionization mass spectrometry, including radioactive sources (e.g., ^{210}Po) (Lee et al., 2014, 2020), vacuum ultraviolet (VUV) light (Northway et al., 2007; Ji et al., 2020), x-ray lamps (Rissanen et al., 2019), dielectric barrier discharge (Albrecht, 2014; Pape and Schmitz, 2024), and corona discharge (CD) (Kürten et al., 2011).

Using VUV in Funmass offers several advantages over other methods. First, it is significantly safer compared to, for example, a radioactive source. In the event of a leak or damage to the ion source, the VUV lamp simply stops emitting light, as it requires a vacuum to function.

More importantly, VUV ionization is more selective than other sources, meaning it ideally ionizes only the reagent ion precursor while minimizing ionization of nitrogen and/or oxygen in the carrier flow. This selectivity enhances measurement accuracy and reduces interference from carrier gases.

In Funmass, two Krypton VUV lamps (Type PKS 106) from Heraeus are mounted illustrated in Figure 3.14. Each lamp has a bulb diameter of 19.6 mm and a length of 53 mm. They are powered by a DC power supply (Type C200) from Heraeus, which operates at 12 V DC and provides an open-circuit output of 1.5 kV to start the lamps. Once running, the

3.1. ASPECTS OF KEY COMPONENTS

current ranges between 0.2 and 2 mA. Each lamp operates at 400 V and draws 0.8 mA.

According to the manufacturer, the expected lifetime of each lamp is approximately 4,000 hours. A key advantage of this lamp type is that it does not require additional cooling, reducing power consumption—an important consideration given the limited power resources available in FunMass-C. Also, the operation does not produce any high extent of electromagnetic disturbances as e.g., discharge sources do.



Figure 3.14: Krypton VUV lamp Type PKS 106 from Heraeus (Lab-Club, 2025).

The window has a diameter of 10.25 mm and is made of magnesium fluoride (MgF_2), a typical material for VUV radiation applications. To connect the lamps to the IMR, a customized mounting system was designed, as shown in Figure 3.15. This mounting was used until the third IMR version (see Subsection 3.1.4).

The mounting consists of two pieces that securely clamp the lamp in a leak-tight manner. A 1/8" tube is welded onto the lower part of the holder. Initially, this tube was used to introduce the reagent ion precursor and nitrogen mix into the VUV light (up to the second IMR version). In the third version, it was repurposed to deliver a small nitrogen purge flow.

For the outlet, a 6 mm compression fitting from Swagelok® was welded to the bottom of the lower part, allowing connection to any type of tubing, e.g., the mixing tube connector.

Given the reactive environment (exposure to VUV radiation and reactive precursor species

such as bis(trifluoromethyl) peroxide (BTP)), selecting suitable sealing materials was crucial. Various materials — including Viton, Perbunan, silicone, fluorosilicone, PTFE, and Indium (the latter applied directly on the window) — were tested. It could be shown that for leak-tightness, there is no significant difference between the tested materials. However, most of the materials tested resulted in impurities due to outgassing and/or interaction with reactive species and/or VUV beam, which could be observed in the mass spectrum. Indium showed the cleanest spectrum and therefore, was used in the final setup.

In the fourth and final version described in subsection 3.1.4, the VUV lamps are directly clamped onto the newly designed mixing tube, utilizing only a modified version of the upper part of the previous mounting system.

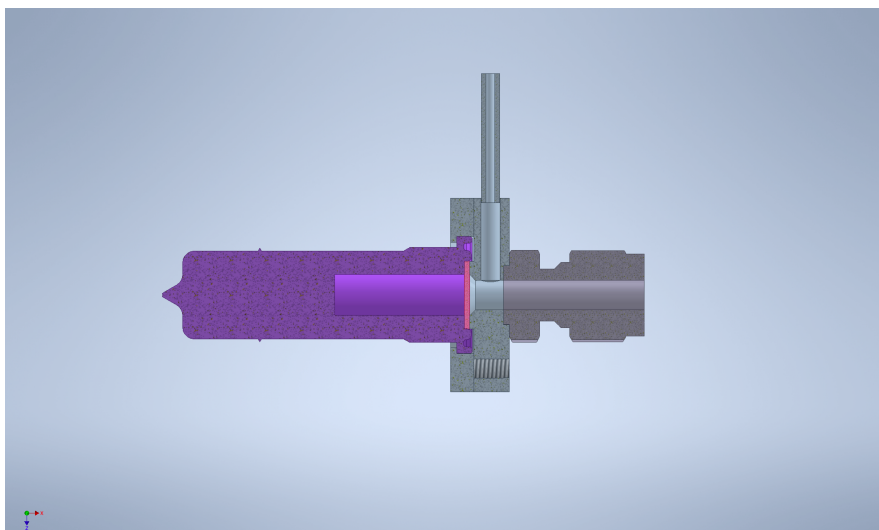


Figure 3.15: Customized mounting for the VUV lamp. Source: Jochen Barthel.

The Krypton lamps emit at two wavelengths: 116.6 nm (10.6 eV) and 123.6 nm (10 eV) (see Figure 3.16). Therefore, precursor substances must have an ionization potential (IP) of 10.6 eV or lower. The VUV light photoionizes these molecules, generating cations and photoelectrons. These electrons can further ionize neutral molecules, leading to the formation of anions.

If the reagent ion precursor is a high-IP electron attacher ($\text{IP} < 10.6 \text{ eV}$), a low-IP substance can be used as a photoelectron donor. This concept is discussed in more detail in Section 3.2.

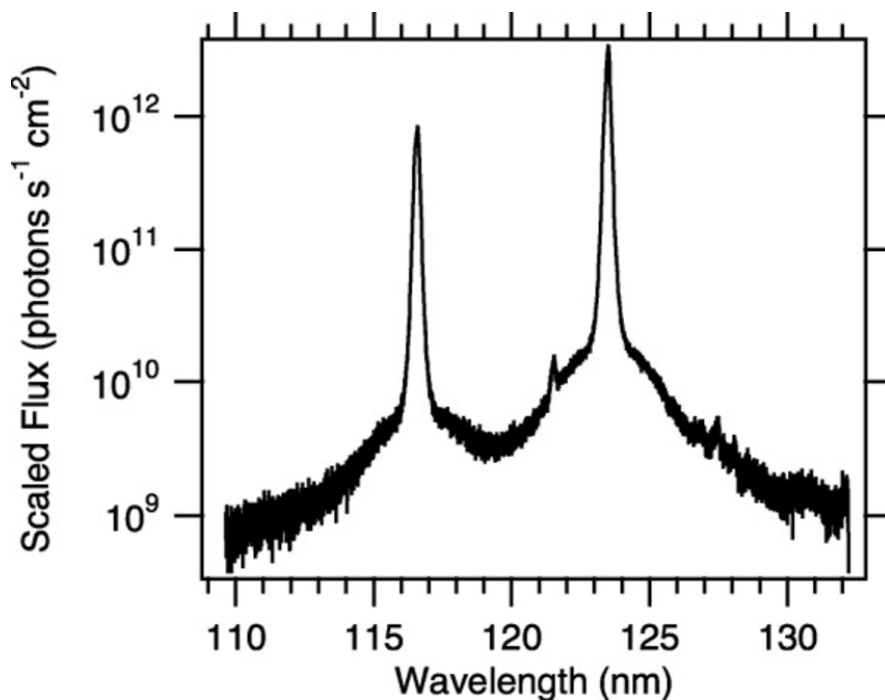


Figure 3.16: VUV spectrum of a Krypton lamp similar to the one used in FunMass-C, showing the two atomic line emissions at 116.5 nm (10.6 eV) and 123.6 nm (10 eV) (Northway et al., 2007). Note that the commercially available lamps are likely much weaker in output.

3.1.4 Ion Molecule Reaction Zone

The ion molecule reaction zone (short: IMR) can be described as a small flow tube system, in which the analyte flow from the inlet and reagent ion flow from the ion source is mixed and ion chemistry and ion cluster formation produce the product ions detected in the MS.

After passing through the scrubber valve (see Figures 3.7), the airflow enters the Ion-Molecule Reaction Zone (IMR). Figure 3.17 provides a schematic of the IMR and the mounted scrubber valve. The IMR consists of four key components: a stainless steel mixing tube (dark blue) that directs the airflow, a PTFE inset (beige) designed to introduce and mix the sample air with the nitrogen flow containing the reagent ions, vacuum ultraviolet (VUV) lamps (violet) serving as the ion source, and an aluminum cylinder (orange) that helps focus the airflow toward the Time-of-Flight (ToF) orifice (dark blue and red).

The stainless steel mixing tube has an inner diameter of 50 mm and features two opposing G 1/8 threads (see Figure 3.18) for mounting the VUV lamps using straight 35 mm long, 6

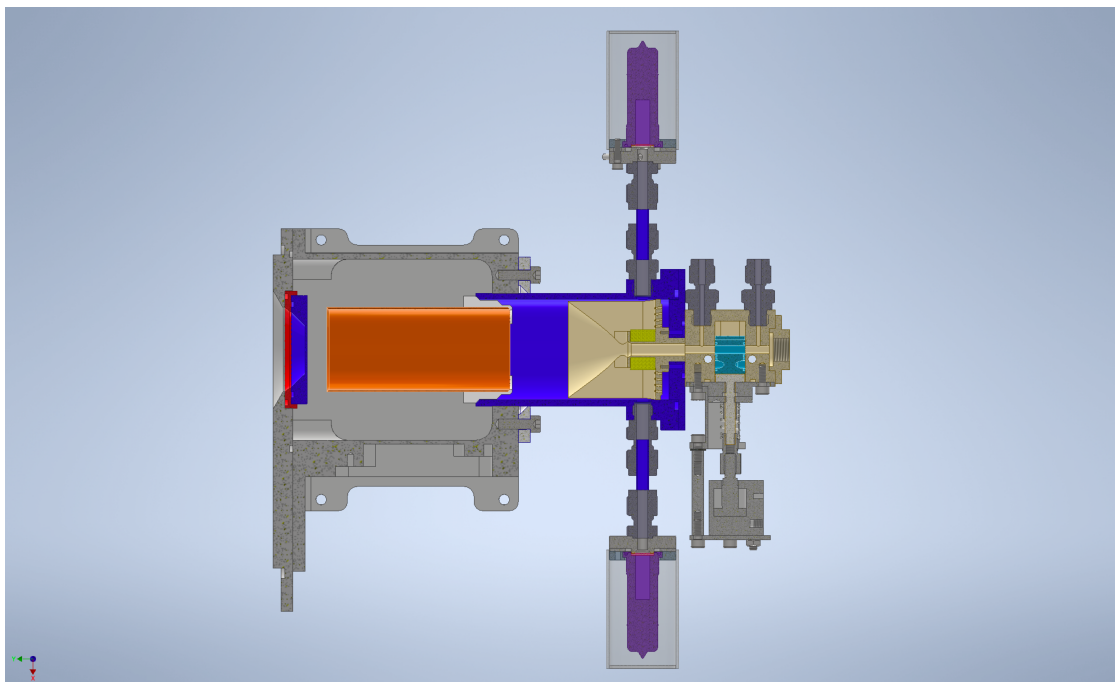


Figure 3.17: A schematic of the IMR (sample airflow from right to left). At the inlet, the scrubber valve (beige) with its inset (turquoise) is visible. The main IMR part is a stainless steel mixing tube (darkblue; 50 mm diameter) with a PTFE inset (beige). On each side of the mixing tube are G 1/8 threads to mount short 6 mm stainless steel tubes (darkblue) to supply VUV light (violet) and a little purge flow to keep the VUV windows (pink) in front of the lamp clean. The VUV beams from the lamps are reflected into themselves by two VUV mirrors (Edmund Optics; yellow) in order to enhance ion generation. A smaller aluminium cylinder (orange) is attached to the mixing tube in order to focus the airflow to the ToF inlet. A stainless steel plate (blue) with a small orifice (0.4 - 0.5 mm) is put in front of the ToF. It is isolated by a ceramic plate (red). The mixing tube is mounted in a 140 mm $\times$ 105 mm $\times$ 112 mm (L $\times$ W $\times$ H) aluminium box.

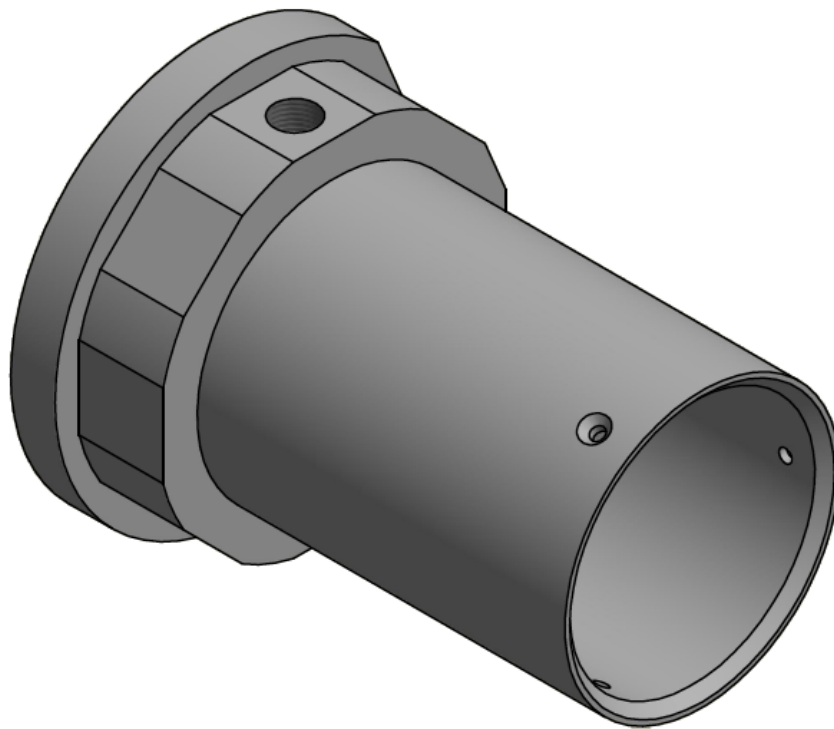


Figure 3.18: The stainless steel mixing tube with a inner diameter of 50 mm and two G 1/8 threads to plug in the ion source. Source: Jochen Barthel

mm stainless steel tubes. To attach the scrubber valve, a front plate with a 6 mm inner diameter inlet hole was manufactured.

Initially, the mixing tube was made of aluminum, which is lighter than stainless steel and more suitable for an airborne instrument. However, due to the possibility of airflow-wall interactions (caused by a non-ideal flow regime), the material was switched to stainless steel, which offers better properties for minimizing interactions with the trace gases of interest. In the future, the mixing tube could be made from PFA- or SilcoNert2000®-coated aluminum (lightweight and inert).

The mixing tube is mounted in a 140 mm $\times$ 105 mm $\times$ 112 mm (L $\times$ W $\times$ H) aluminium box as shown in Figure 3.17. The fore pump line connection is at the front plate (removed due to clarity in Figure 3.17). Importantly, a negative temperature coefficient (short: NTC) thermistor is put through the housing into the IMR airflow. This ensures to measure the IMR gas temperature.

The IMR underwent an evolution of four states. The first three states are using almost the same IMR construction as shown in Figure 3.17, only the PTFE inset (beige) (inserted to the mixing tube) was altered.

In the following, the four IMR versions are briefly explained.

- For the first IMR setup (IMR1), a conical PTFE inset was used. The reagent ions were generated by flowing the reagent ion mixture directly past the VUV lamps. The reagent ion flow was entering the IMR from the side. This introduction could be altered by using different tube lengths and bending. However, the analyte flow could never be shielded from the VUV beam in the a sophisticated version.
- In the second IMR setup (IMR2), the conical PTFE inset was exchanged by a PTFE tube covered by a stainless steel cap. The advantage of this setup was that the analyte flow was protected from the VUV beam. This setup was designed to be a proof-of-concept version as the tube caused turbulence and a enhance surface contact.
- The third IMR version (IMR3) was combining the findings of the two versions before. The PTFE inset has a conical shape while shielding the analyte flow from the VUV

beam. The reagent ion mixture was introduced to the IMR backwards flowing through 24 small little holes of the PTFE inset. The ions were generated by the almost to flow direction perpendicular VUV beam, which was reflected by VUV mirror (Edmund Optics) to enhance ion formation. However, CFX simulation showed turbulence and even backflows inside the IMR due to this configuration, which made the residence time unpredictable and caused enhanced surface contact.

- The fourth IMR version (IMR4), the entire IMR was newly designed based on CFX simulations. It is similar to the VOCUS AIM reactor from TOFwerk(Randel et al., 2010; Aggarwal et al., 2025). The reagent ions are generated in separated compartment and subsequently introduced to the analyte flow almost perpendicularly. The VUV beams are perpendicular to the oblong holes to the IMR and reflected into themselves by VUV mirrors (Edmund optics). This setup keeps the advantages of the previous versions (mainly shielding the analyte flow from the VUV beam) while reducing significantly turbulence and hence, surface contact. Moreover, this setup achieves a better and more controlled mixing between the reagent ion and analyte flow.

In this subsection, only the last two versions are described in more detail as the third version was used for the experiments, detailed described in Chapters 4 and 5, and the fourth and final version will be the IAGOS-CARIBIC setup. The first and second IMR version are described in Section S3.

A PTFE inset was inserted into the mixing tube to improve the mixing of the sampled airflow with the reagent ion flow. In Figure 3.19, the IMR3 is shown. It has again a conical shape with a widening angle of 60 to 70 ° as shown in Figure 3.20. The analyte inlet tube has again an inner diameter of 6 mm, which increases within the cone to 49.5 mm. To the left and to the right of the inlet tube, 3×4 holes with an inner diameter of 1 mm were drilled slightly oriented to the center axis of the IMR3 with an angle of 7.5 ° as shown in Figure 3.19b. This allows better mixing between the reagent ion flow and the sampled airflow. The reagent ion flow enters the IMR3 in the small space between the SS mixing tube and PTFE inset as shown in Figure 3.17. Afterwards the mixture flows through the 24 small little holes

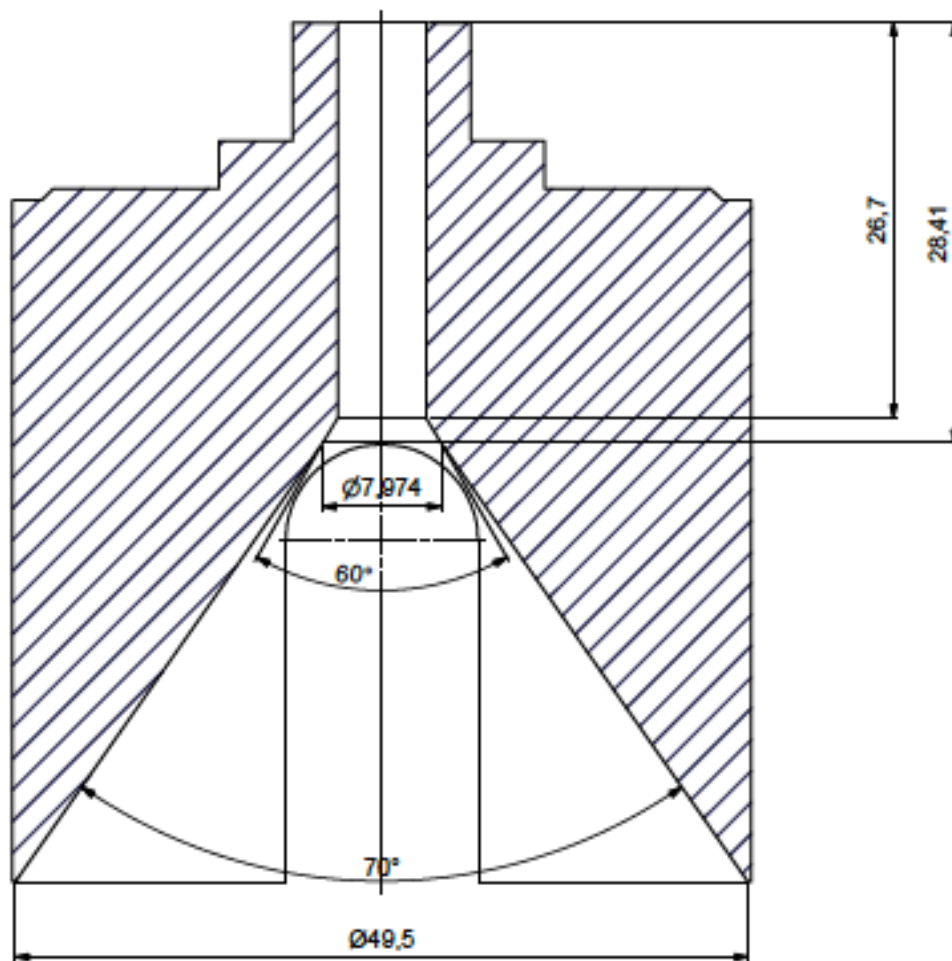


Figure 3.20: Technical drawing of the IMR3 inset made of PTFE. Source: Jochen Barthel.

airflow toward the ToF inlet while preventing mixing with older air masses. It was assumed that air masses not entering the ToF would be immediately removed by the fore pump. However, the backflow undermines this objective.

The backflow is particularly problematic due to the small gap between the aluminum cylinder and the stainless steel mixing tube, which increases wall surface contact. Additionally, this backflow interacts with the sheath flow generated by the nitrogen flow passing the VUV lamps, further complicating the flow dynamics. Another slow backflow is also present along the inner wall of the aluminum cylinder. These backflows create two large vortices on either side near the orifice of the inner cylinder. Although the velocity of these vortices and backflows is significantly lower than that of the main sampled airflow—by a factor of 10—indicating only a minor influence on measurements, their presence is still undesirable. The vortices prolong the residence time of air masses to an unknown extent, which is not ideal.

Another issue with this design is the mismatch between the reagent ion flow and the sampled airflow. The reagent ion flow is considerably slower, leading to inefficient mixing between the two gas flows. Furthermore, a significant fraction of the reagent ions come into contact with the surface of the PTFE inset, resulting in reagent ion loss.

These non-ideal characteristics of the IMR3 ultimately led to the development of the fourth and final IMR version.

Consequently, the IMR4 was designed with the help of fluid dynamic CFX simulations (ANSYS 2022 R1) done by Simon Heger (Josip Heger und Simon Heger GbR) shown in Figures 3.22 and 3.23. After several iterations of designing and simulating, the final version could be found as shown in Figure 3.24. The conical design was initially inspired by the VOCUS AIM reactor from TOFwerk (Randel et al., 2010; Aggarwal et al., 2025). The hyperbolic shape of the FunMass-C IMR4 has approved advantaged in terms of flow compared to the straight conical design of TOFwerk.

The IMR4 consists of three parts, which simplifies the manufacturing process. Figure 3.26 depicts the first part, featuring a 31 mm long inlet tube that gradually widens from an inner diameter of 4 mm to 6.05 mm, corresponding to a widening angle of 6°. The oblong hole, with dimensions of 4 mm $\times$ 1 mm $\times$ 4 mm (L $\times$ W $\times$ H), introduces the reagent ion flow

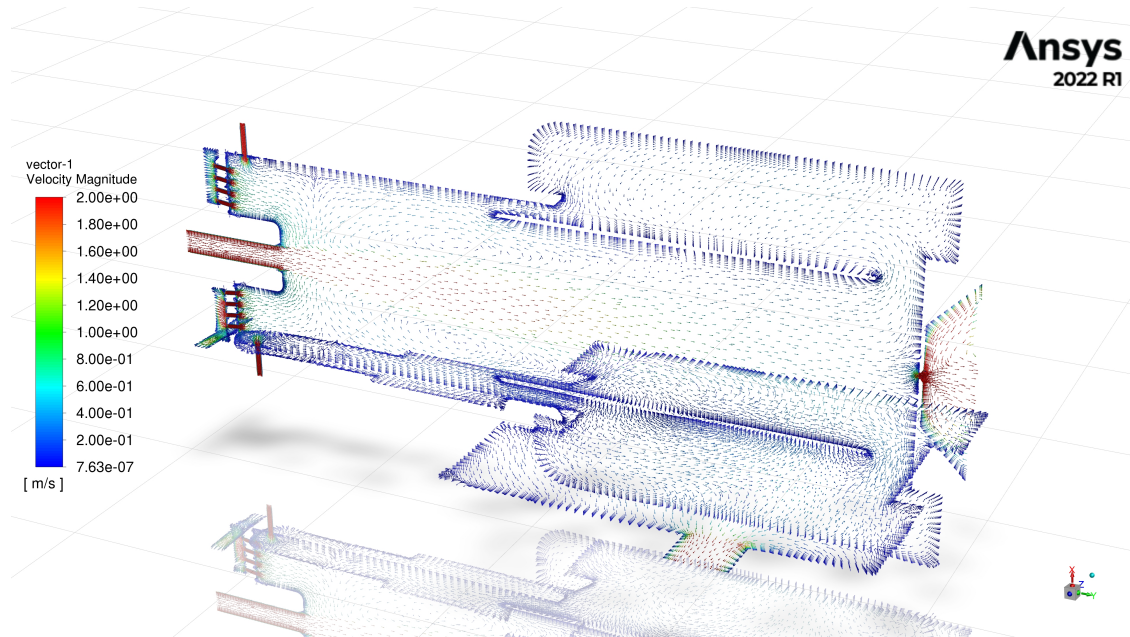


Figure 3.21: Fluid dynamics CFX simulation inside the IMR3 version using ANSYS 2022 R1. The color code represents the velocity of the air in m/s. Source: Simon Heger (Josip Heger und Simon Heger GbR).

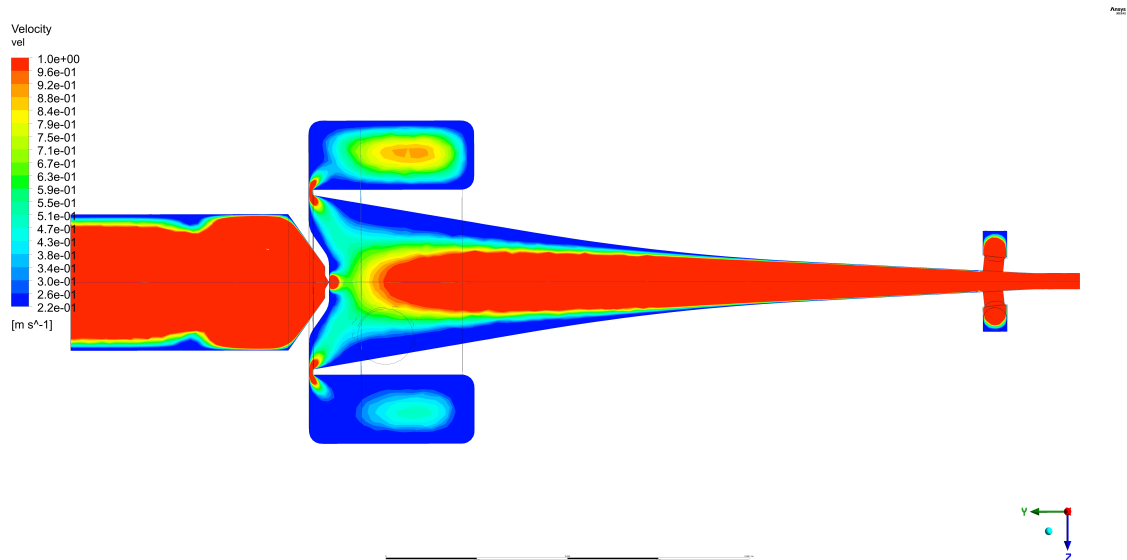


Figure 3.22: Fluid dynamics CFX simulation inside the IMR4 version using ANSYS 2022 R1. The color code represents the velocity of the air in m/s. Source: Simon Heger (Josip Heger und Simon Heger GbR).

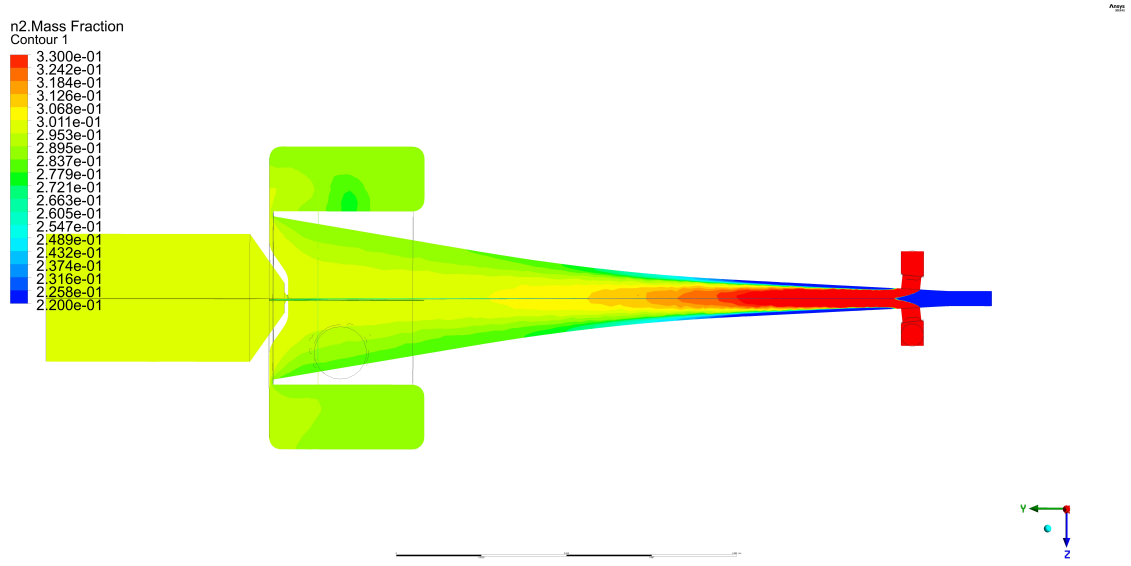


Figure 3.23: Fluid dynamics CFX simulation inside the IMR4 version using ANSYS 2022 R1. The color code represents the N_2 mass fraction introduced via the ion source. If both air flows (air inlet and ion source) are ideally mixed, the N_2 mass fraction should be $2.982 \cdot 10^{-1}$. Source: Simon Heger (Josip Heger und Simon Heger GbR).

after 19.1 mm at an angle of 6° to the analyte airflow illustrated in Figure 3.27. Additionally, this part includes a 10 mm long recess with a threaded inner diameter of 26 mm, allowing the second part (see Figure 3.28) to be securely screwed in.

The second part of the IMR4 has a total length of 79 mm, with the last 13 mm featuring a recess with a threaded inner diameter of xx mm, allowing the third part shown in Figure 3.29 to be securely screwed in. It begins with an inner diameter of 6.05 mm, matching the endpoint of the first part, and gradually expands to an inner diameter of 14.3 mm. However, the widening occurs in two distinct phases. Over the first 37.7 mm, the inner diameter increases linearly at a widening angle of 6° , reaching 10 mm. Beyond this point, the widening transitions into a circular expansion with a radius of 592 mm. This is a result of the CFX simulations showing disturbed flow at purely conical walls. In this section, the inner wall of the IMR4 follows the curvature of an imaginary circle with the specified radius (here: 592 mm). Additionally, a 35 mm long recess (spanning from 16 mm to 51 mm) is incorporated into the middle section to reduce material usage and minimize unnecessary weight.

The third part of the IMR4 begins with an inner diameter of 14.3 mm, matching the endpoint of the second part, and expands to an inner diameter of 43.1 mm over a length of 93

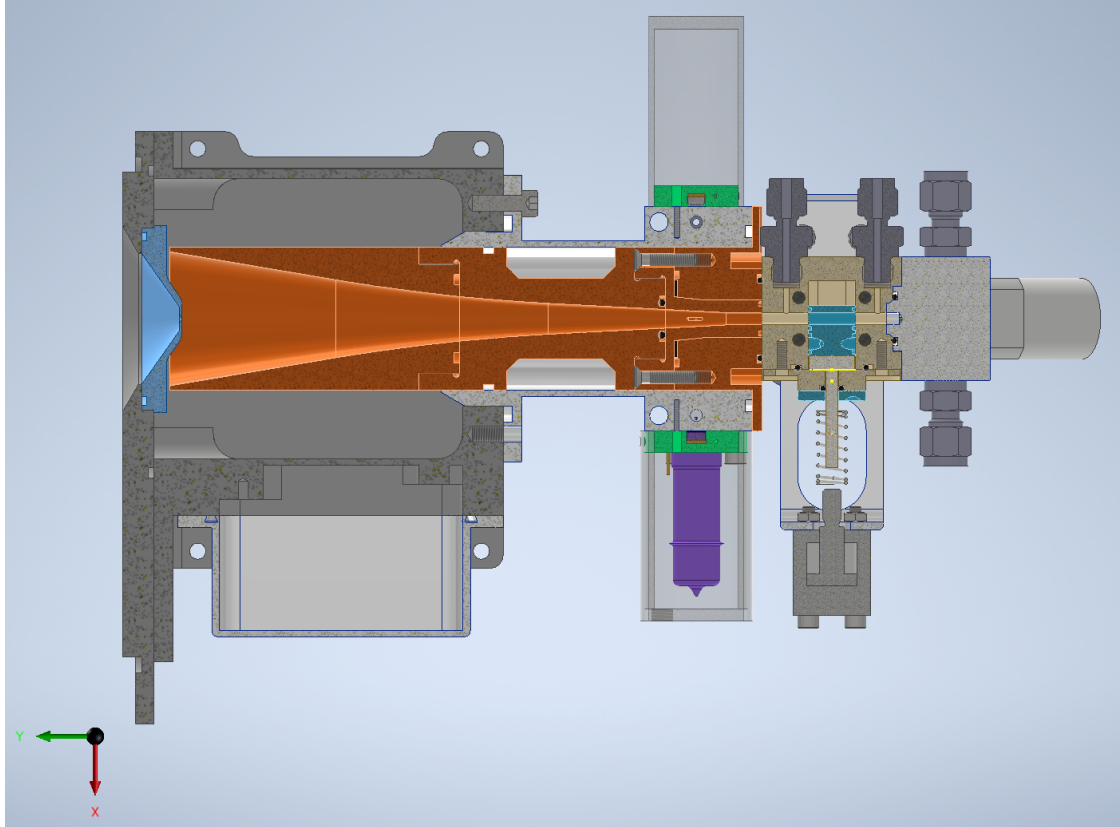


Figure 3.24: Cross-section of the IMR4. The airflow enters the system from the right side, first passing through the scrubber valve (see 3.7). It then enters the IMR, where the IMR inset is divided into three parts to facilitate the manufacturing process. The entire inset is made of SilcoNert2000®-coated aluminum. A portion of the airflow continues into the ToF through a nozzle, also made of SilcoNert2000®-coated aluminum. Perpendicular to the airflow, on both sides, VUV lamps (violet) illuminate channels flushed with a dedicated gas mixture. Source: Jochen Barthel.

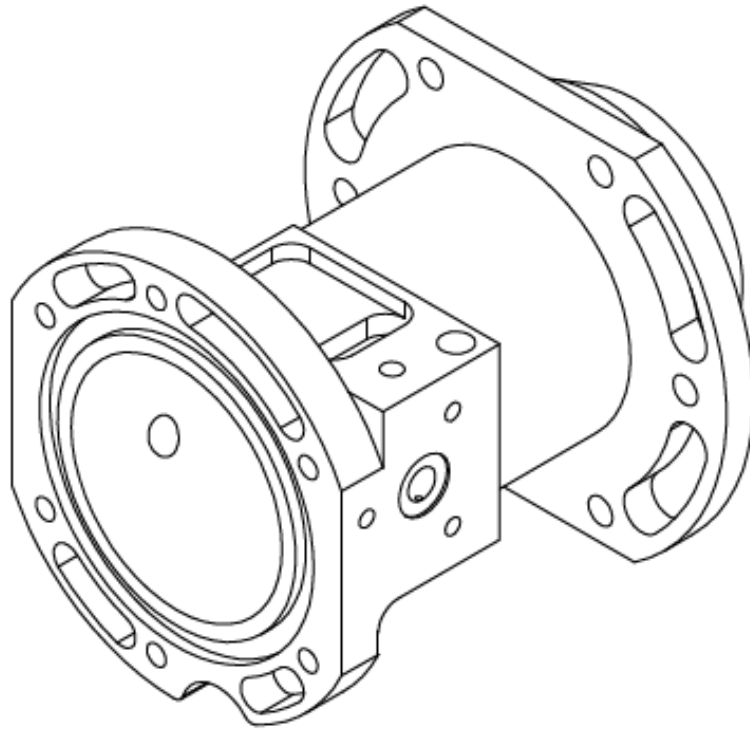


Figure 3.25: The stainless steel mixing tube of IMR4. Source: Jochen Barthel

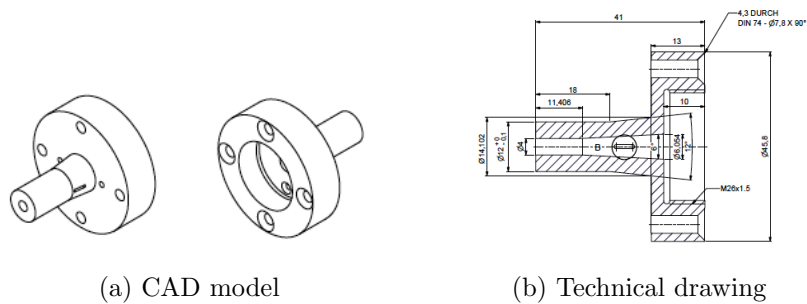
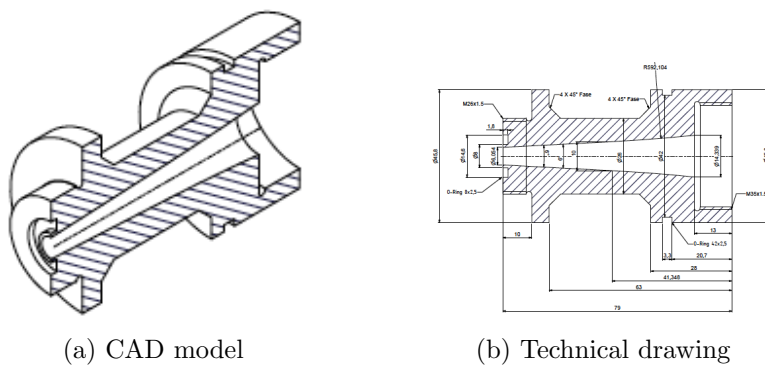
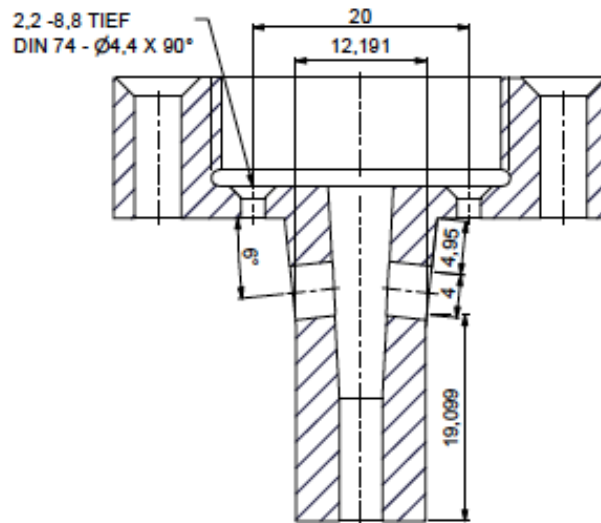


Figure 3.26: First part of the IMR4 made of SilcoNert2000®-coated aluminum. Source: Jochen Barthel.



mm. The first 39.7 mm continues the circular expansion with a radius of 592 mm, consistent with the second part, and reaches an inner diameter of 25 mm at the end of this section. The final 53.4 mm transitions to a linear expansion with a widening angle of 19.2° to meet the required length specifications. Additionally, there is a 1 mm gap between the IMR4 and the front plate of the ToF nozzle, allowing excess air to be efficiently pumped away without causing unintended effects on the gas flow due to suction from the fore pump.

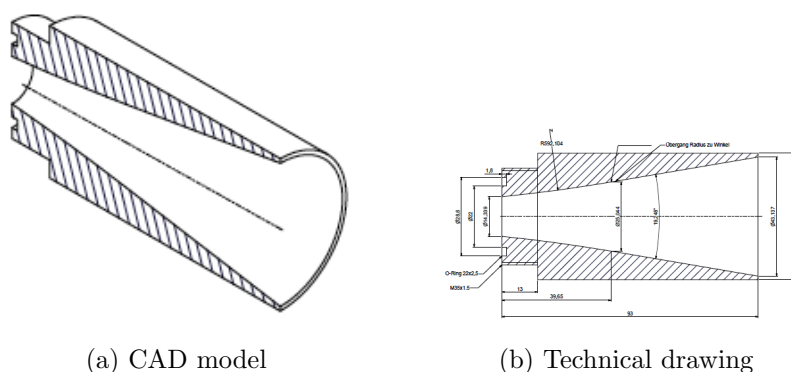


Figure 3.29: Third part of the IMR4 made of SilcoNert2000®-coated aluminum. Source: Jochen Barthel.

The entire IMR4 setup is directly connected to the newly designed front plate of the mixing tube (shown in Figure 3.30), ensuring a precise and reliable 1 mm gap between the IMR4 insert and the front plate of the ToF nozzle.

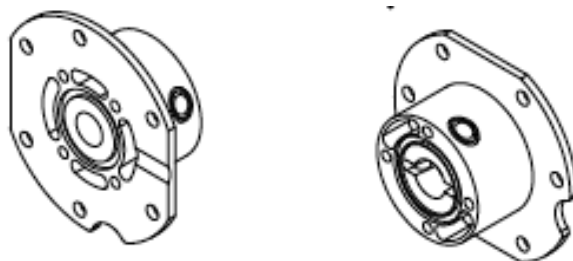


Figure 3.30: Front plate of the mixing tube and second cylinder of the ion source made of SilcoNert2000®-coated aluminum for the IMR4. Source: Jochen Barthel.

As there is not an inner tube inside the IMR4, which protects the sampled airflow from the VUV light of the ion source, the ion source was also redesigned as shown in Figure 3.31). Each VUV lamp (violet) has its own reagent ion mixture supply line, along with a separate

3.1. ASPECTS OF KEY COMPONENTS

nitrogen supply line to keep the windows (pink) clean. Upon entering the ion source tube, the reagent ion mixture flow and the VUV beam are oriented perpendicular to the IMR4 flow, preventing VUV light from entering the IMR4. To enhance ionization, the VUV beam is reflected by a VUV mirror (yellow), effectively doubling the beam path length. The ionized reagent ion flow then enters the IMR4 through the oblong holes. Due to space limitations, both lamps are opposite each other and slightly offset in the z-axis shown in Figure 3.31.

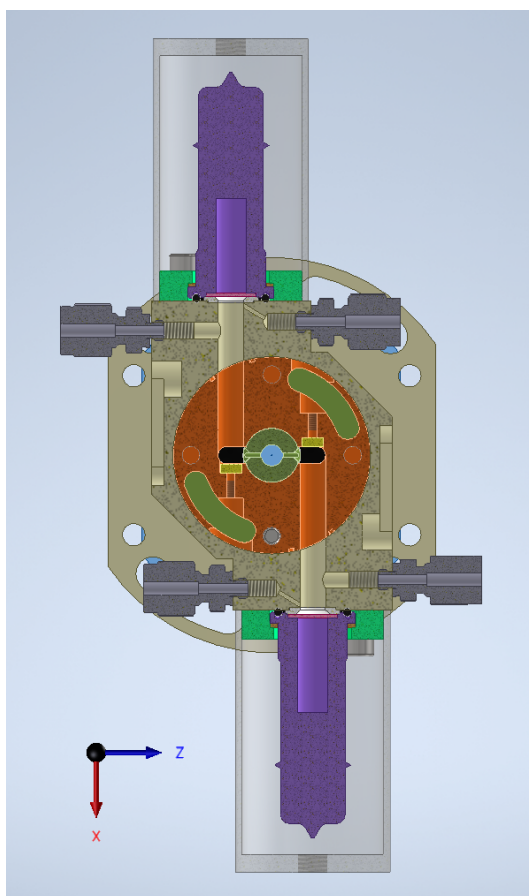


Figure 3.31: Schematic of the ion source for the IMR4. Each VUV lamp (violet) has its own reagent ion mixture supply line, along with a separate nitrogen supply line to keep the windows (pink) clean. Upon entering the ion source tube, the reagent ion mixture flow and the VUV beam are oriented perpendicular to the IMR4 flow, preventing VUV light from entering the IMR4. To enhance ionization, the VUV beam is reflected by a VUV mirror (yellow), effectively doubling the beam path length. The ionized reagent ion flow then enters the IMR4 through the oblong holes. The inner wall of the IMR is illustrated in green to be better distinguished to the IS. Source: Jochen Barthel.

The airflow enters the ToF through a critical orifice, where the flow rate ideally depends

on the pressure difference before (20–80 mbar) and after (10^{-2} mbar) the orifice. Various orifice sizes, ranging from 0.3 mm to 0.5 mm, were tested. A 0.3 mm orifice was found to be too small, leading to a significant signal decrease, while a 0.5 mm orifice could pose challenges for the turbo and small fore pump in the final CARIBIC setup.

With the transition from an aluminum to a stainless steel orifice, the exact orifice size is currently 0.47 ± 0.02 mm. Figure 3.32 illustrates the dependence of the flow into the ToF (black), BSQ pressure (blue), ToF pressure (orange), and Turbo power consumption (red) on the IMR pressure for the IMR3 setup with the stainless steel ToF orifice.

The power consumption of the turbo molecular pump remains well within operational limits, not exceeding 100 W. The maximum allowable power during operation is 120 W, with automatic shutdown occurring if consumption exceeds 150 W. During CARIBIC operation, the IMR pressure is expected to be between 30 and 40 mbar, corresponding to a turbo pump power consumption of approximately 80 W. Additionally, both the BSQ and ToF pressures remain within acceptable ranges for IMR pressures below 50 mbar.

For the CARIBIC setup, the flow into the ToF is between 40 and 45 SCCM, which is sufficient but could ideally be higher. Since both the pressures and the turbo pump power consumption are relatively low for an IMR pressure of 30–40 mbar, there is potential for optimization.

To increase flexibility, the front plate for the ToF has been designed to be changed easily. This modification facilitates easier adjustments, enabling systematic testing to determine the optimal orifice size for the CARIBIC setup. In the final setup, a SilcoNert2000®-coated aluminium front plate is used. This combines the inert surface caused by the coating and the lighter weight due to the use of aluminium instead of stainless steel.

3.1.5 Time-of-Flight Mass Spectrometer

A small fraction of the ionized air sample, approximately 5 – 10 % of the total flow, exits the IMR through the narrow orifice (0.4–0.5 mm) and enters the transfer stage designed by TOFWerk shown in Figure 3.33. The transfer stage consists of two main sections. The first stage, maintained at approximately 10^{-2} mbar, houses a big segmented quadrupole

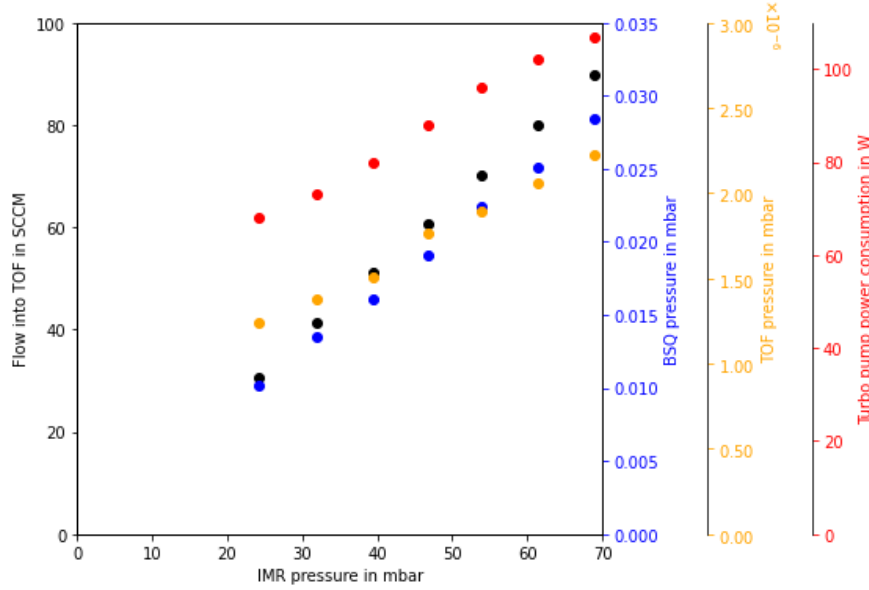


Figure 3.32: The dependence of the flow into the ToF (black) in SCCM, BSQ pressure (blue) in mbar, ToF pressure (orange) in mbar, and Turbo power consumption (red) in W on the IMR pressure in mbar for the IMR3 setup with the stainless steel ToF orifice

(BSQ). After passing through this section, the ions enter the second stage, which contains the ion optics compartment. This stage operates at a lower pressure of around 10^{-5} mbar and serves to focus the ion beam before it enters the ToF analyzer, i.e. the extractor. The pressure further decreases within the ToF chamber, not exceeding $3 \cdot 10^{-6}$ mbar. The transfer stages and the ToF analyzer are maintained at these vacuum conditions by a four-stage turbo molecular pump (SF270, Pfeiffer Vacuum GmbH).

As described in Section 1.3, the core principle of the ToF analyzer is the separation of ions based on their mass-to-charge ratio (m/q). This separation relies on differences in flight time through a field-free drift region of known length. However, for this method to be accurate, two key assumptions must be met: first, all ions must enter the drift region simultaneously, and second, they must have no initial kinetic energy in the flight direction. In FunMass-C, both conditions are satisfied by accelerating the ions perpendicularly to their flight path upon exiting the transfer stage, as illustrated in Figure 3.33.

To achieve this, an extractor (see Figure 3.33) generates an ultra-short electrical field pulse using a pulser. The electrical energy E_{el} introduced to the ions by this pulse is converted into

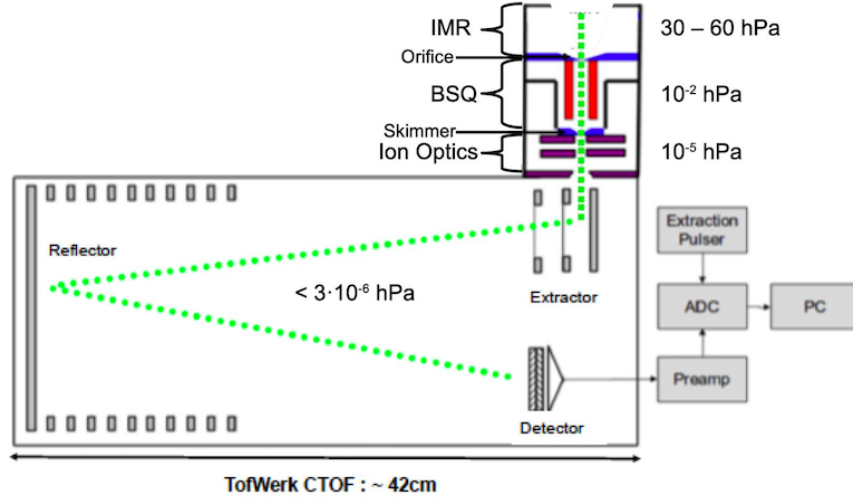


Figure 3.33: Schematic of the ion transfer stages and CToF analyzer

the kinetic energy E_{kin} of the ions, as expressed in equation 3.1. The electric field between the extractor plates is assumed to be homogeneous, allowing the electrical energy to be expressed as $E_{\text{el}} = q \cdot U$, where the charge q of an ion is an integer multiple z of the elementary charge e , i.e., $q = z \cdot e$ (Note: In CIMS, there are hardly any $z > 1$).

$$E_{\text{el}} = q \cdot U = e \cdot z \cdot U = \frac{1}{2} \cdot m \cdot v^2 = E_{\text{kin}} \quad (3.1)$$

The equation 3.1 can be transformed in the equation 3.2.

$$v = \sqrt{\frac{2 \cdot e \cdot z \cdot U}{m}} \quad (3.2)$$

In Equation 3.2, it is shown that the velocity v is a function of the charge of the ion q , the mass of the ion m , and the voltage of the electrical field U . Since the voltage U remains constant over time and space, it is the same for every ion. Consequently, the velocity v in the field-free drift path is proportional to the square root of the ion charge q and inversely proportional to the square root of the ion mass m . This implies that lighter ions and ions with a higher charge travel faster, while heavier or lower-charged ions travel more slowly. The faster an ion moves, the shorter its drift time t . Under the valid assumption of uniform motion, where velocity remains constant over time, the drift time t can be described as function of

3.1. ASPECTS OF KEY COMPONENTS

the drift path length s and the velocity of the ion v (shown in equation 3.3).

$$t = \frac{s}{v} = \frac{s}{\sqrt{2 \cdot e \cdot U}} \cdot \sqrt{\frac{m}{z}} \quad (3.3)$$

Using the equation 3.3, the difference of the drift time Δt between two ions a and b with different m/q can be calculated as described in equation 3.4.

$$\Delta t = \frac{s}{\sqrt{2 \cdot e \cdot U}} \cdot \left[\sqrt{\frac{m_a}{z_a}} - \sqrt{\frac{m_b}{z_b}} \right] \quad (3.4)$$

The larger Δt between two ions with very similar m/q the better these ions can be resolved, resulting in higher mass resolution and improved differentiation. According to equation 3.4, this can be achieved by increasing the path length s or decreasing the kinetic energy E_{kin} . In particular, increasing the flight path length is the most common approach to improving mass resolution. However, extending the flight path is not always feasible for two main reasons.

First, space is always a limited resource, especially for instruments deployed on an aircraft, but also for laboratory-based setups. Second, the maximum possible flight path is constrained by the mean free path l . The mean free path l represents the average distance an atom, molecule, ion, or particle can travel without colliding with another atom, molecule, ion, or particle. Collisions can cause changes in the kinetic energy (velocity) and in the flight direction (Gross, 2006). Thus, the likelihood of collisions should be as low as possible. It is a function of the pressure p , the kinetic diameter of the object d , and the temperature T assuming the ideal gas law and spherical particles (see equation 3.5). The constant k is the Boltzmann constant ($1.38 \cdot 10^{-23} \text{ J K}^{-1}$).

$$l = \frac{k \cdot T}{\sqrt{2} \cdot \pi \cdot d^2 \cdot p} \quad (3.5)$$

The longer the flight path of an ion (i.e., the larger the ToF analyzer), the longer the mean free path must be to minimize collisions. Consequently, the ToF pressure must be lower for a given temperature (e.g., $T = 300 \text{ K}$). Figure 3.34 illustrates the minimum ToF pressure in hPa required to minimize collisions as function of the mean free path in meters at 300 K for

different kinetic diameters: 265 pm (black), 360 pm (blue), and 590 pm (orange).

However, even if a mean free path of 6 m were hypothetically required due to the size of the ToF, the minimum ToF pressure would still be $4 \cdot 10^{-6}$ mbar for larger molecules such as SF_6 , which remains feasible using turbo pumps. In FunMass, a compact ToF (CToF) is employed, as its small size and lightweight design make it well suited for airborne instrumentation. The dimensions of the FunMass ToF are 265 mm $\times$ 175 mm $\times$ 115 mm. Given this, a minimum mean free path of 1 m should be more than sufficient. Assuming a 1 m free path, a maximum pressure of $2.5 \cdot 10^{-5}$ mbar is required (indicated by the red dashed line in Figure 3.34). Due to the high voltages used within the ToF, the pressure must anyways not exceed $3 \cdot 10^{-6}$ mbar to avoid sparks from high-voltage equipment.

To extend the flight path of ions without increasing the physical dimensions of the ToF, reflectors can be used, as illustrated in Figure 3.33. FunMass operates in a single-reflector configuration known as V-mode. Some ToFs utilize two reflectors resulting in three reflections, referred to as W-mode. Increasing the number of reflectors effectively extends the flight path, thereby enhancing mass resolution.

The ions are detected by a microchannel plate (MCP) detector. An MCP consists of millions of tiny tilted channel electron multipliers (called cherron configuration). Two stacked plates are maintained at a voltage between 1900 V and 2500 V (direct current), with the specific voltage depending on factors such as the age and quality of the MCP, as well as the required signal strength.

On nanosecond timescales, ions impact the MCP, triggering electron avalanches within the microchannels. The resulting secondary electron-induced signal pulses are subsequently amplified and digitized by an analog-to-digital converter (ADQ1600, Teledyne Signal Processing Devices Sweden AB), which must operate at extremely high speeds to capture the rapid signal variations. The digitization rate of the ADQ1600 is 1 ns, which means that the dwell time of one data point dealt by the ADQ1600 is 1 ns. The digitized data are then stored on a hard drive or solid-state device during in-flight operation. Moreover, FunMass operates with a maximum extraction frequency of 20 kHz, meaning that a mass spectrum with 21248 data points is recorded every 16.65 μs . It is crucial that the time interval between two consecutive

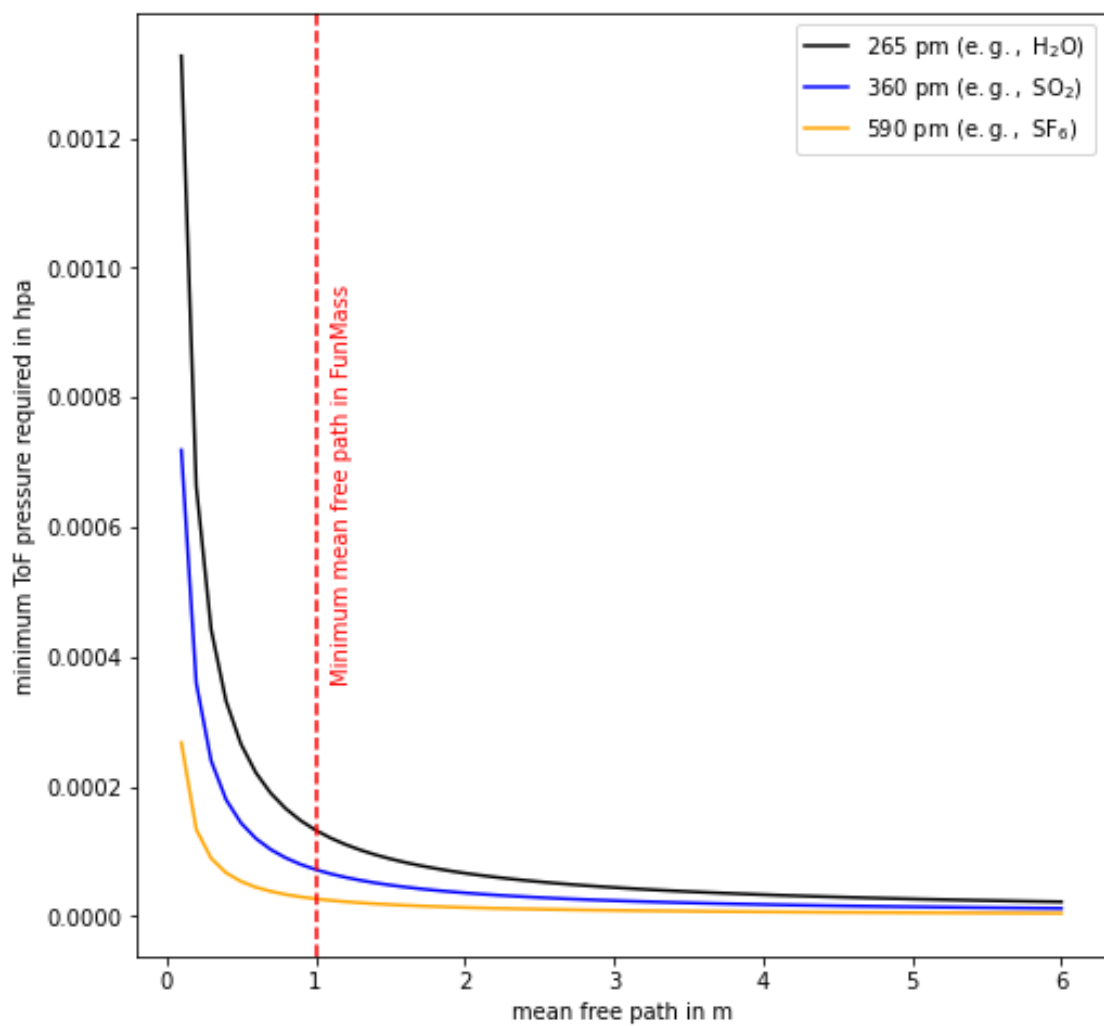


Figure 3.34: The minimum ToF pressure in hPa required to minimize collisions as function of the mean free path in m at 300 K for different kinetic diameters (265 pm (black), 360 pm (blue), and 590 pm (orange)). The red dashed line represents the minimum mean free path needed in FunMass.

mass spectra is not too short. If the interval is too short, high-mass ions from the first mass spectrum may still be in transit when low-mass ions from the subsequent spectrum are detected, leading to signal overlap and interference. To prevent this, a new extraction pulse is only generated once the previous mass spectrum has been fully completed, ensuring proper time separation between successive spectra (pulse delay). A single pulse is not merely a single point at a specific moment in time, rather, it appears as a peak with a pulse width of ± 2000 ns. The acquisition frequency is set to 1.5 Hz (every 0.67 s a data point).

To quantify ion signals within a given time interval (expressed in counts per second, cps), it is necessary to determine the signal strength of an individual ion, referred to as the single ion signal (SIS). TOFwerk provides dedicated software for the automatic determination of SIS values. The SIS is dependent on the m/q , as illustrated in Figure 3.35. A pronounced decline in SIS is observed beyond 55 Th, where the signal drops from approximately $1.7 - 2.2$ mV $\cdot$ ns to $1.2 - 1.4$ mV $\cdot$ ns. This presents a potential limitation, as the TOFwerk software applies a constant, average SIS value across the entire m/q range rather than accounting for its m/q -dependence.

For FunMass, this simplification is generally inconsequential, as trace gas quantification relies on external calibration standards. However, non-linearities in the calibration response may arise when the SIS for specific m/q values falls below approximately 1.2 mV $\cdot$ ns (also shown in Section 4.11). If the average SIS is set near this threshold, certain m/q values, particularly at higher masses, may already exhibit non-linear behavior, despite the global average remaining above the critical value. To avoid such effects, FunMass measurements are typically performed with an average SIS in the range of 1.4 to 1.6 mV $\cdot$ ns, ensuring linearity across all relevant m/q channels.

In Figure 3.36, the time and humidity dependence of the SIS is shown. It is recommended to let the MCP warm up to avoid larger drift effects in the signals. This can also be observed in the SIS. At the beginning, SIS is much larger (around 1.4 mV $\cdot$ ns) and subsequently, decreases to 1.29 - 1.31 mV $\cdot$ ns. TOFwerk suggests a warm up phase of at least 30 minutes, which is in agreement with the measurements shown in Figure 3.36.

An increase in water vapor content leads to a reduction in the SIS, as illustrated by

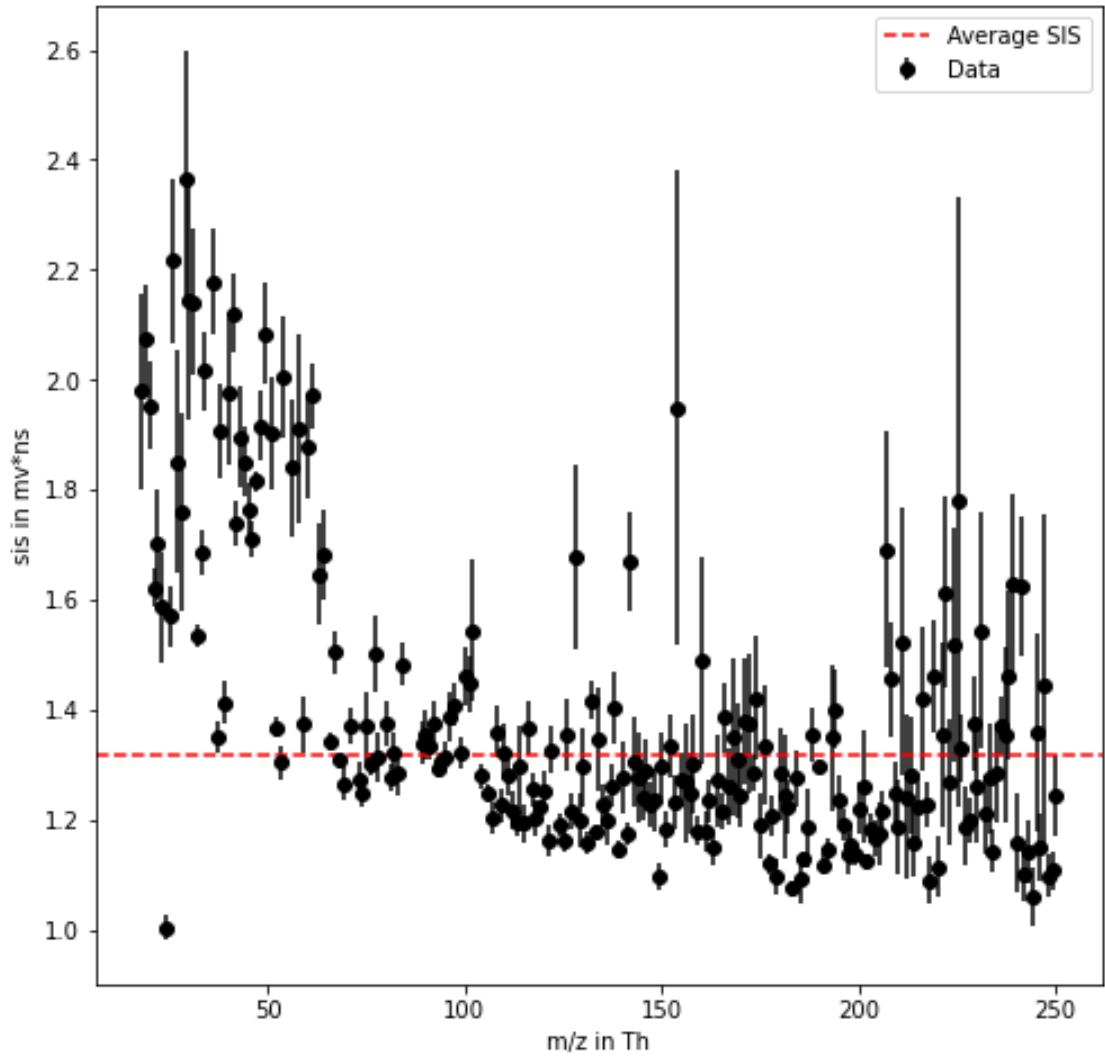


Figure 3.35: SIS (in $\text{mV} \cdot \text{ns}$) as function of the m/z (in Th). The SIS was determined five times within 7 hours under dry conditions and the MCP voltage was set to 2150 V. Average SIS: 1.3 - 1.32 $\text{mV} \cdot \text{ns}$.

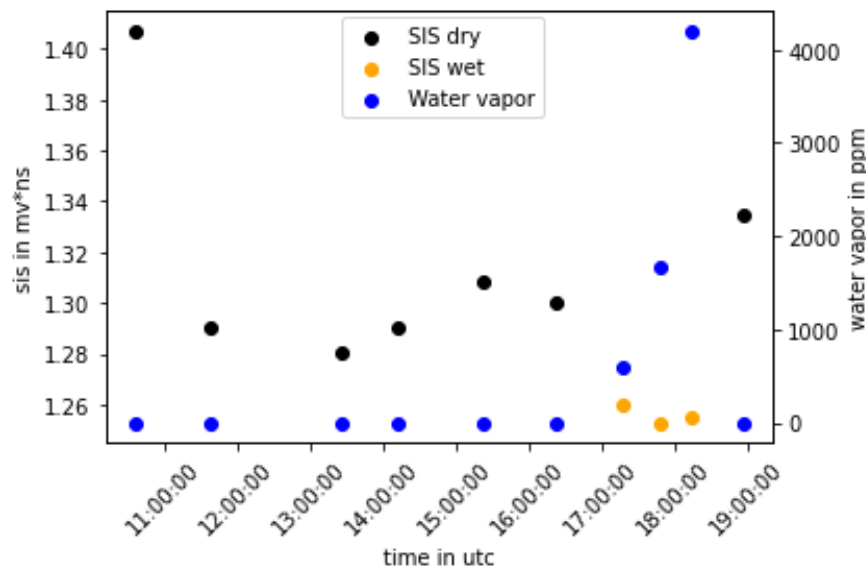


Figure 3.36: SIS (in $\text{mV} \cdot \text{ns}$) over time and for various humidity levels. The SIS under dry condition is represented by black circles and under humidified conditions by orange circles. The blue circles present the water vapor mixing ratios (in ppm). The MCP voltages were turned on between 10:30 and 10:35 UTC.

the comparison between the black and orange circles in Figure 3.36. This decrease, up to approximately 4 %, is attributed to the partial disruption of electron avalanches within the microchannel plates (MCP) caused by water molecules. TOFWerk has acknowledged this effect and defines an acceptable SIS reduction of up to 5 %. Importantly, this reduction is reversible, the SIS typically returns to its baseline value within a maximum of one hour.

In addition to environmental influences, SIS also declines gradually over time due to MCP aging. Consequently, it is recommended to determine and, if necessary, adjust the SIS prior to each measurement. However, during continuous measurement campaigns (e.g., chamber studies), changes to the MCP voltage, used to compensate for SIS decrease, should be approached with caution. Adjusting the MCP voltage does not affect all m/q values uniformly, potentially altering normalized signals by up to 10 %. Although such variations can be corrected by performing calibrations before and after the voltage change, uncertainties arise when only normalized data are available (i.e., in the absence of external standards). In such cases, modifications to MCP voltage within a measurement series may introduce significant systematic errors.

3.2 Chemical ionization within FunMass

Table 3.2: Summary of the applications of reagent ions for measuring trace species. Adapted from (Zhang et al., 2023).

Reagent Ion	Measured Species
I^-	reactive nitrogen (e.g., HONO, N_2O_5 , PAN); reactive halogens (e.g., Cl_2 , Br_2 , HOCl); organics (e.g., HCOOH, $\text{C}_3\text{H}_6\text{O}_3$, organic acids); inorganic acids (e.g., HCl, HBr, HNO_3); HOMs
Br^-	OH, HO_2
NO_3^-	H_2SO_4 , $\text{CH}_3\text{SO}_3\text{H}$, HOMs
CH_3COO^-	organic acids (e.g., HCOOH, $\text{C}_2\text{H}_5\text{COOH}$); inorganic acids (e.g., HCl, HBr, HNO_3); HOMs
CF_3O^-	hydroperoxides (e.g., H_2O_2 , ROOH); inorganic acids (e.g., HCl, HNO_3 , HCN); SO_2 ; organic acids (e.g., HCOOH, CH_3COOH)
CO_3^-	inorganic acids (e.g., HNO_3 , HCN); SO_2
SF_6^-	inorganic acids (e.g., HNO_3 , HCN, HCl); organic acids (e.g., HCOOH, CH_3COOH) SO_2
SF_5^-	inorganic acids (e.g., HNO_3 , HCN, HCl); organic acids (e.g., HCOOH, CH_3COOH) SO_2
H_3O^+	VOCs; amines; organic acids; (thio-)aldehydes and (thio-)ketones
NH_4^+	RO_2 , HOMs
C_6H_6^+	DMS; monoterpenes, sesquiterpenes; amines

The choice of a suitable reagent ion depends on the species to be measured quantitatively. Table 3.2 presents the most commonly used reactant ions in both positive and negative modes, along with examples of substances that can be detected using each ion. In general, iodide (CIMS) and H_3O^+ (PTR-MS) are among the most widely used reagent ions due to their ability to detect a broad range of species with good sensitivity and low detection limits (LOD).

For FunMass, used in the CARIBIC container, the highest priority is the precise and

accurate measurement of SO_2 . Figure 3.37 illustrates the standard Gibbs free energy change of cluster formation between neutral SO_2 and various ions (F^- , Cl^- , Br^- , I^- , O^- , and NO_3^-) in the gas phase. These values serve as a proxy for the binding energy between SO_2 and the respective ions. Certain assumptions are made, such as using the "naked" ion (except for O^-) instead of the actual reagent ion employed. Nonetheless, the data clearly indicate that fluoride-cluster-forming reagent ions are the best choice for SO_2 detection from a thermodynamic perspective. Kinetic considerations are not discussed here, as cluster formation between neutral molecules and ions often occurs near the collision limit.

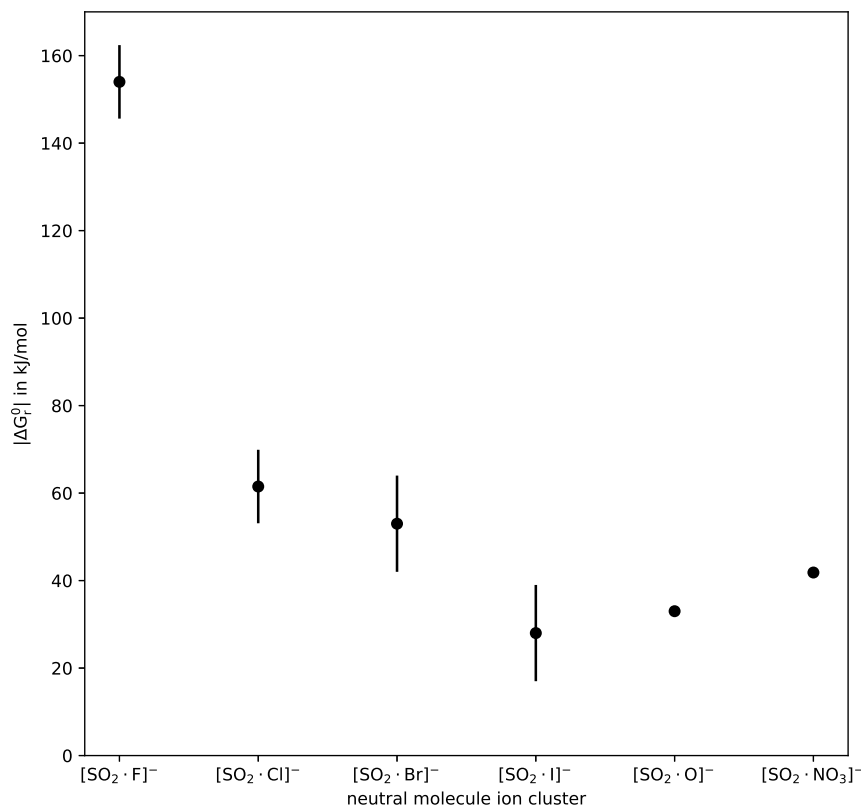


Figure 3.37: Standard Gibbs free energy change of cluster formation, $\Delta_r G_0$ in kJ/mol, between neutral SO_2 and various ions (F^- , Cl^- , Br^- , I^- , O^- , and NO_3^-) in the gas phase. Note: The $[\text{SO}_2 \cdot \text{O}]^-$ cluster is formed through the reaction of SO_2 with CO_3^- . Data adapted from (Fehsenfeld and Ferguson, 1974; Keese et al., 1980; Banic and Iribarne, 1985; Caldwell and Kebarle, 1985; Larson and McMahon, 1985).

3.2.1 Reagent Ion Precursor

In the atmospheric science CIMS community, Bis(trifluoromethyl) peroxide (BTP; CF_3OOCF_3), Trifluoromethylsulfur pentafluoride (CF_3SF_5), and sulfurhexafluoride (SF_6) are typically used as fluorine-containing precursors forming CF_3O^- , SF_5^- , and SF_6^- , respectively. Trifluoromethoxy sulfur pentafluoride (CF_3OSF_5) is a rather special as it forms CF_3O^- as well as SF_5^- .

The reagent ion precursor molecules must exhibit a medium to large absorption cross-section within the two emission lines of the Kr VUV lamp (116.5 and 123.6 nm). Additionally, their ionization energy must be below 10.6 eV to generate sufficient photoelectrons for negatively charged ion formation.

Neither CF_3SF_5 (11.84 ± 0.15 eV) (Bodi et al., 2021) nor SF_6 (15.35 ± 0.02 eV) (Frost et al., 1967) meet this criterion, as their ionization energies are too high to produce photoelectrons for negative ion formation. While no experimental ionization energy data exist for BTP, FunMass-C experiments indicate that almost no negatively charged ions are formed using only Kr VUV lamps and BTP. This suggests that BTP also has an ionization energy exceeding 10.6 eV.

Ji et al. (2020) previously demonstrated that an electron source, such as benzene (with a lower ionization energy of 9.24384 ± 0.00006 eV) (Nemeth et al., 1993), can facilitate reagent ion formation when paired with an electron-attaching compound of higher ionization energy. These electron-providing substances (EP) are generating photoelectrons while being irradiated by the VUV light, as illustrated in Equation 3.6.



In Funmass, benzene is used as an electron source. Additionally, acetone (IP = 9.7 eV) (Traeger et al., 1982) and toluene (IP = 8.8276 ± 0.0006 eV) (Lu et al., 1992) were tested, both performing comparably to benzene. However, since neither provided any significant improvement, benzene remains the preferred choice.

BTP is a well-established precursor for chemical ionization mass spectrometry (CIMS)

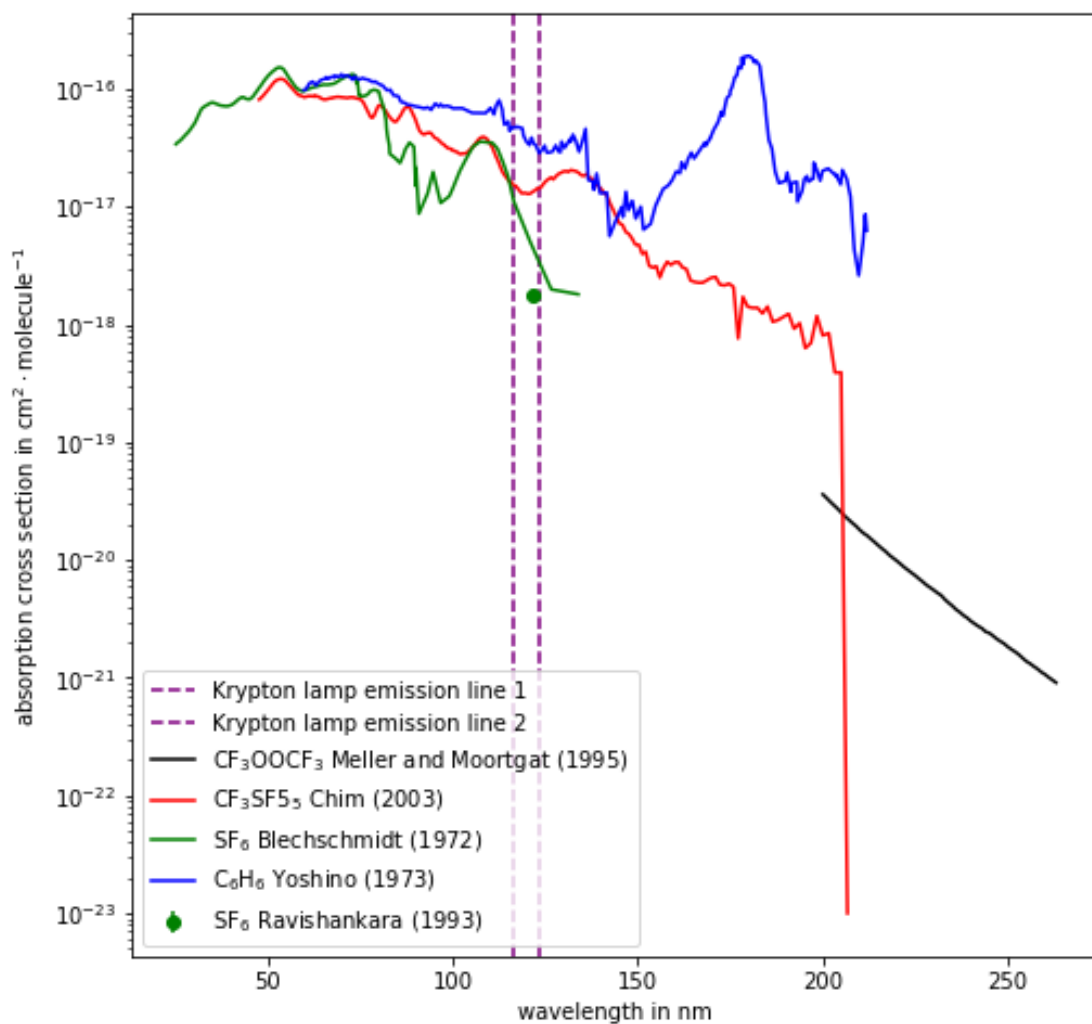


Figure 3.38: Absorption cross section [$\text{cm}^2 \cdot \text{molecule}^{-1}$] in logarithmic scale within the wavelength range of 5 - 275 nm for the molecules CF_3OOCF_3 (black), CF_3CF_5 (red), SF_6 (green), and C_6H_6 (blue) (Blebschmidt et al., 1972; Chim et al., 2003; Meller and Moortgat, 1995; Ravishankara et al., 1993; Yoshino et al., 1973). The purple dashed lines indicate the two emission lines of the Kr VUV lamp (116.5 and 123.6 nm).

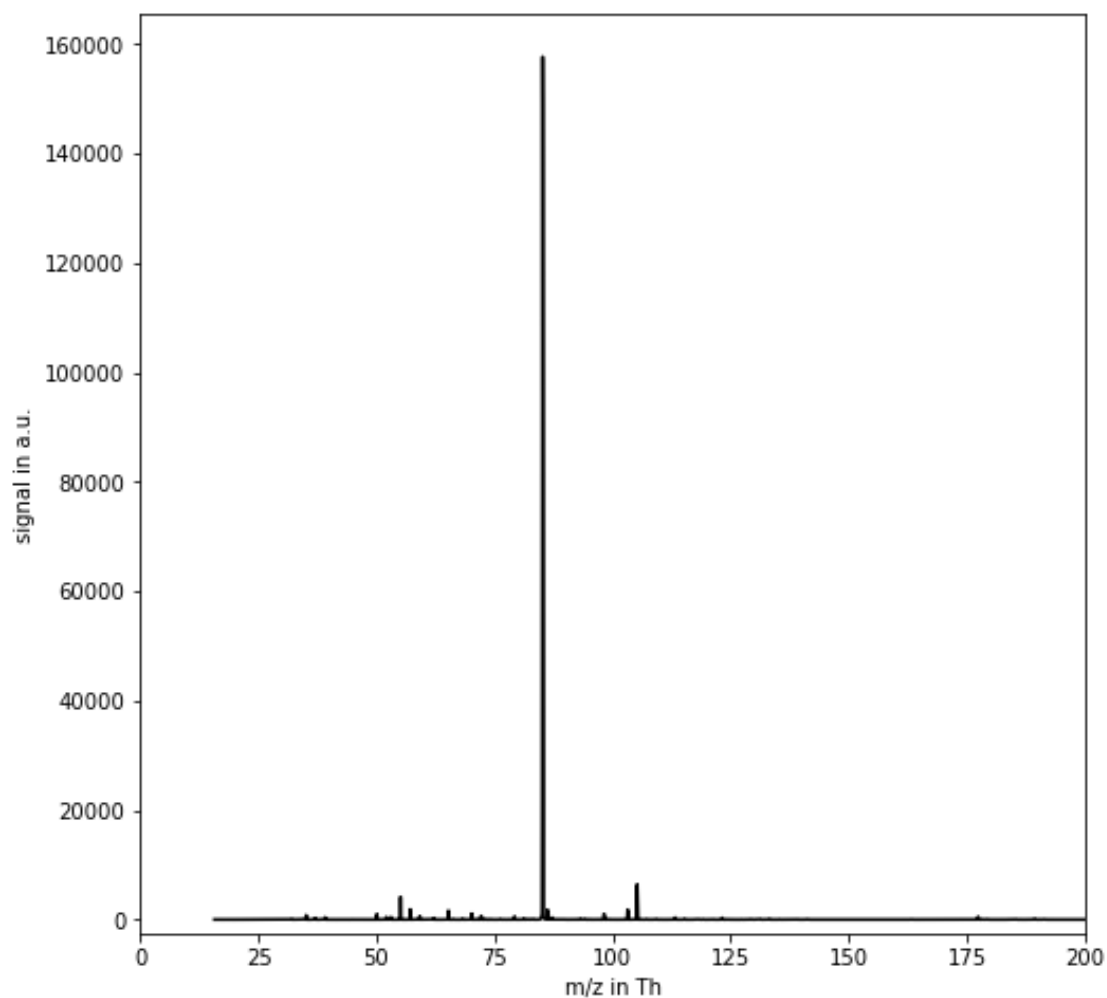


Figure 3.39: Spectrum of FunMass using BTP and benzene as precursor. The main signals are CF_3O^- (85 Th), $[\text{CF}_3\text{O} \cdot \text{H}_2\text{O}]^-$ (103 Th), $[\text{CF}_3\text{O} \cdot \text{HF}]^-$ (105 Th). The three larger impurity peaks can be assigned to HCl ($[\text{HF} \cdot \text{Cl}]^-$; 55 and 57 Th) and HCOOH ($[\text{HF} \cdot \text{HCOO}]^-$; 65 Th)

(Huey et al., 1996; Amelynck et al., 2000; Crounse et al., 2006, 2009; Allen et al., 2021, 2022). The resulting ion clusters can be used to quantify various compounds, including hydrogen peroxide (H_2O_2), organic hydroperoxides such as methyl hydroperoxide (CH_3OOH), organic acids like formic acid (HCOOH) and acetic acid (CH_3COOH), as well as inorganic acids (HCl , HNO_3 , and HCN). Additionally, it can detect sulfur dioxide (SO_2), peroxyntiric acid (HO_2NO_2), and HONO . Especially, due to its high sensitivity with respect to SO_2 and HCN , it is the first choice for Funmass for the IAGOS-CARIBIC deployments.

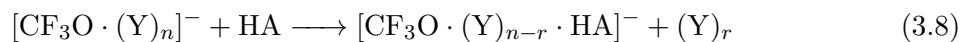
In the following, the possible reaction mechanisms are illustrated using the example analyte molecule HA .



Since the reagent ion trifluoromethoxide (CF_3O^-) readily forms clusters with many neutral molecules, particularly weak acids, equation 3.7 can be generalized to equation 3.8 with $n \geq 0$ and $r \leq n$. Neutral cluster molecules—such as H_2O , HF , and other acids (e.g., formic acid, HCl , etc.)—or any combination thereof are represented by Y .

During aircraft measurements, water clusters are predominant, as water vapor is ubiquitous, especially at lower altitudes. Additionally, hydrogen fluoride (HF) is another trace gas that must be considered in Funmass, as it is intrinsically formed as a byproduct of other chemical reactions. The concentration of HF strongly depends on pressure, temperature, and the presence of other trace gases in the IMR.

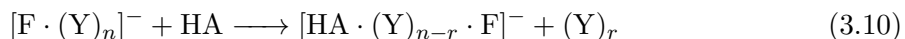
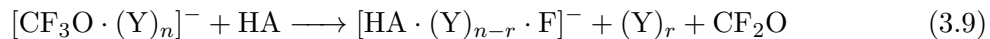
If the integer values n and r in equation 3.8 are both zero, the equation simplifies to equation 3.7. If n is 1 or greater and r is 1, the reaction is referred to as a ligand-switching reaction. In Funmass, the number of molecules per detected cluster ion typically does not exceed three, except in cases where all involved molecules are small, such as HF , HCN , or H_2O .



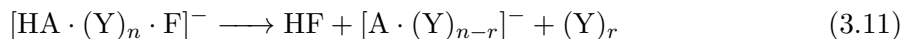
Clusters between the analyte HA and fluoride can also be formed, either directly via CF_3O^-

3.2. CHEMICAL IONIZATION WITHIN FUNMASS

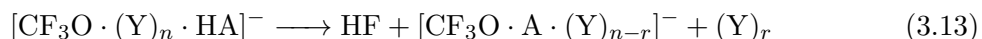
(cf. Equation 3.9 with $n \geq 0$ and $r \leq n$) or through second-generation reactions involving fluoride clusters formed in the first generation (cf. Equation 3.10 with $n \geq 0$ and $r \leq n$).



Furthermore, additional neutral molecules can be attached after the ion molecule clusters are already formed. Acid-containing clusters can release HF or CF_3OH as illustrated in the equations 3.11 and 3.12 ($n \geq 0$ and $r \leq n$).



In rare cases, also the reaction 3.13 can be observed (e.g., for HCN with $n = 0$ and $r = 0$).

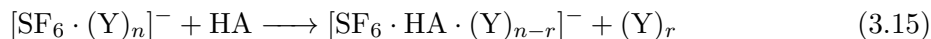


BTP is not commercially available, and therefore, no certified safety data sheet exists. This poses challenges for the certification process. As a fallback option, an alternative precursor is required. Two serious candidates under consideration are trifluoromethylsulfur pentafluoride (CF_3SF_5) (Marcy et al., 2005; Jurkat et al., 2010, 2011) and sulfur hexafluoride (SF_6) (Huey et al., 1995a, 2004; Nah et al., 2018), which are also well-established for quantitative measurements of compounds such as SO_2 , HCl , HNO_3 , and HONO .

The primary reaction in SF_5^- -CIMS is described by Equation 3.14 ($n \geq 0$ and $r \leq n$). However, additional reactions, as outlined in Equations 3.10 and 3.11, may also occur.

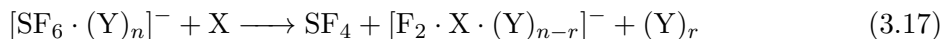


SF_6^- primarily forms F^- or SF_5^- clusters, as shown in Equations 3.15 and 3.16. Similar to CF_3O^- and SF_5^- , the reactions described in Equations 3.10 and 3.11 can also occur with SF_6^- .



For certain analyte molecules X, the reaction described in Equation 3.17 can occur with SF_6^- . The feasibility of this reaction depends on the coordination number of molecule X. For instance, SO_2 undergoes this reaction, driven by the sulfur atom present in both SF_6^- and SO_2 .

Due to its two s-orbital and four p-orbital valence electrons, along with readily available d-orbitals in the third period, sulfur can exist in oxidation states of +2, +4, and +6. Consequently, the formation of SF_4 alongside SO_2F_2^- drives the reaction toward the product side.



However, Huey et al. (1995a) demonstrated that SF_6^- is unsuitable for measurements in environments with elevated ozone concentrations, such as the stratosphere, due to its rapid reaction with ozone.

Trifluoromethoxy sulfur pentafluoride (TMSPF; CF_3OSF_5) was also considered for use in Funmass, as it combines the ion-molecule chemistry of both BTP and CF_3SF_5 . However, its use introduced more challenges than benefits. The presence of two ion chemistry schemes for the IMR increased the likelihood of isobaric interferences, leading to its rejection as a reagent ion option.

Chapter 4

Characterization and Calibration of FunMass-C

Measuring ultra trace gases in the UTLS down to a few ppt requires a special calibration procedure. Especially as water vapor and ozone can vary during flights (see Subsection 3.1.2), calibrations should be carried out under several water vapor and ozone. Therefore, a calibration setup was built to meet these requirements (described in Section 4.1).

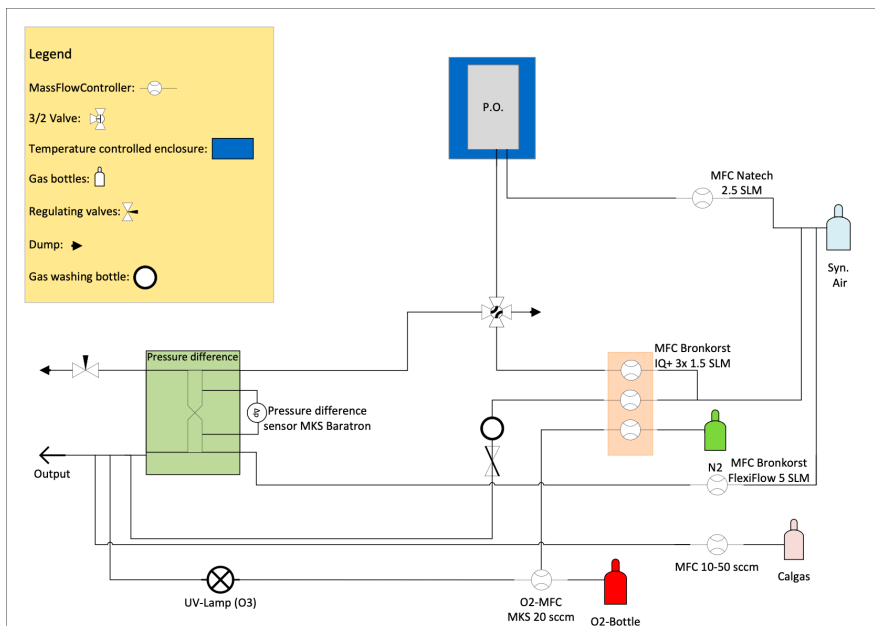
If not separately stated, all the calibration and experiments were carried out using IMR3.

4.1 Calibration Rack

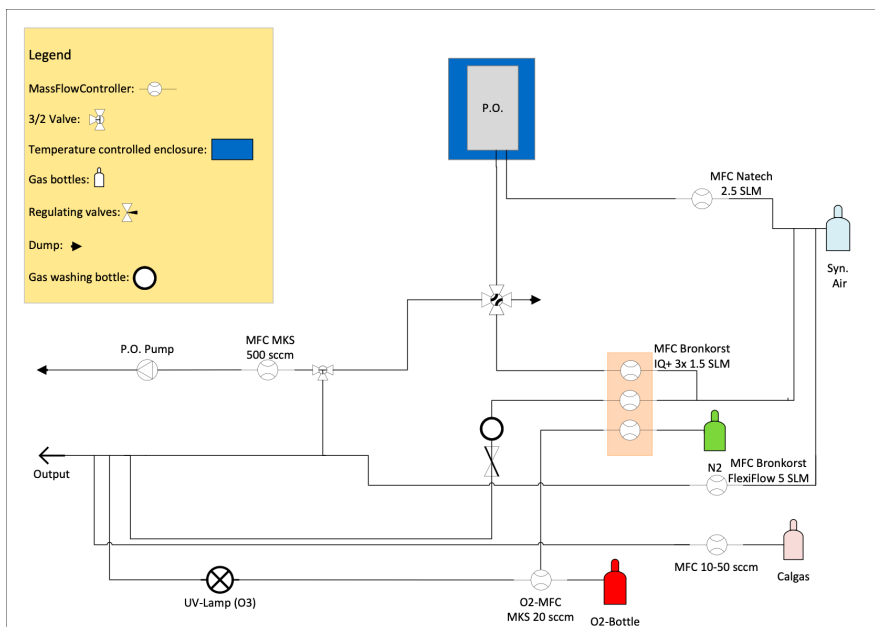
Conducting calibration under various conditions requires a well-designed calibration system. To achieve this, a calibration rack was developed, capable of controlling all necessary parameters. Figure 4.1 illustrates the two different configurations of the calibration rack used. The system consists of four key components: the permeation oven, the water vapor supply, the ozone generator, and a dilution stage. The latter differentiates the two configurations.

The permeation oven is only briefly described here (for further details, see Khattatov (2019); Li (2021)). It consists of a SilcoNert2000®-coated stainless steel tube (outer diameter: 50 mm; inner diameter: 40 mm) with a welded base plate, which houses two 1/8" SilcoNert2000®-coated Swagelok®NPT threads, one for the synthetic air inlet and another

4.1. CALIBRATION RACK



(a) Dilution by a PTFE pressure difference nozzle



(b) Dilution by overflow MKS 500 SCCM MFC

Figure 4.1: Funmass calibration rack. Source: Sarah Honold and Wilhelm Steffes.

one for the PT100 temperature sensor. The top side features a screw cap for inserting and removing permeation tubes. The weight loss over time of two example permeation tubes (SO_2 and HCN with oxalic acid as stabilizer (self-made)) is shown in S4.1.

A 1/4" SilcoNert2000®-coated stainless steel tube is welded a few centimeters below the screw cap as the outlet. Additionally, a 1/8" stainless steel tube connected to the inlet is wrapped around the 50 mm tube for preheating the synthetic air. The entire assembly is enclosed within a Peltier-controlled copper block to maintain a stable temperature (typically 25.0 °C). Inside the 50 mm tube, a precisely fitted PTFE insert is placed, as PTFE offers superior chemical resistance for some substances (e.g., HCOOH , HNO_3 , HCN) analyzed by Funmass compared to SilcoNert2000®-coated stainless steel.

Before the 1/8" stainless steel tube, a 2.5 SLM mass flow controller (Natec Sensors GmbH) regulates the airflow. To prevent gas adsorption, particularly for highly reactive substances like HNO_3 , at least 100 SCCM synthetic air continuously flows through the permeation oven. Under normal operation 500 SCCM is used.

The water vapor supply consists of a gas scrubber bottle filled with either ultra-pure water (Promochem Water HPLC Optigrade®) or moistened molecular sieves (0.5–1.0 nm). The molecular sieve method prevents water vapor spikes caused by bubbling but limits the maximum achievable water vapor mixing ratio to about 4000 ppm at 5 SLM total flow. The scrubber bottle is operated at room temperature in order to prevent condensation in the downstream lines.

A shut-off valve is installed after the gas washing bottle to prevent unintended moisture leakage into the dry main synthetic airflow.

The self-made ozone generator consists of a 3-way PTFE-block (25 mm × 25 mm × 25 mm), housing a UV pen-ray lamp (B-71241 from Penray UVP) is inserted into one port. The other two ports serve as gas inlet and outlet. To ensure temperature stability—critical for maintaining the ozone formation equilibrium—the PTFE block is cooled using a stainless steel block and a fan.

The ozone mixing ratio is controlled by adjusting the pure oxygen flow (0–20 SCCM) within a constant nitrogen flow (100 or 200 SCCM). Within minutes, the ozone mixing ratio

4.1. CALIBRATION RACK

stabilizes within $\pm 5\%$, which is a sufficient accuracy for FunMass-C calibration, which only weakly varies with O_3 concentration.

To quantify water vapor and ozone during ultra-trace gas calibration of Funmass, an LGR DLT-100 (Los Gatos) and an ozone analyzer (Model 211-G Ozone Monitor from 2BTech) are used. Figures 4.2 and 4.3 illustrate the calibration of the water vapor supply and ozone generator, respectively. The accuracy of these two systems is sufficient for Funmass calibration, providing the full range of mixing ratios required for tropospheric and stratospheric conditions encountered during CARIBIC flights: water vapor (0 to >10000 ppm) and ozone (0 to 1 ppb).

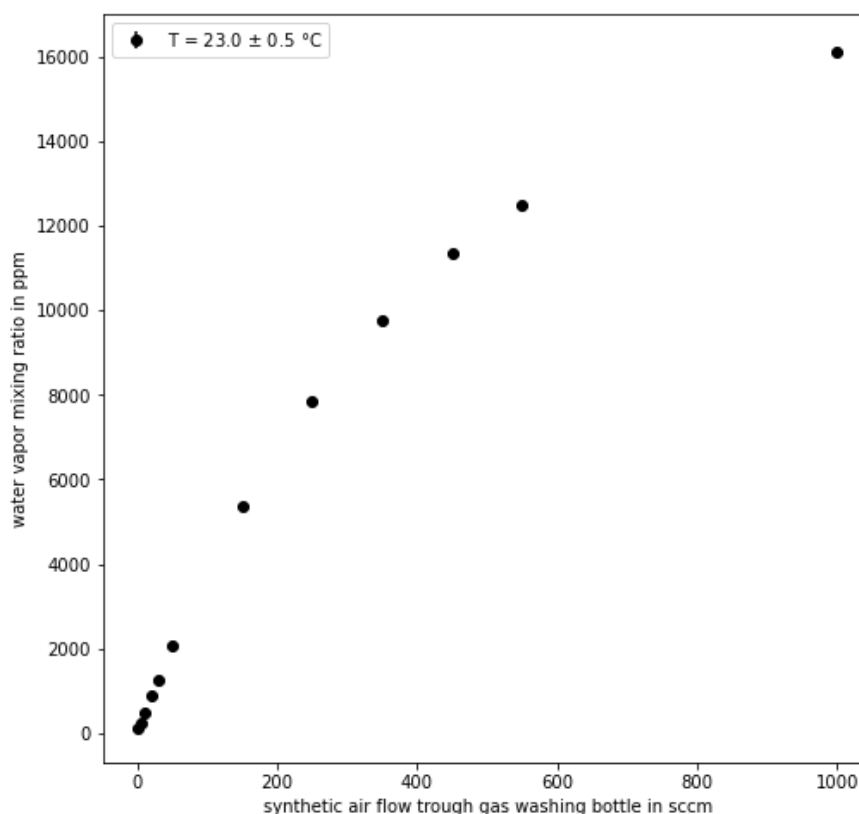


Figure 4.2: Water vapor mixing ratio in ppm for various synthetic airflows in SCCM through the gas scrubber bottle containing liquid HPLC grade water. The main gas flow was set to 700 SCCM.

Additionally, a separate port is installed for direct calibration of analytes using standard gas cylinders and MFCs with maximum flow rates between 10 and 50 SCCM, depending on the MFC model. Comparison between a certified SO_2 standard and the permeation tube

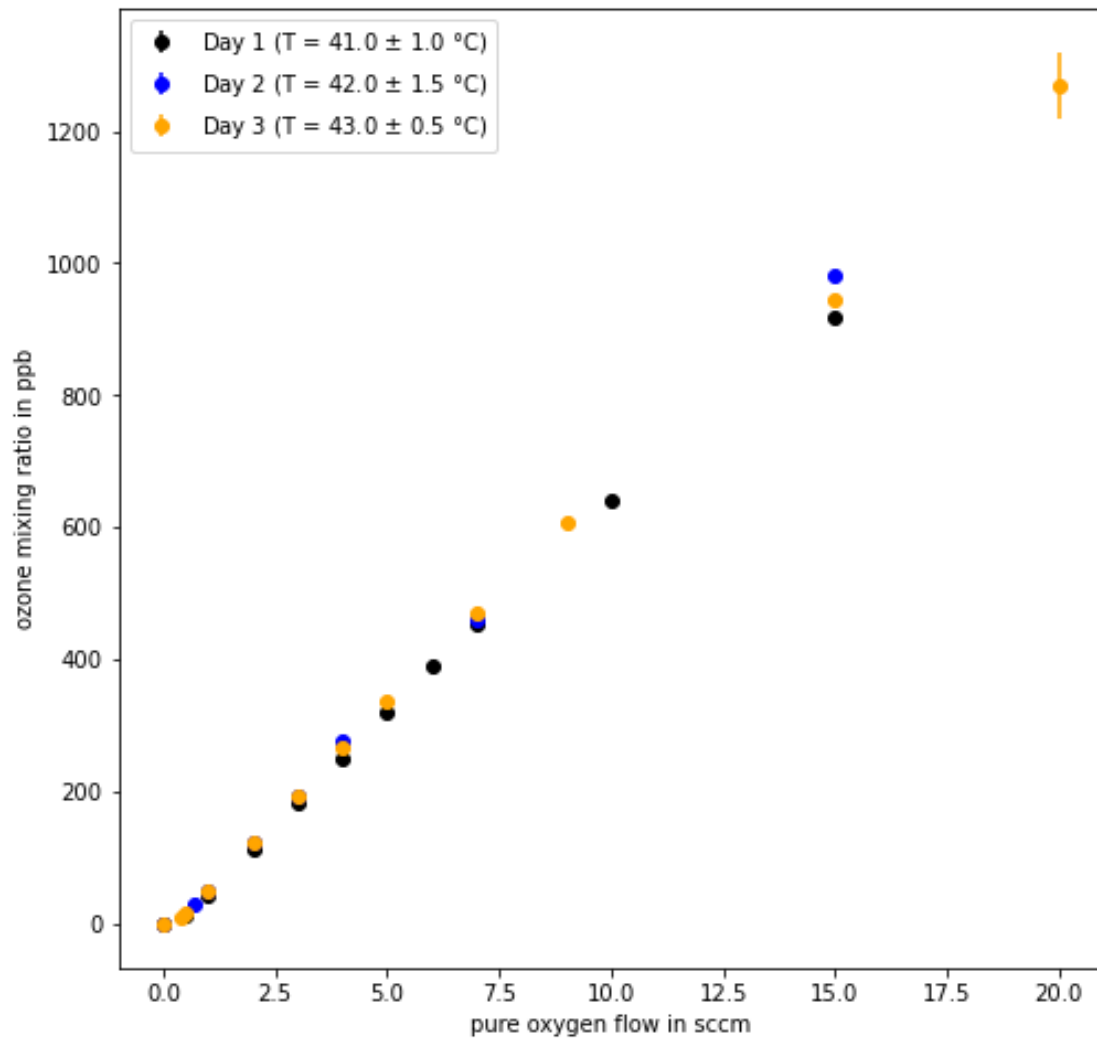


Figure 4.3: Ozone mixing ratio in ppb for varying pure oxygen flow in SCCM mixed into 200 SCCM nitrogen flow on three consecutive days (first day (black), second day (blue), and third day (orange)). The main gas flow was set to 2 SLM.

4.1. CALIBRATION RACK

showed good agreement during calibration of the ICE-4 high-resolution ToF (FunMass-L).

The main synthetic airflow is typically set between 0.5 and 5 SLM (or up to 20 SLM) using a Bronkhorst®Flexiflow MFC.

Using 500 SCCM directly from the permeation oven results in high analyte mixing ratios due to the elevated permeation rate, with minimum mixing ratios of 10 ppb at 500 SCCM. To achieve lower mixing ratios, the calibration flow must be diluted with the main flow (up to 5 SLM). However, even at the highest flow rate, the dilution factor is only approx. 10 (resulting in minimum mixing ratios of approx. 1 ppb). Achieving higher dilution factors requires an MFC with a larger maximum flow (e.g., 20 SLM provides a dilution factor of 40). Since Funmass is designed for ultra-trace gas measurements (sub-ppb levels down to a few tens of ppt), a high dilution factor is essential.

However, high dilution introduces another challenge: the water vapor supply and ozone generator do not provide sufficiently high mixing ratios that can be easily diluted by a factor of at least 40. To address this, two options were considered: optimizing the water vapor and ozone sources or modifying the ultra-trace gas calibration line.

In the Funmass calibration rack, the ultra-trace gas calibration line was optimized. Instead of direct dilution, pre-dilution is applied: ultra-trace gases are pre-mixed with 500 SCCM of synthetic air, and only a fraction of this pre-diluted air (5 – 500 SCCM) is introduced into the main flow (0.5 – 5 SLM). This exists in two variants given in Figure 4.1.

A PTFE critical orifice is used to regulate airflow, as its flow rate depends on the pressure differential. Since the main line is near ambient pressure, a regulating valve upstream of the orifice increases backpressure, creating the necessary pressure gradient. The pressure difference is measured using an MKS Baratron (10 Torr) differential pressure sensor. Initially, the pressure differential was adjusted manually using a needle valve. Later, the system was optimized using a piezo valve (see Figure S1.2), the Baratron sensor, and a custom-programmed PID controller. The PID regulation system significantly improved calibration precision and speed by rapidly stabilizing the pressure difference.

A challenge with the critical orifice is its limited flow range. Ideally, the flow should be adjustable between 5 and 500 SCCM. However, if the orifice is too small, low flows (<30

SCCM) can be controlled easily, but achieving higher flows requires a large pressure gradient (as shown in Figure 4.4), which will propagate back to the permeation oven. This backpressure fluctuation affects temperature stability, compromising the calibration accuracy of the permeation oven or extending the calibration time tremendously. Contrarily, using a larger orifice allows for higher flows, but low flows can no longer be accurately achieved. The optimal solution is to use two separate orifices that can be switched as needed, ensuring full coverage of the entire flow range.

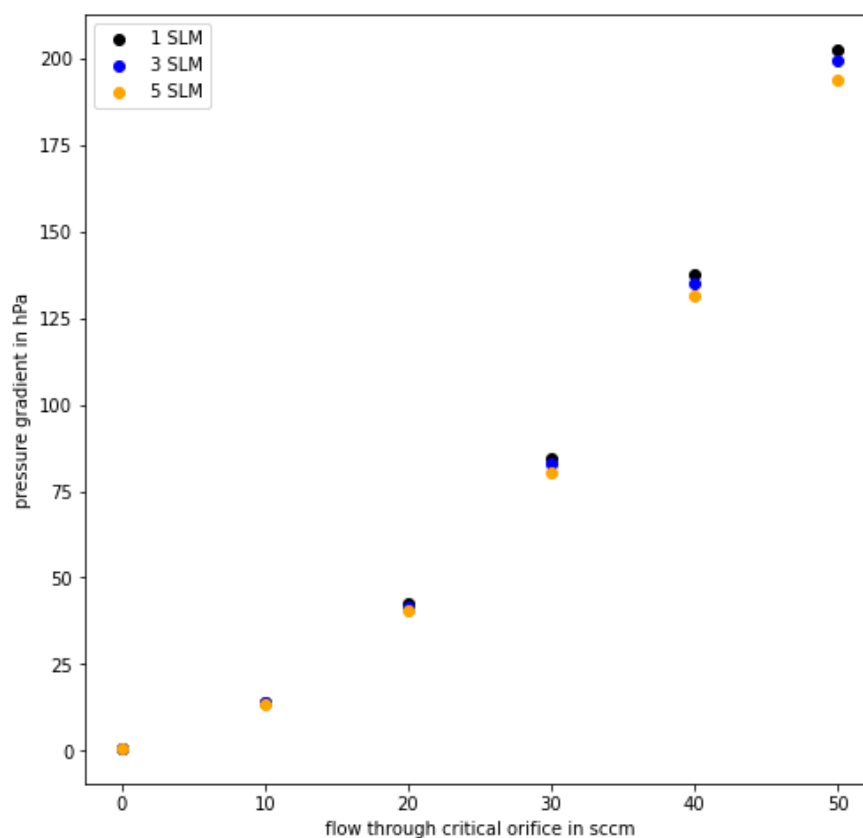


Figure 4.4: The emerging pressure gradient in hPa against the flow through the PTFE critical orifice in SCCM for various main airflows (1 SLM (black), 3 SLM (blue), and 5 SLM (orange)) in the calibration rack.

This issue led to the development of an alternative approach, utilizing a small temperature-controlled pump and a second 500 SCCM MFC (MKS). The pump is installed downstream of the second MFC, creating a controlled flow system.

In this setup, 500 SCCM from the permeation oven is drawn by the pump through the

second MFC. The difference between the permeation oven’s MFC flow rate (typically 500 SCCM, NATEC) and the flow set on the second MFC (MKS) determines the amount of ultra-trace gas introduced into the main gas flow. For example, if the second MFC is set to 480 SCCM, the remaining 20 SCCM of ultra-trace gas from the permeation oven is added to the main airflow.

This method requires precisely calibrated MFCs, as it relies on accurate flow differentials, which can introduce additional uncertainties. Additionally, the pressure gradient before and after the second MFC must remain constant (hence, the need for temperature control), as many MFCs are pressure-dependent. An alternative solution would be to use a pressure-independent MFC, eliminating this dependency.

The main advantage of the MFC approach is that it allows for a single setup to cover the entire flow range (5–500 SCCM) while also enabling more precise flow adjustments on a finer scale compared to the pressure difference method.

Lastly, a double L-valve (NResearch Inc.), connected to both the permeation oven and a second 1.5 SLM MFC from Bronkhorst® (also set to 500 SCCM), is used to maintain a constant total flow when the permeation oven is turned on or off.

All MFCs, valves, and pressure sensors can be monitored and controlled via custom-programmed software, enabling automated calibration. Further improvements and optimizations are planned for the future (see Section 6.1). Additionally, the calibration rack will be expanded with additional permeation ovens to better investigate cross-sensitivities of various trace gases (e.g., SO_2 and formic acid under humid conditions).

4.2 Insides of Detectable Species using CF_3O^-

In this section, Funmass is characterized under ideal conditions, specifically in environments with low water vapor mixing ratios (below 2 ppm) and the absence of ozone (defined as dry conditions). It is capable of measuring both organic (e.g., formic acid (HCOOH), acetic acid (CH_3COOH), oxalic acid) and inorganic acids (e.g., hydrogen chloride (HCl), nitric acid (HNO_3), hydrogen cyanide (HCN), nitrous acid (HONO)). Additionally, it enables

the quantification of perfluorinated acids such as perfluoroacetic acid (TFAA). The use of bis(trifluoromethyl)peroxide (BTP) further allows for the detection of sulfur dioxide (SO_2). Moreover, Funmass can be utilized to measure water vapor mixing ratios in the upper troposphere and lower stratosphere (UTLS) down to levels well below 500 ppm.

Strong acids, such as HCl , HNO_3 , HCOOH , and CH_3COOH , predominantly form fluoride clusters ($[\text{HX} \cdot \text{F}]^-$). Due to decomposition processes, the anionic forms of these acids (X^-) can also be detected. At higher acid mixing ratios, also the formation of CF_3O^- clusters ($[\text{HX} \cdot \text{CF}_3\text{O}]^-$) becomes more pronounced. With increasing concentration, the acids, especially organic acids, begin to cluster with themselves, forming $[\text{HX} \cdot \text{X}]^-$ species. The relative distribution of these clusters, exemplified by HCl , is depicted in Figure 4.5a.

Weak acids, such as HCN and hydroperoxides (e.g., H_2O_2), form similar clusters but with different propensities. Notably, the CF_3O^- cluster ($[\text{HX} \cdot \text{CF}_3\text{O}]^-$) is the dominant species, as illustrated in Figure 4.5a. SO_2 forms mainly the fluoride cluster (cf. Figure 4.5b).

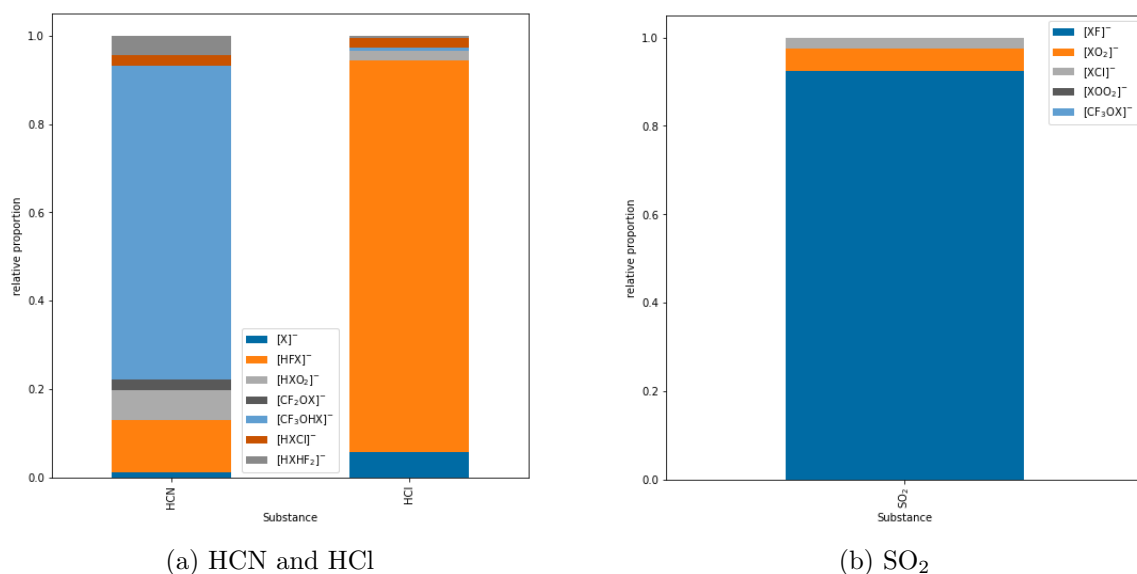


Figure 4.5: Relative proportion of the various clusters formed inside the IMR by 1.8 ppb HCN, 2.6 ppb HCl, and 1.2 ppb SO_2 under dry conditions. X represents CN, Cl, and SO_2 , respectively.

Due to minor impurities from chlorine-containing substances, chloride (Cl^-) clusters are detectable for all analytes. No cleaning procedure, alternative sealing materials, or changes to the ion-molecule reactor (IMR) material were able to eliminate these clusters, leading to

the conclusion that the contamination likely originates from the gas supply.

Superoxide (O_2^-)-containing clusters can be observed for all tested analytes. Superoxide is supposed to be formed through charge transfer processes within the IMR. These clusters were detected in every IMR configuration and could not be eliminated unless nitrogen (N_2) was used instead of synthetic air in the main airflow. Figure 4.6 illustrates the formation of the superoxide anion (orange) and its water cluster (black) when synthetic air (gray-shaded), rather than nitrogen (white-shaded), is used as the carrier flow in the main airflow. The TIC remained approximately constant. Assuming similar transmission properties for the superoxide anion (32 Th) and its water cluster (50 Th), the experiment reveals a threefold increase in the presence of the superoxide-water cluster compared to the naked superoxide. This suggests that water molecules play a critical role in the charge transfer process. However, its impact on the measurements is minimal (small 32 Th and 50 Th signals), causing only minor isobaric interferences (see Section 4.10.3).

4.3 Sensitivity

4.3.1 Theory

The theory of deriving the mixing ratio of an analyte P using a CIMS with the reagent ion R^- is well-known and explained in Huey (2007); Heinritzi et al. (2016); Aggarwal et al. (2025). Here, the basic concept is explained.



Mathematically, the temporal evolution of the ion molecule reaction described in Equation 4.1 can be formulated as:

$$\frac{d[\text{R}^-]}{dt} = -k \cdot [\text{R}^-] \cdot [\text{P}] \quad (4.2)$$

Equation 4.2 can be simplified under assumption of a constant concentration of [P] over the reaction time t (pseudo first order reaction approximation). Moreover, it is assumed

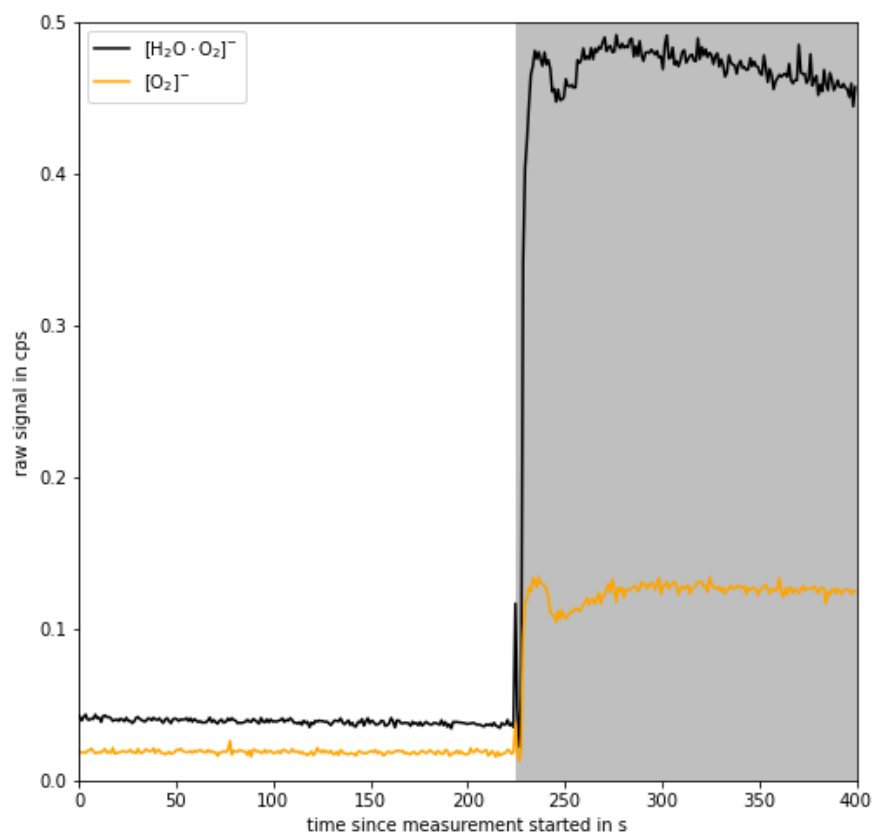


Figure 4.6: Raw signal of superoxide anion (orange) and its water cluster (black) in cps over time (s), with nitrogen (white-shaded) and synthetic air (gray-shaded) as carrier flows in the main airflow.

4.3. SENSITIVITY

that the total amount of charge is constant in the IMR (Heinritzi et al., 2016). With these assumptions, the following expression for the concentration $[P]$ can be derived:

$$[P] = \frac{1}{k \cdot t} \cdot \ln \left[1 + \frac{[P^-]}{[R^-]} \right] \quad (4.3)$$

A first-order approximation of Equation 4.3 is valid for the condition $[P^-] \ll [R^-]$ and results in Equation 4.4 (Heinritzi et al., 2016).

$$[P] \approx \frac{1}{k \cdot t} \cdot \frac{[P^-]}{[R^-]} \quad (4.4)$$

However, a CIMS does not measure directly concentrations of the ions but the ion count rates at the detector. Therefore, the concentrations from Equation 4.4 have to be replaced by the ion count rates, icr .

$$[P] \approx \frac{1}{k \cdot t} \cdot \frac{icr(P^-)}{icr(R^-)} \cdot \frac{1}{T_P} \quad (4.5)$$

The factor T_P is needed as it describes the mass discrimination of R^- relative to that P^- . It depends mainly on the m/q ratio. In general, the signal of analyte depends mainly on the formation rate of its product ion (k), the reaction time in the IMR (t), and the relative transmission efficiency, which is a function of m/q and the magnetic and electric fields, respectively (Aggarwal et al., 2025).

The parameters k , t and T_P can be summarized to the calibration factor C , which also is a function of water vapor content, ozone concentration, pressure, temperature, and airflow. This calibration factor C can be determined by calibration with an external standard (for Funmass the permeation oven). Therefore, also pre, in-flight, and post calibrations are needed for the IAGOS-CARIBIC flights.

In FunMass, unless otherwise specified, the sum of the primary reagent ion CF_3O^- (85 Th) and its water cluster $[CF_3O \cdot H_2O]^-$ (103 Th) is used as reference for signal normalization and sensitivity determination as shown in Equation 4.6. The unit of the normalized signals is called normalized counts per second (short: ncps)

$$P_{\text{norm}} = \frac{icr(P^-)}{\sum icr(R_i^-)} \quad (4.6)$$

4.3.2 FunMass-C Calibration

Table 4.1: Calibration characteristics of FunMass-C.

Characteristic	SO ₂	HCN	HCOOH	CH ₃ COOH	HCl
Sensitivity [ncps · ppt ⁻¹]	2.36 · 10 ⁻⁵	1.54 · 10 ⁻⁵	2.99 · 10 ⁻⁵	2.54 · 10 ⁻⁵	1.46 · 10 ⁻⁵
Sensitivity uncert. [ncps · ppt ⁻¹]	3.38 · 10 ⁻⁷	2.29 · 10 ⁻⁷	4.22 · 10 ⁻⁷	3.40 · 10 ⁻⁷	~ 10 ⁻⁷
LOD(2σ; 10s) [ppt]	2.62	2.15	5.27	3.91	9.81

In this subsection, the calibration parameters for SO₂, HCN, HCOOH, CH₃COOH, and HCl are discussed.

Table 4.1 presents the calibration characteristics of FunMass for SO₂, HCN, HCOOH, CH₃COOH, and HCl. Calibration factors and limits of detection (LODs) are inherently specific to the experimental setup, which includes variables such as tube material, tube length, flow regime inside and outside the IMR, pressure, and temperature.

With the exception of HCl, which was calibrated using a 6 cm PFA tube (4 mm in inner diameter), all other species were measured with a 2 m PTFE tube (4 mm in inner diameter). The IMR pressure was maintained at 35 hPa, and the inlet flow was approximately 406 ± 20 SCCM. The IMR temperature was kept within a range of 30 – 32 °C. Carrier nitrogen flow and VUV lamp purge flow were set to 200 and 20 SCCM, respectively. To generate the reagent ions, 0.2 SCCM of 190 ppm CF₃OOCF₃ in N₂ and 3.5 SCCM of 0.7 % benzene in N₂ were used.

The characteristics summarized in Table 4.1 refer to the most abundant ion cluster formed by each investigated species. For HCOOH, CH₃COOH, HCl, and SO₂, fluoride ion clusters were observed, whereas for HCN, CF₃O⁻ clusters were dominant.

All species examined exhibit sensitivities on the same order of magnitude, approximately 10⁻⁵ ncps · ppt⁻¹. The uncertainties associated with the pure calibration-derived sensitivities

4.3. SENSITIVITY

range between 1–2 %, indicating high precision in the calibration process. However, it is important to note that these uncertainties do not fully capture the accuracy of measurements performed by FunMass-C. Additional experimental factors, such as variations in MFCs, surface effects, and dilution effects, introduce further sources of uncertainty that are not reflected in the calibration data alone.

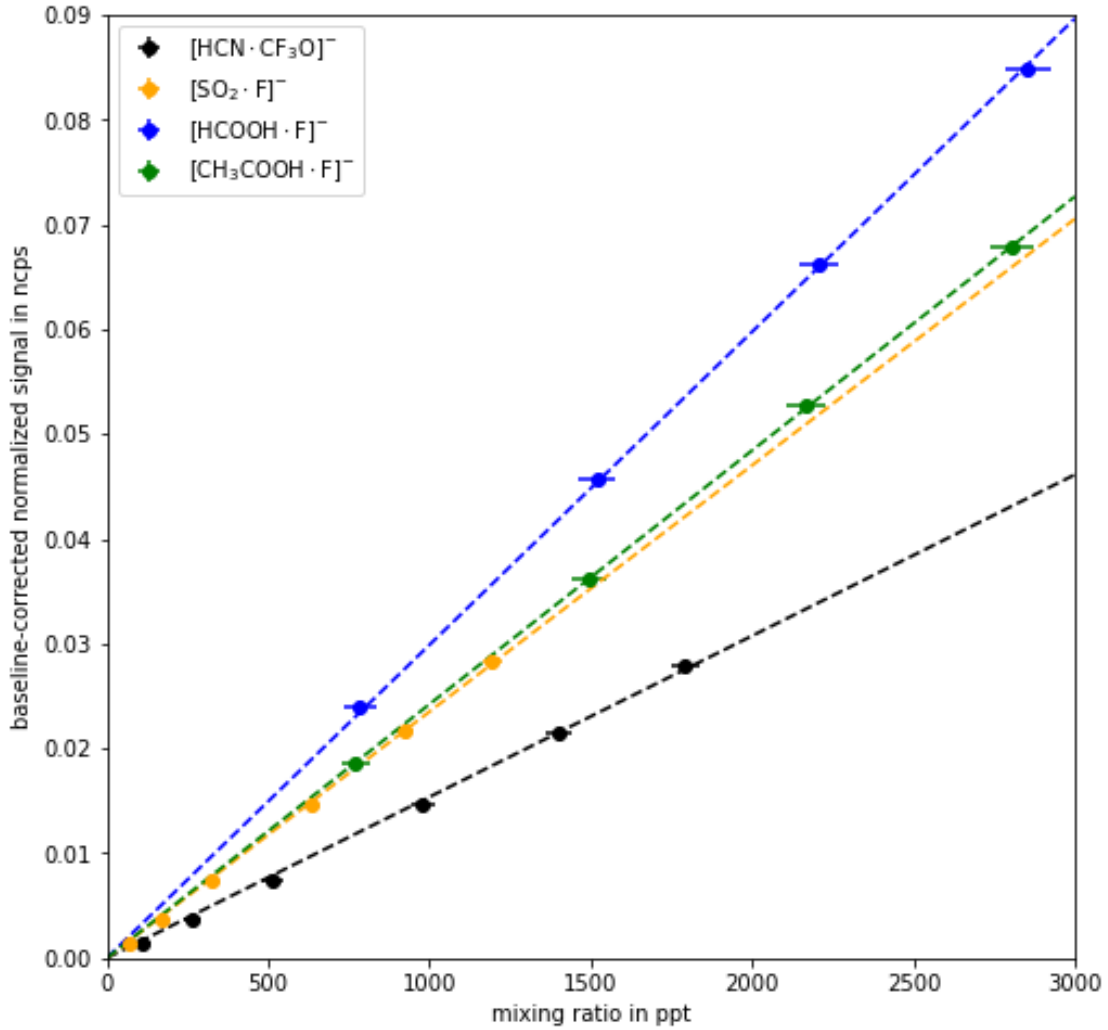


Figure 4.7: Calibration series for HCN (black), SO₂ (orange), HCOOH (blue), and CH₃COOH (green) under dry and ozone-free conditions.

Water vapor can also be quantified using BTP as a reagent ion derived from the [CF₃O · H₂O]⁻ cluster ($m/q = 103$ Th), as illustrated in Figure 4.8. The calibration exhibits linear behavior with a sensitivity of $1.27 \cdot 10^{-3}$ ncps · ppm⁻¹ up to water vapor mixing ratios of

approximately 300 - 500 ppm. The FISH calibration setup, described in Meyer et al. (2015), was used to calibrate up to 120 ppm water vapor and for larger water vapor mixing ratio the LGR DLT-100 from Los Gato was used as a reference. This range is sufficient to cover the typical mixing ratios encountered in the UTLS. The calculated limit of detection ($\text{LOD}(2\sigma, 10 \text{ s})$) is 0.06 ppm, which explains why the water vapor-related signal at 103 Th is consistently detectable in the mass spectra. Even high-purity synthetic air typically contains at least 0.5 ppm of water vapor, ensuring that the signal remains above the detection threshold under standard conditions. It should be noted that the last line gas supply lines used for water vapor calibration will not warrant proper water vapor transmission (PFA was used).

Given these characteristics, the use of CF_3O^- -based CIMS represents a promising approach for water vapor measurements in the UTLS region. However, further investigations are necessary to determine potential interferences from other trace gases that may affect the accuracy and specificity of the water vapor signal.

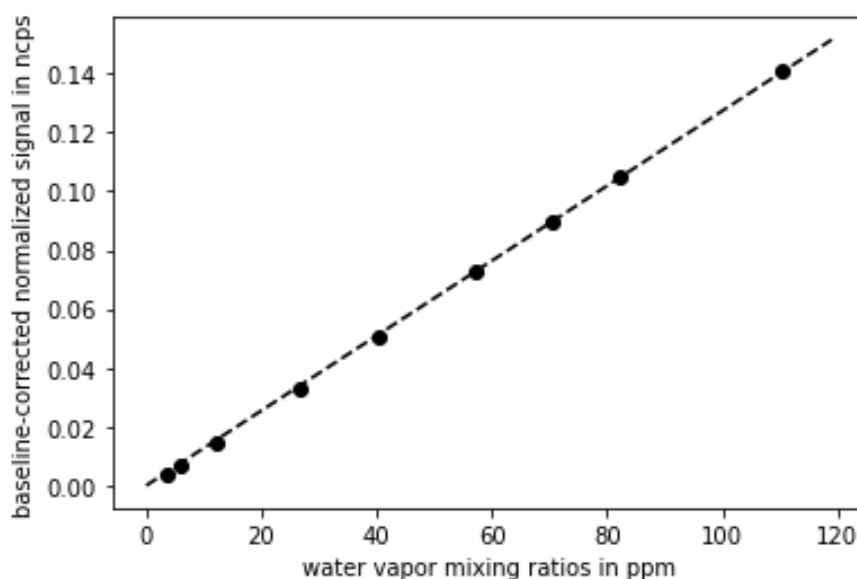


Figure 4.8: Calibration series of water vapor under ideal conditions. The calculated $\text{LOD}(2\sigma, 10 \text{ s})$ is 0.06 ppm.

The lowest limits of detection (LODs) reported in the literature for SO_2 are 8 ppt (1σ , 20 s) using SF_5^- CIMS (Jurkat et al., 2016), 1.8 ppt (1 s) using laser-induced fluorescence (LIF)(Rickly et al., 2021), and 48 ppt (1σ , 10 s) or 56 ppt (2σ , 1 s) using I^- CIMS(Lee et al.,

2018; Eger et al., 2019).

For HCN, reported LODs include 5 ppt (3 s) and 2.58 ppt (3σ , 60 s) using I^- CIMS (Le Breton et al., 2013; Priestley et al., 2018), and <15 ppt ($\text{S/N} = 1$, 0.5 s) reported by DeCarlo et al. (2007).

The highest LODs observed for HCOOH and HCl in this study can be attributed to small interfering impurities at m/q of 65 Th and 55 Th, respectively — corresponding to the fluoride cluster of each species. These signals were enhanced relative to other signals even in the absence of intentional HCOOH or HCl introduction, suggesting the presence of background interference.

In comparison, the literature reports an LOD of 25 ppt (3σ) for HCOOH using I^- CIMS (Le Breton et al., 2012), and 30 ppt (3σ , 150 s) using SF_6^- CIMS. For HCl, Jurkat et al. (2010) reported a 44 ppt (2σ) detection limit.

It is important to emphasize that the LODs determined using the FunMass system were obtained under ideal laboratory conditions, which do not fully replicate the complexities of flight or field environments. Consequently, direct comparison with literature values—often derived under more application-specific conditions — should be approached with caution. Nonetheless, the results indicate that FunMass performs very well when evaluated against other established measurement techniques, demonstrating its potential as a reliable instrument for multiple trace gas analysis.

The two key species for CARIBIC are SO_2 and HCN. Therefore, these species are examined in more detail with respect to their measurement precision. The overlapping Allan deviation (Wallin et al., 2018) was determined by continuously measuring 922 ppt SO_2 and 1017 ppt HCN over one hour (steady state) as shown in Figure 4.9). Both HCN and SO_2 exhibit good precision even at a 2-second integration time, with standard deviations of approximately 5 ppt, corresponding to about 0.5 %. With increasing integration time, the precision improves further, reaching a minimum at 400 seconds: 0.62 ppt for HCN and 1.02 ppt for SO_2 . Since CARIBIC data are typically averaged over 10 seconds, the relevant precision for both species at this integration time is 2.3 ppt, which corresponds to approximately 0.2 %.

The minimum of the Allan deviation occurs at a relatively long integration time (400

s), suggesting that the FunMass instrument is affected by low-frequency noise (e.g., white frequency or flicker noise) or slow instrumental drift (IMR temperature instability or purification of the IMR). One likely contributor is the instability of the IMR temperature, as the heating system was not operational during the measurement period. This lack of temperature control may have introduced drift or fluctuations in the signal. Another point is that Funmass always experiences a slow signal decreasing drift (main signal and TIC decreases over time) indicating e.g., purification of the instrument. In addition, the instrument exhibits some electronic noise, potentially at a frequency of around 10 Hz, and chemical noise, which may further impact measurement stability. Together, these effects can explain the relatively long integration time required to reach the minimum allan deviation.

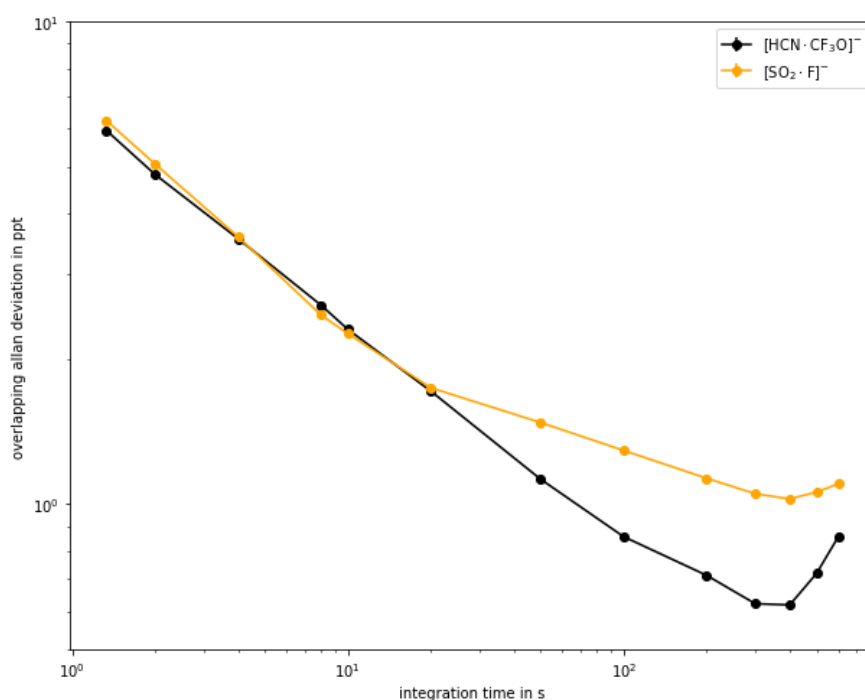


Figure 4.9: Overlapping Allan deviation calculated from continuous calibration measurements of 922 ppt SO₂ and 1017 ppt HCN over 1 hour at a 1.5 Hz sampling frequency.

The temporal response of the calibration signals for various analytes was evaluated to assess the feasibility of online calibrations during airborne or field measurements. For this purpose, a 2 m PTFE tubing was employed to connect the calibration system to the FunMass instrument. The stabilization times, defined as the time required to reach a steady-state

4.3. SENSITIVITY

signal following the initiation of calibration gas flow, were determined for each compound. The calibration signals for HCN (1.8 ppb), SO₂ (1.1 ppb), and CH₃COOH (2.8 ppb) stabilized within approximately 50, 100 , and 200 - 300 s, respectively. HCOOH (2.9 ppb), known for its high surface affinity, achieved a first plateau at 92 % of its steady-state signal within 6 seconds but required additional 150 – 200 s to reach full stabilization.

Another key parameter characterizing the system’s response is the e-folding time τ , which describes the exponential decay of the signal upon termination of the calibration gas. The e-folding time is calculated according to equation 4.7 and provides insight into the desorption dynamics and potential memory effects of the analytes.

$$S = A \cdot e^{\frac{t}{\tau}} + C \quad (4.7)$$

The decay of the normalized signal (in ncps) after the calibration of 1.8 ppb HCN (black), 1.1 ppb SO₂ (orange), 2.9 ppb HCOOH (green), and 2.8 ppb CH₃COOH (green) is shown in Figure 4.10

The determined e-folding times τ for HCN, SO₂, HCOOH, and CH₃COOH were 1.10 ± 0.04 s, 1.77 ± 0.09 s, 2.19 ± 0.09 s, and 2.38 ± 0.07 s, respectively. These results demonstrate that HCN and SO₂ exhibit sufficiently fast response times to enable online calibration, which is particularly advantageous given their planned use in in-flight calibration during CARIBIC. Rapid and reliable calibration is critical for ensuring accurate quantification of trace gases under the dynamically changing conditions encountered in the UTLS. While the response characteristics of HCOOH and CH₃COOH do not preclude online calibration entirely, especially if shorter lines are employed, their comparatively slower stabilization and decay times would significantly extend the duration of the calibration sequence. Therefore, in-flight calibration of these organic acids would be considerably more time-consuming than for HCN and SO₂.

In the following sections, the behavior of SO₂ and HCN under various conditions are investigated.

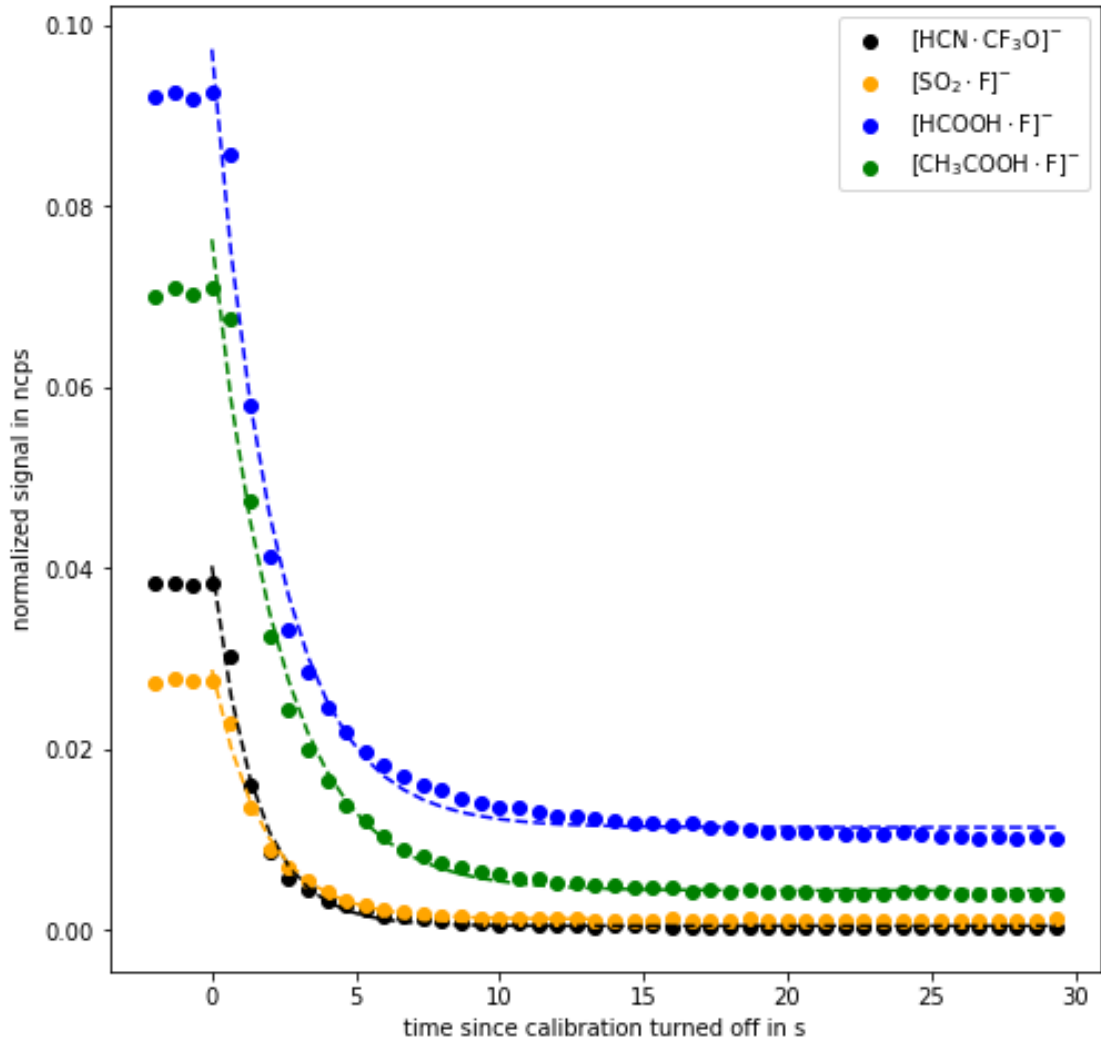


Figure 4.10: The decay of the normalized signal (in ncps) after the calibration of 1.8 ppb HCN (black), 1.1 ppb SO_2 (orange), 2.9 ppb HCOOH (green), and 2.8 ppb CH_3COOH (green). Dashed lines show the exponential fit, described in Equation 4.7, to the decays.

4.4 CF_3OOCF_3 Dependence

To evaluate whether the sensitivity is influenced by the flow rate of a 190 ppm $\text{CF}_3\text{OOCF}_3/\text{N}_2$ mixture, measurements were performed at varying flow rates. This could be expected since weak increasing signals of 123 Th (likely corresponding to CF_5O^-) and 189 Th (likely $\text{CF}_3\text{OOCF}_3 \cdot \text{F}^-$) were observed increasing the BTP flow rate. Figure 4.11 presents the relative sensitivities of SO_2 (orange) and HCN (black) at different $\text{CF}_3\text{OOCF}_3/\text{N}_2$ mixture flow rates. The sensitivity of HCN remains largely unaffected by changes in the BTP mixture flow, with variations below 0.3 %. In contrast, the sensitivity of SO_2 shows a slightly increasing trend with increasing flow rate, although the effect is minimal (less than 1 %) and can be considered negligible. Overall, it can be concluded that using the lowest possible flow rate is preferable to minimize BTP consumption, as higher flow rates do not yield significant sensitivity improvements (e.g., only a 16 % increase of the TIC when increasing the flow from 0.2 to 1.5 SCCM)

At higher BTP mixture flow rates, increased signals are observed at 123 Th and 189 Th, indicative of BTP decomposition products. While these signals peak at elevated flow rates, they subsequently level off afterwards. However, both species exhibit a tendency to adhere to surfaces, suggesting some degree of "stickiness."

These decomposition products typically form when residual BTP mixture remains in the tubing between the MFC and the gas cylinder over night(s). The material of the tubing appears to have no significant influence on this phenomenon. To mitigate this issue, the remaining BTP mixture in the short 1/8" stainless steel tube (only a few centimeters in length) is evacuated, followed by continuously flushing the line with 2 SCCM of high-purity N_2 (5.0). This procedure has proven effective in keeping the decomposition-related signals consistently low.

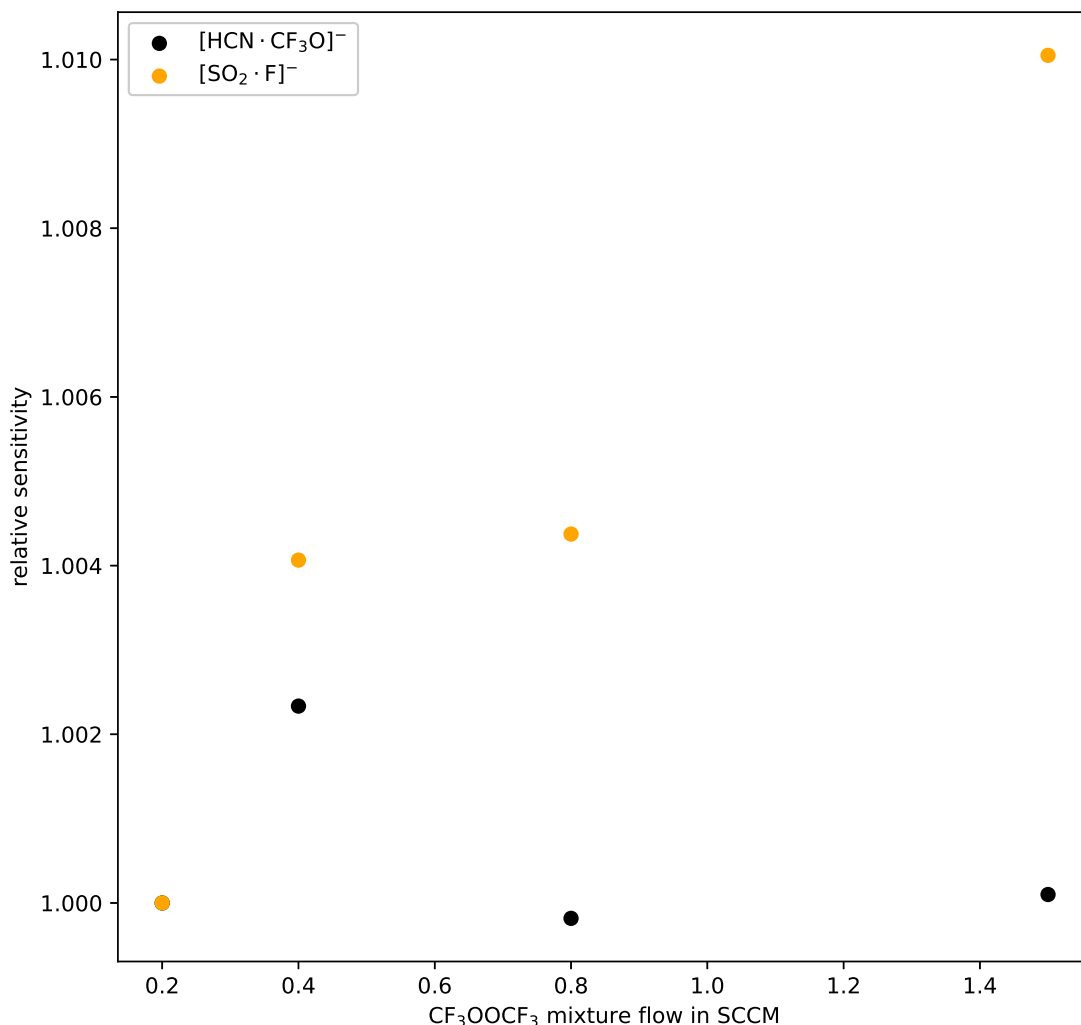


Figure 4.11: Relative sensitivity, which is the sensitivity normalized to the response at 0.2 SCCM of a 190 ppm CF₃OOCF₃/N₂ mixture, shown for various CF₃OOCF₃ mixture flow rates (in SCCM) added to 200 SCCM N₂ (5.0). In orange the fluoride cluster of SO₂ and in green the CF₃O⁻ cluster of HCN are shown.

4.5 Benzene Dependence

Besides BTP, also benzene could have an influence on the sensitivity of the analytes. The flow rate of 0.7 % benzene mixed in N₂ (5.0) was varied. The results are shown in Figure 4.12.

The relative sensitivity of SO₂ increases with rising benzene mixture flow rates, reaching up to a 2.5 % increase. In contrast, the relative sensitivity of HCN decreases by approximately

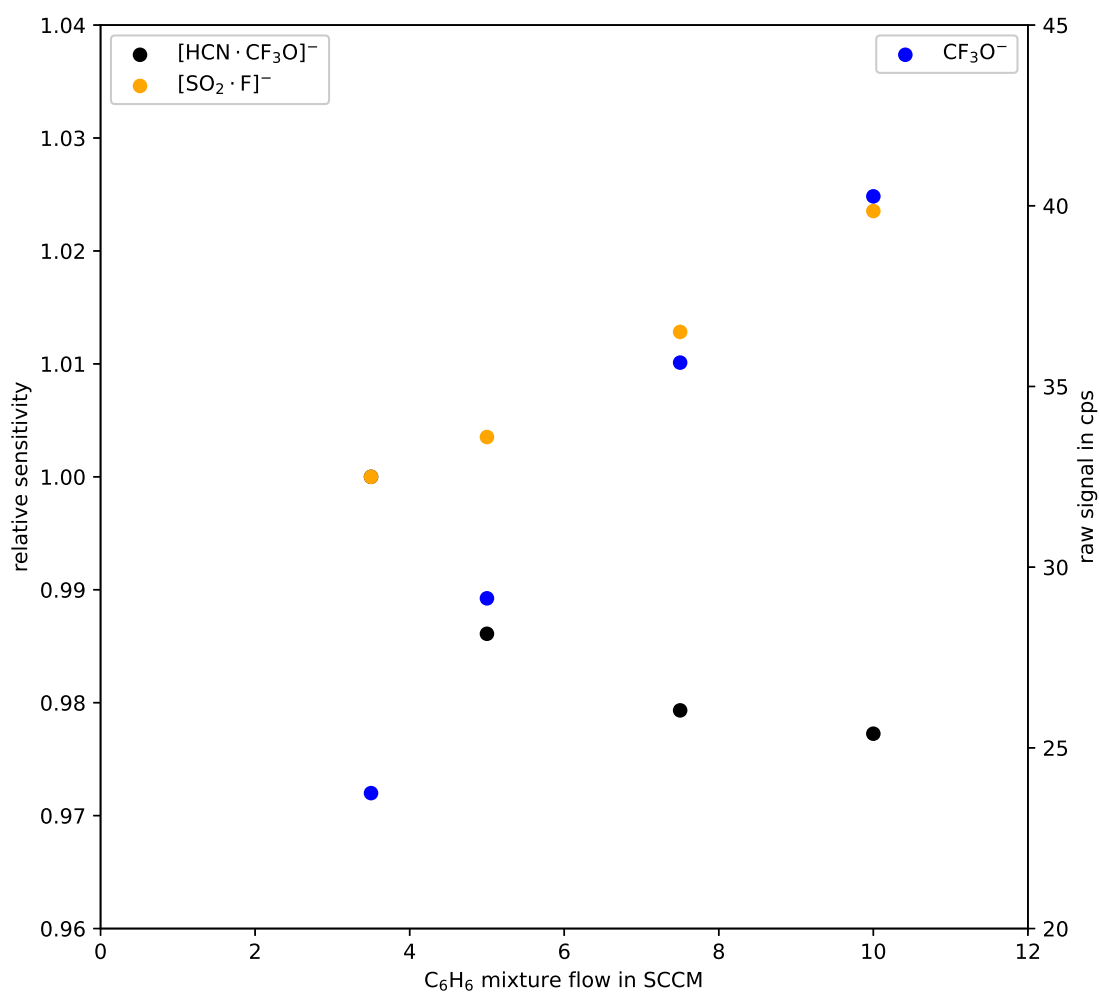


Figure 4.12: Relative sensitivity, which is the sensitivity normalized to the response at 3.5 SCCM of 0.7 % benzene mixed in N₂ (5.0), shown for various benzene mixture flow rates (in SCCM) added to 200 SCCM N₂ (5.0). In orange the relative sensitivity of the fluoride cluster of SO₂, in black the relative sensitivity of the CF₃O⁻ cluster of HCN, and in blue the raw signal of CF₃O⁻ in cps as a proxy for the TIC are shown.

2 %. The CF_3O^- signal also increases with flow rate, suggesting a higher total ion generation, up to approximately 80 % more at elevated flow. Despite this, changes in benzene mixture flow rate do not have a consistent or remarkable effect on sensitivity across all species (e.g., SO_2 vs. HCN), and increases in normalized background signals at certain m/q values are also observed.

To minimize benzene consumption and associated costs, while maintaining adequate sensitivity and limiting background signal, the flow rate was set as low as possible, specifically at 3.5 SCCM.

4.6 IS Flow Dependence

The influence of the IS carrier gas flow on analyte sensitivities was also investigated. As both the IMR pressure (35 mbar) and the total IMR outflow (669 SCCM) were held constant, any change in the IS carrier flow resulted in an inversely proportional change in the sample inlet flow. Consequently, the effective mixing ratio within the IMR, hereafter referred to as the IMR mixing ratio, varied with changes in flow conditions. This ratio was therefore calculated during calibration to account for such variations. Sensitivities were subsequently derived based on the corresponding IMR mixing ratios, ensuring that the results remained directly comparable across different IS carrier flow rates. The mixing ratios of SO_2 and HCN before entering the IMR were 3457 and 3813 ppt, respectively.

Figure 4.13 presents the relative sensitivities of SO_2 (orange) and HCN (black), which is the sensitivity normalized to the response at an IS carrier flow of 200 SCCM N_2 (5.0), across a range of IS carrier flow rates. Additionally, the raw signal of CF_3O^- (in counts per second), used as a proxy for the total ion count (TIC), is shown in blue.

For both SO_2 (measured via its fluoride cluster) and HCN (via its CF_3O^- cluster), sensitivity increases with increasing IS carrier flow. Notably, the sensitivity of SO_2 shows a steep, exponential increase, doubling at 300 SCCM, while HCN exhibits a more moderate increase of approximately 40 % over the same range. In contrast, the CF_3O^- signal (proxy for the TIC) reaches a maximum near 220 SCCM and subsequently decreases at higher flow rates.

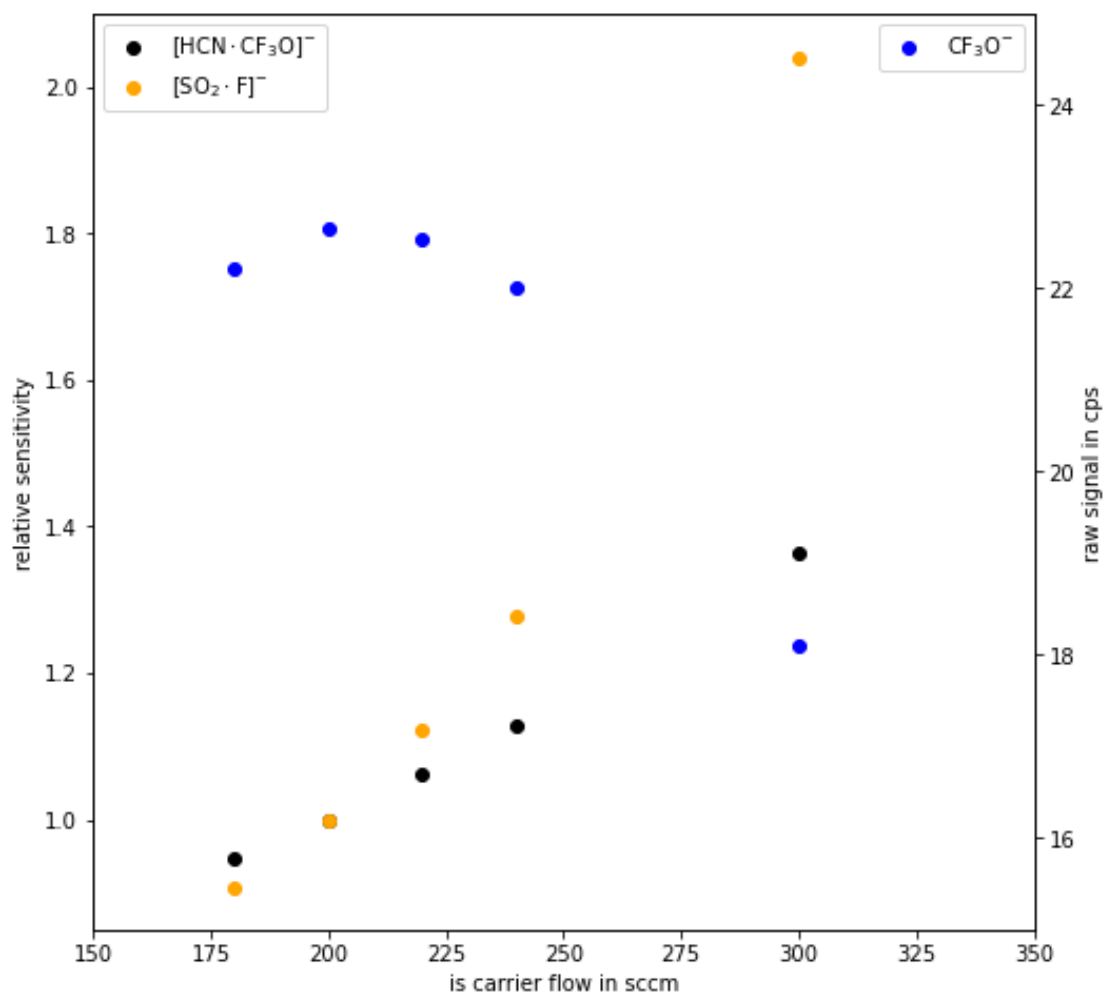


Figure 4.13: Relative sensitivity, which is the sensitivity normalized to the response at 200 SCCM of the IS carrier flow (N₂ 5.0 grade), shown for various IS carrier flow rates (in SCCM). In orange the relative sensitivity of the fluoride cluster of SO₂, in black the relative sensitivity of the CF₃O⁻ cluster of HCN, and in blue the raw signal of CF₃O⁻ in cps as a proxy for the TIC are shown.

This decline in TIC at elevated flow rates may be attributed to reduced VUV exposure time of the reagent ion mixture (BTP, benzene, and N₂), as well as lower mixing ratios of BTP and benzene in the ion source. Both effects likely result in fewer reagent ions and, consequently, a reduction in overall sensitivity.

The primary factor contributing to the observed sensitivity increase is likely enhanced mixing due to increased turbulence at higher IS carrier flows. This is supported by the decrease in TIC beyond 220 SCCM, suggesting that stronger turbulence also promotes ion loss processes such as wall interactions and changes in residence time. The more pronounced increase in SO₂ sensitivity compared to HCN may be explained by the nature of its ion chemistry: SO₂ primarily forms fluoride clusters, which are considered to result from multiple ion–molecule reaction pathways and may represent terminal products in the ion chemistry network. This behavior contrasts with HCN, which is detected mainly as a CF₃O[−] adduct.

Based on these findings, an IS carrier flow rate of 200–220 SCCM was selected as optimal, balancing sensitivity and ion stability while minimizing losses due to turbulence.

The final parameter in the ion source flow configuration is the lamp purge flow. This flow serves two primary purposes. First, to maintain the cleanliness of the lamp windows by preventing the deposition of reactive species, and second, to support the formation of a sheath flow within the IMR, thereby minimizing wall effects and associated ion losses. It should be noted that, for example, a total IS lamp purge flow of 20 SCCM corresponds to 10 SCCM directed through each lamp.

Both SO₂ and HCN sensitivities increase exponentially with increasing IS lamp purge flow. At the highest tested flow rate of 80 SCCM, the sensitivities of SO₂ and HCN increase by approximately 50 % and 25 %, respectively, relative to the baseline. The TIC also increases with increasing purge flow, appearing to saturate or peak at around 80 SCCM.

It was initially hypothesized that higher purge flows might introduce turbulence due to their perpendicular entry relative to the IS carrier flow. However, the observed improvement in performance, particularly up to 40 SCCM per lamp, suggests that the enhanced sensitivity is more likely attributed to the development of a more effective sheath flow. This improved sheath flow likely reduces wall interactions and supports more stable ion generation and

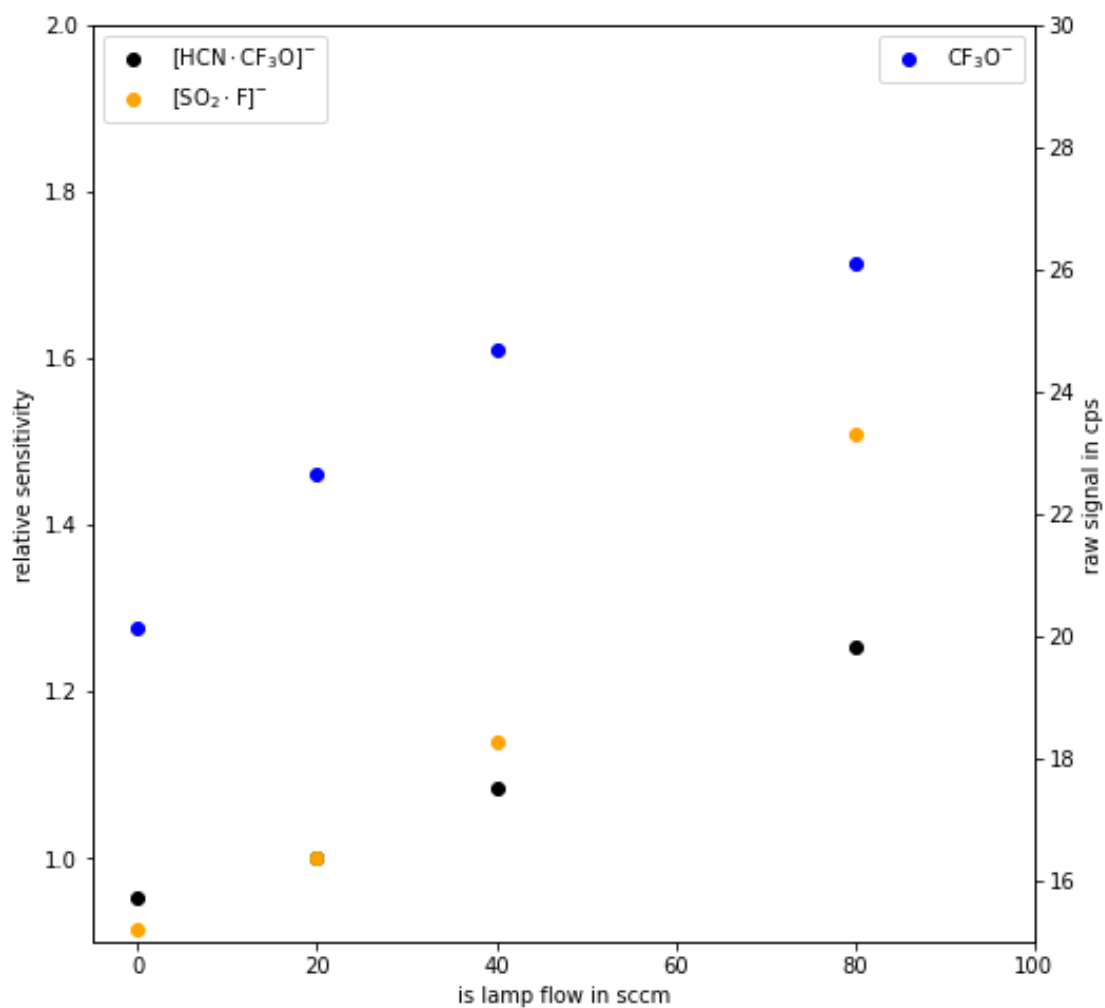


Figure 4.14: Relative sensitivity, which is the sensitivity normalized to the response at 20 SCCM of the IS lamp flow (N_2 5.0 grade), shown for various IS lamp flow rates (in SCCM). In orange the relative sensitivity of the fluoride cluster of SO_2 , in black the relative sensitivity of the CF_3O^- cluster of HCN, and in blue the raw signal of CF_3O^- in cps as a proxy for the TIC are shown.

transmission, thereby enhancing the overall sensitivity of the FunMass-C system.

4.7 IMR Pressure Dependence

The IMR pressure also influences the sensitivity.

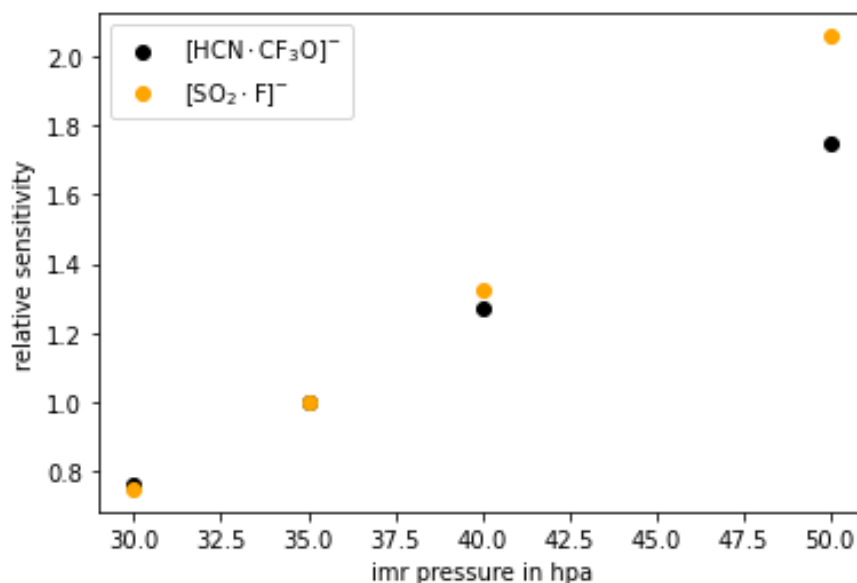


Figure 4.15: Relative sensitivity, which is the sensitivity normalized to the response at 35 mbar, shown for various IMR pressures (in mbar). In orange the relative sensitivity the fluoride cluster of SO₂, and in black the relative sensitivity of the CF₃O⁻ cluster of HCN. All the flows kept constant while varying the IMR pressure.

Figure 4.15 displays the relative sensitivities of SO₂ (orange) and HCN (black), which is the sensitivity normalized to the response at an IMR pressure of 35 mbar, across a range of IMR pressures. For both species, sensitivity increases with rising IMR pressure. The sensitivity of SO₂ seems to behave non-linear for larger IMR pressure ($p_{\text{IMR}} \geq 40$ hPa) since the relative sensitivity approximately doubles between 35 mbar and 50 mbar. In contrast, the sensitivity of HCN exhibits a more linear trend, increasing at an approximate rate of 5 % per mbar.

The observed increase in sensitivity with higher IMR pressure can be attributed to a greater frequency of ion-molecule collisions, which promotes the formation and destruction of ion clusters. Thus, the equilibrium between ion-molecule clustering and declustering is

4.7. IMR PRESSURE DEPENDENCE

shifted. However, the FunMass system operates with a critical orifice that regulates the flow from the IMR to the ToF. Since this flow is primarily governed by the IMR pressure, higher pressures result in increased flow rates to the ToF, leading to higher turbo pump power consumption and increased heat generation.

With a nozzle diameter in the range of 0.4 – 0.5 mm, the maximum stable IMR pressure achievable is approximately 80 mbar. To operate at even higher pressures, a reduction in nozzle diameter would be required to save the turbo pump.

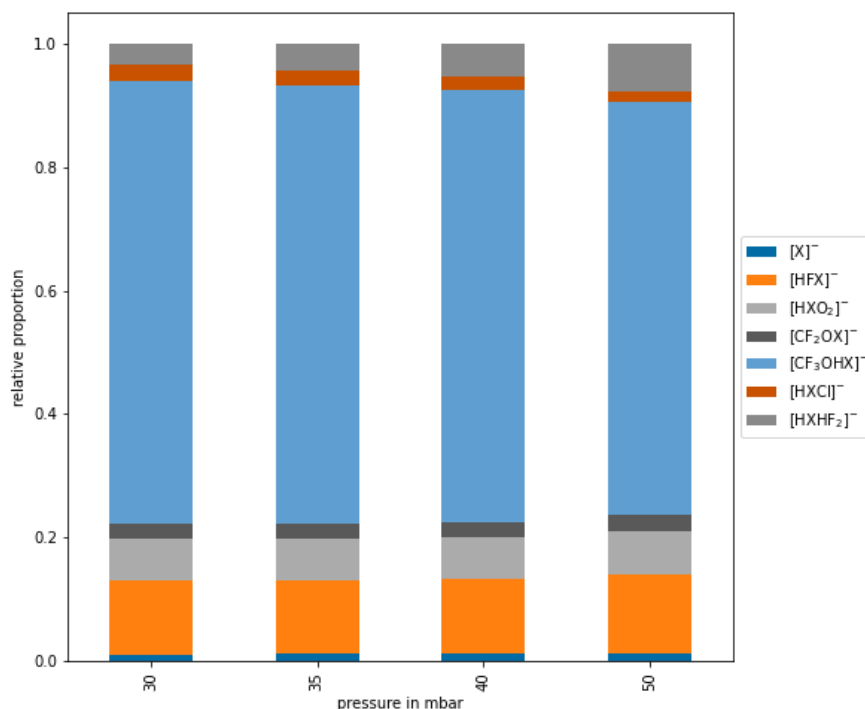


Figure 4.16: Relative proportion of the various clusters formed inside the IMR by adding 1.8 ppb HCN for different IMR pressures (in mbar).

An increase in IMR pressure can also lead to enhanced fragmentation and decomposition of ion molecule clusters. Figure 4.16 illustrates the relative distribution of various ion clusters formed in the IMR upon the addition of 1.8 ppb HCN, across a range of IMR pressures (in mbar). Between 30 and 50 mbar, no significant changes in the cluster distribution are observed. However, slightly higher proportions of fluoride clusters (such as $[HFX]^-$ and $[HXHF_2]^-$) as well as analyte anions ($[X]^-$), are detected at elevated IMR pressures. This shift results in a modest relative decrease in CF_3O^- -based clusters.

Despite these minor changes, the extent of fluoride cluster formation remains limited and does not present a compelling reason to avoid higher IMR pressures. Thus, within the tested pressure range, increased IMR pressure can still be considered beneficial for sensitivity without substantially altering ion chemistry in a detrimental way.

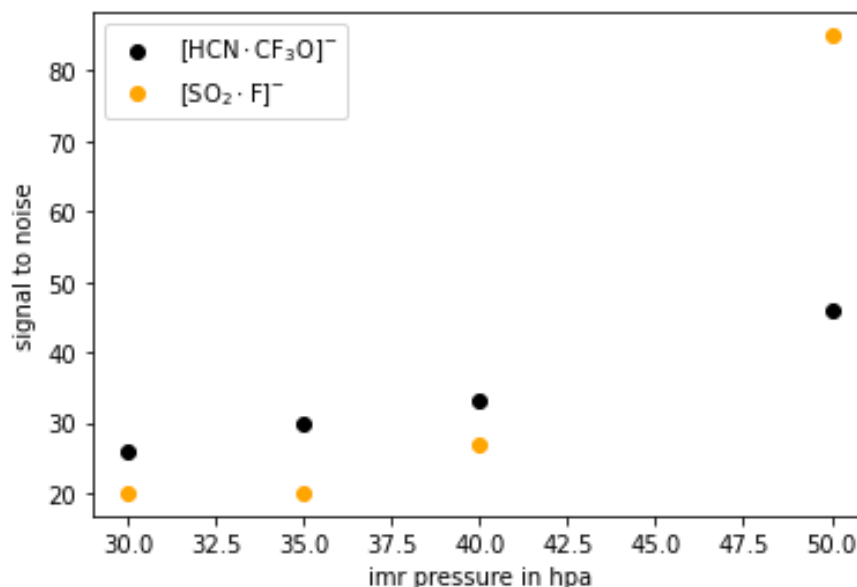


Figure 4.17: Signal to noise ratio (1σ , 10s) for various IMR pressures while adding 109 ppt HCN or 103 ppt SO_2 , respectively. In orange the signal to noise ratio of the fluoride cluster of SO_2 , and in black the signal to noise ratio of the CF_3O^- cluster of HCN

Higher IMR pressure can also contribute to increased signal noise. To evaluate this, the signal-to-noise ratio (S/N; 1σ , 10s) was assessed at low mixing ratios (109 ppt HCN and 103 ppt SO_2) across different IMR pressures, as shown in Figure 4.17. Despite the potential for increased noise, the S/N ratio improves for both SO_2 and HCN with increasing IMR pressure. Since a higher signal-to-noise ratio is always advantageous for detection sensitivity and data quality, elevated IMR pressures are considered beneficial in this context.

4.8 Total IMR Flow Dependence

The ion molecule reactions inside the IMR and the sensitivities are influenced by the reaction time, which can be adjusted by the total flow through the IMR (cf. 4.18).

Hence, different total IMR flows and their effect on the sensitivities were tested. The

4.8. TOTAL IMR FLOW DEPENDENCE

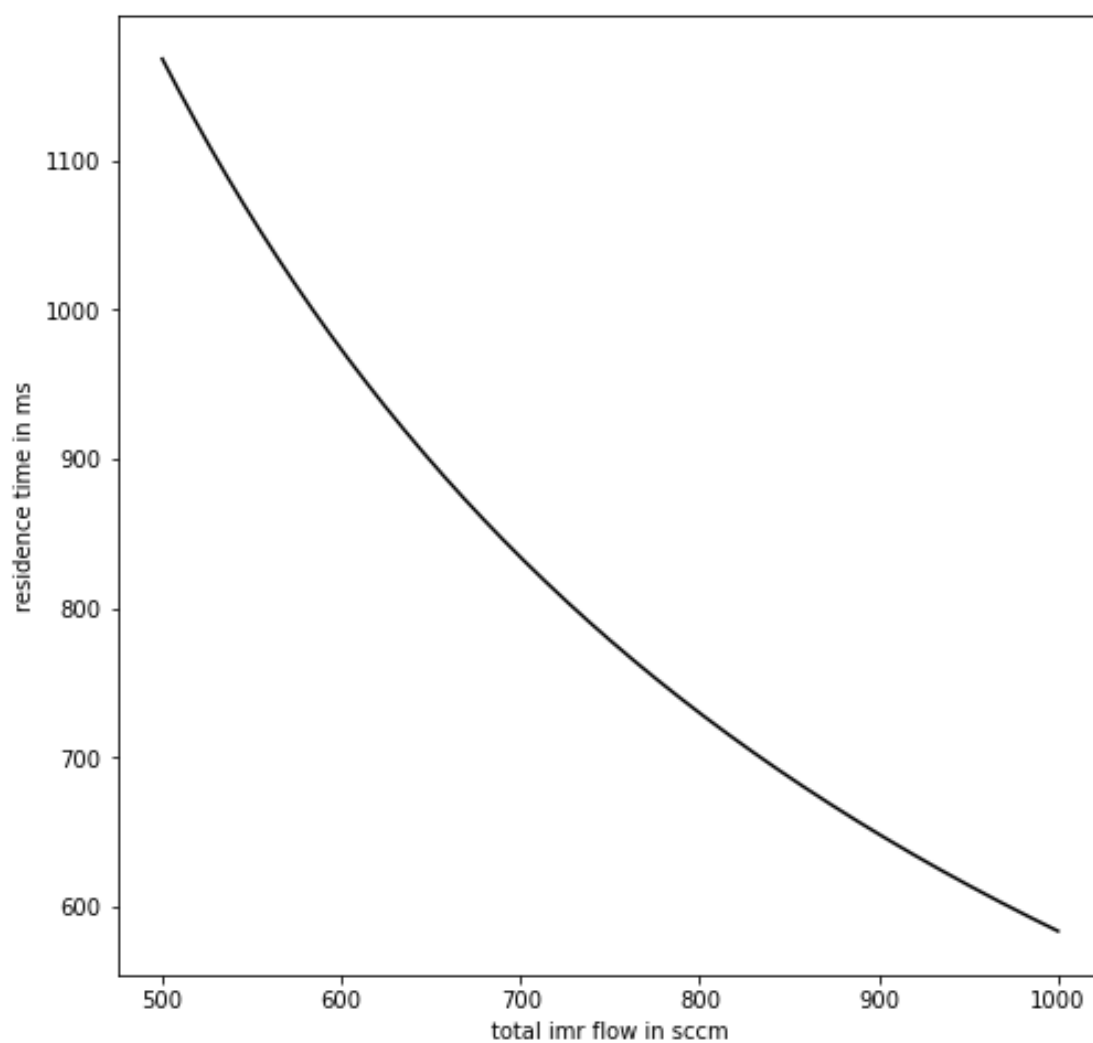


Figure 4.18: Residence time inside the IMR (only for the mixing tube) in ms for various total IMR flows in SCCM. For the calculation of the residence time, ideal cylinders were assumed as well as a IMR pressure and temperature of 35 mbar and 303 K, respectively.

pressure was held constant at 35 mbar as well as the ion source flows (IS carrier flow = 200 SCCM, IS lamp purge flow = 20 SCCM, benzene mixture flow = 3.5 SCCM, and BTP mixture flow = 0.2 SCCM). Thus, changes in the total IMR flow corresponds solely to a change in the inlet flow.

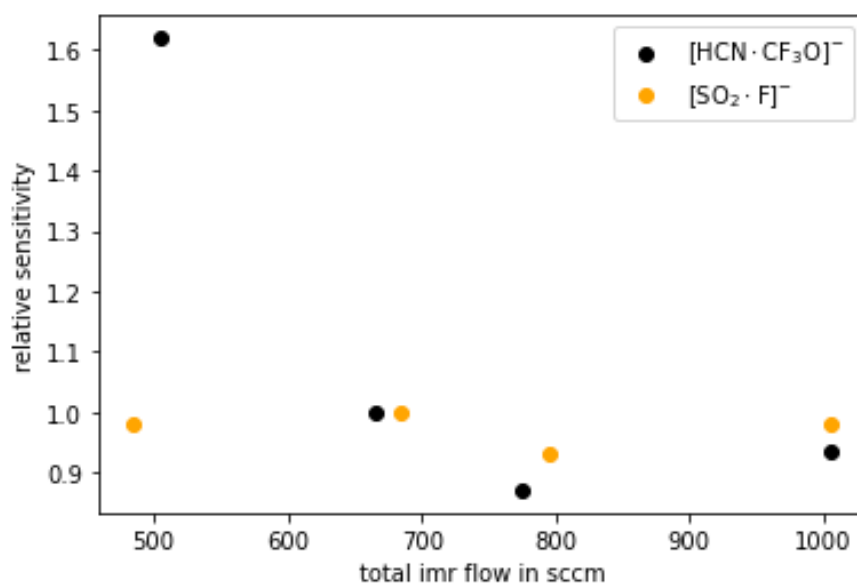


Figure 4.19: Relative sensitivity, which is the sensitivity normalized to the response at a total IMR flow of 665 SCCM (HCN) and 685 SCCM (SO₂) respectively, shown for various total IMR flows (in SCCM). In orange the relative sensitivity the fluoride cluster of SO₂, and in black the relative sensitivity of the CF₃O⁻ cluster of HCN

Figure 4.19 presents the relative sensitivities of SO₂ (orange) and HCN (black), which is the sensitivity normalized to the response at total IMR flows of 685 SCCM (SO₂) and 665 SCCM (HCN), respectively, across a range of total IMR flow rates. The sensitivity of the [HCN · CF₃O]⁻ cluster exhibits a pronounced exponential decrease (approximately 60 %) between 505 and 665 SCCM, after which it appears to slightly reach a saturation. This trend suggests that the ion–molecule reaction between HCN and CF₃O⁻ is relatively slow and kinetically limited or at least mixed-controlled for total IMR flows larger than 505 SCCM. At higher total IMR flow rates, the reduced residence time likely limits the extent of cluster formation.

In contrast, the relative sensitivity of SO₂ remains relatively stable across the same flow range. However, due to measurement limitations and the absence of data covering both the

4.8. TOTAL IMR FLOW DEPENDENCE

low- and high-flow transition regimes, it is not possible to definitively determine whether the ion chemistry of SO_2 lies within a kinetically or thermodynamically controlled regime across the 500 – 1000 SCCM range. Nevertheless, based on the observed stability and the presumed faster reaction kinetics between SO_2 and CF_3O^- or F^- , it is likely that $[\text{SO}_2 \cdot \text{F}]^-$ cluster formation operates under thermodynamic control within the FunMass system.

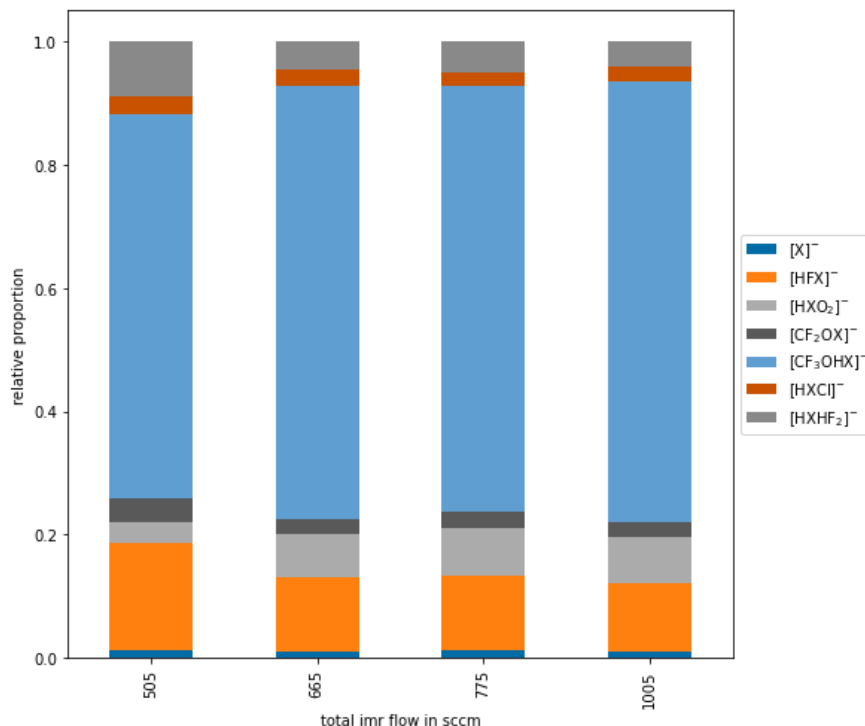


Figure 4.20: Relative proportion of the various clusters formed inside the IMR by adding 0.95 - 1.0 ppb HCN (IMR mixing ratio) for different total IMR flows (in SCCM).

Longer residence times within the IMR, associated with lower total flow rates, can promote increased fragmentation, decomposition, or in general the formation of second-generation products. Figure 4.20 illustrates the relative distribution of various ion clusters formed in the IMR following the addition of 0.95–1.0 ppb HCN (IMR mixing ratio) at different total IMR flow rates (in SCCM). At shorter residence times (i.e., higher flow rates), the formation of CF_3O^- clusters is favored. In contrast, at lower flow rates, there is a somewhat increased formation of fluoride clusters such as $[\text{F} \cdot \text{HCN}]^-$ and $[\text{HF}_2 \cdot \text{HCN}]^-$.

This observation supports the hypothesis that fluoride clusters are primarily formed from CF_3O^- parent clusters. In kinetically controlled systems, longer reaction times facilitate the

formation of second-generation products. Another ion species that shows enhanced formation at lower flow rates is $[\text{CF}_2\text{O} \cdot \text{CN}]^-$. One possible explanation is that it also originates from the decomposition of CF_3O^- clusters, thus behaving similarly to the fluoride clusters. Alternatively, its formation could involve a reaction between CF_2O and CN^- . This pathway would be consistent with the longer formation times observed, as CN^- itself is likely a second- or third-generation product and thus forms more slowly.

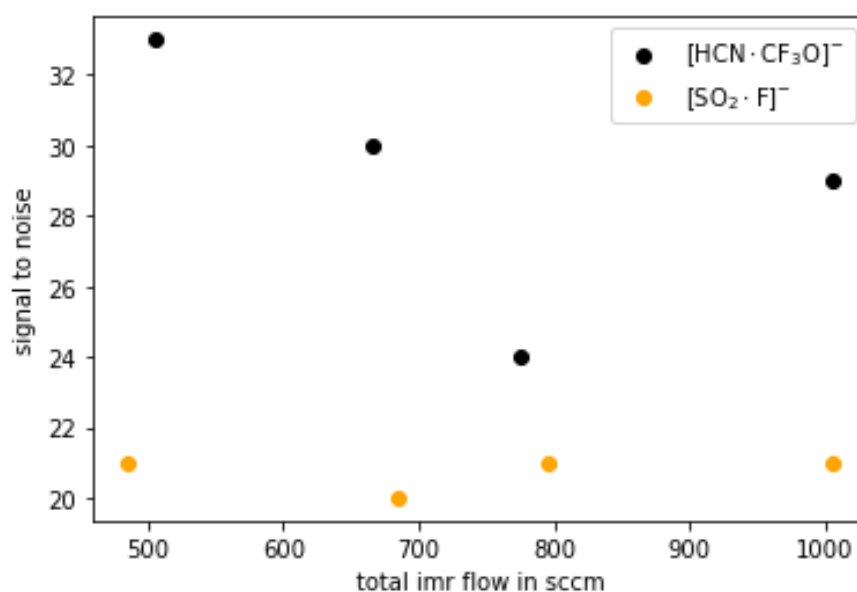


Figure 4.21: Signal to noise ratio (1σ , 10s) for various total IMR flows while adding 61-84 ppt HCN or 46-79 ppt SO_2 (IMR mixing ratios), respectively. In orange the signal to noise ratio of the fluoride cluster of SO_2 , and in black the signal to noise ratio of the CF_3O^- cluster of HCN is shown.

The signal-to-noise ratio (S/N; 1σ , measured over 10 seconds) was evaluated at low IMR mixing ratios (61–84 ppt for HCN and 46–79 ppt for SO_2) across a range of total IMR flows, as shown in Figure 4.21. While the S/N of the SO_2 signal remains largely unaffected by changes in total IMR flow, HCN exhibits a slightly improved S/N at lower flow rates. Notably, a decline in both S/N and sensitivity is observed for HCN at a total IMR flow of 775 SCCM. This drop cannot be attributed to any apparent external factors such as temperature variation, flow instability, or pressure fluctuations.

4.9 IMR Temperature Dependence

Robinson et al. (2022) showed that the sensitivity depends on the IMR temperature using a I⁻ CIMS. Moreover, they observed almost no effect of the ToF temperature on the sensitivity.

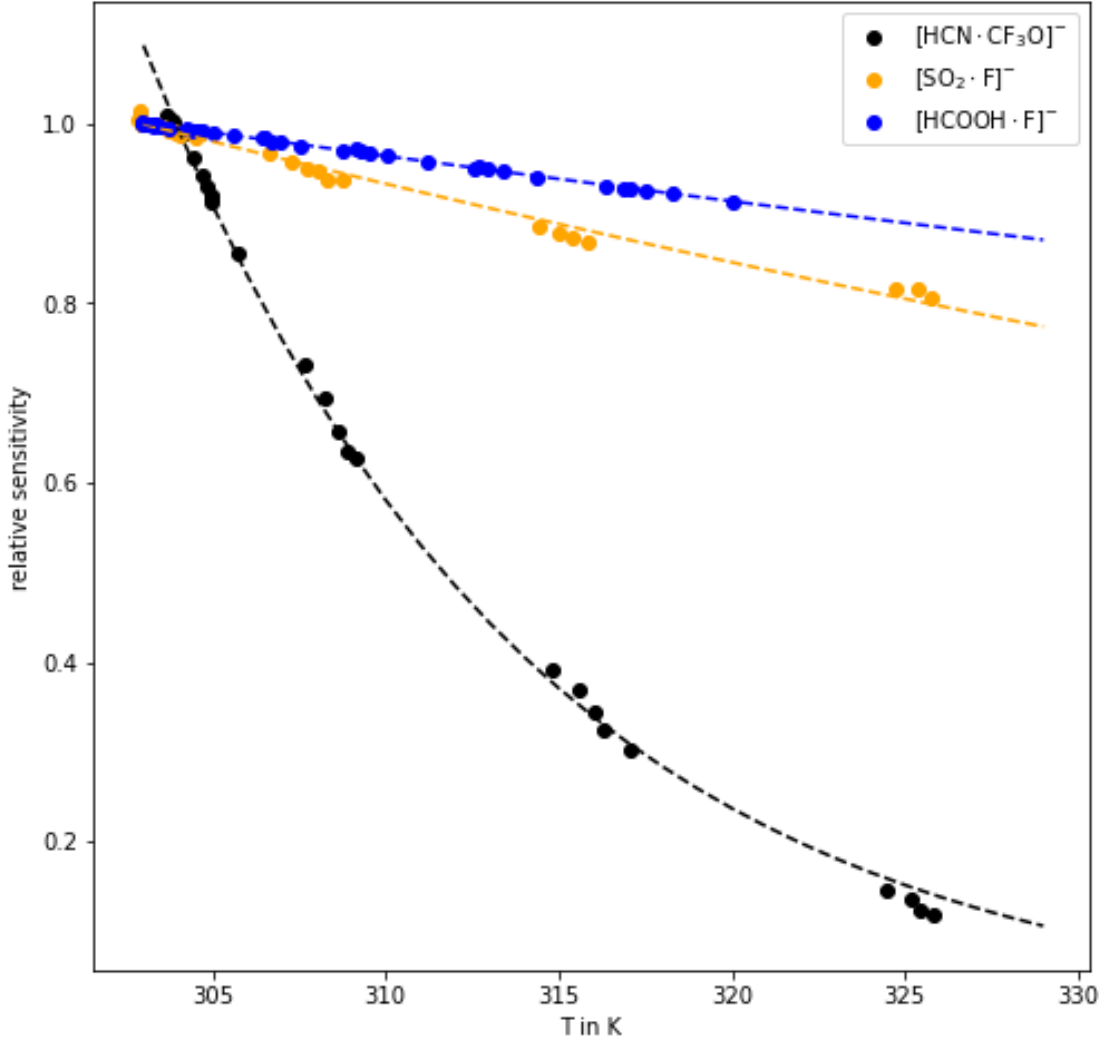


Figure 4.22: Relative sensitivities of HCN (black), SO₂ (orange), and HCOOH (blue), normalized to the response at 303 K, as function of IMR temperature (in K). The dashed lines represent an exponential fit with the function $f(T) = a \cdot e^{-b \cdot (T-303)}$.

Figure 4.22 shows the relative sensitivities of HCN (black), SO₂ (orange), and HCOOH (blue), normalized to their respective responses at 303 K, as function of temperature. All tested species exhibit decreasing sensitivity with increasing IMR temperature. Among them, HCN demonstrates a steep exponential decline, with a rate of approximately $-9\% \cdot \text{K}^{-1}$,

followed by linear declines for SO_2 ($-1 \text{ \%} \cdot \text{K}^{-1}$) and HCOOH ($-0.5 \text{ \%} \cdot \text{K}^{-1}$). Interestingly, the fluoride cluster of HCN also shows a decrease of about $-0.3 \text{ \%} \cdot \text{K}^{-1}$, suggesting that fluoride clusters are less sensitive to temperature variations compared to CF_3O^- clusters.

These results indicate that lower IMR temperatures are preferable to optimize the performance of FunMass, as sensitivity decreases with temperature while normalized background signals for all tested compounds increase by a factor of 3–6 increasing the temperature from 35 to 50 °C, thereby degrading detection limits.

However, the CARIBIC container can reach ambient temperatures of up to 40 °C. Since the IMR in FunMass is equipped only with heating capability, its temperature must be set to 40 °C to ensure consistent sensitivity during flights, avoiding fluctuations due to ambient temperature changes. A potential future improvement would be the integration of a Peltier element to enable both active cooling and heating of the IMR. This would allow operation at temperatures below 40 °C, improving sensitivity, especially for thermally sensitive species like HCN, which is adversely affected at temperatures above 35 °C.

Robinson et al. (2022) suggested to use the van't Hoff equation to determine the standard reaction enthalpy $\Delta_r H^0$.

$$\ln(K_{\text{eq}}) = -\frac{\Delta_r H^0}{RT} + \frac{\Delta_r S^0}{R}, \quad (4.8)$$

with the equilibrium constant K_{eq} , standard reaction entropy $\Delta_r H^0$, absolute temperature T , and universal gas constant R .

The equilibrium constant for the example reaction 3.7 is:

$$K_{\text{eq},3.7} = \frac{c([\text{CF}_3\text{O} \cdot \text{HA}]^-)}{c([\text{CF}_3\text{O}]^-) \cdot c(\text{HA})} \quad (4.9)$$

with the concentration c .

Equation 4.9 closely resembles the rearranged form of equation 4.5, expressed in terms of the calibration factor (sensitivity). Assuming temperature-independent transmission within the IMR, the equilibrium constant K_{eq} can be substituted by the relative sensitivity. This allows the standard reaction enthalpy to be derived from the slope of the linear fit, as illustrated

in Figure 4.23.

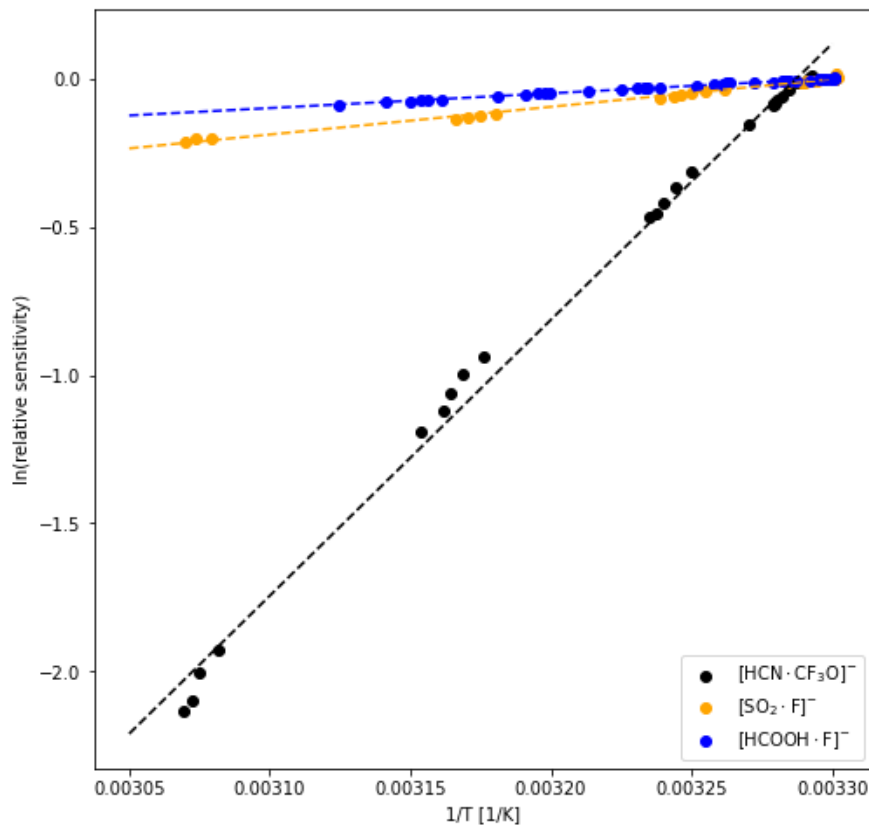


Figure 4.23: The logarithm of the relative sensitivities of HCN (black), SO₂ (orange), and HCOOH (blue), normalized to the response at 303 K, as function of the inverse temperature (in 1/K). The dashed lines represent a linear fit.

The standard reaction enthalpies determined experimentally are -18.56 kcal/mol for HCN, -1.90 kcal/mol for SO₂, and -1.03 kcal/mol for HCOOH. These values are compared with theoretically calculated reaction enthalpies obtained via density functional theory (DFT) using the B3LYP functional with the def2-TZVP basis set.

The comparison is based on four reference reactions:

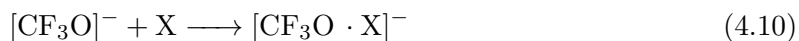




Table 4.2: Reaction enthalpies determined using DFT calculation (B3LYP / def2-TZVP) in kcal/mol for the four reactions at 300 K. Source: Jan Meissner (Heinrichs-Heine University (HHU) in Düsseldorf).

Molecule X	Reaction 1	Reaction 2	Reaction 3	Reaction 4
HCN	-19.83	1.35	-33.87	29.79
SO ₂	-20.21	-2.82	-38.04	-
HCOOH	-31.04	-10.46	-45.68	30.07

Table 4.2 presents the reaction enthalpies calculated via DFT (B3LYP/def2-TZVP) for reactions 4.10–4.13 at 300 K, expressed in kcal/mol. The experimentally determined enthalpy for HCN shows good agreement with the computational result of Reaction 4.10. Minor discrepancies may arise from experimental uncertainties, such as incomplete chemical equilibration or surface effects following temperature changes. Additionally, alternative reaction pathways, such as ligand-switching mechanisms, could influence the observed results. For example, reactions involving H₂O or HF clusters, like reaction 3.8, may contribute to the overall enthalpy, deviating from the idealized single-pathway model. Nevertheless, the observed difference of 1.3 kcal/mol is within an acceptable range and suggests reasonable agreement between theory and experiment.

In the case of SO₂, the formation of the fluoride cluster likely proceeds via reaction 4.11, with the experimental enthalpy of −1.90 kcal/mol aligning well with the theoretical value of −2.82 kcal/mol.

For formic acid, the experimentally determined enthalpy is notably lower than the values predicted for all four reference reactions. This suggests that the fluoride cluster may primarily form through a different reaction pathway, such as ligand-switching, rather than the mechanisms considered in the DFT calculations.

4.10 Sensitivity Dependence on other Trace Gases

In this section, the dependence on the sensitivity of SO_2 and HCN on other trace gases is investigated. The main focus is on water vapor and ozone as both play a crucial role during airborne measurements in the UTLS due to their relatively high abundance and variability.

4.10.1 Water Vapor

Water vapor is highly abundant in Earth's atmosphere; however, its mixing ratio decreases rapidly with increasing altitude. During the second phase of the CARIBIC project, the third quartile of the water vapor mixing ratio was 85.3 ppm for measurements conducted above 5000 m (cf. Figure 3.5). The relative sensitivities of HCN (black), SO_2 (orange), and HCOOH (blue) were evaluated under varying water vapor mixing ratios (in ppm), as illustrated in Figure 4.24. For SO_2 , an additional test was performed in 2023 (indicated by triangles), following an atmospheric chamber campaign. The results show overall good agreement across years, confirming the reproducibility of the measurement. Both tests were conducted under nearly identical conditions.

The sensitivities of HCN and HCOOH decrease significantly with increasing water vapor mixing ratios. At 1000 ppm of water vapor, the relative sensitivities drop by approximately 50 % and 55 % for HCN and HCOOH , respectively. In contrast, SO_2 exhibits a different behavior: its sensitivity initially increases slightly (by up to 2.5%) over the 0–200 ppm range. Beyond this point, a decline is observed, and at 1000 ppm, the sensitivity of SO_2 is reduced by only about 10 % compared to dry conditions. Thus, SO_2 appears to be less affected by water vapor than HCN and HCOOH . At mixing ratios exceeding 2000 ppm, the relative sensitivities for HCOOH seem to reach a saturation point.

These trends demonstrate a well-known fact that water vapor plays a significant role in ion–molecule chemistry within the IMR region. There are mainly three key points where it influences the clustering equilibria.

Additional water molecule(s) can alter the reaction rate of the equilibrium reactions (clustering and declustering) as it introduces new pathways (ligand switching instead of direct

clustering).

Water molecules can influence cluster ion formation by stabilizing or destabilizing reagent or product ions via the formation of hydration shells. This can either enhance or suppress the efficiency of product ion formation depending on the molecular species involved.

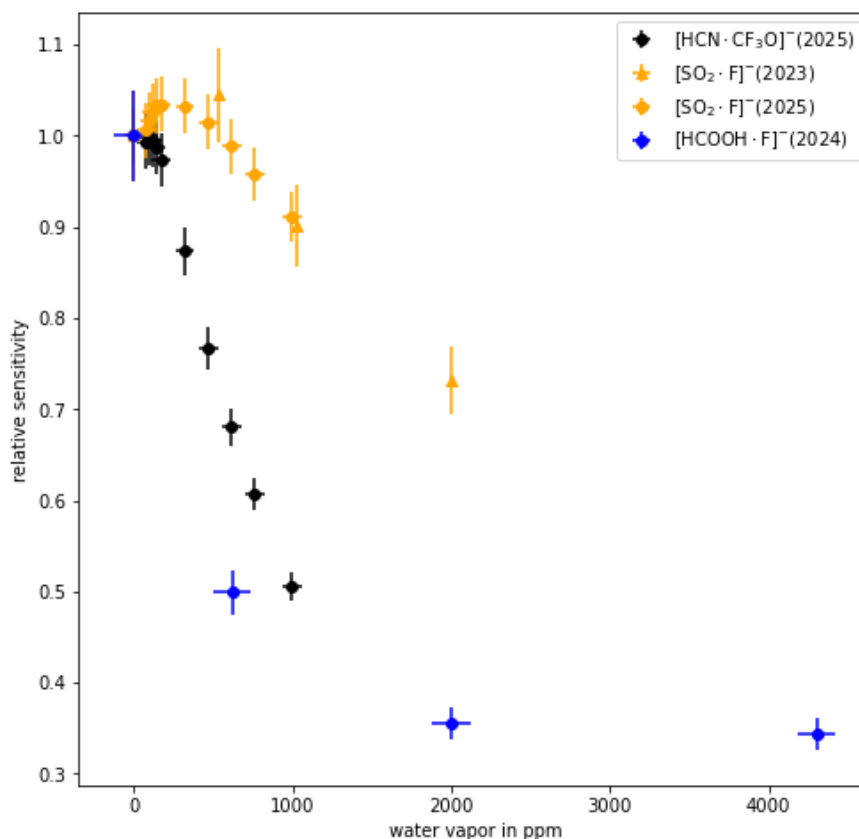
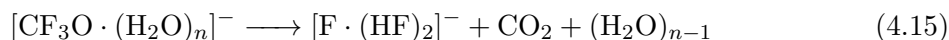


Figure 4.24: Relative sensitivities of HCN (black), SO₂ (orange triangles (2023) and circles (2025)), and HCOOH (blue), normalized to the response at 0 ppm water vapor as function of water vapor content (in ppm).

First, increasing water vapor mixing ratios promote the formation of hydrated reagent ions such as $[\text{CF}_3\text{O} \cdot (\text{H}_2\text{O})_n]^-$, which alters the ion-molecule reaction pathways. The target molecule is more likely (de-)ionized by ligand-switching via hydrated CF_3O^- ions instead of direct (de-)clustering by unhydrated CF_3O^- ions the higher the water vapor content inside IMR is. The different (de-)clustering reaction may have different reaction rates and hence, the equilibrium can be shifted. The hydrated CF_3O^- are also susceptible to decomposition, which reduces the availability of (unhydrated) CF_3O^- ions, which can additionally alters the

equilibrium of the (de-)clustering of the target molecule. This reduction becomes particularly relevant at higher analyte mixing ratios, as the saturation behavior of the CIMS detection is altered due to the lower effective concentration of the primary reagent ion.

This effect has been previously described by Huey et al. (1996) (cf. Equations 4.14 and 4.15), who detailed the decomposition mechanisms of hydrated CF_3O^- clusters, further supporting the observed sensitivity trends.



These decomposition reactions not only reduce the concentration of active reagent ions but also alter the overall chemical environment within the IMR. The generation of additional fluoride ions and HF as byproducts can shift the reaction equilibrium, potentially favoring alternative reaction pathways and further complicating the interpretation of sensitivity behavior under humid conditions.

Secondly, water vapor can influence the product ion distribution. As for FunMass-C, only the primary product ions are used, this variation can result in a sensitivity change as the hydration and secondary clustering processes shift the equilibrium of ion–molecule reactions within the IMR, leading to a redistribution of signal across multiple cluster ions.

The observed decrease in the relative sensitivity of the fluoride cluster of SO_2 is primarily attributed to the formation of its corresponding water cluster, $[\text{SO}_2 \cdot \text{H}_2\text{O} \cdot \text{F}]^-$, which increases in relative sensitivity by approximately a factor of 8. This cluster formation effectively reduces the abundance of the unhydrated fluoride cluster and thus alters the quantification of SO_2 under humid conditions.

A similar behavior is observed for HCN. As water vapor mixing ratio increases, the formation of both water and HF clusters is enhanced, resulting in a significant reduction in the sensitivity of the primary HCN product ions, namely, the fluoride cluster and the CF_3O^- cluster.

Finally, water molecule(s) can catalyze decomposition of a ion-molecule cluster. In the case of HCOOH, Amelynck et al. (2000) proposed a decomposition pathway that leads to the formation of $[\text{HF}_2]^-$, as described by equation 4.16.

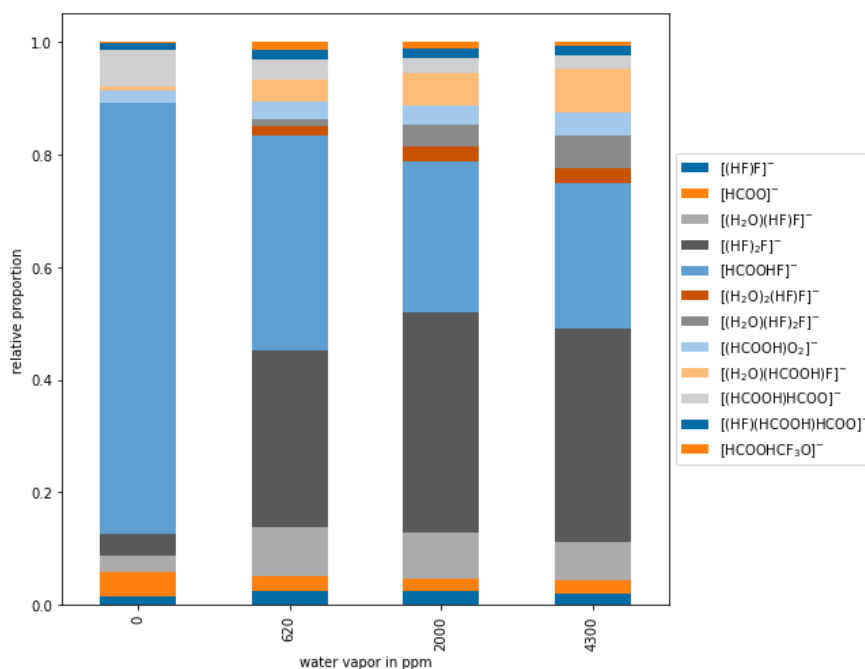
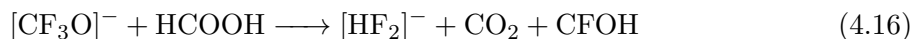


Figure 4.25: Relative proportion of the major clusters formed inside the IMR by adding 4.0 - 4.8 ppb HCOOH under various water vapor mixing ratios (in ppm).

Figure 4.25 presents the relative distribution of major ion clusters formed in the ion-molecule reaction (IMR) region following the introduction of 4.0–4.8 ppb HCOOH under varying water vapor mixing ratios (in ppm). Similar to the other trace gases studied, HCOOH forms an increasing number of water-containing clusters at elevated humidity levels, such as $[\text{H}_2\text{O} \cdot \text{HCOOH} \cdot \text{F}]^-$.

However, in contrast to HCN and SO_2 , HCOOH also shows a pronounced enhancement in the formation of HF-rich clusters including $[\text{HF}_2]^-$, $[(\text{H}_2\text{O}) \cdot (\text{HF}) \cdot \text{F}]^-$, and in particular, $[(\text{HF})_2 \cdot \text{F}]^-$, with increasing water vapor mixing ratios. These observations support the hypothesis proposed by Amelynck et al. (2000), who suggested that HCOOH may undergo a

4.10. SENSITIVITY DEPENDENCE ON OTHER TRACE GASES

decomposition pathway, as described in equation 4.16. The presence of water and HF likely facilitates this process by acting as catalysts or stabilizing intermediates, thereby enhancing the formation of HF-containing product ions. This decomposition further complicates the detection and quantification of HCOOH, particularly under conditions of elevated humidity, where fluoride ions and water molecules are more abundant and reactive.

Water vapor also affects the baseline signal and its noise. Thus, a proper background measurement with the actual amount of water vapor is crucial as the effect can be up to 60 ppt at 2000 ppm water vapor (cf. Subsection 3.1.2).

Additionally, the noise increases. Larger noise and decreasing sensitivity can degrade the limit of detection.

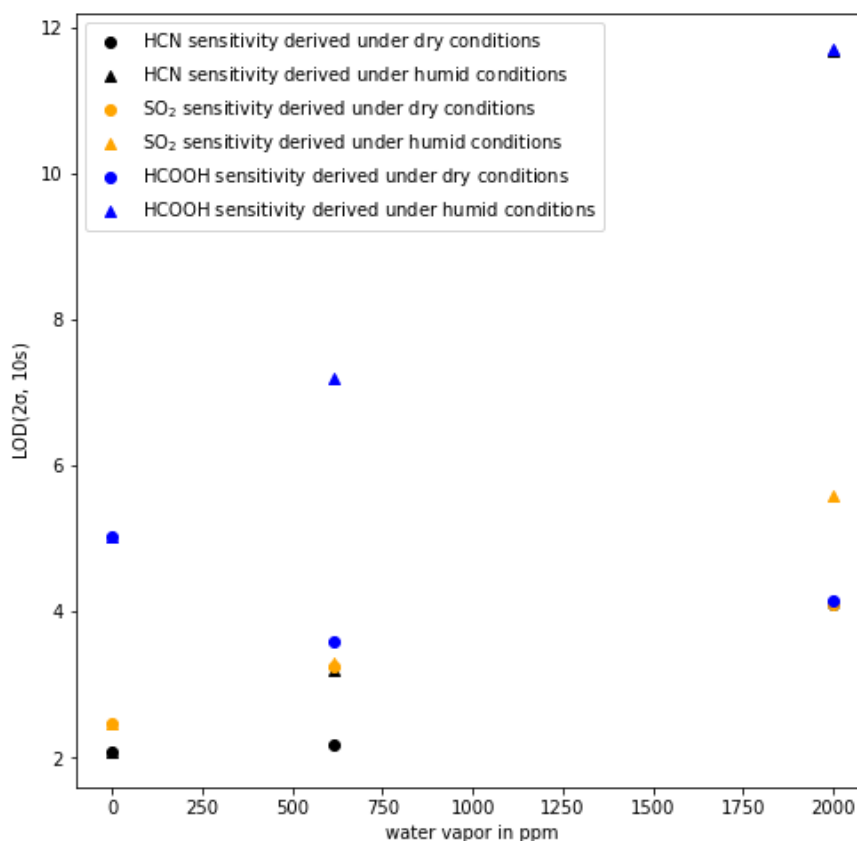


Figure 4.26: LOD(2σ , 10s) of HCN(black), SO₂ (orange), and HCOOH (blue) at various water vapor mixing ratios (in ppm). The circles and triangles represent LOD calculated using the sensitivities under dry condition and water vapor-corrected sensitivities, respectively.

Figure 4.26 illustrates the influence of water vapor on the limit of detection (LOD, defined

as 2σ over 10 seconds) for HCN (black), SO₂ (orange), and HCOOH (blue). The data points represented by circles correspond to LOD values calculated using a constant sensitivity under dry conditions. These values reflect the effect of increased noise resulting from elevated water vapor mixing ratios. As shown, the noise increases only modestly, resulting in a doubling of the LOD at 2000 ppm H₂O for both HCN and SO₂. In contrast, HCOOH exhibits a slight reduction in baseline noise under higher humidity, leading to a marginal decrease in LOD of approximately 1 ppt. This behavior can be attributed to minor HCOOH impurities present within the FunMass system, which contribute to an elevated background signal at the HCOOH signal under dry conditions, thereby increasing its corresponding LOD. As the water vapor mixing ratios increases, HCOOH starts forming hydrated clusters, such as [HCOOH · H₂O · F]⁻. This cluster shares the same nominal mass as the fluoride cluster of SO₂, leading to an increased background signal in the SO₂ channel and a concomitant decrease in the background signal of the fluoride cluster of HCOOH. As a result, under humid conditions, the LOD for HCOOH slightly decreases, while that for SO₂ increases, highlighting the complex interplay of humidity-dependent cluster formation and isobaric interferences in CIMS measurements (also shown in Subsection 4.10.3).

However, since the LOD is a function of both signal noise and sensitivity, the sensitivity corrected for water vapor influence must be considered to accurately quantify detection limits. The triangles in Figure 4.26 represent LOD values computed using the humidity-dependent sensitivity. As the sensitivity for all three species decreases with increasing water vapor content, the corresponding LODs increase substantially. Under high humidity conditions (2000 ppm), the LOD(2σ , 10 s) reaches 5.6 ppt for SO₂, and 11.7 ppt for both HCN and HCOOH.

Overall, the figure demonstrates that the decline in sensitivity due to water vapor has a more pronounced effect on the LOD than the increase in signal noise. This highlights the importance of applying water vapor corrections in the quantitative interpretation of trace gas measurements, particularly under humid conditions.

4.10.2 Ozone

Along with water vapor, ozone is the most abundant trace gas and also highly variable in the stratosphere (0 - 10 ppm). As the CARIBIC flights also reach the lowermost stratosphere (approx. 0 - 1 ppm O_3), the dependence of analyte species on ozone mixing ratios is important.

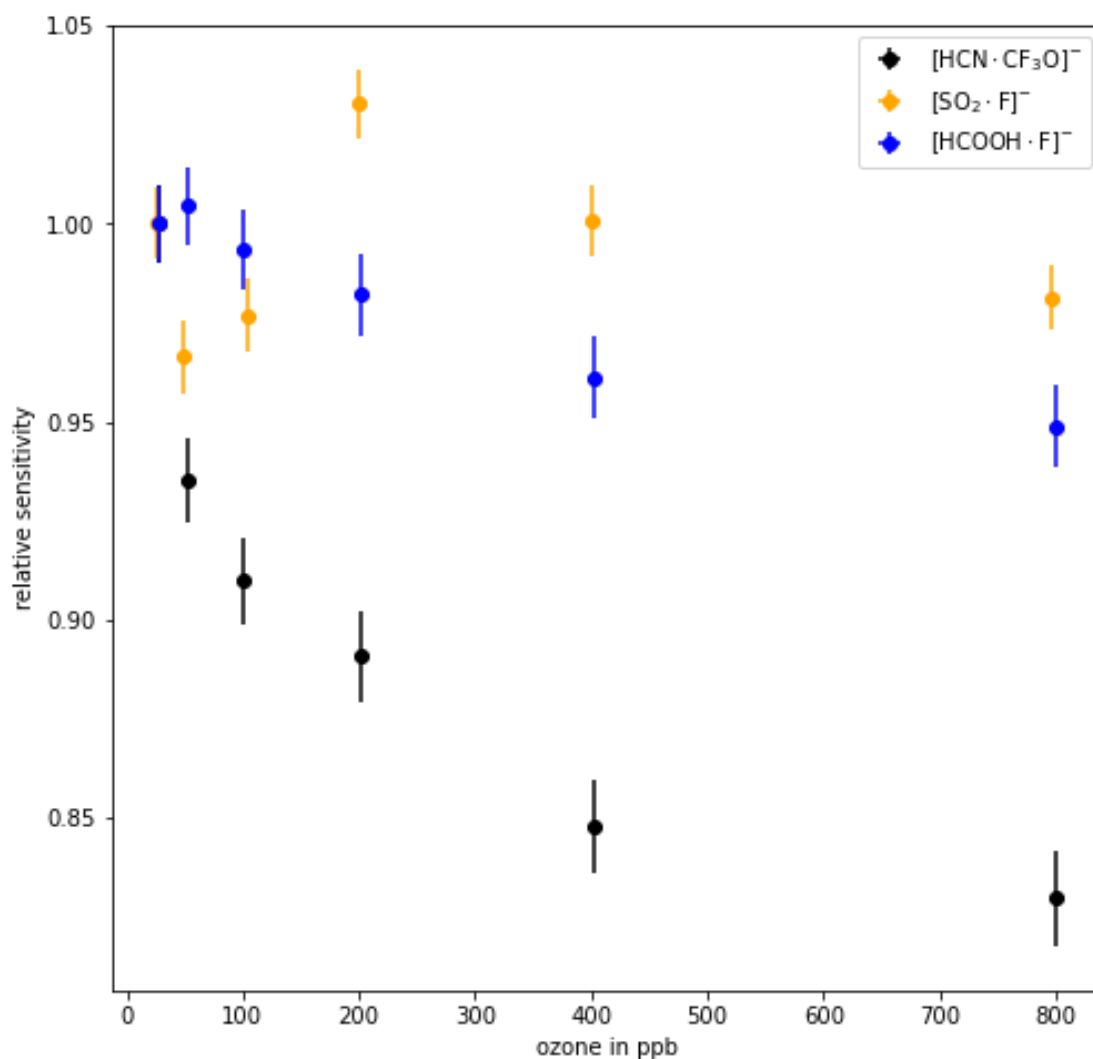


Figure 4.27: Relative sensitivities of HCN (black), SO_2 (orange), and $HCOOH$ (blue), normalized to the response at 20 ppb ozone as function of ozone mixing ratios (in ppb) for dry conditions.

The relative sensitivities of HCN (black), SO_2 (orange), and $HCOOH$ (blue), normalized to the response with 20 ppb added ozone, were evaluated as function of ozone mixing ratios (in ppb), as shown in Figure 4.27.

The CF_3O^- cluster of HCN exhibits the largest decrease in sensitivity, with a reduction of approximately 17 % at elevated ozone levels (800 ppb). In contrast, ozone has a minor effect on the fluoride clusters formed by SO_2 and HCOOH . SO_2 shows no significant correlation between ozone mixing ratio and relative sensitivity. HCOOH displays a slightly negative trend, with a reduction of around 5 % at 800 ppb ozone.

Further insight can be gained by examining the fluoride cluster of HCN, which shows a modest decrease in sensitivity (approximately 4 % at 800 ppb ozone), similar to HCOOH . This observation suggests that the ozone dependence differs between the formation mechanisms of CF_3O^- clusters and fluoride clusters. While both HCN clusters decrease in relative sensitivity with increasing ozone, the signals at 42 Th and 62 Th, corresponding to $[\text{CNO}]^-$ and $[\text{HCNO} \cdot \text{F}]^-$, respectively, exhibit significant increases. Specifically, the relative sensitivities of these two clusters increase by a factor of approximately 2.2 at 800 ppb ozone. However, both $[\text{CNO}]^-$ and $[\text{HCNO} \cdot \text{F}]^-$, like the original HCN clusters, tend to reach a plateau at higher ozone mixing ratios. This indicates that the observed signal loss for HCN is largely due to its conversion into HCNO and subsequent cluster formation. Future work will aim to calibrate HCNO to enable quantification of its formation within the IMR during combined HCN and ozone injection experiments.

Ozone also affects the sensitivity of HCOOH , likely due to its decomposition through reaction with ozone, producing CO_2 , O_2 , and H_2O , as reported by Beltrán et al. (2023). This reaction may be further facilitated by catalytic effects involving e.g., fluoride ions or HF .

As previously noted, the fluoride cluster of SO_2 exhibits no significant sensitivity change in response to ozone. However, Figure 4.5b shows that SO_2 can form a superoxide anion cluster, $[\text{SO}_2 \cdot \text{O}_2]^-$, which is affected by ozone and subsequently transforms into $[\text{SO}_5]^-$. The latter has a nominal m/q of 112 Th and may interfere with the CF_3O^- signal of HCN, as discussed further in Section 4.10.3.2.

As water vapor, ozone does also affect the background signals and its noise level. Hence, the influence of ozone on the limit of detection is also investigated.

Figure 4.28 illustrates the effect of ozone on the limit of detection (LOD, defined as 2σ over 10 seconds) for HCN (black), SO_2 (orange), and HCOOH (blue). The data points indicated

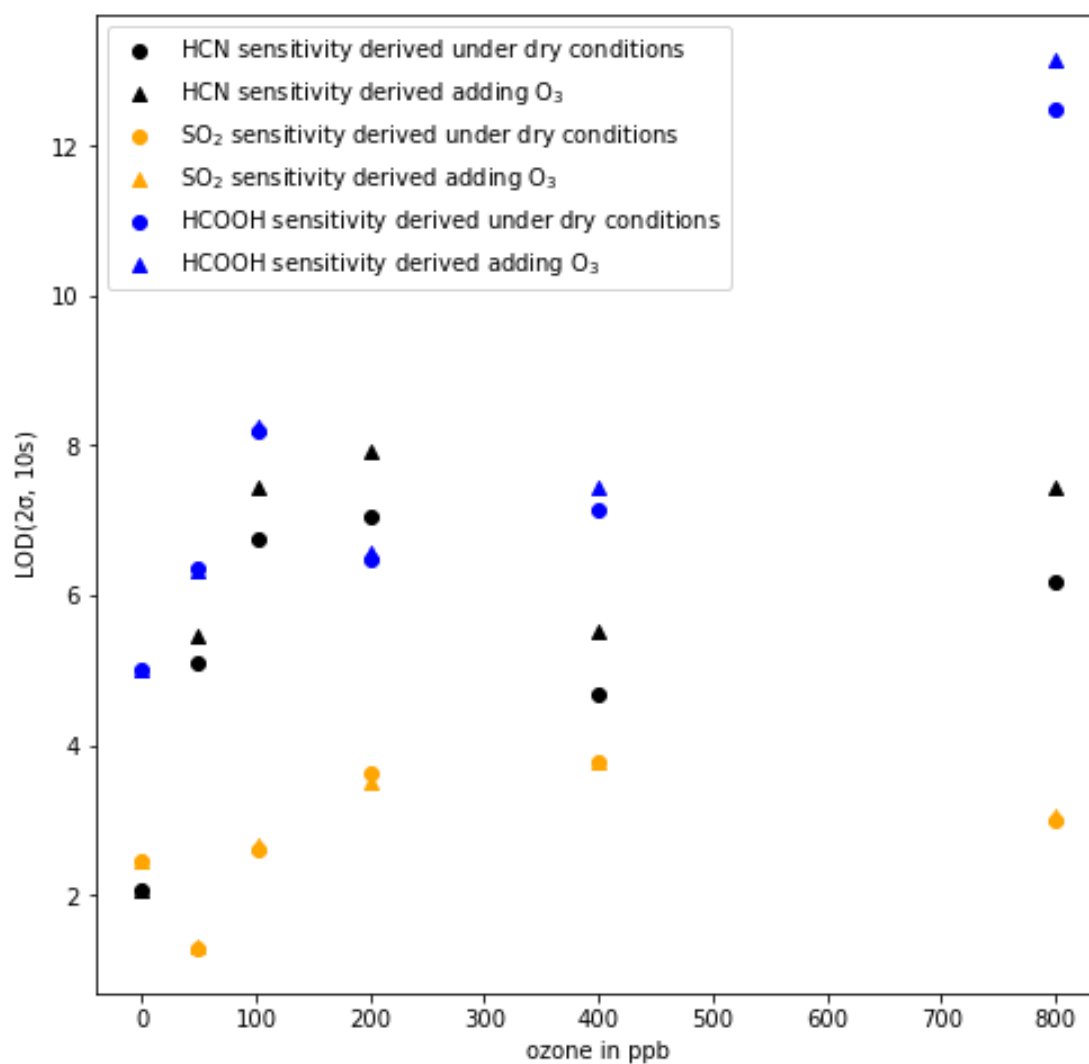


Figure 4.28: LOD(2σ , 10s) of HCN(black), SO₂ (orange), and HCOOH (blue) at various ozone mixing ratios (in ppb). The circles and triangles represent LOD calculated using the sensitivities under ozone-free conditions and ozone-corrected sensitivities, respectively.

by circles represent LOD values calculated using a fixed sensitivity derived under ozone-free conditions. These values primarily reflect changes in the instrumental noise as function of increasing ozone mixing ratio. As shown, the presence of ozone substantially increases the baseline noise for HCN, resulting in elevated LODs ranging from 5 to 7 ppt in ozone-containing environments. HCOOH exhibits a comparable trend, with LODs increasing from 6 to 8 ppt across 40–400 ppb ozone. However, due to a higher baseline LOD under ozone-free conditions, the relative impact on HCOOH is less pronounced. At higher ozone levels (800 ppb), a large increase in HCOOH’s LOD is observed, reaching 12.3 ppt. The LOD of SO₂ only increases by 1 - 1.5 ppt.

In contrast to the pronounced impact of water vapor, ozone has a relatively minor effect on sensitivity. Therefore, the observed changes in LOD under elevated ozone conditions are predominantly attributed to increased noise levels. This noise enhancement is most likely driven by the desorption or release of (semi-volatile) compounds from the internal surfaces of the IMR due to oxidative interactions with ozone, rather than sensitivity degradation.

4.10.3 Isobaric Interference

A major challenge in CIMS measurements is isobaric interference, a situation in which two or more ion clusters share the same nominal m/q resulting in overlapping peaks. This issue can often be resolved using high-resolution mass spectrometry and advanced peak fitting algorithms (Stark et al., 2015). However, the FunMass instrument, being a CToF, has limited mass resolution ($R < 1000$). As a result, it is generally not capable of resolving individual peaks within an isobaric cluster.

To minimize associated uncertainties and potential errors in quantification, it is essential to identify and quantify all relevant isobaric interferences for each analyte in order to correct for that.

Isobaric interference can lead to larger detected mixing ratios of a species i , as the abundance of an isobaric interfering species j increases the peak at the $(m/q)_i$. This is only valid if both species i and j are scrubbed during the background measurement mode. Otherwise, if the interfering species j is not scrubbed, which is unlikely, the isobaric effect will be canceled

out due to the background subtraction. Therefore, it is important to know all possible interfering substances for a species i and ideally, perform laboratory calibration of these species under various atmospheric conditions (varying water vapor and ozone) to quantify their effects on the signal of species i ($(m/q)_i$). Note that for this procedure the interfering species must be measured by FunMass-C on separated mass (ideally) and/or another instrument onboard of the aircraft.

This section discusses the most prominent known interferences affecting the species analyzed in this study.

4.10.3.1 SO₂

The largest known isobaric interference of SO₂ is HCOOH under humid conditions as HCOOH forms $[\text{H}_2\text{O} \cdot \text{HCOOH} \cdot \text{F}]^-$.

To investigate the influence of HCOOH on the nominal mass of 83 Th and hence, on SO₂ quantification, 4.0 - 4.8 ppb HCOOH (rather extreme case) was added to a humidified airflow (0 - 4300 ppm) as shown in Figure 4.29. The HCOOH mixing ratio decreases from 4.8 to 4.0 ppb due to larger dilution since the total gas flow increases while injecting larger amounts of water vapor.

Figure 4.29 demonstrates that HCOOH has a non-negligible impact on the quantification of SO₂ under humid conditions. This interference effect appears to saturate at higher water vapor mixing ratios, with the SO₂ equivalent signal leveling off at approximately 450–500 ppt for an HCOOH mixing ratio of 4 ppb. Even under nominally dry conditions, bearing in mind that synthetic air (grade 5.0) still contains residual water vapor between 0 and 2 ppm, a measurable interference is observed, with an SO₂ equivalent signal of 38 ppt for 4.8 ppb HCOOH.

As this initial test represents an extreme case designed to define the upper bound of interference, an additional experiment was conducted under more atmospherically relevant conditions. In this second test, presented in Figure 4.30, the water vapor mixing ratio was held constant at approximately 600 ppm, while the HCOOH mixing ratio was varied between 85 and 2128 ppt. The resulting signal at 83 Th, attributed to HCOOH induced interference,

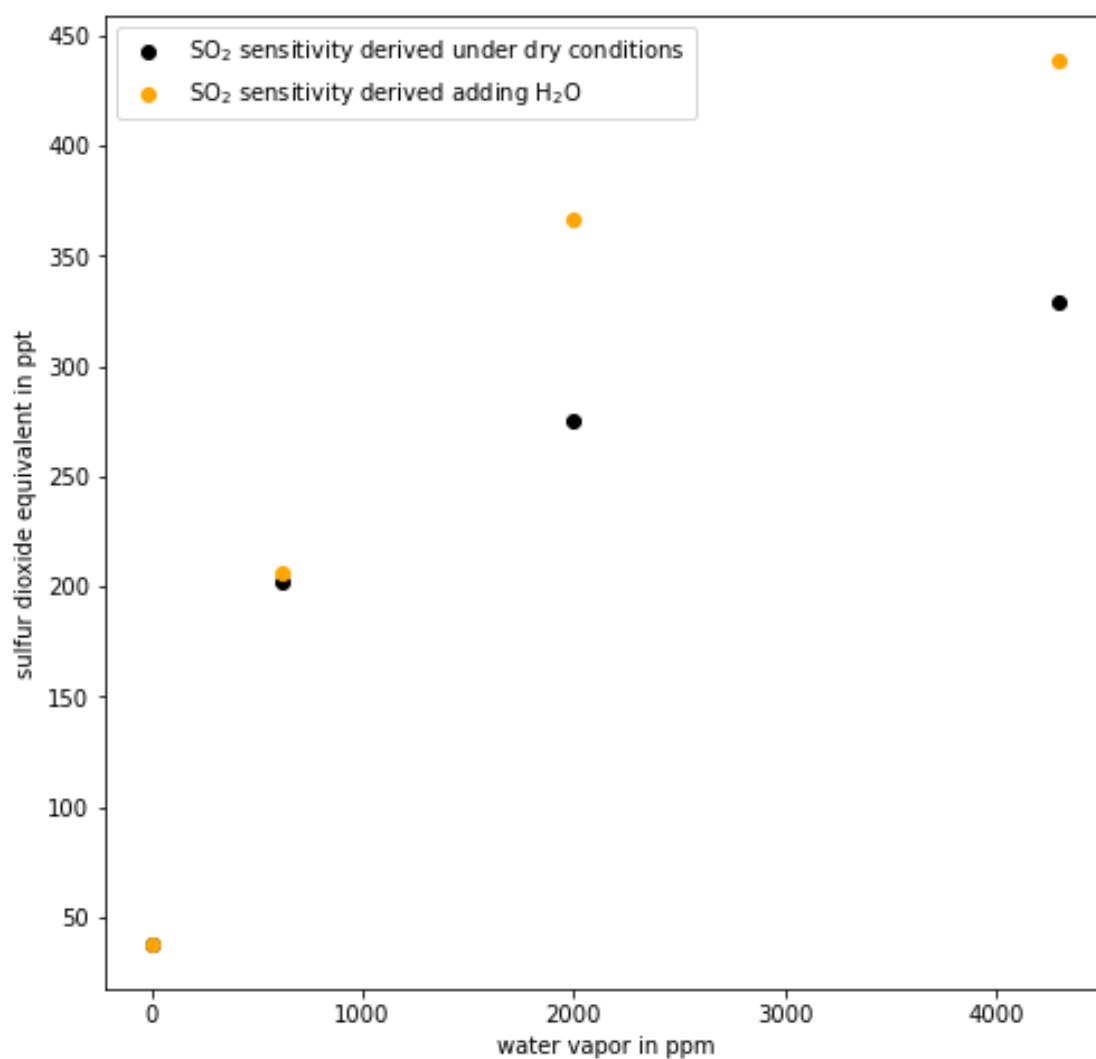


Figure 4.29: SO₂ equivalent signal resulting from the addition of 4.0 – 4.8 ppb HCOOH under varying water vapor mixing ratios. The black circles represent the calculated SO₂ equivalent using the sensitivity determined under dry conditions, while the orange circles show the values corrected for water vapor effects using the SO₂ sensitivity derived under humid conditions.

4.10. SENSITIVITY DEPENDENCE ON OTHER TRACE GASES

exhibited a linear relationship with the formic acid mixing ratio, characterized by a slope of 0.054 ppt SO₂ equivalent per 1 ppt HCOOH.

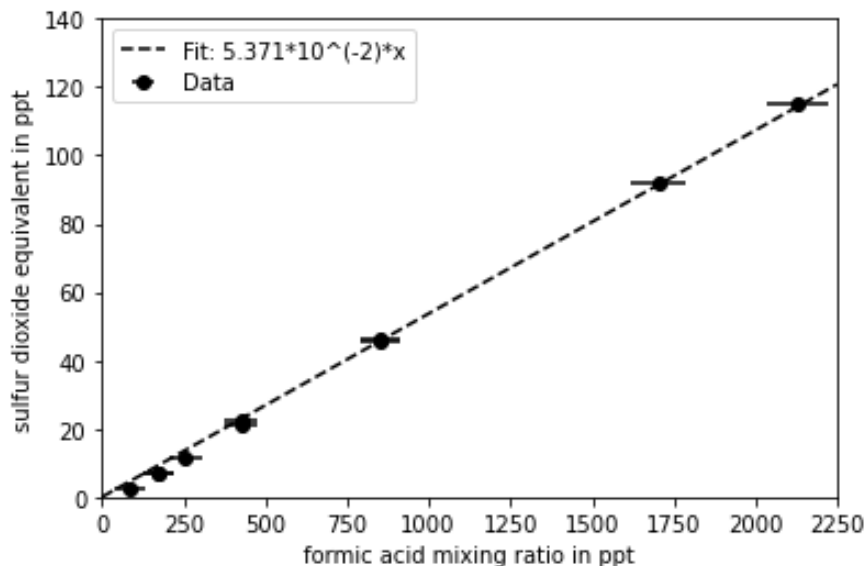


Figure 4.30: SO₂ equivalent signal resulting from the HCOOH addition at a water vapor mixing ratio of 600 ppm.

Figure 4.31 presents the SO₂ equivalent signal, expressed in ppt per 1 ppt HCOOH, as function of water vapor mixing ratio (in ppm). The interference effect increases sharply with rising humidity and tends to plateau at higher water vapor levels. Overall, the SO₂ equivalent increases by nearly a factor of 8 when comparing dry conditions to 4200 ppm water vapor.

However, when comparing this trend to the slope derived from the calibration series conducted at a constant water vapor level of around 600 ppm (orange data in Figure 4.30), a discrepancy of approximately 0.012 ppt SO₂ equivalent per 1 ppt HCOOH is observed. This suggests that the interference at 83 Th not only saturates with increasing water vapor mixing ratio, but is also a function of increasing HCOOH mixing ratio. Such nonlinear effects must be considered when correcting for formic acid interference in SO₂ quantification, particularly under humid conditions or at elevated HCOOH levels.

An additional isobaric interference may arise under conditions where both HCOOH and HCl are present at elevated mixing ratios. Under such circumstances, the formation of the [HCOOH.³⁷Cl][−] cluster ion is possible. This interference could also be relevant for the Fun-

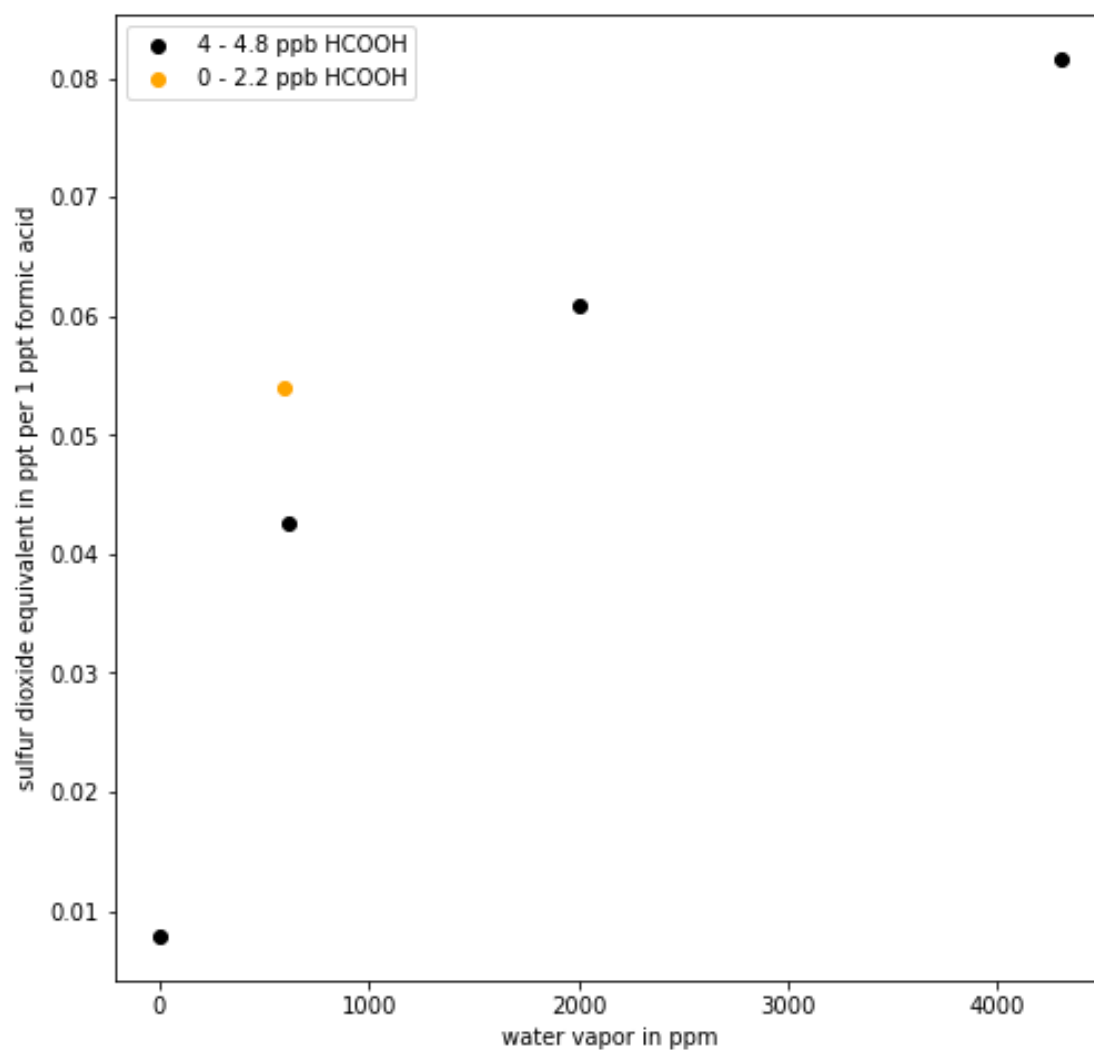


Figure 4.31: SO_2 equivalent in ppt per 1 ppt HCOOH for various water vapor mixing ratios (in ppm). The black circle values are derived by adding 4 - 4.8 ppb HCOOH, while the orange circles are determined by a calibration row varying the HCOOH mixing ratios between 0 - 2.2 ppb.

Mass instrument due to trace chlorine-containing impurities. However, the naturally lower isotopic abundance of ^{37}Cl , approximately one third that of ^{35}Cl , suggests that the overall contribution of this cluster should remain relatively minor. Nevertheless, future work will aim to characterize and quantify this potential source of uncertainty more precisely.

Given that one of the primary objectives of FunMass onboard CARIBIC is the long-term monitoring of global background SO_2 mixing ratios in the UTLS, which typically range from 1 to 100 ppt, it is essential to accurately quantify and correct for the influence of HCOOH and water vapor. Failure to account for these effects could lead to significant biases in the derived SO_2 mixing ratios.

4.10.3.2 HCN

Although HCN is detected at a higher nominal mass (112 Th) than SO_2 , relatively few isobaric interferences have been identified to date. The most prominent interference observed so far originates from SO_2 , particularly under elevated ozone mixing ratios, due to the formation of the $[\text{SO}_5]^-$ cluster ion. Ozone facilitates the further oxidation of the $[\text{SO}_4]^-$ cluster, which is generated via reactions involving the superoxide anion within the IMR (see Figure 4.5b).

Figure 4.32 displays the SO_2 -induced HCN sensitivity (ppt HCN equivalent per 1 ppt SO_2) as function of ozone mixing ratio, respectively. The results show a behavior analogous to that of the SO_2 equivalent signal caused by HCOOH under varying humidity. Specifically, the interference increases sharply with rising ozone mixing ratio and appears to saturate at higher ozone levels. In total, the HCN equivalent signal increases by approximately a factor of 27 when comparing ozone-free conditions to an ozone mixing ratio of 800 ppb.

As background mixing ratios of HCN are typically much higher than those of SO_2 , the relative impact of SO_2 induced interference on the HCN signal is comparatively smaller than the influence of HCOOH and water vapor on SO_2 quantification. Nevertheless, accurate correction for SO_2 -related interferences is still required for HCN measurements during CARIBIC flights. Moreover, any uncertainty or error in the SO_2 correction directly propagates into the derived HCN signal, showing the importance of precise interference characterization and correction strategies.

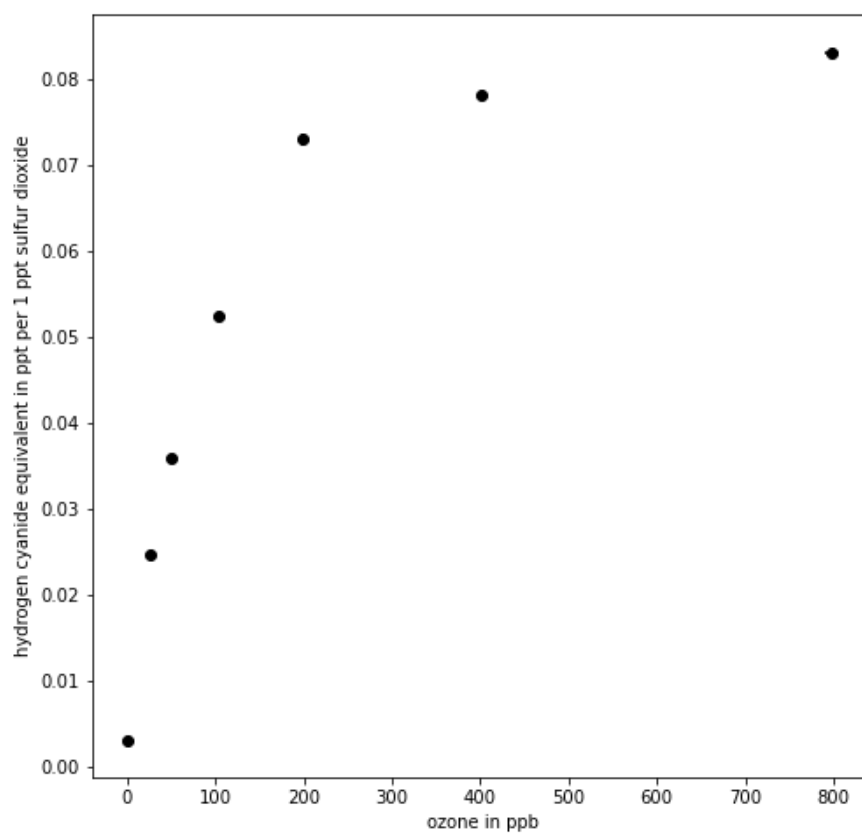


Figure 4.32: HCN equivalent in ppt per 1 ppt SO_2 for various ozone mixing ratios (in ppb).

Water vapor also influences the formation of the $[\text{SO}_5]^-$ cluster ion. An increase in water vapor mixing ratio up to approximately 500 ppm promotes the formation of $[\text{SO}_5]^-$; however, beyond this threshold, the signal begins to decline. Despite this reduction, the net interference effect on the HCN signal remains significant, as it is overcompensated by the concurrent decrease in HCN sensitivity with increasing water vapor, which is described in Subsection 4.10.1 (as indicated by the orange circles). Nevertheless, since water vapor mixing ratios are generally low above 5000 m altitude, this effect is less critical for HCN quantification in the UTLS compared to ozone-related interferences.

4.11 Sensitivity Dependence on MCP Voltage

As already described in Subsection 3.1.5, the SIS influences the calibration (e.g., linearity) and the sensitivity of the analytes. SO_2 was chosen as the example species.

Figure 4.34 illustrates the relative sensitivity of SO_2 as function of the SIS (in $\text{mV} \cdot \text{ns}$), which is directly related to the MCP voltage. As the SIS increases, the relative sensitivity of SO_2 also increases, demonstrating an approximately linear trend above $1.1 \text{ mV} \cdot \text{ns}$, with a slope of 6.35 % per $0.1 \text{ mV} \cdot \text{ns}$. This behavior reflects the fact that higher MCP voltages amplify ion signals, thereby enhancing sensitivity.

However, below approximately $1.1 \text{ mV} \cdot \text{ns}$, the sensitivity exhibits a strong decline, dropping to less than 65 % of the sensitivity measured at $1.37 \text{ mV} \cdot \text{ns}$. This rapid decrease suggests the existence of a threshold SIS below which ToF detection becomes significantly less efficient. While TOFWERK specifies a minimum SIS of $1.2 \text{ mV} \cdot \text{ns}$ for optimal operation, the observed data indicate that the actual performance threshold may lie slightly below this value.

Figure 4.35 presents the calibration curves for SO_2 acquired at two different SIS settings: $1.37 \text{ mV} \cdot \text{ns}$ (black) and $0.95 \text{ mV} \cdot \text{ns}$ (orange). At the lower SIS, the calibration exhibits clearly non-linear behavior, highlighting the onset of non-linearity effects when the SIS falls below a certain threshold. This non-linearity is attributed to insufficient signal amplification at low MCP voltages, resulting in a compromised ion detection efficiency likely due to too

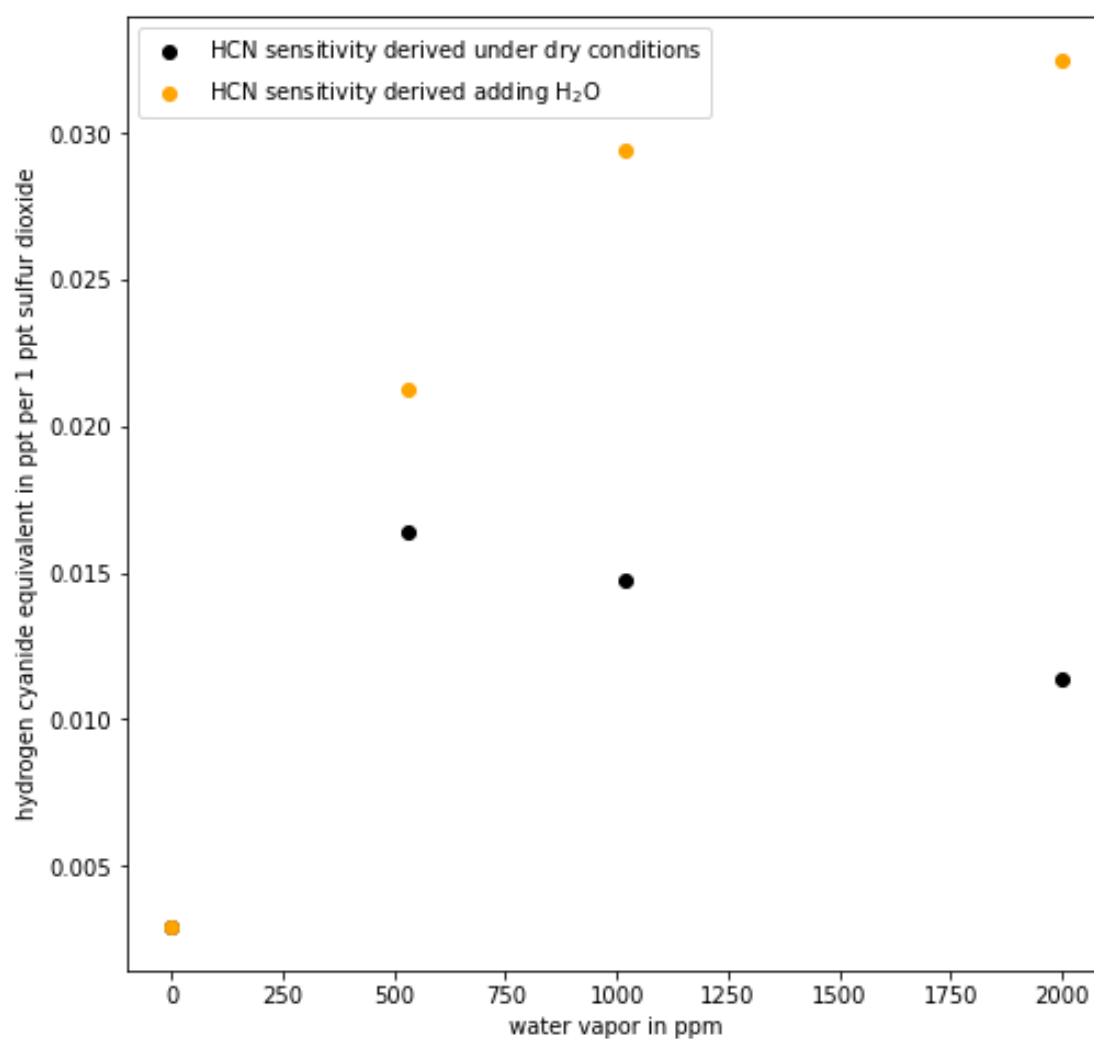


Figure 4.33: HCN equivalent in ppt per 1 ppt SO₂ for various water vapor mixing ratios (in ppm). The black circles represent the calculated HCN equivalent using the sensitivity determined under dry conditions, while the orange circles show the values corrected for water vapor effects using the sensitivity derived under humid conditions.

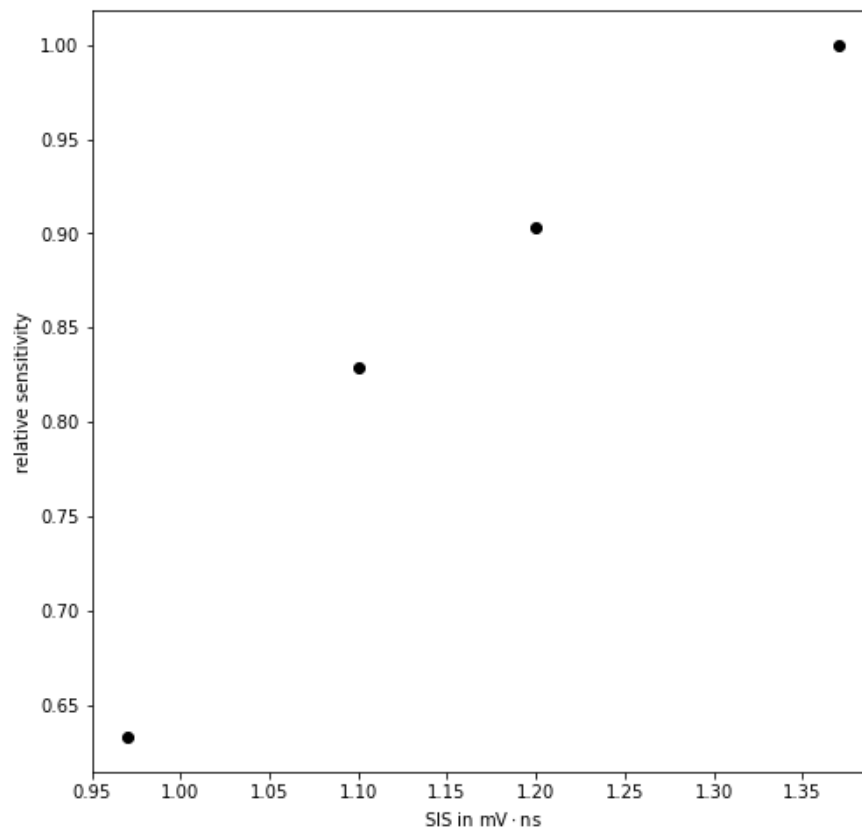


Figure 4.34: Relative sensitivity of SO₂, which is the sensitivity normalized to the response at 1.37 mV · ns for various SIS (in mV · ns).

large electronic noise compared to the signal strength.

Similar observations were reported by Müller et al. (2014) using a PTR-ToF-MS, where reduced MCP gain led to deviations from linearity in calibration functions. Furthermore, their findings also demonstrated that the relative sensitivity tends to plateau at higher MCP voltages, suggesting the presence of an upper SIS limit beyond which increases in voltage no longer enhance sensitivity due to detector saturation effects.

These results underscore the importance of empirical SIS assessment during operation to ensure consistent and reliable quantification.

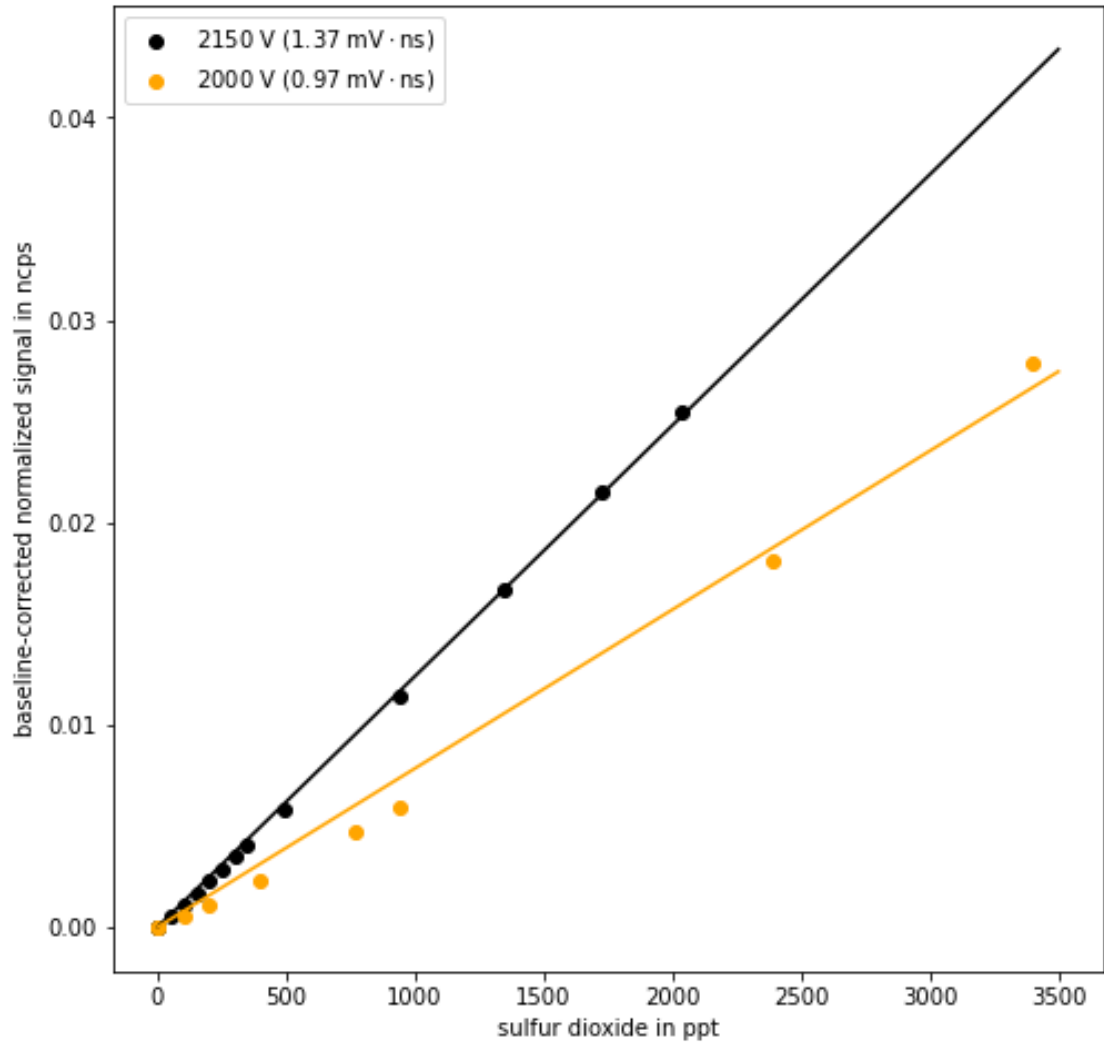


Figure 4.35: The background-corrected normalized signal of the fluoride cluster of SO_2 in ncps as function of SO_2 mixing ratio in ppt. The black circles and orange circle represent calibrations using a SIS of $1.37 \text{ mV} \cdot \text{ns}$ and $0.95 \text{ mV} \cdot \text{ns}$ (at MCP voltages of 2150 and 2000 V), respectively.

4.12 Computational Investigation of the CF_3O^- Ion Chemistry

In Section 4.2, the different behavior of weak and strong Bronsted acids with respect to cluster formation in CF_3O^- ionization was discussed. The tendency of weak acids forming a cluster with CF_3O^- and strong acids forming predominately the fluoride cluster was already observed and discussed in the past (Huey et al., 1996; Amelynck et al., 2000; Crounse et al., 2006; Paulot et al., 2009). Moreover, Hyttinen et al. (2018) carried out a computational study of various reagent ions including CF_3O^- to investigate the cluster formation of these reagent ions with ten different products derived from the OH radical-initiated oxidation of butadiene. However, to our knowledge there is no mechanistical study why weak and strong acid have a different behavior up to date. In literature only, the acidity, the fluorine affinity and rotational degree of freedom are used as a qualitative explanation.

In this section, the preliminary results of a computational study carried out together with the group “Theory and Simulation of Complex Systems” of the Heinrich-Heine University in Düsseldorf are presented and discussed.

The relative free energies of the various clusters (in kcal/mol) were calculated using Coupled Cluster level of theory DLPNO-CCSD(T)/cc-pVQZ // B3LYP/def2-TZVP, as shown in Figure 4.36 and table S5.1.

The CF_3O^- cluster forming a hydrogen bond to the oxygen, $\text{HX}(\text{CF}_3\text{O}^-)$, appears to always be the most stable cluster for every acidic molecule regardless its acidic strength. Coordinating via the fluorine atoms, $\text{HX}(\text{CF}_3\text{O}^-)^{\S}$, is less favorable compared to the cluster coordinated via the oxygen atom as the negative charge is mainly located at the oxygen atom. However, it should be noted that it is statistically more likely to cluster via a fluorine atom than the oxygen atom (3:1).

Weak acids form less stable fluoride clusters compared to strong acids. Thus, a fluoride abstraction of $\text{HX}(\text{CF}_3\text{O}^-)^{\S}$ is less likely for weak acids. The clusters coordinated via oxygen or fluorine cannot be distinguished based on the mass spectra alone.

On the other hand, strong acids form stable fluoride clusters as their corresponding base can stabilize the negative charge. This explains the pronounced occurrence of the fluoride

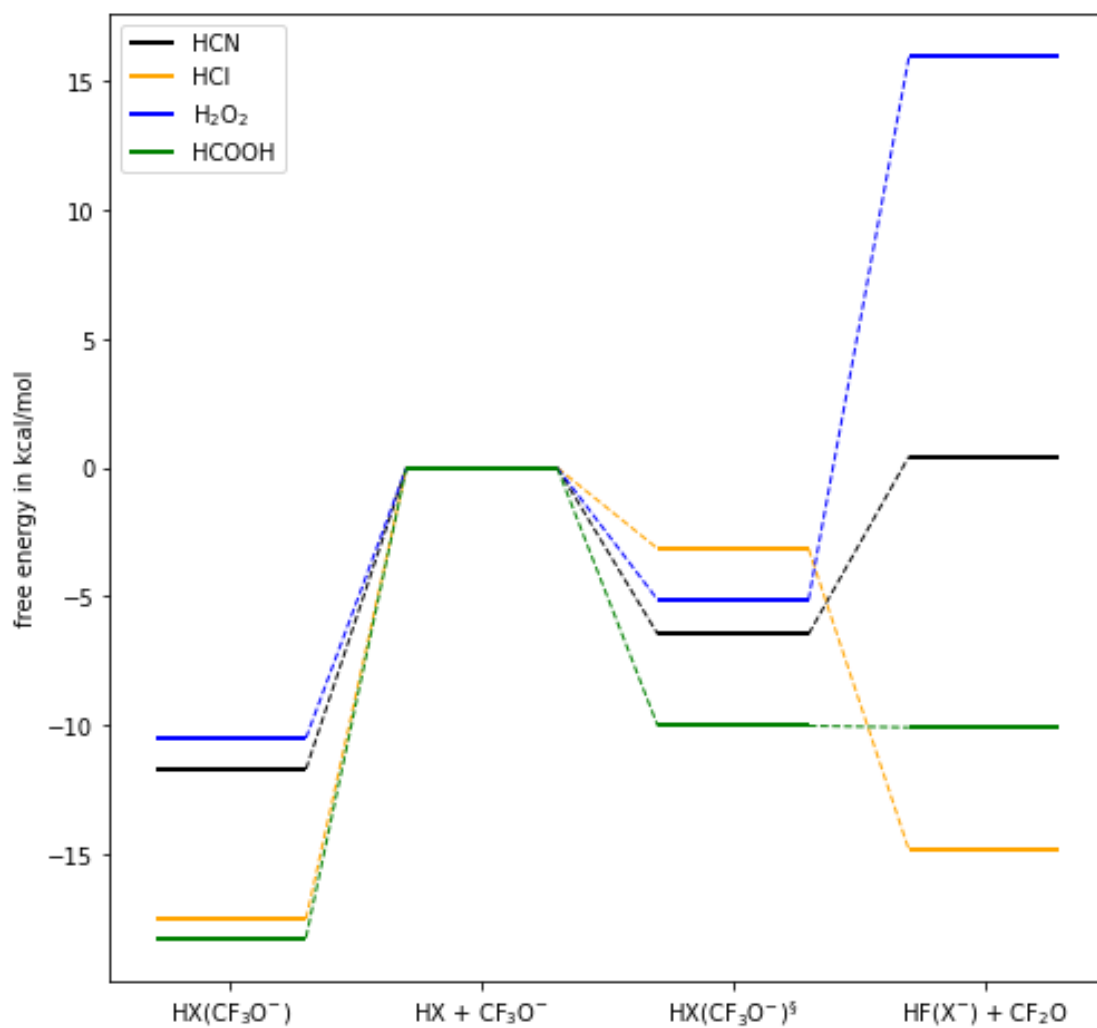


Figure 4.36: Calculated relative energies for complexes formed between CF_3O^- and various interacting acids (HX). All energies are presented in kcal/mol, based on Coupled Cluster level of theory DLPNO-CCSD(T)/cc-pVQZ // B3LYP/def2-TZVP. “§” indicates bonding via fluorine atoms.

cluster for strong acids. In contrast to weak acids, the $\text{HX}(\text{CF}_3\text{O}^-)^\S$ cluster decomposes by a fluoride abstraction for strong acids. However, it cannot explain the absence of the CF_3O^- cluster. It is unlikely that acids only form $\text{HX}(\text{CF}_3\text{O}^-)^\S$, although it is statistically favored. As the $\text{HX}(\text{CF}_3\text{O}^-)$ is also the most stable cluster for strong acids, it should be detected as well. However, this cluster is either absent or only weakly observed in the case of strong acids.

For the $\text{HX}(\text{CF}_3\text{O}^-)$ cluster of strong acids, the proton is mainly located close to the oxygen of the CF_3O^- as CF_3OH is a rather weak acid. Thus, these clusters can rather be described as $\text{CF}_3\text{OH}(\text{X}^-)$. It is known that CF_3OH can decompose spontaneously to CF_2O and HF (Schneider et al., 1996). Hydrogen bond acceptors/donors as H_2O , acids (e.g., HCOOH), bases (e.g., NH_3), or ions can act as catalyst, which promotes the H-shift during the decomposition (Buszek and Francisco, 2009; Long et al., 2011; Parandaman et al., 2018). Especially, water vapor is always present as even the driest synthetic air has at least 0.5 ppm water vapor content, typically 1 ppm and larger. Compared to the reagent ion mixing ratios (10^2 - 10^3 ppb level) and analyte mixing ratio (lower than 15 ppb; typically ppt level), water vapor is in large excess. Long et al. (2011) showed with their computational calculation that a single water molecule or a water-dimer can reduce the activation barrier of the decomposition of CF_3OH from $45.1 \text{ kcal} \cdot \text{mol}^{-1}$ to 17.7 or $4.8 \text{ kcal} \cdot \text{mol}^{-1}$, respectively. Moreover, Buszek and Francisco (2009) observed a reduction of the activation barrier using a radical-catalyzed mechanism including a water molecule and a hydroxyl radical (OH radical). In their study, the activation barrier was even reduced from $45.9 \text{ kcal} \cdot \text{mol}^{-1}$ to $11.0 \text{ kcal} \cdot \text{mol}^{-1}$.

Additionally, Gulvi et al. (2021) investigated various decomposition pathways, including the HF elimination, O-H bond dissociation, and C-O bond dissociation, and compared their theoretical results with the findings of Huey et al. (1995b). They showed that the HF elimination is the predominate decomposition pathway, which also agrees well with the results of Huey et al. (1995b).

As weak acids do not protonate CF_3O^- , no CF_3OH is formed, which can decompose.

Therefore, strong acids (e.g. HCl) mainly form fluoride clusters. Intermediate strong/weak acids (e.g. HCN) can form both and depending on their acidity the proportion between fluoride and CF_3O^- clusters changes. Weak acids (e.g. H_2O_2) only form the CF_3O^- cluster.

It can be concluded that the weaker the acidity of a substance the more CF_3O^- clusters relative to the fluoride clusters will be formed as the weak acids can not protonate CF_3O^- . If CF_3O^- is protonated the CF_3OH decomposes via a catalytic pathway.

4.13 Positive Mode

4.13.1 C_6H_6^+ - CIMS in FunMass

Benzene is employed as the electron donor for BTP, as previously described in Subsection 3.2.1. This process inherently leads to the generation of benzene cations (C_6H_6^+) and their corresponding fragment ions. The concept explored here is that, by simply reversing the polarity of the applied voltages from negative to positive while maintaining the same IMR configuration, a C_6H_6^+ -CIMS operation mode becomes feasible. Previous studies, such as those by Kim et al. (2016) and Lavi et al. (2018), have demonstrated the utility of C_6H_6^+ as a reagent ion, underscoring the versatility of benzene as a CIMS precursor. In this section, preliminary tests and the overall feasibility of operating FunMass in C_6H_6^+ -CIMS mode are presented. This is mainly motivated by the chance to also be capable to measure some (in-)organic precursor molecules like e.g., DMS or NH_3 .

Figure 4.37 displays a representative mass spectrum obtained using C_6H_6^+ as the reagent ion. The dominant peak corresponds to the benzene cation itself (C_6H_6^+ , 78 Th) along with its isotopologues. A smaller peak at 156 Th is also observed and can be attributed to the benzene cation dimer (C_6H_6) $_2^+$. Another prominent signal appears at 94 Th, which is tentatively assigned to $\text{C}_6\text{H}_6\text{O}^+$. In addition, several minor peaks at lower m/q values are present and likely result from fragmentation of C_6H_6^+ .

Due to the high mixing ratio of C_6H_6 used and its efficient ionization via VUV radiation, the resulting spectrum is relatively clean and predominantly composed of well-defined and assigned signals.

In the literature, several reaction pathways of chemical ionization initiated by benzene cations have been described (Kim et al., 2016; Lavi et al., 2018). The primary mechanism involves charge transfer reactions, depending on the ionization energy of the analyte, as

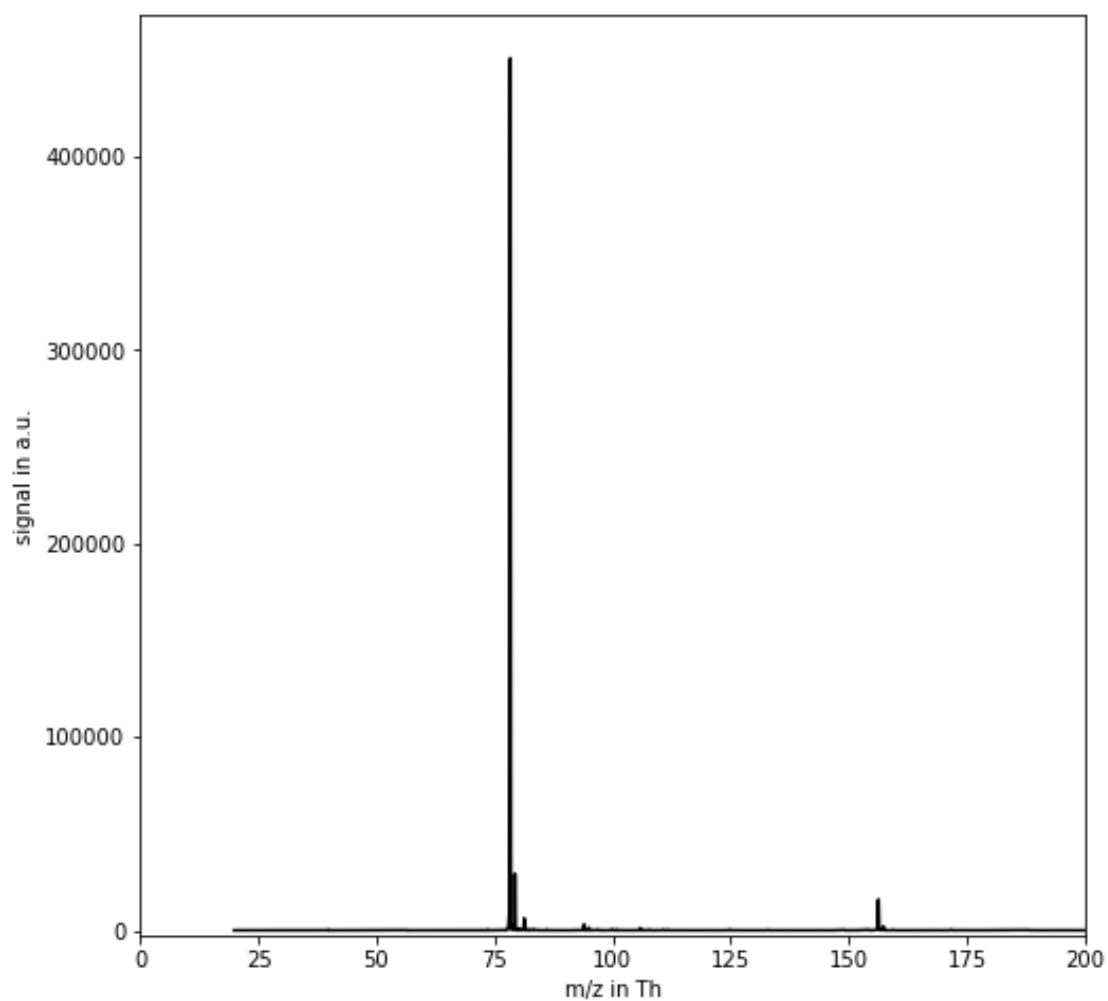
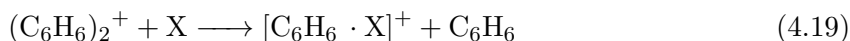


Figure 4.37: Reagent ion spectrum of FunMass in the positive mode with C_6H_6^+ as a reagent ion

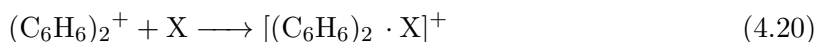
illustrated in Equation 4.17.



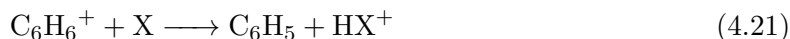
Also, the analyte can cluster with C_6H_6^+ either by direct reaction with C_6H_6^+ or by a ligand-switching reaction with the dimer (cf. equations 4.18 and 4.19).



In some rare cases, also the cluster with the dimer itself is possible (see reaction 4.20).



The last common reaction is the proton transfer as shown in equation 4.21.



Several species were tested, among other things HCN, SO_2 , OCS, DMS, and ammonia (NH_3). However, only DMS and NH_3 show reasonable signal responses as shown in Subsection 4.13.2

4.13.2 Calibration of DMS and NH_3

Dimethyl sulfide (DMS) can be quantitatively analyzed using C_6H_6^+ -CIMS. In this setup, DMS primarily reacts via proton transfer, and to a lesser extent through clustering with the C_6H_6^+ reagent ion. The measured sensitivities for the protonated cluster and the C_6H_6^+ adduct are $4.24 \cdot 10^{-5}$ and $4.40 \cdot 10^{-6}$ ncps $\cdot$ ppt $^{-1}$, respectively. These values are comparable to those obtained with CF_3O^- -CIMS. Moreover, the corresponding detection limits (2σ , 10s) are relatively low, with 0.6 ppt for the protonated cluster and 3.6 ppt for the C_6H_6^+ cluster. Owing to its higher sensitivity and low detection limits, FunMass is well-suited for detecting

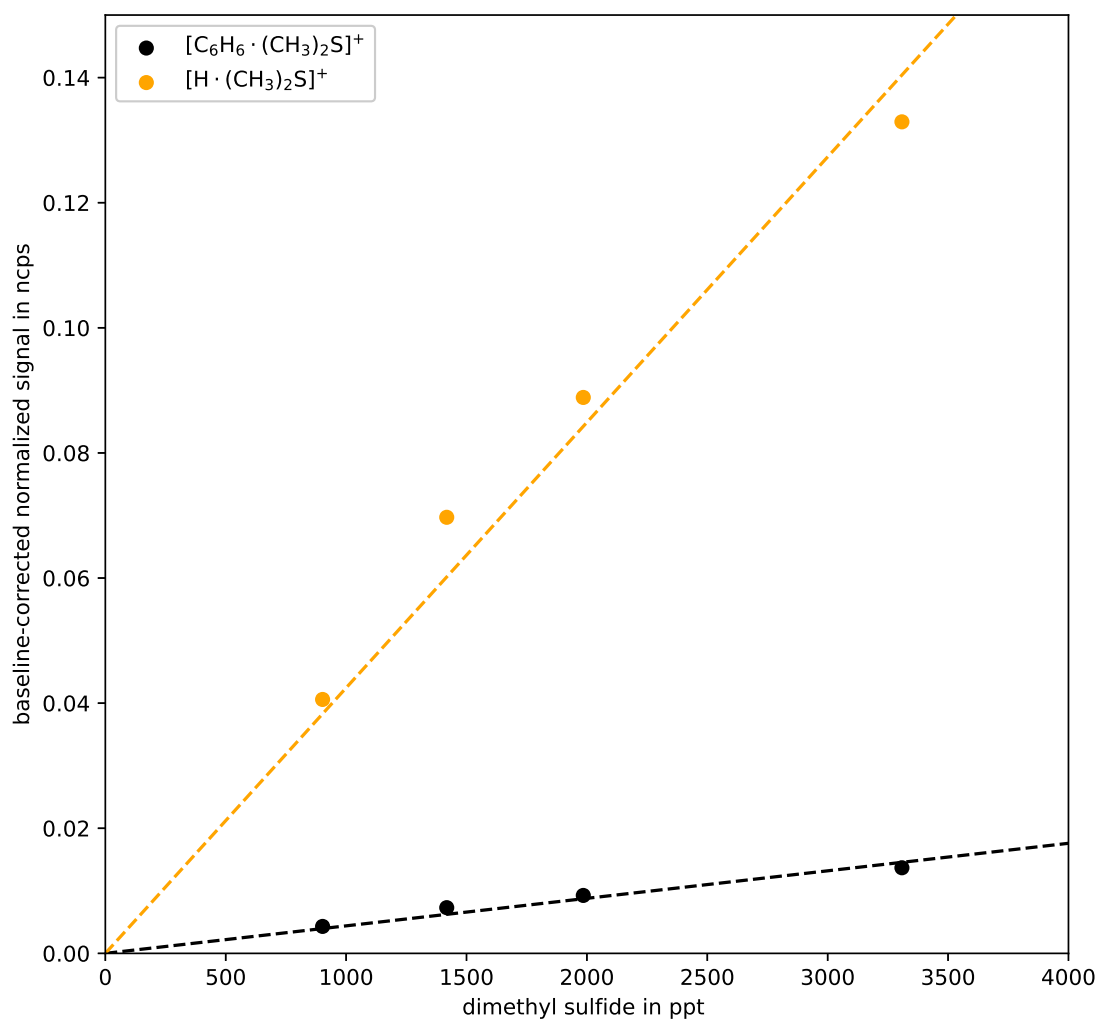


Figure 4.38: Calibration using C_6H_6^+ - CIMS for DMS. The C_6H_6^+ cluster and the H^+ cluster of DMS (140 Th and 63 Th, respectively) are presented in black and orange, respectively.

DMS in the free and upper troposphere, where ambient mixing ratios typically remain below 10 ppt and the impact of atmospheric water vapor is low.

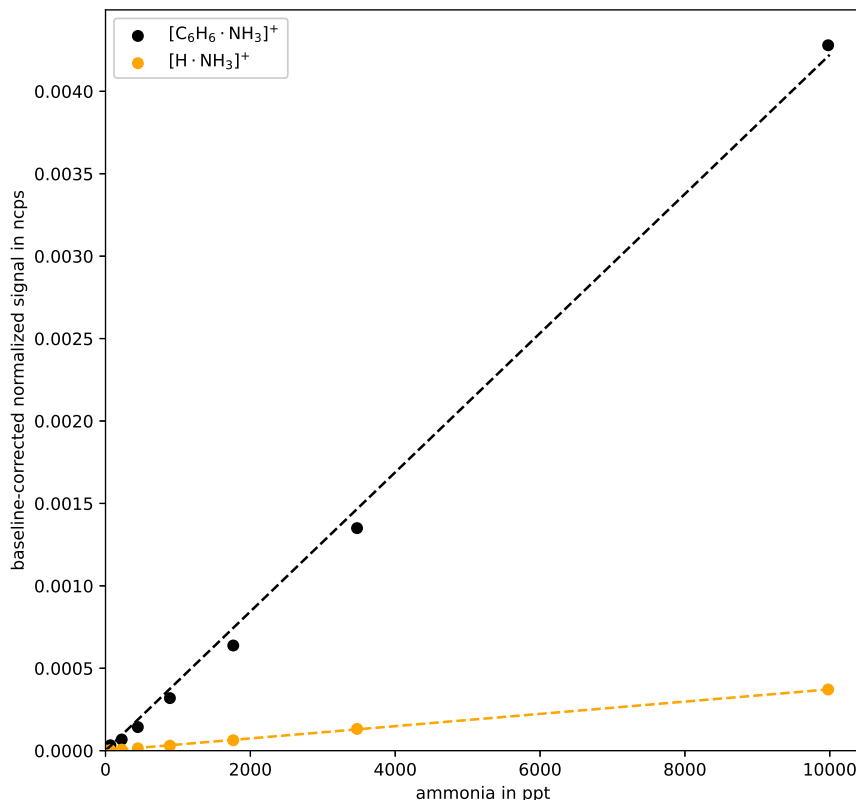


Figure 4.39: Calibration using C_6H_6^+ -CIMS for NH_3 . The C_6H_6^+ cluster and the H^+ cluster of NH_3 (95 and 18 Th, respectively) are presented in black and orange, respectively.

Another analyte that can be detected using C_6H_6^+ -CIMS is ammonia (NH_3). The primary ionization pathway is clustering with C_6H_6^+ , while proton transfer constitutes a secondary reaction channel. The sensitivities for the protonated and clustered species are $4.22 \cdot 10^{-7}$ and $3.72 \cdot 10^{-8}$ ncps · ppt⁻¹, respectively. Compared to DMS, the C_6H_6^+ -CIMS exhibits lower sensitivity for NH_3 . Correspondingly, the detection limits (2σ , 10s) are higher, at 72 ppt for the protonated species and 71 ppt for the cluster ion, likely due to the lower sensitivities.

While the current performance of this method is insufficient for airborne measurements where detection of a few ppt is often required, it is nonetheless adequate for field or chamber studies, particularly where NH_3 mixing ratio exceed 100 ppt or where longer integration times are feasible. Future improvements should aim to enhance the ionization efficiency of

NH₃, thereby reducing detection limits and broadening its applicability to more demanding atmospheric measurement campaigns.

Future work will focus on further development and optimization of the positive ionization mode. This includes refining the experimental setup with respect to gas flow dynamics, pressure conditions, and ion optical parameters (e.g., voltages applied to the ion optics). Additionally, a broader range of analytes, such as organic acids and acetonitrile (CH₃CN), will be investigated to expand the range of compounds detectable with C₆H₆⁺-CIMS. Furthermore, the influence of atmospheric constituents such as water vapor and ozone on the calibration accuracy and ionization efficiency will be systematically characterized to improve the robustness and reliability of this method under varying environmental conditions.

Chapter 5

DMS oxidation at SAPHIR-STAR

5.1 Theory

Dimethyl sulfide (DMS) oxidation has a large environmental impact and hence, its investigation is important for the atmospheric composition and climate. DMS emitted from the ocean is the largest natural sulfur source in the atmosphere. The emission rates of oceanic DMS are about 28 Tg(S) a^{-1} (Lana et al., 2011). In 1972, Loevelock et al. measured DMS for the first time at the ocean surface. The observation indicated that DMS was ubiquitous in the surface ocean waters. The explanation for this observation is the production of DMS by marine phytoplankton. It was known for years that there has to be a significant flux of a sulfur-containing species from the oceans to the atmosphere. This missing compound was found to be DMS. Moreover, a correlation between the blooming of marine phytoplankton and high DMS concentration could be shown (Kettle et al., 1999). As phytoplankton needs UV light to bloom, there is a seasonal cycle of DMS production in the oceans and hence, also a seasonal cycle of DMS flux from the oceans to the atmosphere (Andreae and Raemdonck, 1983). Furthermore, DMS abundance depends on diurnal variations (Andreae and Barnard, 1984). Typically, the DMS mixing ratio is between 5 - 400 ppt in the marine boundary layer (MBL), but if the water is eutrophic, the DMS mixing ratio can reach values above 1 ppb (Lelieveld et al., 1997). In the free troposphere, the mixing ratio decreases fast with increasing altitude to only a few ppt, since it is oxidized rapidly by the hydroxyl radical (OH),

nitrate radical (NO_3), bromine oxide (BrO), and chlorine radical (Cl). This results in a short tropospheric lifetime of DMS (see Subsection 2.2). In general, there are two main channels of the the DMS oxidation: First, the addition pathway, in which OH or Cl are added to DMS, and second, the abstraction pathway, where OH , Cl , or NO_3 remove a hydrogen atom from a methyl-group of DMS yielding a peroxy radical through O_2 addition. The latter can react onwards in two sub-channels : the bimolecular reaction of the RO_2 radical and the RO_2 isomerization. The oxidation channels lead to the formation of other atmospherically important sulfur-containing products, such as SO_2 , sulfuric acid (H_2SO_4), dimethyl sulfoxide (DMSO ; $\text{CH}_3\text{SCH}_3\text{O}$), methane sulfonic acid (MSA ; $\text{CH}_3\text{SO}_3\text{H}$), and OCS , a subject of intensive current research. These oxidation products play a role in tropospheric aerosol and cloud formation as well as for the Earth's climate (Charlson et al., 1987; Quinn and Bates, 2011; Sanchez et al., 2018). In 1994, Barnes et al. could show that DMS is a source of OCS , the most prominent non-volcanic sulfur source for the stratosphere since it is transported to the stratosphere due to its long average atmospheric lifetime of 2.5 years (Montzka et al., 2007). Hence, DMS or better its oxidation pathways and products, play an important role for Earth's climate (e.g., Kremser et al., 2016).

DMS oxidation has been extensively studied over the past decades. OCS direct emission sources are oceans (Von Hobe et al., 2001), wetlands (Watts, 2000), and anoxic soils (Devai and DeLaune, 1995). Moreover, it is formed in the atmosphere through the oxidation of carbon disulfide (CS_2) (Chin and Davis, 1993) and, as already mentioned, DMS (Barnes et al., 1994). Lastly, it is also emitted by anthropogenic activities (Zumkehr et al., 2018). In the troposphere, OCS is mainly taken up by soils and plants as well as consumed by the reaction with OH (Kettle et al., 2002). In the stratosphere on the other hand, its main sink is photooxidation. For many decades, OCS sources and sinks were thought to be balanced within errors, since its average tropospheric mixing ratios were measured to be constant around 500 ppt. However, inverse modeling studies led to a revision of the OCS sinks (Suntharalingam et al., 2008; Berry et al., 2013). According to satellite observations and inverse modeling studies, it is suggested that either the terrestrial OCS sink is overestimated or there is an OCS source, located in the tropical Pacific, which is unaccounted for until today (Berry et al.,

2013; Glatthor et al., 2015a; Kuai et al., 2015; Davidson et al., 2021; Ma et al., 2021). These observations provide evidence that at least part of the missing source is located over the oceans and moreover, it is likely that this source is a chemical production of OCS, since the OCS cycling in seawater is well understood. Lennartz et al. (2017, 2021) could show that the direct emissions of oceanic OCS are well constrained and the uncertainty of the oceanic OCS flux is also too small to be the elucidation of the missing source. The indirect marine OCS source could be the atmospheric oxidation of CS₂ and/or DMS, both emitted from the ocean. However, the formation of OCS from marine CS₂ is currently seen as unlikely to explain the gap (at least partly). In most literature, a uniform yield of 0.7 %, which was determined in laboratory experiments (Barnes et al., 1994, 1996; Albu et al., 2008), is used to calculate the indirect marine OCS source from DMS emitted by the ocean (Kettle et al., 2002). In the recent years, theoretical studies (Wu et al., 2015; Khan et al., 2021; Jernigan et al., 2022b; Jacob et al., 2024), chamber and laboratory experiments (Berndt et al., 2019; Ye et al., 2021, 2022; Shen et al., 2022; Jernigan et al., 2022b; Novelli et al., 2022; Assaf et al., 2023; von Hobe et al., 2023; Alber et al., 2024), and field studies (Veres et al., 2020; Vermeuel et al., 2020; Siegel et al., 2023) suggested new pathways in the DMS oxidation as shown in Figure 5.1 and come to the conclusion that OCS production is not evenly distributed globally. In 2015, Wu et al. could show, based on their theoretical simulations, that the first and (rate-limiting) isomerization reactions in the DMS oxidation scheme at low concentrations of nitrogen oxides (NO_x) and peroxy radicals (HO₂ and RO₂), which are present in remote areas like oceans. Wu et al. (2015) suggested an isomerization rate constant of 2.1 s⁻¹ (298 K) for the primary RO₂, called methylthiomethyl peroxy radical (MTMP; CH₃SCH₂O₂), formed following the hydrogen atom abstraction of DMS. MTMP isomerizes to a stable intermediate, hydroperoxymethyl thioformate (HPMTF; HOOCH₂SCH=O), which has been observed in substantial amounts in marine environments (Veres et al., 2020; Vermeuel et al., 2020).

Recently, in other laboratory studies the isomerization rate constant was also constrained as shown in Figure 5.2, calculating values of 0.23 ± 0.12 s⁻¹ (295 K; (Berndt et al., 2019)), 0.1 s⁻¹ (298 K; (Jernigan et al., 2022b)), 0.09 s⁻¹ (293 K; (0.03–0.3 s⁻¹, 1 σ_g , geometric standard deviation; (Ye et al., 2021)), 0.041 s⁻¹ (293 K; (Veres et al., 2020)); and theoretically

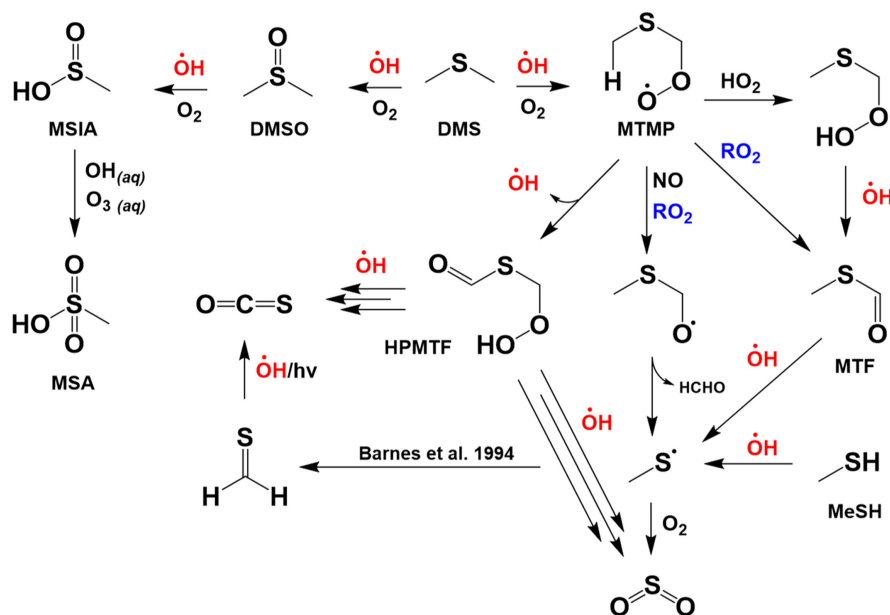


Figure 5.1: Chemical mechanism for the gas-phase OH-oxidation of dimethyl sulfide. Simplified chemical mechanism for the production of carbonyl sulfide (OCS) in the gas-phase OH-oxidation of dimethyl sulfide and methanethiol. The mechanism shown here combines the work of Barnes et al. (1994) and the hydroperoxymethyl thioformate (HPMTF)-derived OCS production pathway proposed in Jernigan et al. (2022b). Source: Jernigan et al. (2022b)

calculated 0.037 s^{-1} and experimentally determined 0.06 s^{-1} (298 K; (Assaf et al., 2023)). The isomerization will be the dominant loss process of MTMP under pristine marine conditions (low NO_x) even assuming the slowest isomerization rate constant. Wu et al. (2015) have already suggested the formation of OCS via the reaction of HPMTF with OH. In the last decade, various chamber and laboratory experiments have been carried out (Jernigan et al., 2022b; Ye et al., 2022; Shen et al., 2022; Novelli et al., 2022; von Hobe et al., 2023; Alber et al., 2024) to investigate the DMS oxidation by OH under low- $\text{NO}_x/\text{HO}_2/\text{RO}_2$ conditions. All of them observed significant HPMTF formation, and some studies also measured OCS and found OCS yields of several percent. These yields are much higher than the previously assumed 0.7 %, based on earlier laboratory studies (Barnes et al., 1994, 1996; Albu et al., 2008). But these experiments were conducted at high precursor concentrations resulting in large RO_2 , which reduced the lifetime ($<5 \text{ s}$) of peroxy radicals due to amplified bimolecular chemistry between two RO_2 . Likely, this has reduced the formation of HPMTF. A major revision of the traditional DMS oxidation mechanism concludes that the isomerization pathway accounts

for 30 % to 46 % of the total global DMS consumption in the atmosphere (Vermeuel et al., 2020; Novak et al., 2021; Fung et al., 2022). HPMTF, the major product of this isomerization channel, is mainly oxidized to SO_2 or OCS , or lost to clouds or aerosols (Vermeuel et al., 2020; Novak et al., 2021). However, also the rather short-lived thioperformic acid (TPA) and thioformic anhydride (TFA) are typical intermediates formed by the (photochemical) oxidation of HPMTF (von Hobe et al., 2023). Especially, TFA is an intermediate in the OCS -producing oxidation channel of HPMTF. Moreover, the formation of thioformic acid (HC(=O)SH , hereafter TFO) via decomposition of HPMTF has been widely discussed in the literature, primarily in the context of aqueous-phase chemistry (Jernigan et al., 2022a, 2024; Vereecken et al., 2025). However, due to the incomplete understanding of this mechanism, the possibility of TFO formation in the gas phase cannot be excluded up to date.

In the addition channel, the oxidant (often OH) is added to DMS and a DMS-OH adduct is formed. This adduct has been observed in gas and aqueous phases (Bonifacic et al., 1975; Barone et al., 1996; Janik and Tripathi, 2013). Under NO_x -free conditions, this adduct reacts with O_2 forming DMSO. DMSO₂ (Arsene, et al., 1999), SO_2 , MSA, methanesulfinic acid (MSIA; $\text{CH}_3\text{S(O)OH}$), and depending on the water vapor content, H_2SO_4 are further oxidation products of DMSO (Sørensen et al., 1996; Arsene et al., 2002).

In the gas phase, DMSO is mainly formed via the addition channel with the oxidants OH (daytime) and BrO (nighttime) for cloud-free conditions in the MBL. During cloudy conditions in the MBL, DMS is mainly oxidized by dissolved O_3 . DMSO is further oxidized by OH in either gas or aqueous phase (Barnes et al., 2006; Hoffmann et al., 2016). However, Zhu et al. (2006) showed in a theoretical study that dissolved SO_4^- and Cl_2^- could also play a significant role in DMSO oxidation in the aqueous phase if their concentrations are large enough. Its main oxidation products are MSA and SO_2 . Besides chemically, DMSO is also lost via dry and wet deposition, since DMSO is highly soluble in water.

Mostly, MSIA is formed by the reaction of DMSO and OH in both gas and aqueous phase. The loss processes are the further oxidation by OH and O_3 also in both gas and aqueous phase. Another oxidant, which removes MSIA, is dissolved Cl_2^- (Barnes et al., 2006; Zhu et al., 2006; Hoffmann et al., 2016). The product of its oxidation is mainly MSA. However, the gas phase

reaction of MSIA with OH can additionally form SO₂.

Another compound formed by DMS oxidation is MSA. Importantly, DMS oxidation is the only source of MSA in the marine troposphere. Hence, it is an important proxy for both DMS emission flux and chemistry. Due to its high water solubility, it is mainly removed from the atmosphere via wet (and dry) deposition. Its atmospheric lifetime is limited to about a week (Hezel et al., 2011). Modeling studies also suggest chemical MSA removal via oxidation by dissolved OH in the aqueous phase (formation of dissolved sulfate). However, the significance of this process (2 - 27 %) is still discussed and not well constrained due to the high uncertainty of the concentration of dissolved OH radicals (Von Glasow and Crutzen, 2004; Zhu et al., 2006; Hoffmann et al., 2016)

Depending on the channel and the phase of the DMS oxidation, the effects on the Earth's climate system can be different. While the gas phase production of H₂SO₄ and MSA can lead to nucleation of new particles since they act as aerosol and cloud condensation nuclei (Kulmala et al., 2000; Chen et al., 2015), the formation of sulfate and MSA in the aqueous phase does not influence new particle formation. Instead, they will affect the aerosol size distribution and therefore, the cloud microphysical properties can change (Kreidenweis and Seinfeld, 1988; Kaufman and Tanré, 1994).

DMS oxidation is still not well understood and there are many open questions.

Mechanistically, it is not well constrained which (sub-)channels (addition or abstraction and isomerization or bimolecular reaction within the abstraction channel) are dominant under which conditions. Thus, which are the environmental factors (e.g., NO_x concentration, humidity, temperature, sunlight, etc.) influencing this balance and how large is their influence (Barnes et al., 2006).

There is often a discrepancy between field measurements and model predictions. The exact yields of the key products SO₂, OCS, HPMTF, DMSO, MSIA, MSA, and sulfate can not be predicted reliably with the current chemistry models, pointing to missing chemical reactions or processes, wrongly determined chemical kinetics, or errors in the experimental data (e.g., using CIMS or PTR-MS). Jacob et al. (2024) could show in their DMS oxidation mechanism intercomparison that most of the mechanisms only work well for the (chamber) study used

to develop this certain mechanism. Most mechanisms have been developed using only one or at maximum a small subset of experimental chamber studies (in recent publication, only one individual chamber study was used to improve the mechanism). Since parameters and settings of such chamber studies vary, the conditions are not the same either. Moreover, individual results of such chamber studies are limited by the instrumentation used. The experimental results always have to be questioned with respect to the precision and accuracy of the data and if all parameters and species are quantified to determine the kinetics. This can result in different yields and kinetics. Jacob et al. (2024) suggested to use as many as possible experimental data available to develop a synthesis mechanism. Especially, the large discrepancy of rate constants for the isomerization channel forming HPMTF is mainly discussed and investigated recently as shown in Figure 5.2. Furthermore, the uptake of HPMTF in clouds or aerosols and its heterogeneous chemistry are not well constrained as pointed out by Veres et al. (2020) and exemplary shown in Jernigan et al. (2022a, 2024, e.g.).

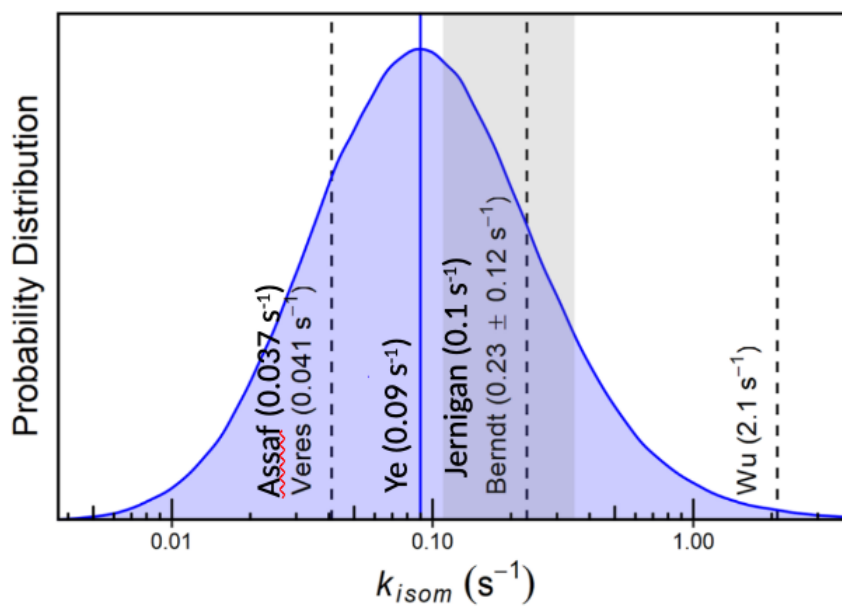


Figure 5.2: Probability distribution of the estimated k_{isom} adapted from Ye et al. (2021). The dotted lines are retrieved using the data of Wu et al. (2015) (293 K), Berndt et al. (2019) (295 K), Veres et al. (2020) (298 K), Jernigan et al. (2022a) (298 K), Ye et al. (2021) (298 K), and Assaf et al. (2023) (298 K). The gray area represents the uncertainty range in Berndt et al. (2019).

Another open question, which is even more important, is the quantification of HPMTF,

one of the major products of the DMS oxidation. As HPMTF is a stable intermediate, but not stable enough to be isolated or formed quantitatively in-situ, there is no standard or technique to calibrate HPMTF reliably. Published studies quantified HPMTF indirectly using other sensitivities, voltage scanning, etc. (Veres et al., 2020; Vermeuel et al., 2020; Siegel et al., 2023). It is still a task of the ongoing research to reliably constrain mixing ratios of HPMTF with a small error. Moreover, the dependency of sensitivity of the HPMTF measurement using CIMS on other trace gases (e.g., water vapor, ozone, nitrogen oxides), temperature, and surfaces are also not well understood yet.

Accurate quantification of HPMTF and its decomposition products are therefore essential to improve our understanding of the OCS formation pathways and its relevance in atmospheric sulfur cycling. To address this knowledge gap, the oxidation of DMS was investigated under a range of controlled conditions using the SAPHIR-STAR chamber (Simulation of Atmospheric PHotochemistry In a large Reaction chamber – Stirred Atmospheric flow Reactor) in fall 2023 and 2024. In addition, the formation and loss processes of hydroperoxymethyl thioformate (HPMTF) and SO_2 were systematically examined.

5.2 SAPHIR-STAR

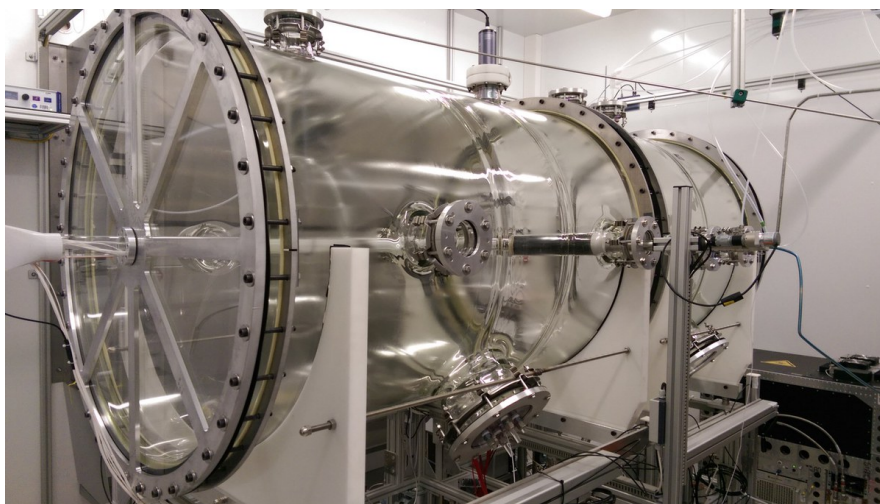


Figure 5.3: Photograph of the SAPHIR-STAR chamber. Source: Sören Zorn.

The SAPHIR-STAR chamber, located at Forschungszentrum Jülich GmbH and depicted

in Figure 5.3, represents an evolution of the earlier Jülich Plant-Atmosphere Chamber facility (JPAC) setup (Mentel et al., 2009). While maintaining the core design principles of its predecessor, SAPHIR-STAR introduces comprehensive programmability, enabling full control, adjustment, and real-time monitoring of all operational parameters.

The chamber itself is cylindrical, with a length of 2.5 m and a diameter of 1 m, and is constructed from borosilicate glass. All internal components are composed either of glass or SilcoNert2000®-coated stainless steel (SilcoTek GmbH) to ensure chemical inertness and minimize surface reactions. The entire glass cylinder is located in a large thermostat chamber to maintain a defined temperature within ± 0.5 °C

Unlike other atmospheric simulation chambers, SAPHIR-STAR is operated as a continuously stirred tank reactor (CSTR), with a typical total gas flow rate of $32 \text{ L} \cdot \text{min}^{-1}$, resulting in an average gas residence time of approximately 61 minutes. Homogeneous mixing is facilitated by an internal fan oriented perpendicularly to the chamber’s axis, ensuring thorough mixing within minutes. The in- and outflow control keeps the pressure within the chamber constant at approximately atmospheric pressure. Due to the fully automated system, the inflow is always kept constant.

The gas inflow, a mixture of nitrogen (N_2) and oxygen (O_2) that can optionally be humidified, is split into two separate streams. To one stream, oxidants such as e.g., H_2O_2 and/or O_3 can be added. The precursor (e.g., DMS) to be oxidized, and other trace gases as needed (e.g., CO) can be added to the second stream. Both gasflows are introduced into the chamber via a circular glass inlet equipped with evenly spaced holes, ensuring homogeneous distribution of the gases throughout the chamber.

For the generation of radicals, two UV lamps are installed in the center of the chamber. A UV-C lamp (254 nm) is aligned along the central axis of the chamber within a sealed quartz tube, while a UV-A lamp (365 nm) is mounted perpendicularly in a similar quartz enclosure. The light intensity, and thus the radical production rate, can be precisely regulated by adjusting a motorized shielding system encasing the lamps.

5.3 Experimental Details

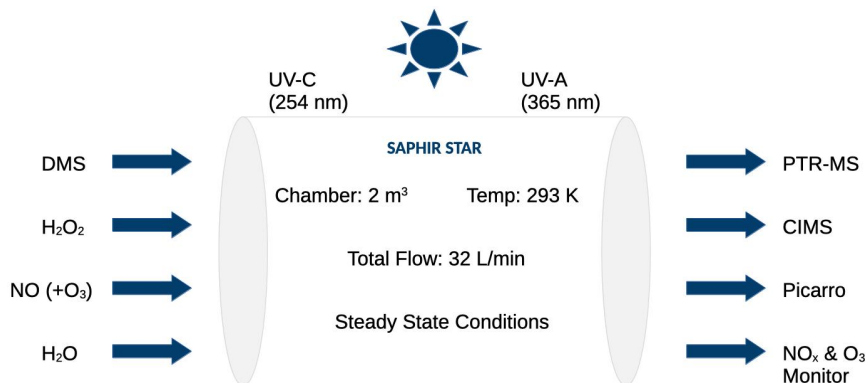
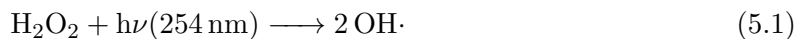


Figure 5.4: Schematic of the SAPHIR-STAR chamber during the DMS oxidation experiments in 2023.

5.3.1 The 2023 Campaign

All experiments were conducted in the SAPHIR-STAR chamber under controlled atmospheric conditions. Hydroxyl (OH) radicals were generated exclusively via the photolysis of H_2O_2 (see Equation 5.1), chosen over alternative methods (e.g., $\text{H}_2\text{O}/\text{O}_3$ or tetramethylethene (TME)/ O_3) due to several advantages: the chamber remained effectively dry (relative humidity $<3\%$), no additional ozone was required, and the formation of excessive RO_2 radicals was avoided. To introduce H_2O_2 into the chamber, a synthetic air gas flow of 0.1 or $0.2 \text{ L} \cdot \text{min}^{-1}$ was passed through a 30% aqueous H_2O_2 solution (supplier: Sigma-Aldrich), which was then mixed into the primary flow.



A 110 ppm DMS mixture in N_2 (5.0) was prepared in-house using pure DMS (supplier: Sigma Aldrich). The DMS was introduced into the main gas stream using a MFC at flow rates of 0.006 or $0.012 \text{ L} \cdot \text{min}^{-1}$, resulting in chamber mixing ratios of 11 and 22 ppb , respectively.

5.3. EXPERIMENTAL DETAILS

To investigate the influence of water vapor, the gas stream was humidified using self-purified water (18.2 MOhm), adjusting the relative humidity (RH) in the chamber to discrete levels of 0 %, 20 %, 40 %, and 60 %.

For experiments involving nitrogen monoxide (NO), an additional flow containing 20 ppm NO in N₂ (supplier: Messer) was added to the chamber. Flow rates ranged from 0.003 to 0.018 L·min⁻¹, corresponding to target NO mixing ratios of 5, 10, 20, and 30 ppb.

The oxidation of DMS by nitrate radicals (NO₃) was investigated under dark conditions. To facilitate sufficient NO₃ formation, 100 ppb of O₃ and 25 ppb of NO (using at 0.015 L · min⁻¹) were introduced into the chamber. Following the dark reaction period, both the UV-C and UV-A lamps were activated for two hours to study the subsequent photolysis of oxidation products.

Throughout all experiments, the chamber temperature was maintained at 293.15 K (20 °C) to ensure consistent thermal conditions.

Due to infrastructure issues related to the water supply, only two weeks of measurement time were available in fall 2023.

A detailed overview of all experimental conditions and configurations is provided in Table 5.1.

Table 5.1: Summary of the four DMS oxidation experiments in 2023

Parameters	Exp. 1	Exp. 2	Exp. 3	Exp. 4
DMS injection [ppb]	11 or 22	22	22	11
H ₂ O ₂ flow [L · min ⁻¹]	0.1 or 0.2	0.2	0.2	0
T [°C]	20	20	20	20
RH [%]	<2	<2 - 60	<2	<2
NO injection [ppb]	0	0	5 - 30	25
O ₃ injection [ppb]	0	0	0	100
UV-C shielding [%]	50 - 100	100	100	0 or 100
UV-A shielding [%]	0	0	100	0 or 100

Dimethyl sulfide (DMS) concentrations were monitored using proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS; Ionicon GmbH).

A key aspect of this campaign was the deployment of three different CIMS, as summarized

in Table 5.2. These included:

- an APi-LToF-CIMS (ToFwerk Ltd.) operated with both nitrate and bromide ion sources and capable of voltage scanning,
- a CIMS-HToF (ToFwerk Ltd.) utilizing iodide ion chemistry, and
- the FunMass instrument, employing CF_3OOCF_3 as the reagent ion precursor to form i.e., CF_3O^- .

In the APi-LToF-CIMS (referred to here as MION), the nitrate ionization mode enables the detection of a broad range of sulfur-containing oxidation products, including H_2SO_4 , MSA, and HPMTF. Additionally, the bromide ionization mode of the same instrument is employed primarily for the detection of hydroperoxy radicals (HO_2).

The iodide-CIMS configuration allows for the measurement of a variety of atmospherically relevant species, including HPMTF, MSA, and HCOOH .

The FunMass instrument is primarily used for monitoring SO_2 , HPMTF, HCOOH , and H_2O_2 .

This combination of instruments enabled comprehensive detection and intercomparison of sulfur-containing oxidation products and intermediates under varying experimental conditions.

Table 5.2: Summary of the CIMS used during the DMS oxidation experiments in 2023.

Reagent Ion	I^-	CF_3O^-	NO_3^- or Br^-
Inlet	IMR	IMR	MION
Pressure [mbar]	110 - 120	35	1 atm
Mass resolution	2500 - 3000	700 - 950	8000 - 9000

CO_2 , CO and H_2O (G2401 cavity ring-down spectrometer, Picarro Inc.); NO and NO_x (NCLD899, Eco Physics GmbH with a home-built photolytic converter); and O_3 (O342e, Envea GmbH) were additionally monitored.

5.3.2 The 2024 Campaign

An extended dimethyl sulfide (DMS) oxidation campaign was conducted in the SAPHIR-STAR chamber during fall 2024, following a similar experimental design as the 2023 campaign.

The experimental setup was largely consistent with that of the previous year. OH radicals were again generated via the photolysis of hydrogen peroxide (H_2O_2). In the first experiment, $0.012 \text{ L} \cdot \text{min}^{-1}$ of a 99.79 ppm DMS in N_2 mixture was introduced into the chamber, resulting in an initial DMS mixing ratio of approximately 20 ppb. Simultaneously, a gas flow of $0.2 \text{ L} \cdot \text{min}^{-1}$ was passed through a 30 % aqueous H_2O_2 solution (at 21 °C) to introduce the oxidant into the chamber.

In the initial phase of this experiment, the UV-C lamp intensity was systematically varied between 0 % and 60 % to study the photolytic sensitivity of DMS oxidation. Subsequently, carbon monoxide (CO) was introduced into the chamber at a mixing ratio of 2.5 ppm, achieved by injecting $1.5 \text{ mL} \cdot \text{min}^{-1}$ of a 10 mol% CO/ N_2 gas mixture (supplier: Messer). CO addition reduces OH concentration and hence, the consumed DMS. The UV-C intensity was incrementally increased, up to a maximum of 95 %, to match the DMS consumption observed in the absence of CO to get the same OH production. The OH chemistry was the same for both cases and only the photolysis rate was different.

After the CO addition phase, oxidation experiments were conducted at UV-C intensities of 75 % and 95 % to evaluate the effect of UV-C intensity on DMS oxidation without CO addition.

The chamber air was also humidified to assess the influence of water vapor on the oxidation process. The relative humidity (RH) was adjusted to 30 % and the change of oxidation products of the UV-C light intensity (25, 50, 75, and 95 %) was investigated under humid conditions injecting 20 ppb DMS. Additionally, the effect of CO addition was also examined under humid conditions. The UV-C lamp was operated at 60 % intensity. Following this, 2.5 ppm CO was again introduced into the humidified system, and the UV-C intensity was raised to 95 % to reproduce conditions analogous to those used during the CO addition under dry conditions.

The second experiment was designed to investigate the influence of nitrogen oxides (NO_x) on DMS oxidation. The same DMS and H_2O_2 concentrations as in the previous experiment were maintained, with the UV-C and UV-A lamp operated at a constant intensity of 75 %. The chamber NO mixing ratio was systematically increased in discrete steps (0, 1, 2, 5, and 10 ppb) by injecting gas from a cylinder containing 101 ppm NO and 1 ppm NO_2 in N_2 (supplier: Messer). This experiment was subsequently repeated under humidified conditions with a relative humidity of 30 % to assess the role of water vapor in NO_x -influenced oxidation chemistry.

The third and final experiment focused on the oxidation of DMS via nitrate (NO_3) radicals under dark conditions. The first phase aimed to evaluate the formation of dinitrogen pentoxide (N_2O_5), which has the same molecular mass as hydroperoxymethyl thioformate (HPMTF), and could potentially interfere with its mass spectrometric detection. For this purpose, 150 ppb O_3 was introduced to the chamber along with variable NO concentrations (5, 10, and 20 ppb).

In the second phase, the NO concentration was held constant at 20 ppb, and the DMS concentration was gradually increased (5, 10, 20, and 30 ppb) to investigate the reactivity and product distribution under NO_3 -dominated conditions. All measurements in this experiment were performed under dry and dark conditions to prevent interference from OH and photolytic reactions.

Throughout all experiments, the chamber temperature was consistently maintained at 294.15K (21°C). A brief summary of all experiments can be found in Table 5.3.

Almost the same experimental setup as during the experiments in 2023 was used (see 5.3.1). The Iodide-CIMS (HToF) was replaced by an Amine CIMS (HToF). Additionally, an Iodide FIGAERO-CIMS was added to the CIMS list. Moreover, OCS could be measured using a Mid-Infrared Cavity enhanced Absorption spectrometer (MICA), which is described in more detail in Kremser et al. (2020).

Table 5.3: Summary of the three DMS oxidation experiments in 2024

Parameters	Exp. 1	Exp. 2	Exp. 3
DMS injection [ppb]	20	20	0 - 30
H ₂ O ₂ flow [L · min ⁻¹]	0.2	0.2	0
T [°C]	21	21	21
RH [%]	<2 or 30	<2 or 30	<2
CO injection [ppm]	0 or 2.5	0	0
NO injection [ppb]	0	0 - 10	0 - 20
O ₃ injection [ppb]	0	0	150
UV-C shielding [%]	0 - 95	75	0
UV-A shielding [%]	0	100	0

5.4 FunMass at SAPHIR-STAR

5.4.1 Setup

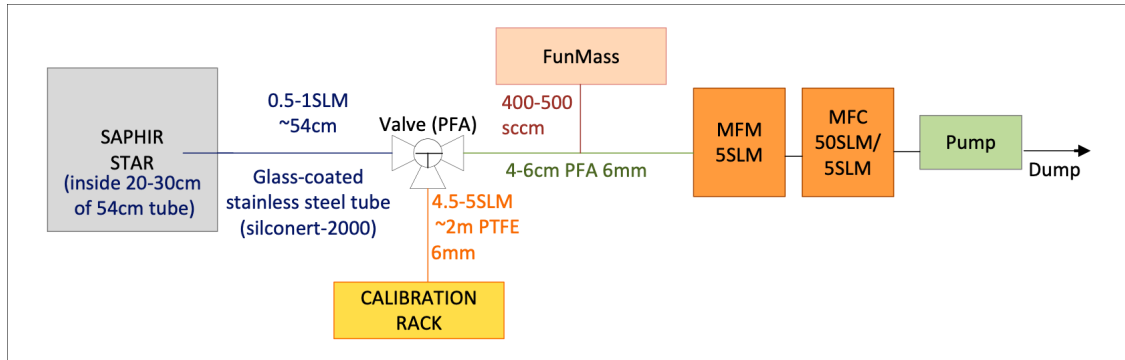


Figure 5.5: Setup of FunMass during the DMS oxidation experiment at SAPHIR-STAR in 2023 and 2024.

The FunMass instrument was connected to the chamber using 53 cm of a 6 mm (o.d.) SilcoNert2000®-coated stainless steel (SS) tube (SilcoTek GmbH). The orifice of this tube was positioned 20 cm away from the nearest chamber wall, extending a total of 30 cm into the chamber. This SilcoNert2000®-coated SS tube was coupled to a PTFE 3-way valve, which was further connected to the FunMass inlet via a 4 cm long 6 mm (o.d.) PFA tube. The third port of the 3-way valve was linked to the calibration rack, located outside the thermostat, using a 2 m long 6 mm PTFE tube.

The gas flow line, from which FunMass draws the analyte air, was routed to an external pump via a MFM (5 SLM) and a MFC (2023: 50 SLM and 2024: 5 SLM), both manufactured by MKS. The MFC regulated the volume of air drawn from the chamber by the external pump. The total flow extracted from the chamber was the sum of the FunMass inlet flow (typically 400–500 SCCM) and the flow set by the MKS MFC. The 3-way valve also allowed for complete isolation of the chamber, enabling operation solely with the gas flow from the calibration rack.

FunMass employs CF_3O^- as a reagent ion, which is highly sensitive to H_2O_2 and water vapor (Crounse et al., 2006). Elevated concentrations of H_2O_2 , and occasionally water vapor, necessitated dilution of the sampled chamber air. Dilution factors of approximately 5.5 (2023) and 11 (2024) were applied to reduce H_2O_2 levels, which otherwise would fully deplete the CF_3O^- ion population. The external pump and FunMass drew 5 and approximately 0.5 SLM, respectively, resulting in a total flow of 5.5 SLM. The synthetic air from the calibration rack was supplied at 4.5 (2023) or 5 (2024) SLM, yielding a net chamber sampling rate of 1000 (2023) and 500 (2024) SCCM, respectively.

A major challenge during both measurement campaigns was that FunMass was not fully integrated into the final measurement setup, specifically, the Gasdeck (which includes an automatic calibration system) was not in place, yet. As a result, the calibration and data acquisition procedures were modified. All flow controllers (MFCs within the calibration rack, and the MFM/MFC preceding the external pump) and pressure sensors (at the IMR and along the inlet line) were monitored. However, IMR temperature data acquisition was only available from December 2024 onward. FlowSuite (Bronkhorst, version 1) and a custom-written program were used to log flow and pressure data from the MKS 647C and MKS PR4000B devices.

An automatic calibration routine was implemented to regularly introduce 500 SCCM of SO_2 and occasionally HCOOH into the system, corresponding to concentrations of 943 ppt and 2105 ppt, respectively. During the second campaign, an extended automatic calibration sequence (including varying calibration flows) was developed, although it was used only intermittently. In most cases, single-point online calibrations were performed.

A LabJack T7-Pro device was employed to automate actuation of the PTFE valve (NRe-

search). Since the LabJack T7-Pro is only capable of supplying a maximum of 5 VDC, and the electronic valve required 24 VDC, a relay circuit was implemented. This relay was triggered by the 5 VDC output of the LabJack T7-Pro and subsequently provided the required 24 VDC to actuate the valve.

5.4.2 SO₂ Calibration

An important source of uncertainty was whether the calibration performed through a 2 m PTFE tube (6 mm o.d.) significantly differed from that performed using a combination of a 53 cm SilcoNert2000®-coated stainless steel (SS) tube (6 mm o.d.), a 4 cm PFA tube (6 mm o.d.), and a PTFE 3-way valve. To assess this, both setups were reconstructed in the laboratory after the measurement campaign, and calibrations using SO₂ were conducted.

Figure 5.6 shows the SO₂ calibration curves for the two configurations: one using a 2 m PTFE tube (6 mm) and the other using a 53 cm SilcoNert2000®-coated stainless steel (SS) tube (6 mm o.d.) connected to a 4 cm PFA tube (6 mm o.d.) via a PTFE 3-way valve. The results indicate no significant difference of the sensitivity between the two setups (<3 %), suggesting that the online 1-point SO₂ calibration performed via the 2 m PTFE tube during the campaign is representative of the SO₂-containing air sampled from the chamber through the 53 cm SilcoNert2000®-coated SS tube.

The influence of water vapor and ozone on the SO₂ calibration has been discussed in Subsection 4.10.1. Water vapor, in particular, has a significant impact on the calibration, especially at high concentrations. Consequently, it was hypothesized that the elevated H₂O₂ concentrations present in the chamber might similarly affect the SO₂ calibration.

Figure 5.7 shows the decrease in the relative sensitivity of the SO₂ calibration as a function of the [H₂O₂ · CF₃O]⁻ to [CF₃O]⁻ ratio in %, which serves as an indicator of changing H₂O₂ concentration. In addition to changes in formation rates, enhanced cluster formation also contributes to the observed decrease in the relative sensitivity of the fluoride cluster of SO₂. In particular, the intensities of [H₂O₂ · SO₂ · F]⁻ and its decomposition product [SO₂ · HO₂]⁻ increase with rising H₂O₂ levels. Therefore, the majority of the decline in relative sensitivity observed in Figure 5.7 is attributed to additional clustering and subsequent decomposition

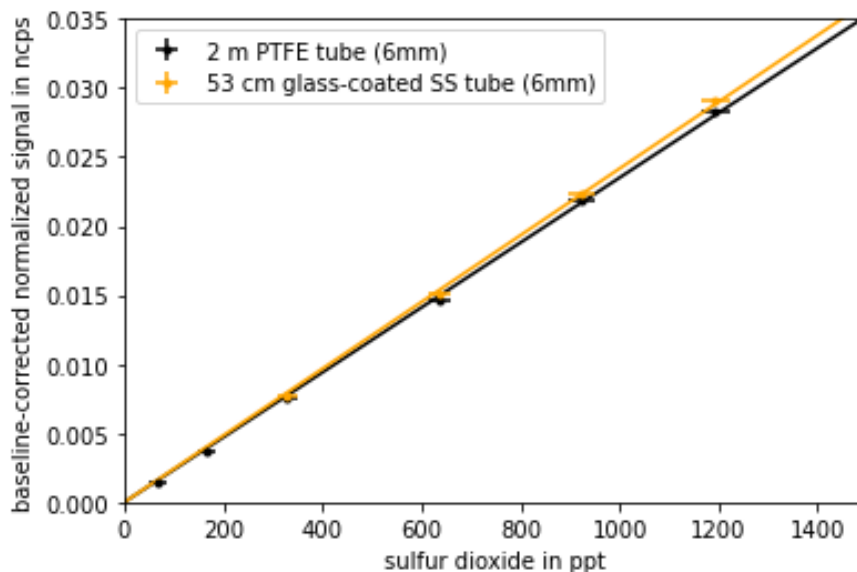


Figure 5.6: Comparison of the SO_2 calibration using the 2 m PTFE tube (6 mm) and the other using the 53 cm SilcoNert2000®-coated SS tube (6 mm) connected to the 4 cm PFA tube (6 mm) via a PTFE 3-way valve.

processes induced by H_2O_2 . Another reason is the decomposition of CF_3O^- and its cluster (e.g., $[\text{CF}_3\text{O} \cdot \text{H}_2\text{O}_2]^-$) with increasing H_2O_2 (or water vapor) leading to more $[(\text{HF})_n \cdot \text{F}]^-$ clusters as well as ion loss. As the signals are normalized to CF_3O^- and its cluster signal, this is not taken into account. This can also contribute to the normalized signal loss. The loss in the sum of the four major CF_3O^- signals (CF_3O^- , its HF-, H_2O -, and H_2O_2 -cluster is calculated to be maximum 15 % if the ratio $[\text{H}_2\text{O}_2 \cdot \text{CF}_3\text{O}]^- / [\text{CF}_3\text{O}]^-$ is 100 %.

5.5 Results

The campaign in 2023 was more a proof-of-concept whether sensible DMS oxidation measurements were feasible in SAPHIR-STAR as not much time was available. Moreover, there were significant problems with measuring and calibrating DMS. This resulted in unreliable DMS mixing ratios making quantitative and sometimes even qualitative analysis impossible.

The second campaign in 2024 was carried out with the objective to retrieve HPMTF mixing ratios and get insights into the kinetics under various conditions. Therefore all the major sulfur containing species (DMS , SO_2 , H_2SO_4 , MSA , MSIA , DMSO , DMSO_2 , HPMTF,

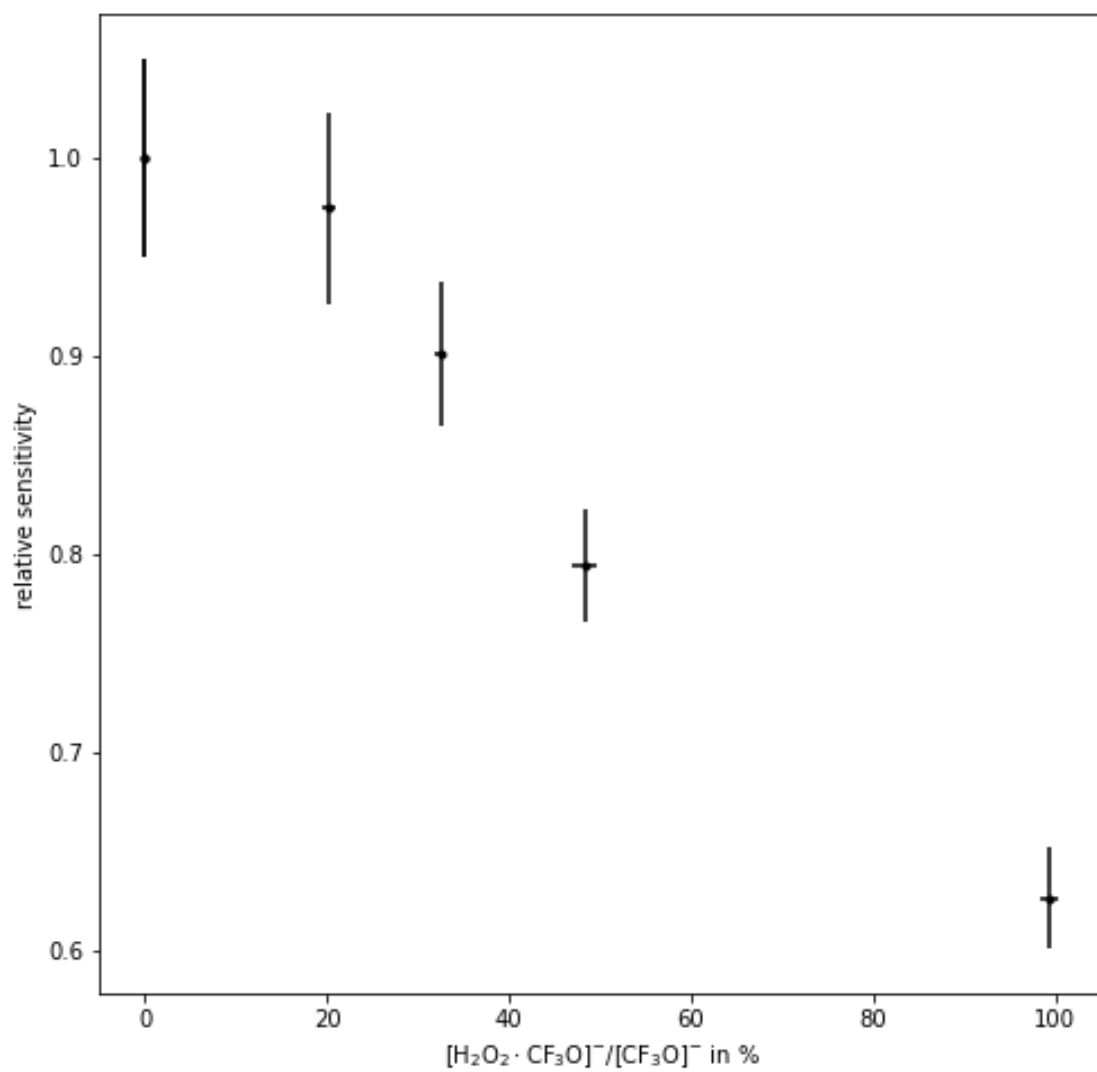


Figure 5.7: The relative sensitivity of the SO₂ calibration using its fluoride cluster as a function of the [H₂O₂ · CF₃O]⁻ to [CF₃O]⁻ ratio in %.

TPA, TFA, and OCS) should be monitored and ideally quantified reliably. However, up to this date, only SO_2 , OCS, and partly DMS data could be carefully calibrated.

5.5.1 Dry Conditions

The first experiments were done under dry conditions ($\text{RH} < 3\%$). This experiment should show if DMS can be oxidized significantly in SAPHIR-STAR using H_2O_2 as OH radical precursor.

Time series of observed radicals, trace gases, stable intermediates, and other relevant parameters (e.g., temperature and relative humidity) during the oxidation of dimethyl sulfide (DMS) under dry conditions in 2023 are presented in Figure 5.8.

An increase in light intensity, and consequently in OH radical concentrations, leads to enhanced formation of sulfur-containing products including SO_2 , HPMTF, MSA, H_2SO_4 , TFA, and TPA. SO_2 concentrations approximately double from 350 ppt to 700 ppt. This increase in SO_2 is accompanied by an increase in OH radicals, which in turn leads to higher levels of H_2SO_4 (see Figure 5.8c). The reaction mechanism responsible for this process, particularly under the presence of water molecules, is described in Subsection 2.2. OH radicals oxidize SO_2 to HSO_3 and subsequently to SO_3 . Additionally, the presence of H_2O_2 , OH, and even trace amounts of water vapor (< 1 ppm) can contribute to minor H_2SO_4 formation.

The increase in H_2SO_4 with more lamp opening is clearly observed. However, it should be noted that the NO_3^- mode of the MION instrument is highly sensitive in detecting H_2SO_4 , and the observed increase likely corresponds to only a few tens of ppt. At the time, a full calibration of H_2SO_4 had not yet been implemented.

The normalized signal of HPMTF increases by approximately 35 %. Unlike SO_2 , which is a stable end product under dry conditions, HPMTF is an intermediate species and subject to various sink processes. While enhanced light intensity increases OH radical production and DMS oxidation—leading to larger HPMTF formation, photolysis and OH-induced degradation of HPMTF also become more efficient. As a result, the relative net increase in HPMTF is smaller compared to e.g., SO_2 .

A modest rise (16–19 %) in the HO_2 signal is also observed with increasing light intensity.

5.5. RESULTS

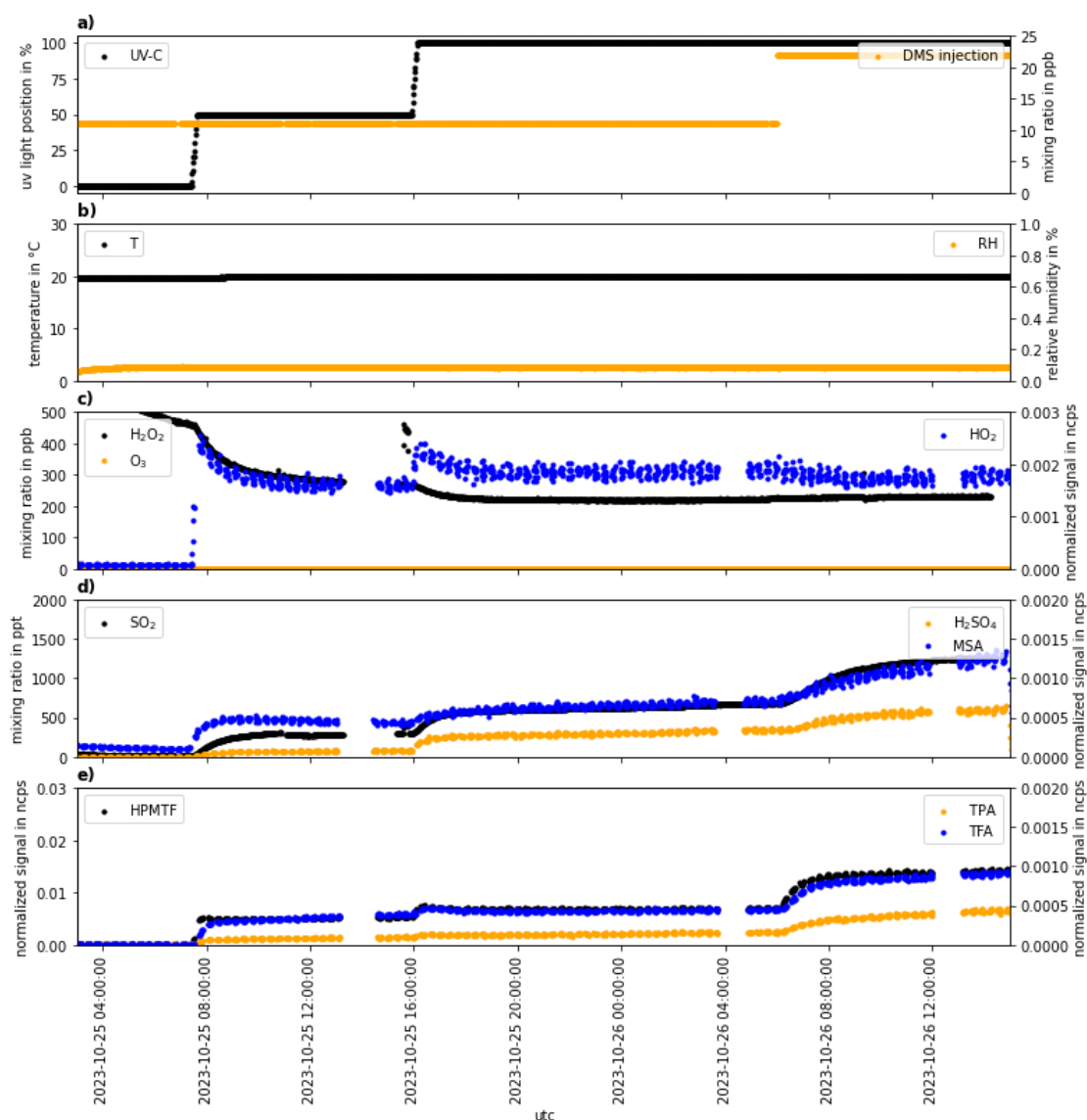


Figure 5.8: DMS oxidation under dry conditions in 2023. **(a)** UV-C lamp opening (black; in %) and DMS concentration injected (orange; in ppb). **(b)** Temperature (black; in °C) and relative humidity (orange; in %). **(c)** Time series of H_2O_2 (black; in ppb), O_3 (orange; in ppb), and HO_2 measured by the Br^- mode of the MION (blue; in ncps). **(d)** SO_2 measured by FunMass (black; in ppt), H_2SO_4 (orange; in ncps), and MSA (blue; in ncps) measured by the NO_3^- mode of the MION. **(e)** Normalized signals (in ncps) of HPMTF (black), thioperformic acid (TPA; orange), and thioformic anhydride (TFA; blue) using the Br^- mode of the MION.

The formation of HPMTF involves isomerization (H-shift) of the MTMP, a pathway that competes with reactions involving HO_2 , NO , and other RO_2 radicals (Berndt et al., 2019). As demonstrated by Ye et al. (2022), in high RO_2 regimes, $\text{RO}_2 + \text{HO}_2$ (or $\text{RO}_2 + \text{RO}_2$) termination reactions dominate, suppressing the isomerization route and reducing HPMTF yields. However, in environments like the global remote MBL, where DMS is mostly emitted and HO_2 levels are relatively low (Veres et al., 2020), the intramolecular H-shift reaction is favored.

Novak et al. (2021) reported a high HPMTF yield ($f_{\text{isom}} = 0.95$) from the abstraction pathway, underscoring the importance of isomerization under such conditions. Importantly, SO_2 can be produced through both the addition and abstraction pathways, making it a dominant product under dry conditions, where SO_2 sinks are minimal.

Doubling the DMS injection rate under constant OH conditions nearly doubles the production of both SO_2 and HPMTF, thereby confirming the linearity of DMS oxidation in SAPHIR-STAR. Enhanced DMS input also increases concentrations of MSA, TPA, and TFA.

Notably, TPA and TFA, both direct decomposition products of HPMTF, correlate strongly with HPMTF (see Figure 5.8e), further supporting their similar formation pathway.

HPMTF was successfully detected using all four CIMS systems employed during the 2023 DMS oxidation campaign. The reagent ions applied in the negative ion mode were NO_3^- , Br^- , I^- , and CF_3O^- , as illustrated in Figure 5.9. These results demonstrate the capability of HPMTF detection across a range of reagent ions, emphasizing the robustness of its measurement under various ionization schemes.

Among the instruments, the Br^- -CIMS exhibited the highest sensitivity, with normalized signals reaching up to order of magnitude of 10^{-2} ncps. The I^- - and CF_3O^- -CIMS instruments showed similar sensitivities, both in the range of 10^{-3} ncps, with I^- -CIMS being approximately three times more sensitive than CF_3O^- -CIMS. In contrast, NO_3^- -CIMS exhibited the lowest sensitivity, with maximum normalized signals around 10^{-5} ncps and the highest associated signal noise.

It is important to emphasize that sensitivity differences cannot be attributed solely to the reagent ions. Instrumental parameters such as inlet configuration, transmission efficiency,

5.5. RESULTS

ion–molecule reaction conditions (e.g., pressure, temperature, flow rates), and background contamination also significantly affect sensitivity. Therefore, these results do not represent an absolute sensitivity ranking of the reagent ions. However, the NO_3^- - and Br^- -CIMS were operated on the same MION instrument with identical instrumental settings, allowing for a more direct and meaningful comparison between the two.

All four CIMS systems recorded consistent time-resolved trends in HPMTF concentrations. For example, doubling the DMS injection rate led to a corresponding doubling in the HPMTF signal across all instruments.

A key advantage of employing multiple reagent ions lies in minimizing the impact of isobaric interferences, as different reagent ions are variably affected by potential chemical interferences. Furthermore, the use of a high-resolution mass spectrometer (MION) enabled the resolution of overlapping peaks with identical nominal masses, thereby improving confidence in compound identification. This intercomparison is particularly valuable for instruments with lower mass resolution, such as FunMass, and underscores the benefit of parallel measurements using multiple ionization schemes.

In fall 2024, the DMS oxidation experiments were repeated under dry conditions (see Figure 5.10). The DMS injection was held constant, while the UV-C light intensity was varied between 25 % and 95 %. To investigate the role of photolysis, CO was added to suppress OH via scavenging. In these experiments, the light intensity was increased to compensate for the resulting OH loss, ensuring comparable DMS consumption rates to those observed without CO. This approach was intended to maintain consistent OH levels while increasing the contribution from direct photolysis.

In order to estimate if the OH radical concentration was at atmospherically relevant levels, the steady state OH concentration is estimated using the method described in Kiendler-Scharr et al. (2009) and Baker et al. (2023). This is necessary as the OH radical could not be measured in SAPHIR-STAR due to the too high analyte flow requirements of the LIF instrument.

$$[\text{OH}]_{\text{ss}} = \frac{\frac{F}{V} \cdot \frac{[\text{DMS}]_{\text{in}} - [\text{DMS}]_{\text{ss}}}{[\text{DMS}]_{\text{ss}}}}{k_{\text{OH}}} \quad (5.2)$$

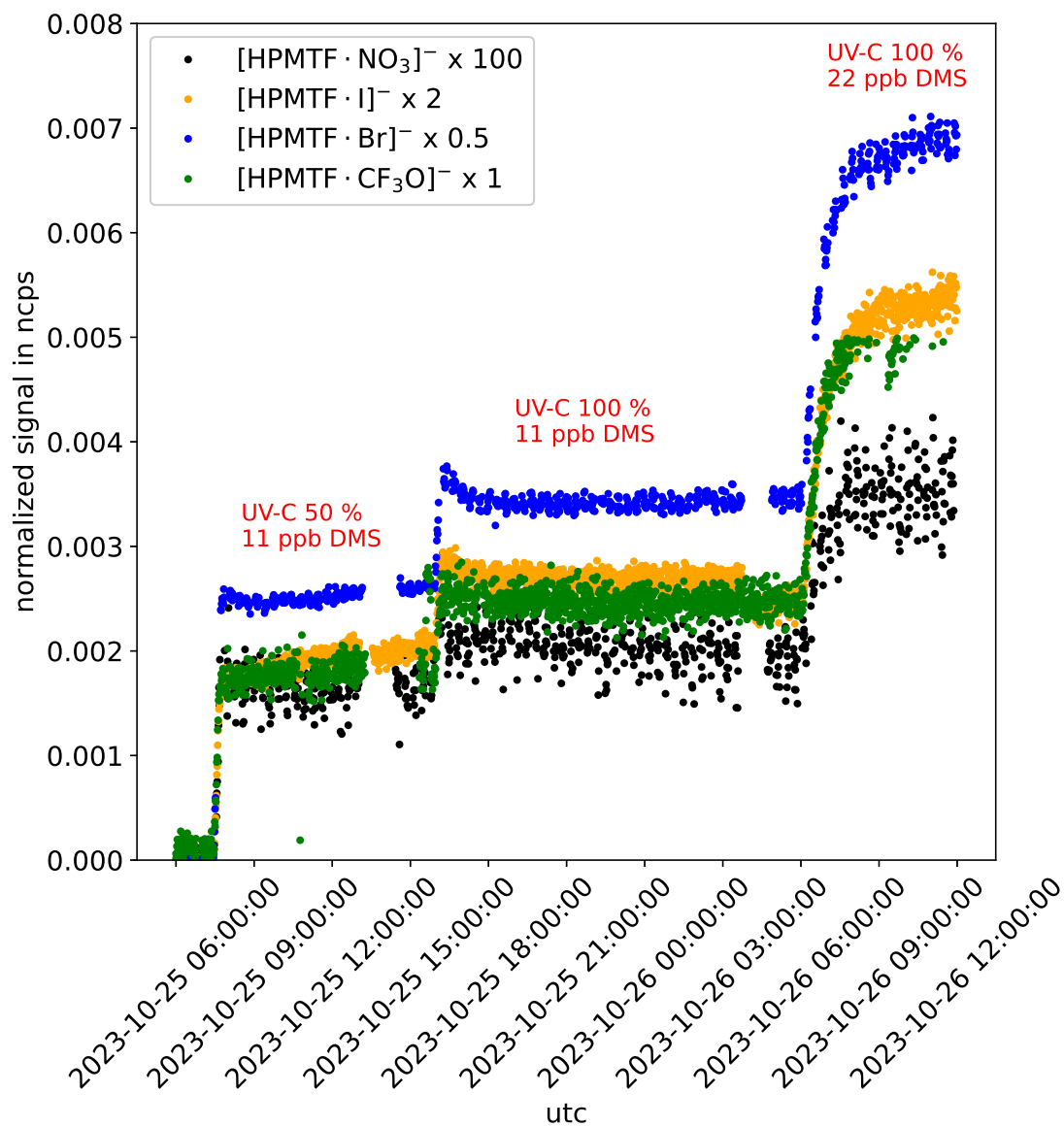


Figure 5.9: Time series of the normalized HPMTF signals measured by NO_3^- mode MION (black; $100 \cdot \text{ncps}$), I^- HToF (orange; $2 \cdot \text{ncps}$), Br^- mode MION (blue; $0.5 \cdot \text{ncps}$), and CF_3O^- FunMass (green; $1 \cdot \text{ncps}$) during the DMS oxidation campaign in 2023 under dry conditions.

5.5. RESULTS

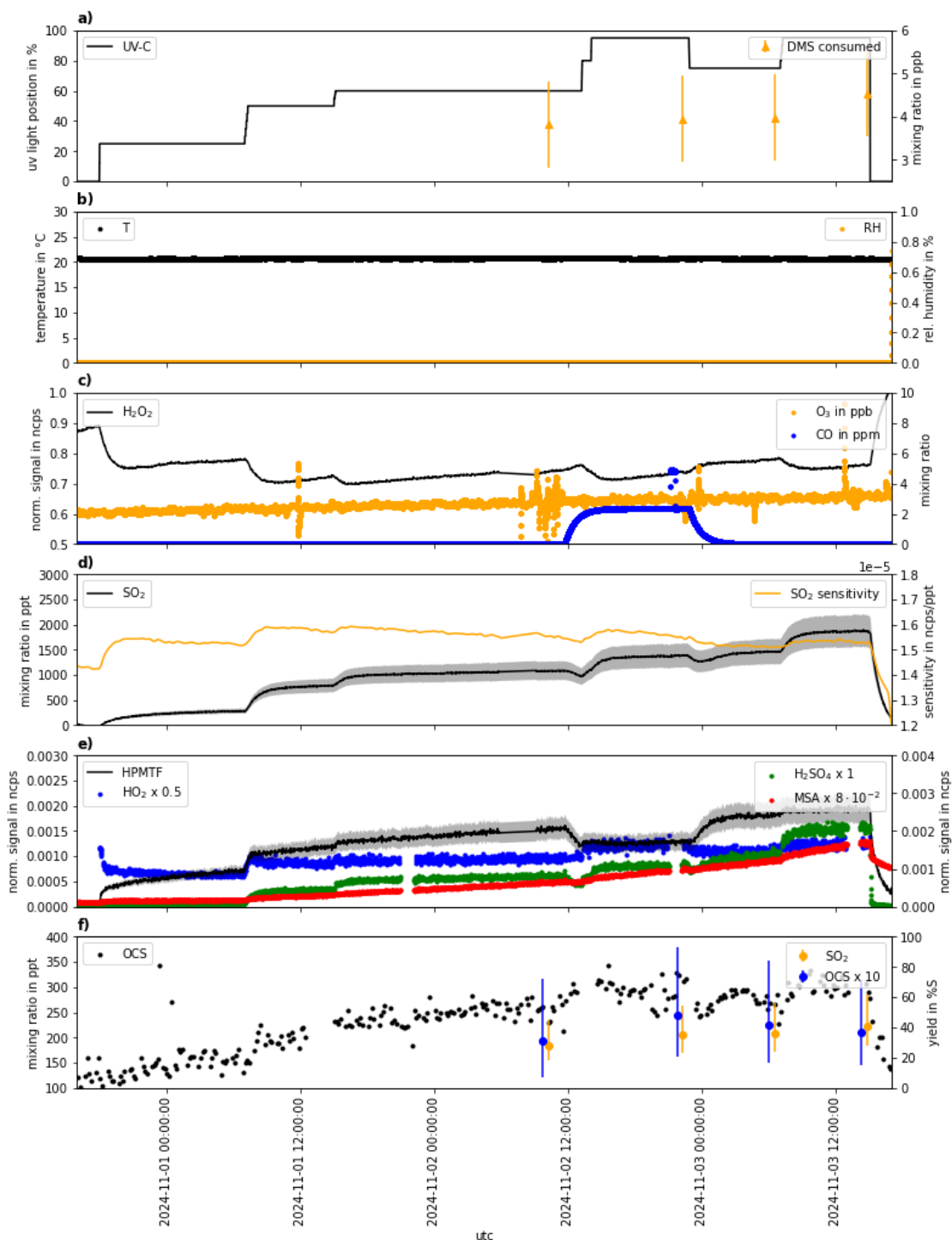


Figure 5.10: DMS oxidation under dry conditions in 2024. (a) UV-C lamp opening (black; in %) and the DMS consumption (orange; in ppb). (b) Temperature (black; in °C) and relative humidity (orange; in %). (c) Time series of H_2O_2 (black; in ppb), O_3 (orange; in ppb), and CO (blue; in ncps). (d) SO_2 (black; in ppt) and its sensitivity (orange, $\text{ncps} \cdot \text{ppt}^{-1}$). (e) Normalized signal (in ncps) of HPMTF (black, FunMass), HO_2 multiplied by 0.5 (blue; MION), H_2SO_4 (green; MION), and $\text{MSA} \cdot 8 \cdot 10^{-2}$ (red; MION). (f) OCS (black; in ppt) and the yield of SO_2 (orange; in %S) and OCS (blue; in $10 \cdot \text{S}$).

The steady-state concentration of OH radicals, denoted as $[\text{OH}]_{\text{SS}}$, can be estimated using Equation 5.2, which incorporates the total chamber flow rate F , chamber volume V , the injected concentration of dimethyl sulfide (DMS), $[\text{DMS}]_{\text{in}}$, the steady-state DMS concentration, $[\text{DMS}]_{\text{SS}}$, and the bimolecular rate constant k_{OH} for the reaction between DMS and OH (Baker et al., 2023). The recommended value for k_{OH} , as provided by the Jet Propulsion Laboratory (JPL), is $6.74 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Burkholder et al., 2020). It is important to account for both primary reaction pathways—hydrogen abstraction and OH addition, when determining k_{OH} , as each contributes to the overall reactivity. The uncertainty associated with $[\text{OH}]_{\text{SS}}$ determined using this method is estimated to be approximately 20% (Wildt et al., 2014). As this approach was originally developed for volatile organic compounds (VOCs), its application to other compounds such as DMS may introduce additional uncertainties in the calculated OH radical concentrations.

Figure 5.11 demonstrates that the steady-state concentrations of OH radicals lie within the atmospherically relevant range of 10^6 to 10^7 molecules cm^{-3} . An increase in the UV-C lamp aperture results in a higher photon flux, which in turn enhances the photolysis rate of H_2O_2 . Consequently, the steady-state OH concentration, $[\text{OH}]_{\text{SS}}$, increases with increasing lamp intensity.

The general behavior observed in 2023 was reproduced in the 2024 experiments. As the UV-C light intensity increased, net SO_2 production increased significantly, while normalized HPMTF signal was comparatively less affected. Only at the experiments with UV-C openings above 50 %, calibrated DMS mixing ratios were available.

SO_2 formation scaled with the degree of DMS consumption, resulting in a relatively constant SO_2 yield of approximately 28 - 40 [19 -61] %. Comparison of these values to literature data must be approached with caution due to chamber-specific differences such as wall losses, temperature, background impurities, and residence time.

However, Patroescu et al. (1998) conducted similar experiments using 254nm UV light and 25ppmv H_2O_2 as an OH precursor, with DMS injections of 6.5 ± 0.5 ppmv. They reported SO_2 yields of 32.8 ± 4 %S and 53 ± 5 %S at 4 ± 2 % and 10 ± 5 % DMS conversion, respectively. The results indicate that the yield of SO_2 is influenced by the reaction time. In

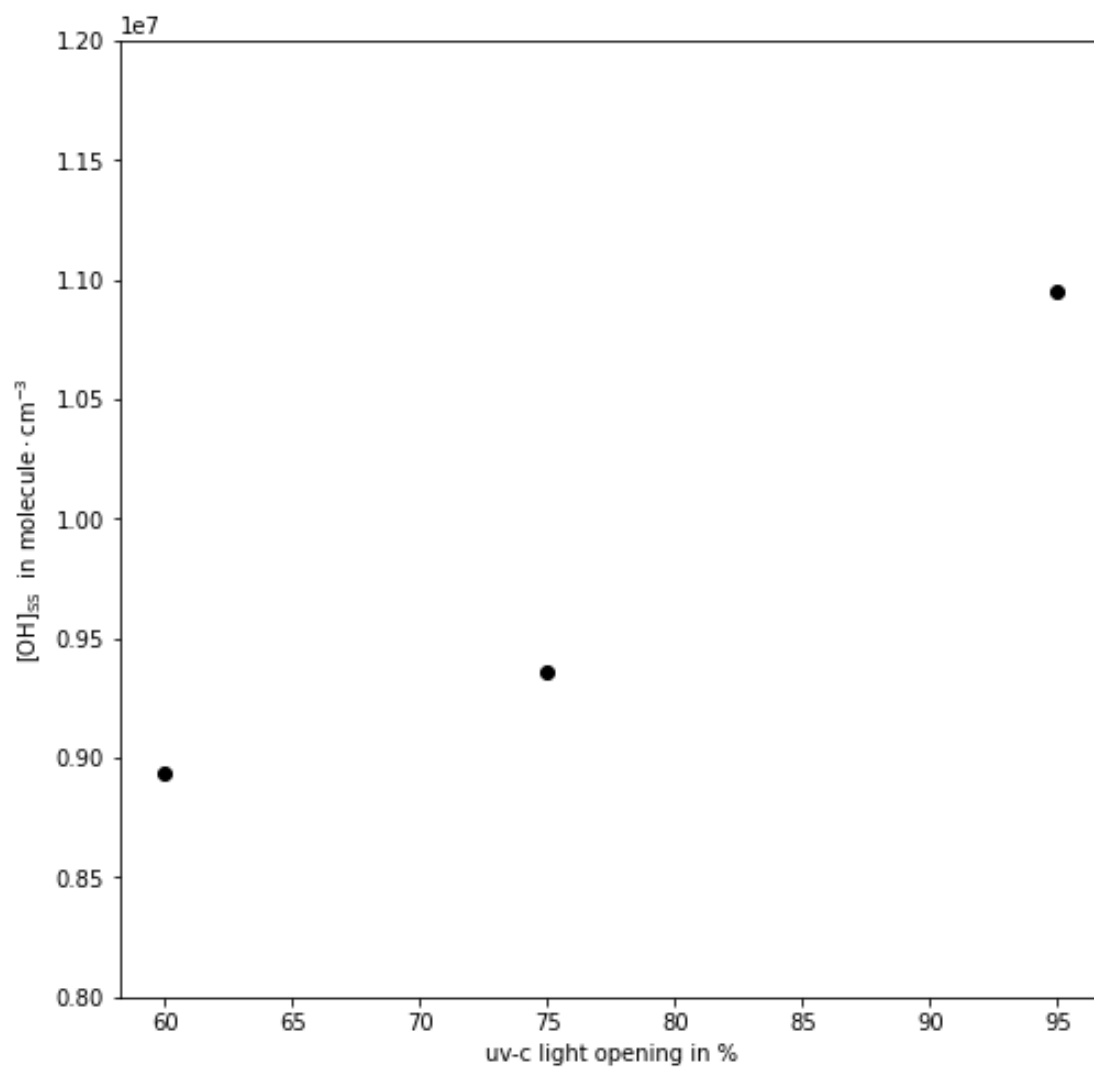


Figure 5.11: Estimated steady state OH concentration $[\text{OH}]_{\text{ss}}$ in molecules $\cdot \text{cm}^{-3}$ for various UV-C lamp opening positions in %.

this work, the DMS conversion ranged from 10 % to 20 %, and the resulting SO₂ yields are broadly consistent with those reported by Patroescu et al (1998).

von Hobe et al. (2023) observed SO₂ yields of 20 – 40 % under various conditions, including humidified air and Cl₂ addition. These findings are in good agreement with the present results. However, other chamber studies under dry conditions have reported substantially higher or lower SO₂ yields, depending on the experimental setup (e.g., Barnes et al., 1994; Jernigan et al., 2022b). For instance, Ye et al. (2022) observed a SO₂ yield of 15 - 18 %S for dry and low-NO_x conditions. This variability highlights the importance of carefully considering chamber-specific characteristics when interpreting yield data. Ideally, intercomparison across different chambers should be leveraged to develop a universally valid model for DMS oxidation product formation under controlled conditions (Jacob et al., 2024).

The formation of H₂SO₄ can also be observed with the MION using the NO₃⁻ mode. As expected it correlates fairly well with the SO₂ signal as SO₂ is its direct precursor. Unfortunately, no calibration of H₂SO₄ was done up to date by ICE-3. However, this is planned for the summer 2025.

MSA exhibits a steadily increasing trend in its signal, with a signal enhancement correlating with increasing OH radical concentrations. This behavior suggests that a steady-state equilibrium for MSA is not fully established under the experimental conditions. This observation can be explained by a slow formation process of MSA itself or one of its precursors. As the concentration of OH radicals increases, DMSO levels also increase, which correlates with an increase in the MSA signal. Therefore, the delayed equilibrium may result from DMSO or another intermediate that contributes to MSA formation, effectively propagating the signal over time.

OCS concentrations were observed to increase slightly with both light intensity and experimental duration. However, since OCS is not considered a primary or early-generation oxidation product like HPMTF, its formation rate was expected to be relatively low. This is consistent with the limited average residence time of air masses in the chamber (61 minutes). OCS is hypothesized to be formed primarily via decomposition of HPMTF, initiated either by OH radicals or through photolysis, specifically targeting the hydroperoxide functional group.

The maximum OCS concentration measured in the absence of CO was 168 ± 85 ppt.

The OCS yield was estimated to range between 3 - 5 [1 - 9] %S across several steady states, as shown in Figure 5.10 f). These findings are in good agreement with recent literature (Jernigan et al., 2022b; Ye et al., 2022; von Hobe et al., 2023), which report higher OCS yields than those determined in the 1990s (0.7 %) (Barnes et al., 1994).

For HPMTF, absolute yields could not be determined due to the lack of calibration. However, relative signal changes can still be meaningfully analyzed. Similar to SO₂, the effect of incrementally opening the UV-C lamp shielding shows a decreasing trend and saturates with increasing opening percentage, as illustrated in Figure 5.12. Notably, the relative signal increase for HPMTF declines more rapidly compared to SO₂, indicating that HPMTF undergoes more significant degradation via OH radical reactions and photolysis.

Overall, the magnitude of the relative signal increase diminishes with each successive shielding step. This is attributed both to the smaller incremental changes in shielding and to the nonlinear relationship between shield opening and photon flux, which arises from the specific configuration of the UV-C lamp and shielding system.

A key experimental modification compared to previous campaigns (e.g., 2023) was the addition of CO. Under CO addition at 95 % light opening, the DMS consumption rate was comparable to that observed at 75 % light opening without CO, indicating similar OH radical concentrations. Despite comparable OH levels, HPMTF concentrations decreased by approximately 30 %, suggesting an increased role of photolysis in its degradation. Since OH-driven formation and decomposition of HPMTF should remain constant under equal OH concentrations, the enhanced UV-C intensity is likely responsible for accelerating photolysis rates.

The photolysis rate of HPMTF is typically estimated based on known rates for aldehydes (RCHO) and hydroperoxides (ROOH), with a representative photolysis rate on the order of magnitude of $j = 10^{-6} \text{ s}^{-1}$. In particular, photolysis of the -OOH group is expected to contribute directly to OCS production. As illustrated in Figure 5.10 panel f), a slight increase in OCS (approximately 12 %) was observed during CO addition. However, this increase must be interpreted cautiously due to significant measurement uncertainty at low ppt OCS concentrations (± 85 ppt).

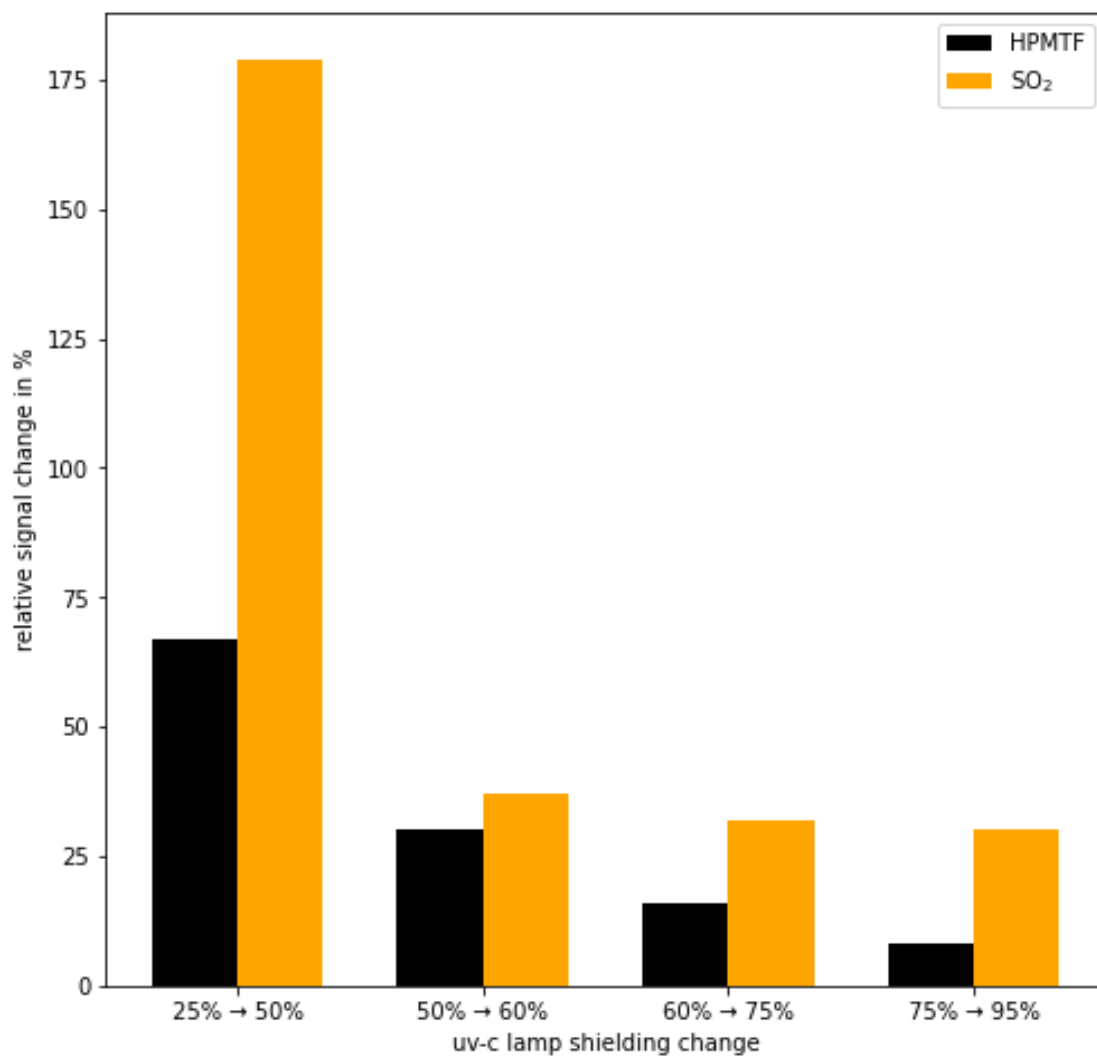


Figure 5.12: The relative signal change in % of HPMTF (black) and SO₂ (orange) for several UV-C lamp shielding changes under dry conditions.

Notably, the SO₂ yield [28 %, 35 %, 36 %, and 40 %] increases with increasing OH concentration due to more UV-C irradiation. Comparing the steady state with CO addition (95 % UV-C lamp opening) and without CO addition (75 % UV-C lamp opening), the DMS consumption was almost the same indicating the same OH concentration as already described earlier. As the SO₂ yield is also the same, it can be suggested that SO₂ yield is not sensitive to UV-C irradiation (photolysis).

The mechanism developed by Jacob et al. (2024) shows that HPMTF photolysis can lead to HOOCH₂S and OCH₂SCHO. While the first decomposition radical will likely lead to SO₂ (especially under the presence of O₃ or NO₂), the second will mainly result in OCS. There are also pathways which lead to OCS via HOOCH₂S but these are much slower and/or need additional O₃ or NO₂. According to literature, both photolysis channels of HPMTF have a rate constant in the order of magnitude of 10⁻⁶ s⁻¹. Up to date, there are no robust rate constants of HPMTF, therefore the rate constants used in models are based on structure similarities with MTF and CH₃OOH. The findings of this work support that HPMTF is likely photolyzed via its hydroperoxy group rather than its aldehyde group. However, as already said, such interpretations must be treated cautiously.

Additional processes may also influence these observations. Adding CO also leads to more HO₂ formation. The bimolecular reaction between MTMP and HO₂ competes with the isomerization reaction of MTMP (see more in subsection 5.5.4). Thus, elevated HO₂ concentrations due to CO addition (see Figure 5.10 panel e) could suppress HPMTF formation, thereby decreasing f_{isom} . Further investigations, including more calibrated datasets and the application of a comprehensive kinetic model, are necessary to evaluate these mechanisms in more detail. However, the increase in HO₂ due to the CO can not be assessed quantitatively since there is no HO₂ calibration available.

It should be noted that photolysis of HPMTF has likely minor contribution compared to photochemical loss process via reaction with e.g., OH radicals. According to literature, the photolysis rate is assumed to be a factor 10 slower than the reaction with OH.

Moreover, for many intermediates and substances, the surface uptake and consequently heterogeneous chemistry is a major loss process, which could be also influenced by changed

UV-C light intensity.

In addition to chemical loss processes and photolytic degradation, wall losses must also be considered when evaluating species lifetimes in the chamber. To assess these contributions, the UV-C lamps were switched off, and the signal decay of selected compounds, specifically HPMTF and SO₂, was monitored. The corresponding signal loss was analyzed under dry conditions, and is presented in Figure 5.13. The data are shown as logarithmically normalized signal of HPMTF (black circles) and SO₂ (orange circles) plotted against time, allowing for a clearer assessment of the first-order loss processes (linear behavior) attributable to wall interactions.

The normalized signals of HPMTF and SO₂ display a relatively good linear trend with a slope of $-3.2 \cdot 10^{-4} \text{ s}^{-1}$ and $-3.3 \cdot 10^{-4} \text{ s}^{-1}$ respectively, corresponding to a negligible effective wall loss as the dilution rate is $2.7 \cdot 10^{-4} \text{ s}^{-1}$. Low wall loss rates (HPMTF: $-5 \cdot 10^{-5} \text{ s}^{-1}$ and SO₂: $-6 \cdot 10^{-5} \text{ s}^{-1}$) can be explained by a fully equilibrated surface adsorption–desorption process

To improve the reliability of future measurements, dedicated sensitivity studies involving H₂O₂ should be conducted for species where direct calibration is not feasible. These studies can be performed by introducing controlled amounts of H₂O₂ into the instrument sampling lines, without altering the chamber chemistry.

The wall loss rates determined for SO₂ and HPMTF are much smaller than those rates of other relevant loss processes (chemical reaction with OH or dilution). Specifically, the loss of HPMTF due to reaction with OH radicals is estimated to be in the range of 10^{-5} - 10^{-4} s^{-1} , depending on the ambient OH concentration, while the photolysis rate is assumed to be approximately 10^{-6} s^{-1} . However, accurate quantification of wall losses is in any case essential for robust modeling of the chemical kinetics within the chamber. Neglecting or underestimating these wall interactions could lead to significant discrepancies between modeled and observed concentrations.

Switching off the UV-C lamps significantly alters the chamber conditions, notably leading to a rapid increase in H₂O₂ concentrations due to the absence of photolysis. This change in composition can affect the instrument sensitivity, contributing to the observed signal dynam-

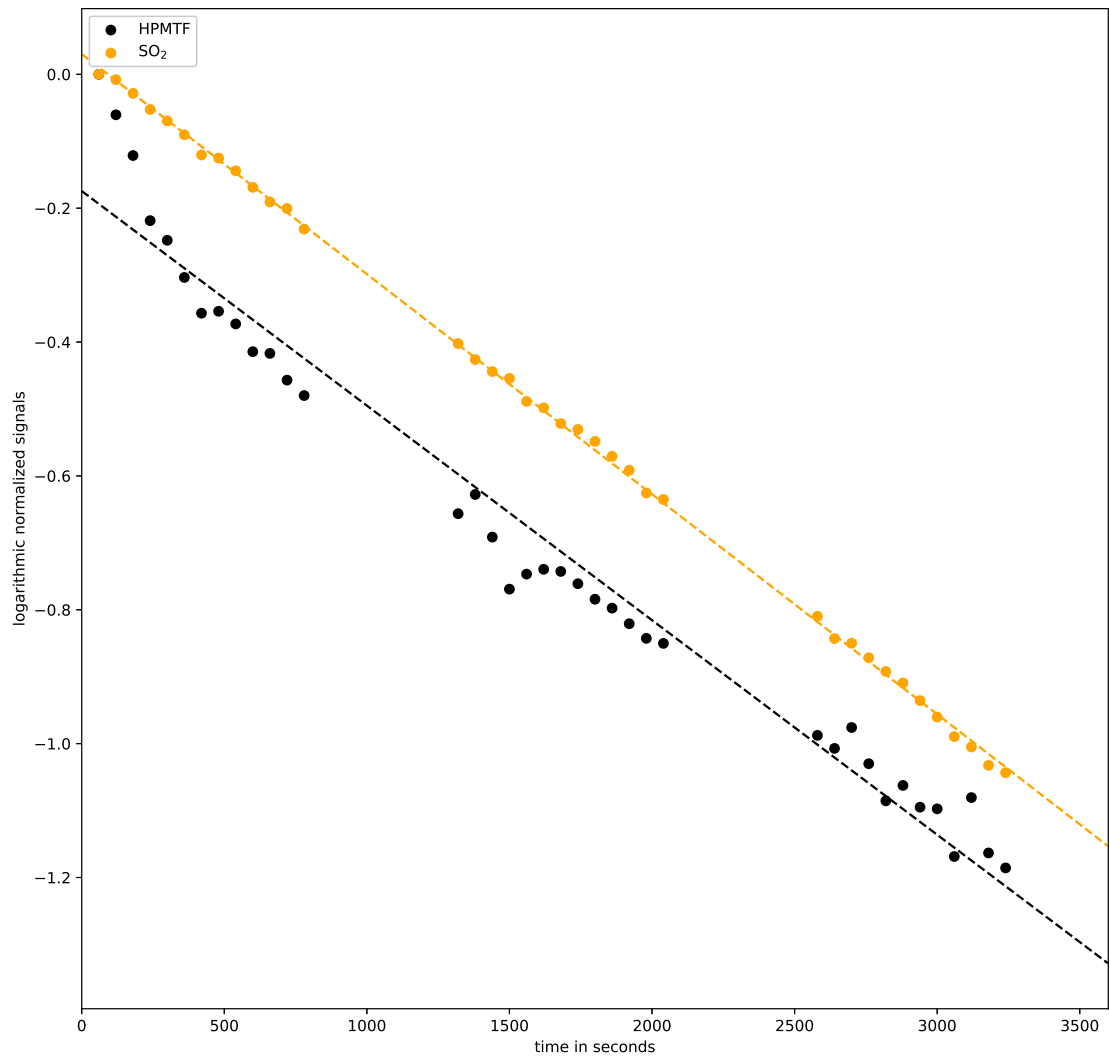


Figure 5.13: The logarithmic normalized signal of HPMTF (black) and SO₂ (orange) as a function of time since the lamp was turned off in seconds under dry conditions.

ics.

Indeed, a SO_2 sensitivity reductions of up to 25 % were observed, coinciding with the rise in H_2O_2 signal (cf. Figure 5.10). The impact of H_2O_2 on instrument sensitivity is further discussed in Section 5.4.2. Consequently, the normalized signal decay represents a combination of both wall loss and sensitivity-related effects. While sensitivity loss occurs more slowly than wall loss (by a factor of 5–10), it still follows an exponential decay (also apparent on a logarithmic scale), thus it might distort the expected linear trend. This could explain the non-linear behavior of HPMTF at the beginning of the decay in Figure 5.13.

To improve the reliability of future measurements, dedicated sensitivity studies involving H_2O_2 should be conducted for species where direct calibration is not feasible. These studies can be performed by introducing controlled amounts of H_2O_2 into the instrument sampling lines, without altering the chamber chemistry.

The FunMass instrument exhibits high sensitivity towards acids, particularly organic acids such as formic acid (HCOOH). Consequently, the detection of TFo, a possible degradation product of HPMTF (cf. Section 5.1), should be feasible, provided that its atmospheric lifetime is sufficiently long for it to be observed.

Figure 5.14 presents the time series of the normalized signals for HPMTF and TFo (detected via its fluoride cluster) under dry conditions.

A significant correlation between HPMTF and TFo signals is observed, suggesting that their formation pathways may be closely linked. This supports the hypothesis that TFo is either a direct decomposition product of HPMTF or that both compounds originate from a common precursor, such as MTMP. Moreover, the TFo signal saturates much faster which can be due to a faster formation process than HPMTF.

To validate the assumption that the detected compound is at least an organic acid, most likely TFo, a correlation analysis was performed between its fluoride cluster (81 Th) and the corresponding anion (61 Th). The resulting correlation plot (cf. figure 5.15) supports the identification of the compound as an acid, confirming its acidic character.

The correlation between TFo and HPMTF is also observed for the other experiments (high NO_x and NO_3 -initiated DMS oxidation).

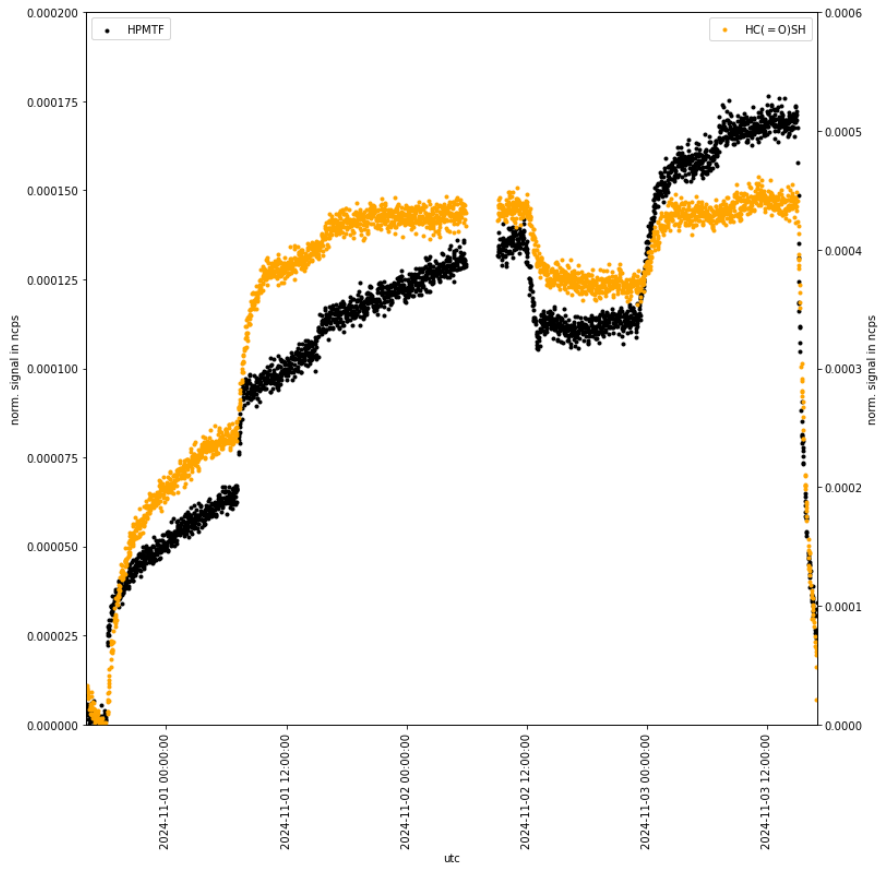


Figure 5.14: Time series of the normalized signals of HPMTF (black) and TFO (orange) in ncps under dry conditions.

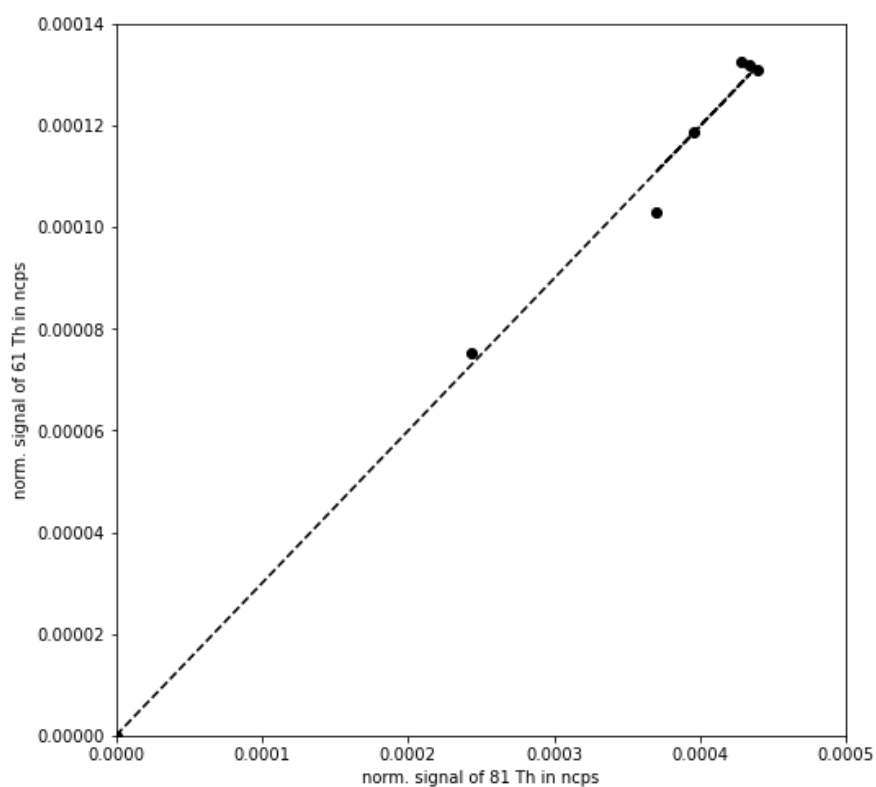


Figure 5.15: Correlation between the baseline-corrected normalized signal of 81 Th in ncps against the baseline-corrected normalized signal of 61 Th in ncps under dry conditions. Dashed line represents the linear fit ($y = mx$).

The simultaneous investigation of TFO, HPMTF, and OCS offers valuable insights into the complex and not yet fully elucidated atmospheric chemistry of HPMTF. In particular, TFO and formic acid (HCOOH) are proposed as the major products of heterogeneous HPMTF degradation. Thus, a better understanding of TFO formation mechanism could provide critical constraints for refining current mechanistic models of HPMTF processing in both gas and condensed phases.

A future objective will be to constrain the sensitivity of TFO detection using FunMass, in order to improve the reliability of its quantification and assess its atmospheric relevance more accurately.

5.5.2 Humidification

As a next step, the experiments were repeated humidifying the air to get more atmospherically realistic conditions (see figure 5.16). The relative humidity was set to approximately 30 % and 20 ppb DMS was injected to the chamber. The UV-C light opening was varied between 25 and 95 %.

Increasing relative humidity can enhance wall losses, as the formation of a thin water film on the chamber walls increases their affinity for polar species. Additionally, the presence of water vapor modifies the gas-phase and heterogeneous chemistry. For instance, H₂O plays a crucial role in the further oxidation of SO₂ to H₂SO₄, and it promotes heterogeneous reactions that are less significant under dry conditions. Consequently, changes in both product yields and signal intensities are expected.

Under humid conditions, a similar dependence on photon flux as observed under dry conditions is retained: increasing light intensity leads to enhanced DMS consumption and greater formation of HPMTF, OCS, and SO₂, as shown in Figure 5.16. This behavior is consistent with expectations. However, the quantification of DMS is associated with a high degree of uncertainty due to baseline fluctuations, with an estimated uncertainty of ± 3.2 ppb. This issue remains unresolved and propagates substantial uncertainties into the calculated yields of SO₂ and OCS. The induced large and asymmetric error margins preclude any meaningful quantitative interpretation, particularly in the case of OCS, for which yield analysis has

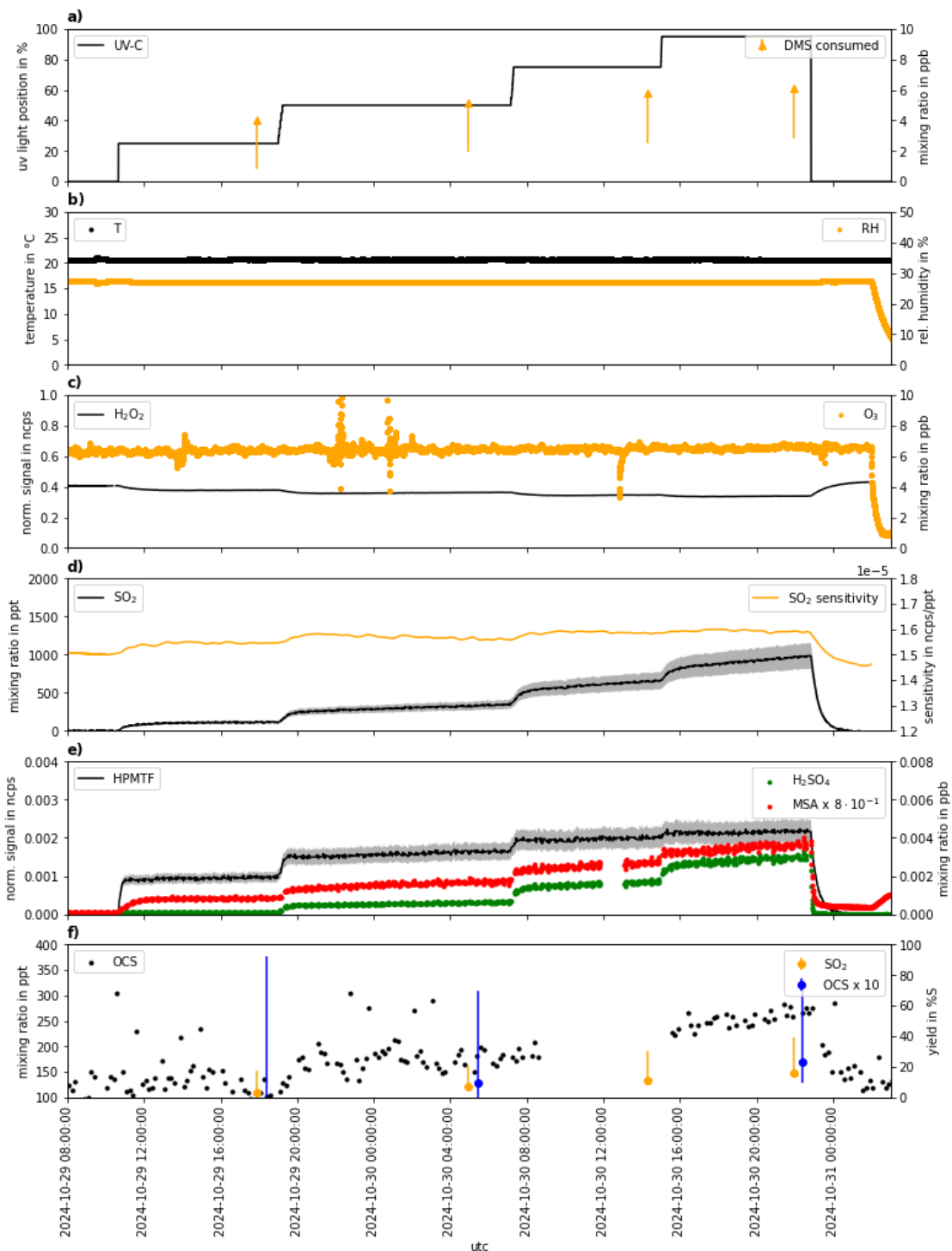


Figure 5.16: DMS oxidation under humid conditions in October 2024. **(a)** UV-C lamp opening (black; in %) and DMS consumption (orange; in ppb). **(b)** Temperature (black; in °C) and relative humidity (orange; in %). **(c)** Time series of H_2O_2 (black; in ppb, FunMass), O_3 (orange; in ppb), and CO (blue; in ncps). **(d)** SO_2 (black; in ppt; HCOOH -corrected) and its sensitivity (in orange, $\text{ncps} \cdot \text{ppt}^{-1}$), both measured by FunMass. **(e)** Normalized signal (in ncps) of HPMTF (black, FunMass), of H_2SO_4 (green, MION), and MSA multiplied by 0.8 (red, MION). **(f)** OCS (black; in ppt) and the yield of SO_2 (in %S) and OCS (in 10 · %S).

therefore been omitted.

Nonetheless, despite the uncertainties, a noticeable decrease in SO_2 yield is observed under humid conditions, with values up to 16 ± 24 %S lower than in the dry case. This could be in general agreement with the findings of Ye et al. (2022), who reported SO_2 yields in the range of 3–5 %S at 60 % relative humidity. Moreover, Ye et al. (2022) employed seed particles (NaCl or NaNO_3) to promote particle formation, which can enhance the uptake of gas phase species through heterogeneous processes and lead to additional losses via partitioning onto particles. The lower SO_2 yield under humid conditions may be attributed to increased wall uptake, enhanced heterogeneous conversion to sulfuric acid, and altered gas-phase chemistry.

Thus, the observed differences between dry and humid experiments, and also between the present humid experiment and that of Ye et al. (2022), are plausible and highlight the importance of considering and investigating both physical (e.g., wall interactions) and chemical (e.g., secondary oxidation pathways) changes introduced by water vapor in chamber studies.

A comparison of Figure 5.12 and Figure 5.17 reveals that increasing relative humidity does not significantly affect the relative signal change of HPMTF in response to variations in photon flux. This suggests that the overall dependence of HPMTF production and loss processes on photon flux remains largely unchanged under humid conditions, or that production and loss processes are influenced proportionally.

Additionally, it can be observed that the linear increasing trend of MSA observed under dry conditions has vanished. This suggests that humidification enables faster equilibration of (at least) MSA in the chamber. Moreover, the normalized signal is almost doubled. Taking into account the established DMS oxidation mechanism, humidification and with that corresponding enhanced heterogeneous chemistry can lead to more MSA formation. However, since these signals are not sensitivity shift - corrected, this interpretation should be treated cautiously.

The normalized H_2SO_4 signal measured by the MION instrument shows only a small increase compared to the dry conditions. Compared with the decrease in SO_2 , a larger increase was initially expected. However, as most of the SO_2 is likely lost on the walls and there converted heterogeneously to H_2SO_4 , it is possible that most of the formed H_2SO_4 stays

on the surfaces and hence, is not detected.

In contrast, SO_2 exhibits a noticeably different behavior under humid conditions compared to the dry case. The relative signal change decrease with increasing photon flux is less pronounced, indicating a shift in the balance between SO_2 formation and loss processes. Humidified air enhances OH radical production through increased UV-C-induced photochemistry, potentially resulting in a higher SO_2 formation rate that offsets or exceeds the rate of SO_2 loss under these conditions (e.g., more OH leads also to more HO_2). Alternatively, and more plausibly, humidity-dependent loss processes, such as heterogeneous uptake or conversion to H_2SO_4 , may reach saturation more quickly with increasing photon flux and with that correlating SO_2 formation (especially if the relative humidity is not large enough).

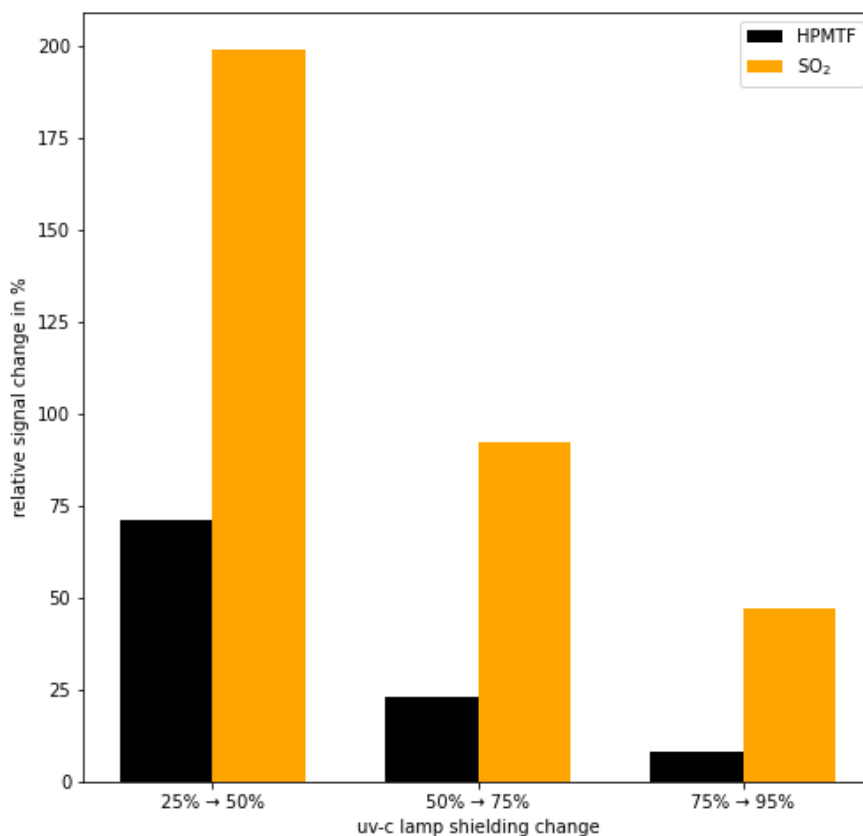


Figure 5.17: The relative signal change in % of HPMTF (black) and SO_2 (orange) for several UV-C lamp shielding changes under humid conditions.

As for the dry conditions, also the wall losses were investigated as shown in Figure 5.18. This results in nearly identical wall loss rates for HPMTF ($5.0 \cdot 10^{-4} \text{ s}^{-1}$) and SO_2 ($4.5 \cdot 10^{-4}$

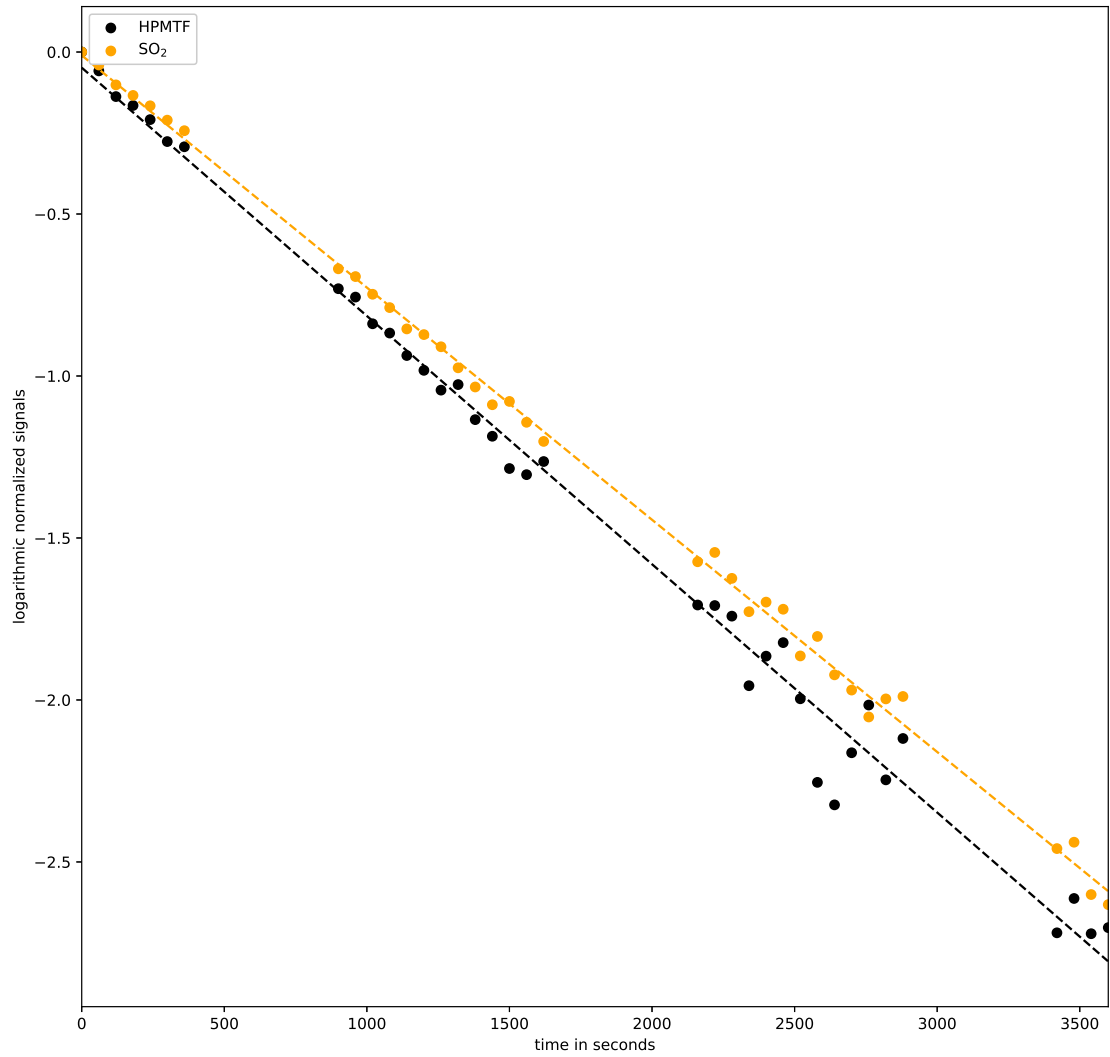


Figure 5.18: The logarithmic normalized signal of HPMTF (black) and SO₂ (orange) as function of the time since the lamp was turned off in seconds under humid conditions (RH = 30 %).

s^{-1}). Compared to the wall loss rates derived under dry conditions (HPMTF: $-5 \cdot 10^{-5} \text{ s}^{-1}$ and SO_2 : $-6 \cdot 10^{-5} \text{ s}^{-1}$). This is a significant increase in wall loss due to humidification.

In humidified conditions, the formation of a thin water film on the chamber walls can significantly affect the partitioning behavior of polar compounds. Such a layer can enhance the adsorption or dissolution of polar species. Consequently, these compounds may experience extended residence times on the walls, as reevaporation becomes less favorable compared to dry conditions. In addition, heterogeneous chemical processes can further contribute to the degradation of wall-deposited substances. The decomposition of a compound within the aqueous layer drives continued uptake from the gas phase, thus amplifying wall loss beyond that expected from physical partitioning alone. Given the water solubility and polar character of both HPMTF and SO_2 , their wall losses increase with rising humidity and water vapor concentrations. Furthermore, acidification of the chamber walls under humidified conditions may also play a significant role in enhancing these wall loss processes (Vereecken et al., 2025).

The surface loss tends to have a major impact on the yields. The humidification experiment was redone, also to investigate the CO addition under humid conditions, four days later after the experiment under dry conditions in November 2024. The wall loss rates changed to $1.28 \cdot 10^{-4} \text{ s}^{-1}$ (HPMTF) and $2.01 \cdot 10^{-4} \text{ s}^{-1}$ (SO_2). This results in larger SO_2 yields under humid conditions of 48 S%, with a range due to uncertainties of between 33 and 71 S%. This loss rates are smaller compared to the losses measured in the first humidified experiment in October 2024. Moreover, these yields also exceed the 35 S% for SO_2 under the same UV-C light intensity (60 %) in October 2024, which is likely due to the decreased loss rates. This was not anticipated and is not in agreement with the current literature-based mechanism. The time series of the second humidified experiment (November 2024), as shown in Figure 5.20, indicates that the SO_2 signal of FunMass might not have established its equilibrium and hence, larger SO_2 yields are calculated. The only difference between the two experiments was the experiment under dry conditions carried in between the both experiments under humid conditions. That could result in changed surfaces (new conditioning of the chamber walls). Moreover, the time how long the surfaces are exposed to the certain trace gases (as HPMTF or SO_2) under certain conditions can play a crucial role in the surface conditioning.

In Figure 5.19, the wall loss rates of SO₂ over the time period of the experiments are shown. The wall loss rates decrease during the DMS oxidation experiments conducted in 2024 and reach values well below $2.7 \cdot 10^{-4} \text{ s}^{-1}$ (dilution rate). Consequently, wall losses are primarily relevant at the beginning of an experimental series and appear to become negligible over time.

As long as experimental conditions remain constant, the wall loss rates decrease as the chamber surfaces gradually equilibrate with the chemical species present during the experiments. However, substantial changes in experimental conditions may alter this behaviour. For example, the pronounced increase in the wall loss rate between 3rd November (dry conditions) and 4th November (humid conditions) suggests that the addition of water vapour affected the surface processes. Similar behaviour has also been reported for other experimental series conducted in the SAPHIR-STAR chamber. Also in experiments, where the relative humidity was kept constant, the wall losses decrease to an order of magnitude of 10^{-5} s^{-1} or even smaller (source: private communication).

These aspects should be considered in future studies to improve experimental reproducibility. In particular, wall loss rates should be assessed for each experiment, especially when significant changes in conditions that may influence chamber surfaces are introduced.

During the campaign in 2023, the dependency of the relative humidity on the CIMS HPMTF sensitivity was investigated. The lamp opening, temperature, and DMS injection was held constant and only the relative humidity was increased gradually (shown in Figure 5.21).

The NO₃⁻, I⁻, and CF₃O⁻-based CIMS instruments show an increase in HPMTF sensitivity with increasing relative humidity. However, all three exhibit a saturation effect at higher humidity levels (see Figure S6.1). The largest relative increase is observed for the NO₃⁻ mode of the MION, where the HPMTF signal is enhanced by a factor of 10 at 60 % relative humidity. In contrast, the I⁻ and CF₃O⁻-based CIMS signals increase by factors of approximately 4 and 3, respectively. Notably, the Br⁻ mode of the MION shows a substantial decrease in HPMTF sensitivity, with signal suppression up to a factor of 33 at 60 % relative humidity. This decrease is likely due to the high sensitivity of the Br⁻ mode to elevated con-

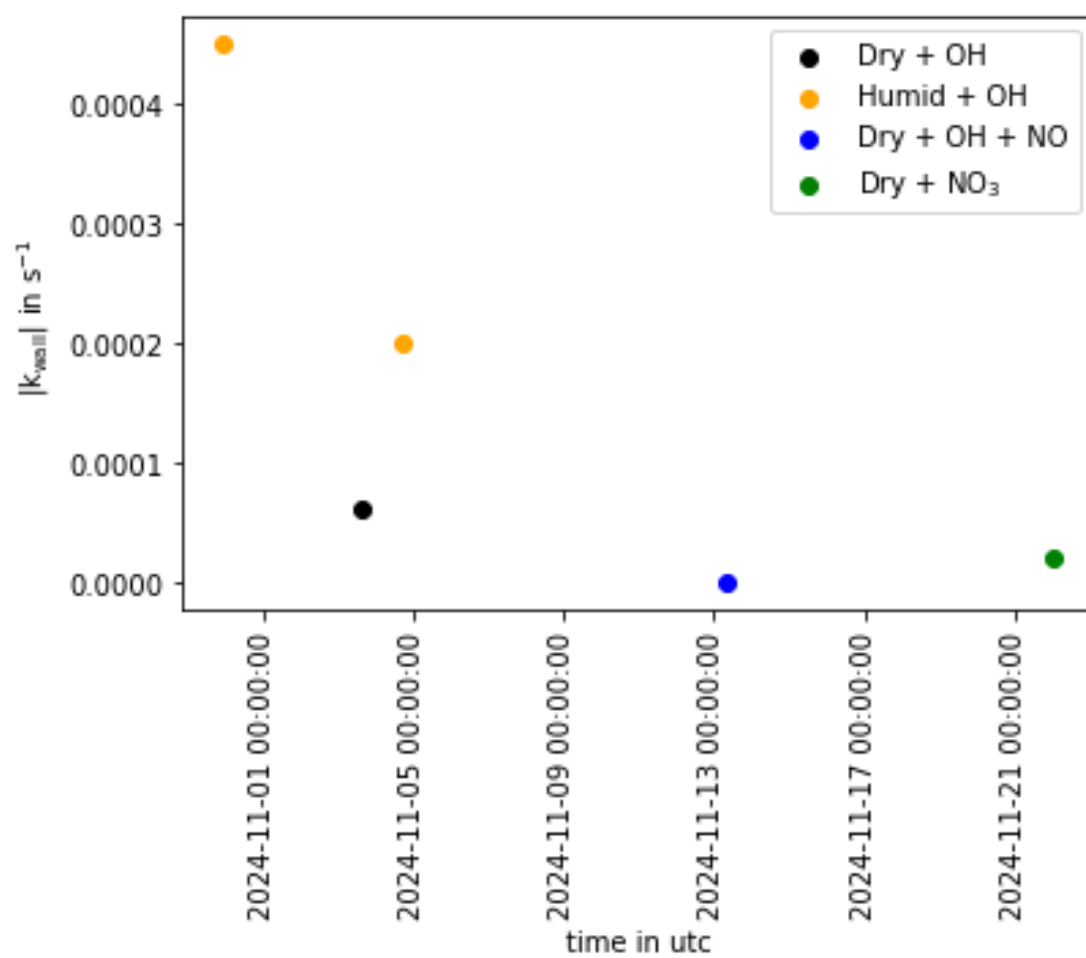


Figure 5.19: The time series of the SO₂ wall loss rates k_{wall} in s^{-1} for the several conditions: dry + OH (black), humid + OH (orange), dry + OH + NO (blue), and dry + NO₃ (green).

5.5. RESULTS

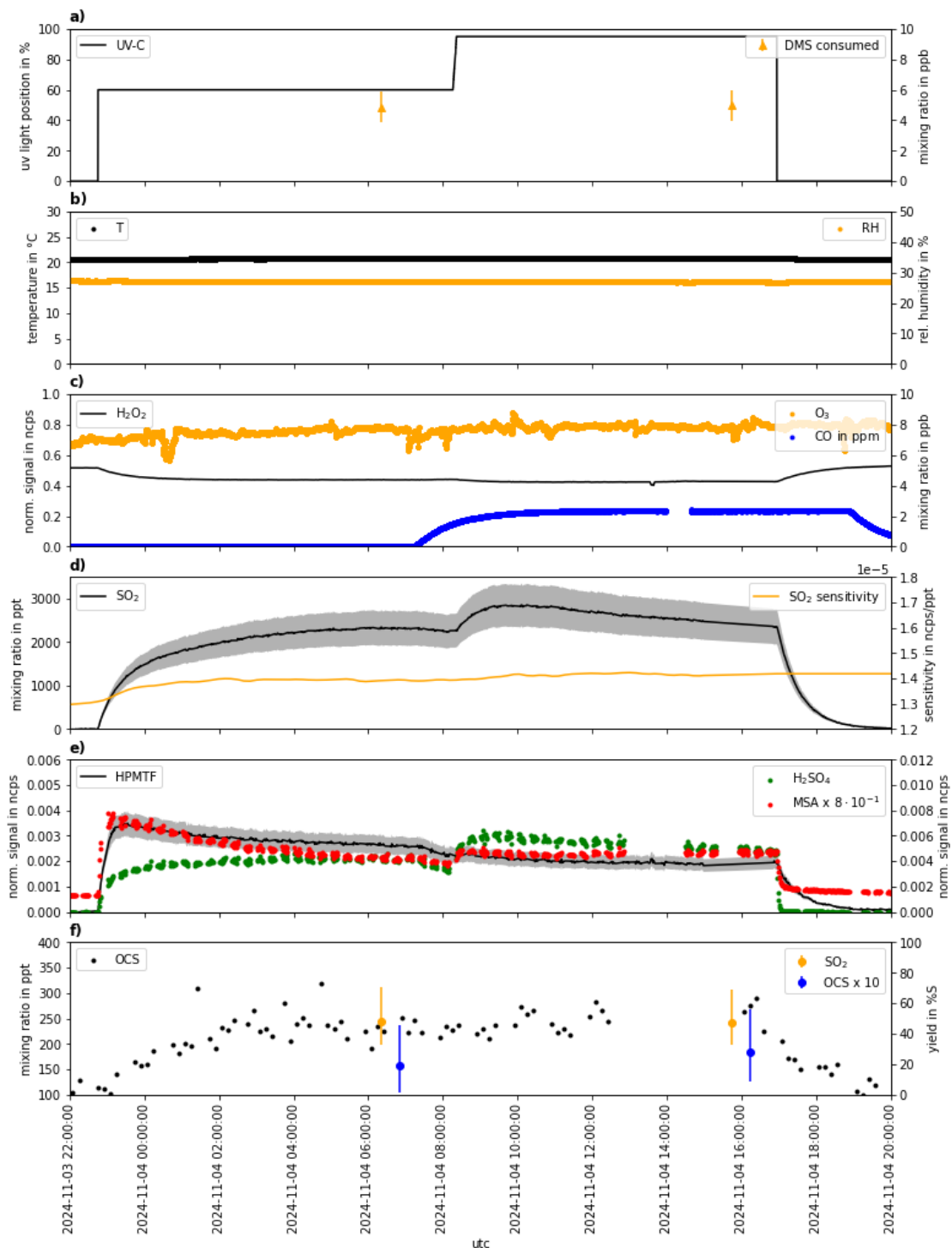


Figure 5.20: DMS oxidation under humid conditions in November 2024. **(a)** UV-C lamp opening (black; in %) and DMS consumption (orange; in ppb). **(b)** Temperature (black; in °C) and relative humidity (orange; in %). **(c)** Time series of H_2O_2 (black; in ppb, FunMass), O_3 (orange; in ppb), and CO (blue; in ncps). **(d)** SO_2 (black; in ppt; HCOOH-corrected) and its sensitivity (in orange, $\text{ncps} \cdot \text{ppt}^{-1}$), both measured by FunMass. **(e)** Normalized signal (in ncps) of HPMTF (black, FunMass), of H_2SO_4 (green, MION), and MSA multiplied by 0.8 (red, MION). **(f)** OCS (black; in ppt) and the yield of SO_2 (in %S) and OCS (in $10 \cdot \text{S}$).

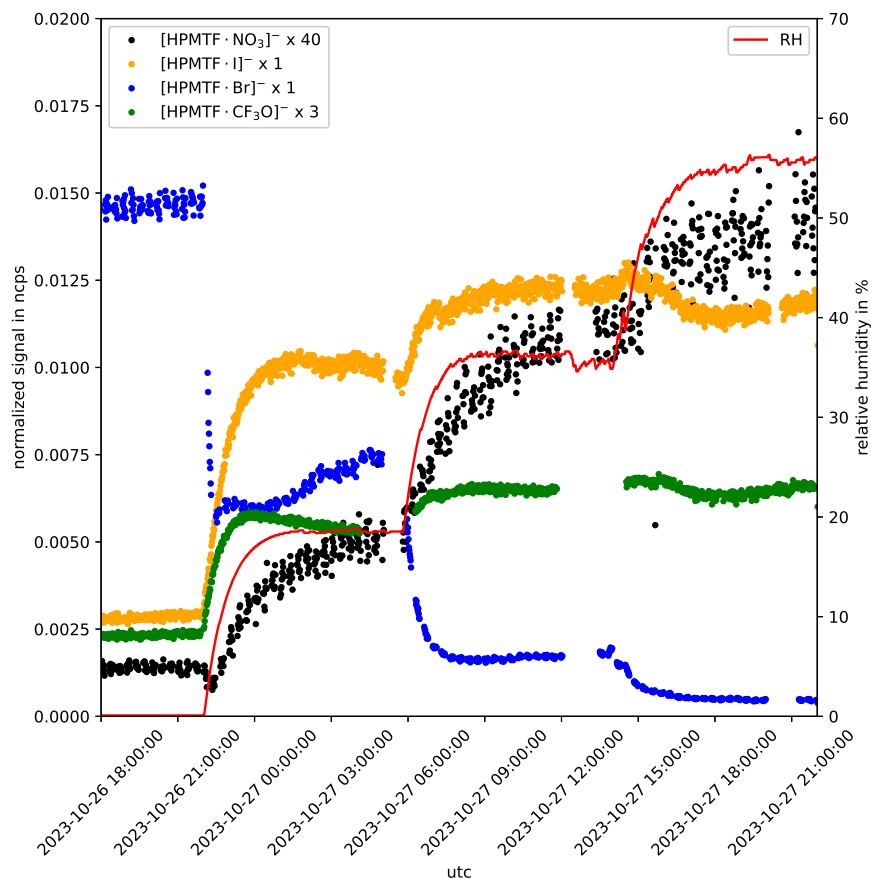


Figure 5.21: The normalized signal of HPMTF using the MION NO₃⁻ mode (in black; 40 · ncps), HToF I⁻ mode (in orange; ncps), MION Br⁻ mode (in blue; ncps), and FunMass CF₃O⁻ (in green; 3 · ncps) during the DMS oxidation campaign in 2023 for various relative humidity levels set (0, 20, 40, and 60 %) . Additionally, the relative humidity in the chamber (in %) is shown in red.

5.5. RESULTS

centrations of interfering trace gases such as water vapor, O_3 , and nitric acid (HNO_3); the latter is discussed in more detail in subsection 5.5.3.

To exclude that this effect is caused by a baseline shift while increasing the relative humidity, DMS was shut off and the relative humidity was incrementally decreased (60, 40, 20, 10, and 0 %) to investigate the behavior of the HPMTF signal (shown in Figure S6.2). The baseline increases by a few percent, which cannot explain the signal increase.

Moreover, a similar HPMTF signal trend is observed for the two CIMS operated with an IMR under low-pressure conditions, compared to the NO_3^- - based MION operated at atmospheric pressure. This suggests a pressure dependence in the ion–molecule reaction kinetics or clustering behavior relevant to HPMTF detection with certain reagent ions. This effect is further examined in subsection 5.5.3.

A positive effect of water vapor on analyte sensitivity is not unusual and has been observed previously (e.g., Crounse et al., 2006). However, within the FunMass system, HPMTF is the first species to exhibit such humidity-dependent behavior (see subsection 4.10.1). Since this response was unprecedented for FunMass and potential chamber-related effects, such as altered gas-phase and/or heterogeneous chemistry or surface interactions, could not be entirely excluded, an additional test was conducted during a dry experiment in 2024. In this test, the relative humidity at the FunMass inlet was systematically varied while in the chamber steady-state condition was held for longer time (to ensure stable HPMTF concentration). Unfortunately, no space was available in SAPHIR-STAR for deploying the dedicated water vapor instrument of the FunMass group, so it is relied on the internal water vapor signal of FunMass as a proxy for relative humidity. This approach is suboptimal for two reasons: first, the water vapor signal in FunMass exhibits linearity only up to approximately 300–500 ppm; second, the signal is strongly influenced by the H_2O_2 concentration, which differed between the two campaigns. Consequently, the results from this test should be interpreted solely as a qualitative assessment.

Figure 5.22 illustrates the relative sensitivity change of HPMTF measured by the CF_3O^- CIMS (FunMass) as a function of the normalized water vapor signal (in ncps). The data includes results from the chamber experiment in 2023 with varying relative humidity (in

black), as well as from the 2024 dry steady state experiment, in which the relative humidity was altered directly at the FunMass inlet (in orange).

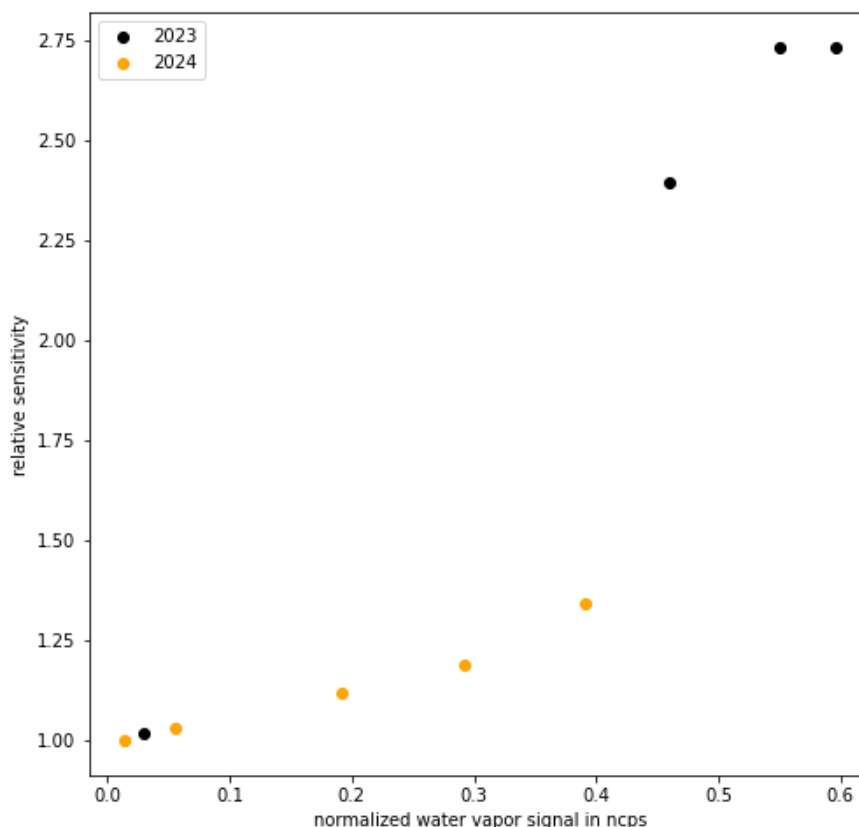


Figure 5.22: The relative sensitivity of HPMTF using the FunMass CF_3O^- - CIMS for the chamber experiment in 2023 (black) and the water vapor addition to the inlet flow of FunMass in 2024 as function of the normalized water vapor signal in ncps.

It can be observed that the relative sensitivity increases by up to 34 % with increasing water vapor content when water vapor is added solely to the FunMass inlet. This suggests that water vapor indeed enhances the formation of the $[\text{HPMTF} \cdot \text{CF}_3\text{O}]^-$ cluster under high H_2O_2 conditions. However, it is important to note that this effect must not be observed under completely dry conditions — i.e., in the absence of several hundred ppb of H_2O_2 , as would be more typical in the atmosphere. Therefore, a potential interaction between H_2O_2 and water vapor influencing HPMTF sensitivity cannot be ruled out. With increasing water vapor concentration, a rearrangement of the four major CF_3O^- clusters ($[\text{CF}_3\text{O}]^-$, $[\text{H}_2\text{O} \cdot \text{CF}_3\text{O}]^-$, $[\text{HF} \cdot \text{CF}_3\text{O}]^-$, and $[\text{H}_2\text{O}_2 \cdot \text{CF}_3\text{O}]^-$) is also observed, potentially altering the overall

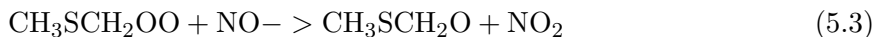
formation rate of the $[\text{HPMTF} \cdot \text{CF}_3\text{O}]^-$ cluster resulting in an enhanced signal.

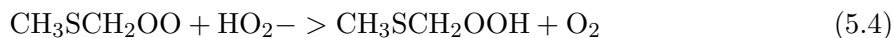
Unfortunately, the water vapor supply from the calibration rack could not provide sufficiently high mixing ratios under the setup used during the campaign (e.g., main flow set to 5 SLM), preventing an overlap in water vapor signal between the 2023 and 2024 experiments. As a result, a potential chamber effect on the HPMTF signal cannot be entirely excluded. Nevertheless, the observed sensitivity changes with increasing relative humidity were clearly demonstrated. Both scenarios remain plausible: a strong sensitivity increase at normalized water vapor signals above 0.4 ncps or additional chamber effects contributing to the observed signal enhancement.

5.5.3 NO Addition

The competition between the two reaction pathways of MTMP, isomerization (reaction 5.5) and bimolecular reactions (reactions 5.3 and 5.4), has been discussed extensively in previous studies (Wu et al., 2015; Berndt et al., 2019; Veres et al., 2020; Jernigan et al., 2022b; Ye et al., 2021, 2022; Assaf et al., 2023) as well as in previous sections of this work. Due to the large uncertainty in the isomerization rate constant ($k_{\text{isom}} = 0.04\text{--}2.1 \text{ s}^{-1}$) and the strong variability of NO and HO₂ concentrations depending on the environment, predicting the branching behavior of MTMP in both pristine and polluted regions remains challenging, particularly in areas influenced by anthropogenic emissions (Ye et al., 2022).

In this section, the effect of NO addition (and consequently, NO_x) is investigated to simulate conditions in polluted environments. It has been shown that HPMTF reacts with both NO and HO₂, ultimately leading to a shared reaction mechanism. While the HO₂ channel forms an additional intermediate—methylthioformate (MTF), which decomposes into the CH₃S radical, the subsequent reactions converge with the NO pathway, as described in Ye et al. (2022) and shown in Figure S6.3. The dominant products resulting from these mechanisms are MSA and SO₂. Both trace gases are important for aerosol formation and therefore, this channel is crucial to be understood better.





In Figure 5.23, the key species and parameters associated with the NO addition experiment conducted in 2023 are presented. During this experiment, the signals of HPMTF, TPA, and TFA were obtained using the I^- - CIMS, as NO addition effectively suppresses the Br^- - CIMS signal. MSA and H_2SO_4 were detected using the NO_3^- mode of the MION instrument, while SO_2 and H_2O_2 were monitored by FunMass. Due to instability in the H_2O_2 supply within the chamber, the final step involving the injection of 30 ppb NO is considered invalid and was thus excluded from the analysis.

As NO is incrementally added, resulting in elevated NO_x levels, a corresponding increase in SO_2 , MSA, and H_2SO_4 concentrations is observed, consistent with previous studies (Jernigan et al., 2022a; Ye et al., 2021, 2022; Jacob et al., 2024). Specifically, SO_2 concentrations increase by up to a factor of 2.5 when comparing baseline conditions (no NO addition and UV-A light) with 20 ppb NO injection. MSA and H_2SO_4 signals increase by factors of approximately 4 and 7, respectively. However, these enhancements should be interpreted with caution, as no instrument calibration was performed for MSA and H_2SO_4 , and NO injection may have influenced sensitivity through secondary effects such as HNO_3 formation, which can alter ion chemistry in the MION (e.g., the Br^- mode is rendered inoperative under NO-rich conditions).

The signal intensities of HPMTF and its decomposition products (TPA and TFA) remain largely stable but show a slight decline at the 20 ppb NO level. While this may initially appear counterintuitive, the critical parameter is not the amount of NO injected, but rather the concentration of NO available for reaction with HPMTF. This effective NO concentration is challenging to determine without a detailed chemical model, owing to complex gas-phase and heterogeneous processes, including wall interactions. Therefore, the steady-state NO mixing ratio is used as a proxy for NO availability. For an injection of 20 ppb NO, the measured steady-state concentration is only 0.5 ppb. Consequently, the absence of a significant HPMTF

5.5. RESULTS

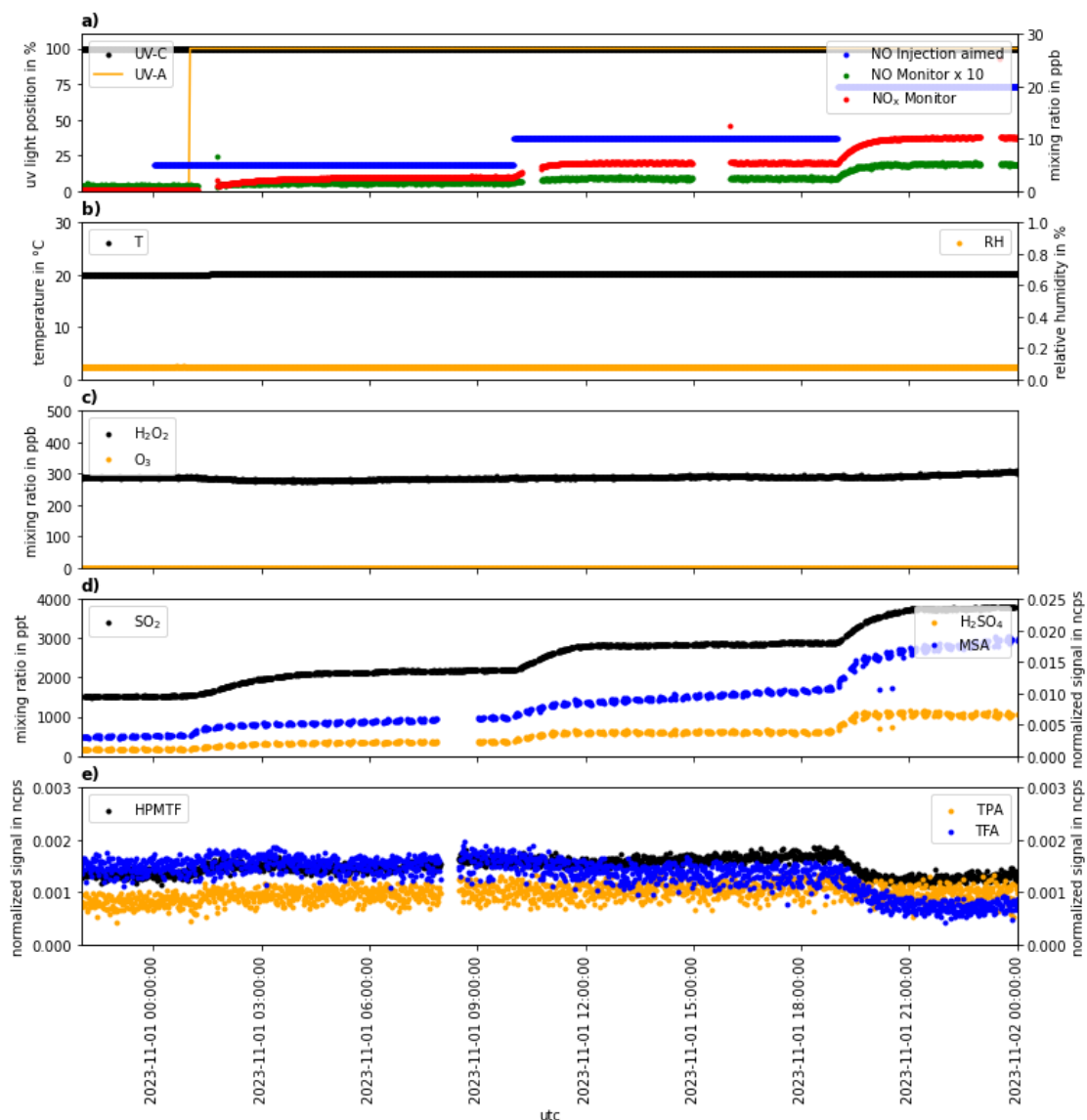


Figure 5.23: DMS oxidation adding NO in 2023. (a) UV-C lamp opening (black; in %), UV-A lamp opening (orange; in %), NO injection aimed (blue; in ppb), NO monitor (green; in $10 \cdot \text{ppb}$), and NO_x monitor (red; in ppb). (b) Temperature (black; in $^{\circ}\text{C}$) and relative humidity (orange; in %). (c) Time series of H_2O_2 (black; in ppb), O_3 (orange; in ppb), and HO_2 measured by the Br^- mode of the MION (blue; in ncps). (d) SO_2 measured by FunMass (black; in ppt), H_2SO_4 (orange; in ncps), and MSA (blue; in ncps) measured by the NO_3^- mode of the MION. (e) Normalized signals (in ncps) of HPMTF (black), thioperformic acid (TPA; orange), and thioformic anhydride (TFA; blue) using the I^- - CIMS.

decrease at lower NO additions (5 and 10 ppb) may be justifiable.

Another possible explanation for the observed stability in the HPMTF signal is a compensatory increase in detection sensitivity or the occurrence of isobaric interferences. For instance, formation of N_2O_5 during high NO_x conditions could potentially overlap with the HPMTF signal. While a change in sensitivity cannot be conclusively ruled out due to the absence of supporting calibration data, isobaric interference is considered unlikely. Apart from N_2O_5 , no significant interfering species are known under high NO_x conditions. Furthermore, most N_2O_5 formed is expected to undergo rapid photolysis under the chamber's UV-A and UV-C illumination, making its detection during the experiment improbable. Additional discussion on potential isobaric interferences of N_2O_5 is provided later in this subsection.

Unfortunately, no DMS data are available for this experiment due to calibration issues.

Nevertheless, the observed increase in SO_2 production, likely accompanied by elevated MSA and H_2SO_4 formation, can be explained by enhanced OH radical recycling resulting from NO addition. The presence of NO can effectively increase the OH concentration by a factor of 2 - 5. This elevated OH concentration would lead to an increased DMS oxidation rate. However, the simultaneous reaction of NO with MTMP through bimolecular pathways may suppress the formation of HPMTF by diverting reactive intermediates away from the isomerization channel.

At higher NO and NO_2 concentrations, competing reactions can also lead to net OH consumption via the formation of HONO and HNO_3 , with the latter primarily lost to chamber surfaces. The formation of both species can also be observed by FunMass (see Figure S6.4). Additionally, the presence of NO may alter the loss mechanisms of HPMTF, particularly with respect to heterogeneous processes such as wall losses.

To resolve these uncertainties and quantitatively assess the impact of NO on the observed chemical pathways, a detailed modeling study using the SAPHIR-STAR model of ICE-3 is necessary. The model should be optimized against the available calibrated data and high-resolution time series. Without such modeling efforts, further interpretation remains speculative due to the lack of DMS and other supporting measurements.

Figure 5.24 shows the comparison of the four reagent ion schemes under various NO

injections levels.

At first glance, the MION data appear reasonable, as both the NO_3^- and Br^- modes exhibit a rapid decrease in the HPMTF signal with increasing NO injection, which aligns with expected chemical behavior. However, upon closer inspection, this response, particularly in the Br^- mode, can largely be attributed to interference from other trace gases, such as HNO_3 , rather than reflecting a true change in HPMTF concentration. Consequently, measurements from the Br^- -CIMS cannot be considered reliable under these conditions.

Similarly, the NO_3^- mode warrants scrutiny. Notably, signal intensities related to HNO_3 increase significantly with NO injection. Voltage scanning analyses of the MION, carried out by ICE-3, revealed that the binding energy of the $[\text{HPMTF}\cdot\text{NO}_3]^-$ cluster is substantially lower than that of other species such as HNO_3 , MSA or H_2SO_4 (source: private communication). This weaker cluster stability is consistent with the generally low HPMTF sensitivity observed in the NO_3^- mode. The increasing concentration of strong acids combined with the high collision frequency at atmospheric pressure likely promotes declustering of $[\text{HPMTF}\cdot\text{NO}_3]^-$, resulting in an apparent sensitivity loss.

Given that two independent CIMS instruments operating with an IMR under reduced pressure conditions, namely FunMass and the I^- HTof of ICE-3, yielded comparable HPMTF responses (trend), their monitored HPMTF time series are considered to be more likely for the NO addition experiments compared to the MION HPMTF data. Nevertheless, minor sensitivity changes or isobaric interferences in both the I^- -CIMS and FunMass instruments during NO injection cannot be completely ruled out as the HPMTF signal increases slightly. However, here also more OH could be the reason. This should be addressed in future investigations (e.g., model or experimental).

Based on the current dataset, atmospheric-pressure CIMS (e.g., MION) are not recommended for the quantitative detection of HPMTF under conditions involving high NO or NO_x levels. IMR-based CIMS instruments—particularly those operating with I^- or CF_3O^- reagent ions—demonstrate higher reliability and are better suited for such measurements across a broader range of environmental conditions.

In 2024, this experiment was redone as shown in Figure 5.25. The I^- -CIMS was unfor-

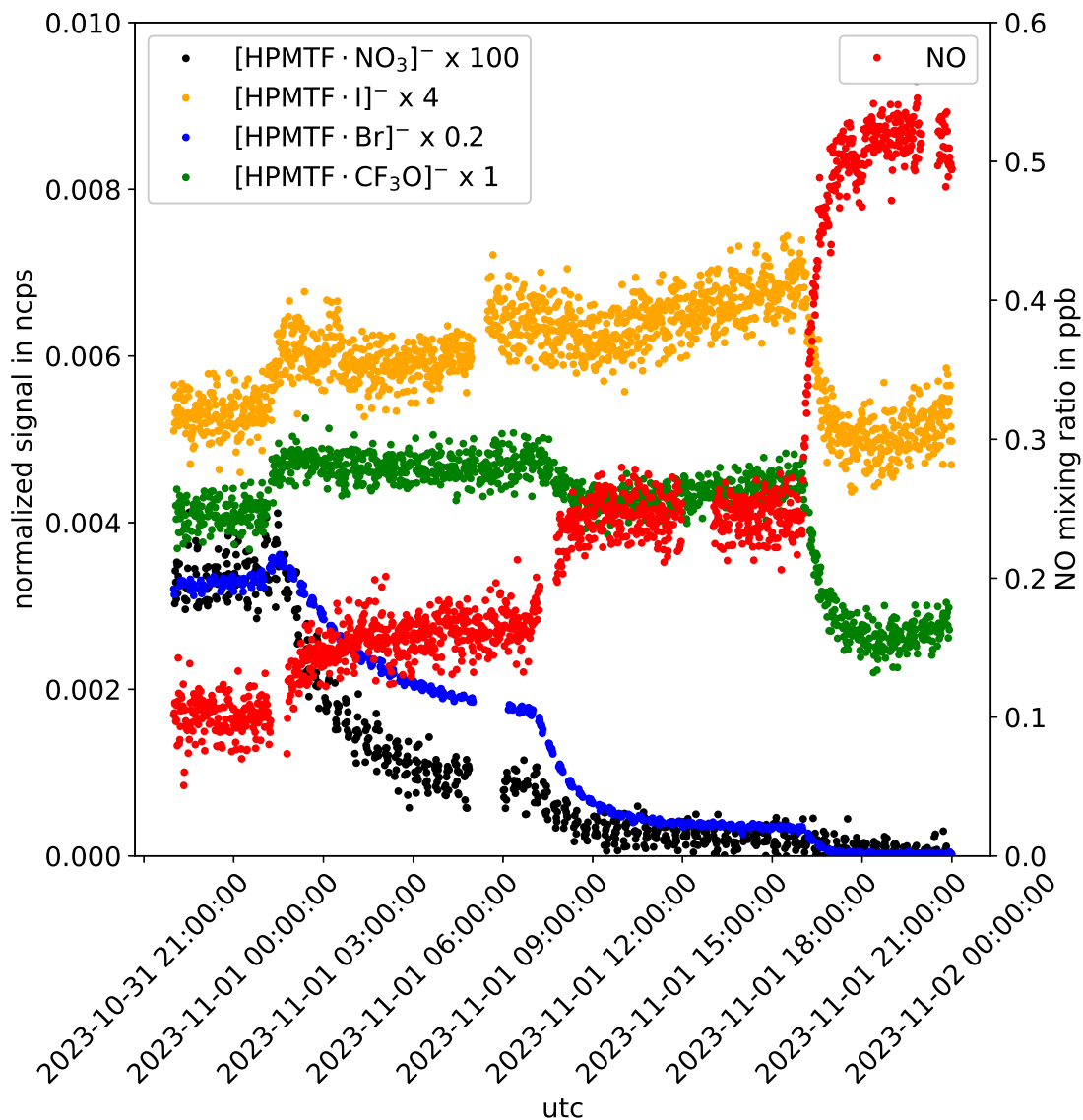


Figure 5.24: Time series of the normalized HPMTF signals measured by NO₃⁻ mode MION (black; 100 · ncps), I⁻ HToF (orange, 4 · ncps), Br⁻ mode MION (blue, 0.2 · ncps), and CF₃O⁻ FunMass (green; 1 · ncps) during the DMS oxidation campaign in 2023 for various NO injections (0, 5, 10, and 20 ppb). Additionally, the NO in the chamber (in ppb) is shown in red.

tunately not available and the NO monitor was not operational.

The results obtained from the 2024 experiments confirm the main findings from the 2023 campaign.

The SO₂ mixing ratios are in good agreement with those observed in 2023 under comparable experimental conditions, supporting the reproducibility of the measurement. In contrast, no significant change in the HPMTF signal is observed due to the relatively small amount of NO injected. Notably, the apparent increase in HPMTF signal following the addition of 10 ppb NO is not considered to reflect a true concentration change but is instead attributed to a sensitivity shift. This shift results from a sudden decrease in H₂O₂ levels by a few percent (see Figure 5.25, panel c), which is also reflected in a corresponding increase in the SO₂ sensitivity (panel d).

Applying a rough correction by scaling the HPMTF signal using the relative change in SO₂ sensitivity due to the H₂O₂ drop yields an adjusted HPMTF signal comparable to that observed at 5 ppb NO. This adjusted value aligns well with the results from the 2023 experiments, further supporting the consistency of the observations across both campaigns.

The NO addition experiments again reveal that the MSA signal exhibits a slow drift over time, making its quantification under these conditions uncertain.

The increased consumption of DMS observed during this experiment compared to the low-NO_x experiment can be attributed to the elevated H₂O₂ levels, which result in enhanced OH radical formation (cf. Panels c of Figures 5.10 and 5.25). The higher oxidation capacity subsequently leads to increased production of secondary trace gases, including SO₂, compared to the dry reference case. However, the SO₂ yield remains within the same range as under dry conditions, between approximately 30 - 36 % [21 - 49 %]. Upon the addition of 10 ppb NO, a slight increase in SO₂ yield (+3 - 5 %) and no change in OCS yield are observed. These variations lie within the experimental uncertainty and may partially result from the observed decline in H₂O₂, which is not accounted for in the DMS calibration and is expected to influence DMS sensitivity.

The introduction of NO may promote OH recycling, thereby enhancing the overall DMS oxidation rate. Consequently, not only the DMS consumption but also the concentrations of

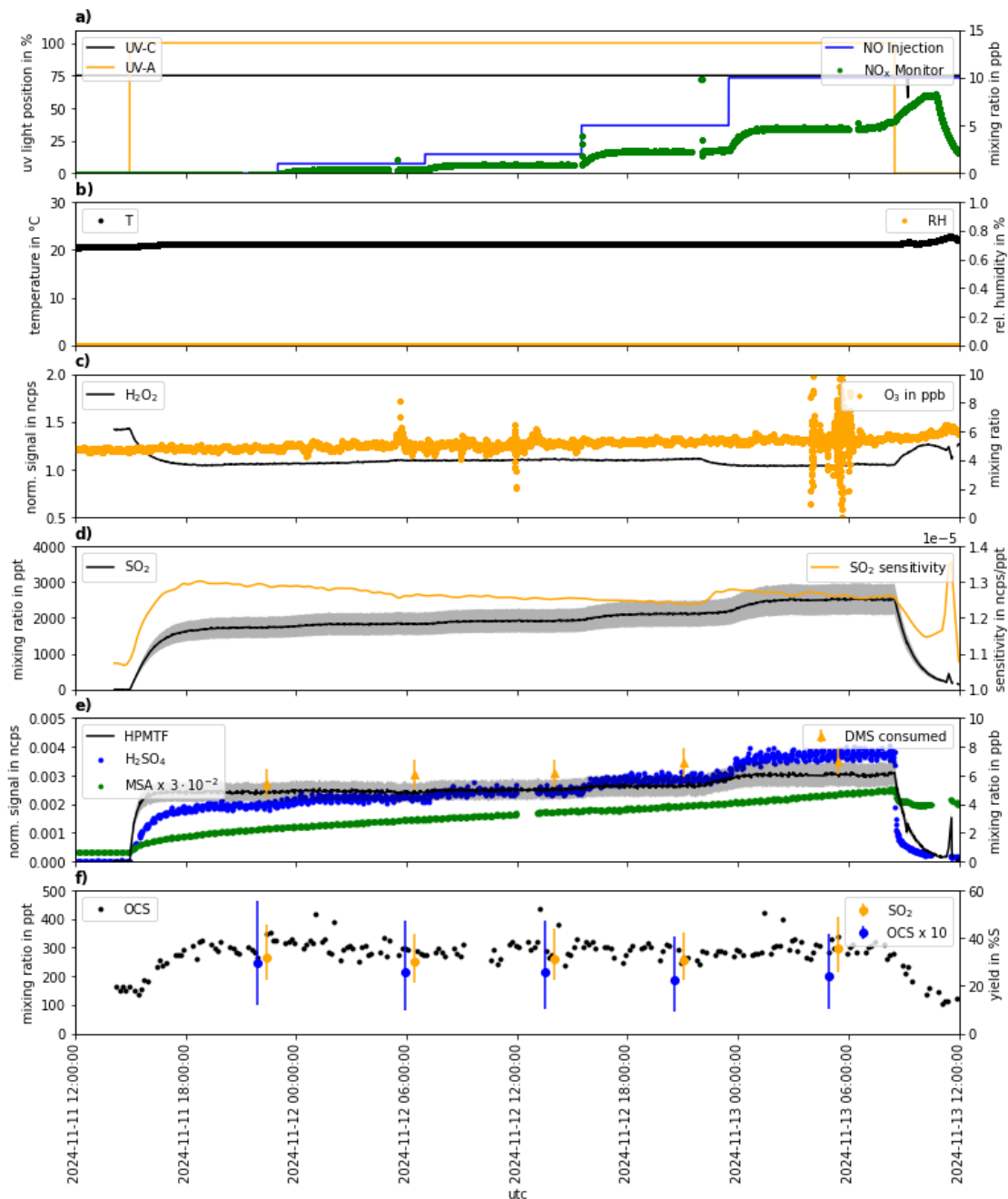


Figure 5.25: DMS oxidation adding NO in 2024. (a) UV-C lamp opening (black; in %), UV-A lamp opening (orange; in %), NO injection aimed (blue; in ppb), and NO_x monitor (green; in ppb).. (b) Temperature (black; in °C) and relative humidity (orange; in %). (c) Time series of H₂O₂ (black; in ppb), O₃ (orange; in ppb), and CO (blue; in ncps). (d) SO₂ (black; in ppt) and its sensitivity (orange, ncps · ppt⁻¹). (e) Normalized signal (in ncps) of HPMTF (black, FunMass), H₂SO₄ (blue; MION), and MSA multiplied by $3 \cdot 10^{-2}$ (green; MION), and the DMS consumption (orange; in ppb). (f) OCS (black; in ppt) and the yield of SO₂ (orange; in %S) and OCS (blue; in 10 · %S).

oxidation products such as SO_2 , H_2SO_4 , and to a lesser extent HPMTF, are elevated.

N_2O_5 is a well-known isobaric interference of HPMTF frequently discussed in the literature. To assess and potentially exclude its influence during NO addition experiments, a dedicated control experiment was conducted under ideal N_2O_5 formation conditions. Specifically, 150 ppb O_3 was introduced to the chamber, followed by incremental additions of 5, 10, and 20 ppb NO (shown in Figure 5.26). The experiment was performed in the dark and under H_2O_2 -free conditions to prevent OH radical formation and photolysis of N_2O_5 . This setup was chosen to closely mimic the NO concentration ranges applied in previous experiments investigating the influence of NO_x on DMS oxidation and NO_3 -initiated DMS oxidation.

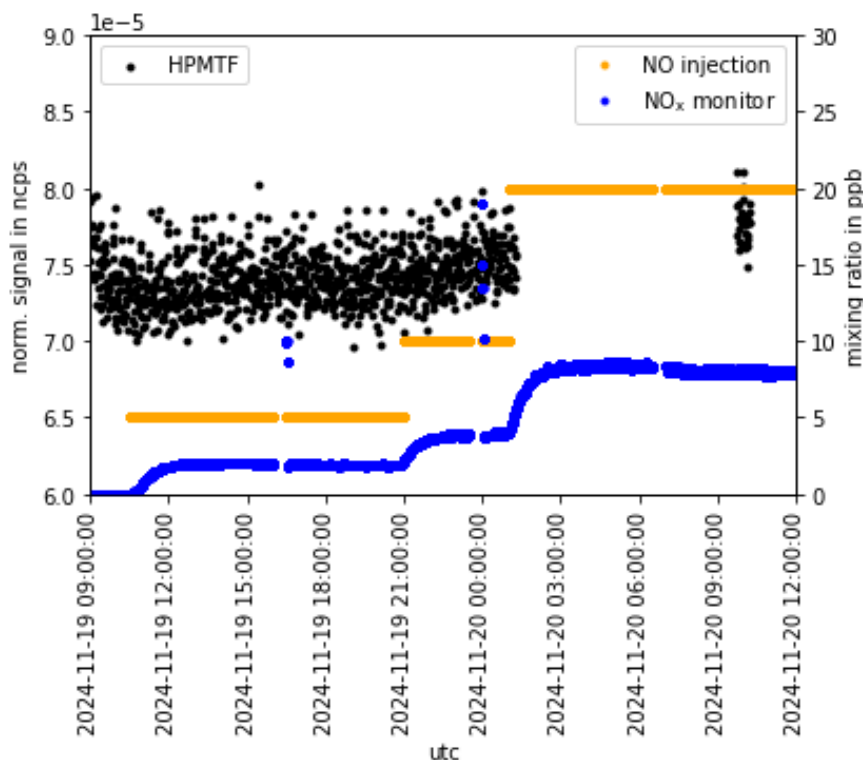


Figure 5.26: Normalized signal of HPMTF in ncps using FunMass under varying NO additions (5, 10, and 20 ppb) and 150 ppb O_3 .

Figure 5.26 illustrates the response of the HPMTF signal of FunMass at 193 Th (CF_3O^- - cluster) during the N_2O_5 interference experiment. Despite minor instrumental gaps, data were available for all steady-state periods. A slight increase in the HPMTF signal is observed upon NO addition, potentially attributable to the formation of N_2O_5 . However, this increase

corresponds to a maximum relative deviation of less than 5 %, which is well below the overall measurement uncertainty of approximately 17 %.

It should be noted that the absence of a pronounced signal increase at 193 Th may also be due to losses of N_2O_5 during transport to FunMass, likely caused by surface adsorption or chemical decomposition. Specifically, the $[\text{N}_2\text{O}_5\cdot\text{CF}_3\text{O}]^-$ cluster may decompose to NO_3^- and CF_3ONO_2 , as proposed by Huey et al. (1996). An increase in the NO_3^- signal with increasing NO concentration supports this hypothesis. However, a definitive attribution to N_2O_5 remains uncertain, as NO_3^- could also originate from other chamber processes, including HNO_3 formation.

Furthermore, NO addition under these conditions results in a slight baseline increase in several species, including SO_2 (10–30 ppt), which may originate from secondary effects within the chamber or the IMR, such as altered gas phase chemistry or enhanced wall interactions.

In summary, the observed signal changes are minor relative to the absolute HPMTF signal intensities recorded during the main experiments. Therefore, it can be concluded that NO addition does not introduce significant interference in the HPMTF detection, particularly under illuminated (UV lamp on) conditions for the CF_3O^- - CIMS.

In conclusion, the addition of NO at the tested levels (up to 10 ppb) does not significantly influence the DMS oxidation pathways or associated product yields. The SO_2 yield remains largely constant across the NO addition range, indicating that the effective NO concentration in the chamber was insufficient to drive substantial changes in oxidation chemistry. Nonetheless, minor effects due to enhanced OH recycling cannot be fully excluded.

5.5.4 Estimation of the HPMTF Calibration Factor for FunMass

The primary objective of the 2024 campaign was to close the sulfur budget under a range of atmospheric conditions, including dry conditions, humid conditions ($\text{RH} = 30\%$), experiments with NO addition, and dark experiments utilizing NO_3 radicals to suppress OH-initiated oxidation pathways. Achieving sulfur closure, by accounting for the major calibrated sulfur-containing products of DMS oxidation (namely DMS, DMSO, DMSO_2 , SO_2 , OCS, MSA, MSIA, and H_2SO_4), would allow for indirect quantification of HPMTF. This, in turn, en-

ables the determination of its calibration factor across different experimental conditions and detection systems.

However, due to limited availability of calibrated data, an alternative approach was adopted. Under dry conditions (excluding experiments with CO addition), HPMTF's calibration factor was estimated using literature-based constraints and steady-state assumptions.

The key principle of this method is the application of steady-state conditions, wherein the production and loss rates of a species are balanced. This relationship is described in equation 5.6.

$$\text{production rate} = \text{loss rate} \quad (5.6)$$

By explicitly considering the known production and loss processes of HPMTF, equation 5.7 can be derived. This equation incorporates the branching ratio between the isomerization pathway and the bimolecular reaction of MTMP (f_{isom}), as well as the branching ratio between the abstraction and addition pathways in the OH-initiated oxidation of DMS (f_{abs}). It further includes the rate coefficient for the reaction of DMS with OH radicals ($k_{\text{DMS+OH}}$), the steady-state concentrations of DMS ($[\text{DMS}]_{\text{ss}}$) and OH radicals ($[\text{OH}]_{\text{ss}}$), and the steady-state normalized signal of HPMTF ($[\text{HPMTF}]_{\text{ss}}$). The calibration factor of HPMTF is denoted as α_{HPMTF} , while $k_{\text{HPMTF+OH}}$, k_{wall} , k_{dil} , and J_{HPMTF} represent the rate coefficients for the reaction of HPMTF with OH radicals, the wall loss rate, dilution rate, and the photolysis rate of HPMTF, respectively.

$$f_{\text{isom}}f_{\text{abs}}k_{\text{DMS+OH}}[\text{DMS}]_{\text{ss}}[\text{OH}]_{\text{ss}} = \frac{[\text{HPMTF}]_{\text{ss}}}{\alpha_{\text{HPMTF}}} (k_{\text{HPMTF+OH}}[\text{OH}]_{\text{ss}} + k_{\text{wall}} + J_{\text{HPMTF}} + k_{\text{dil}}) \quad (5.7)$$

Since the steady-state concentrations are monitored or derived mathematically and the corresponding reaction rate constants have either been determined experimentally or obtained from the literature, equation 5.7 can be simplified to equation 5.8 by introducing a constant C_{HPMTF} .

$$\alpha_{\text{HPMTF}} = \frac{C_{\text{HPMTF}}}{f_{\text{isom}}} \quad (5.8)$$

$$\text{with } C_{\text{HPMTF}} = \frac{[\text{HPMTF}]_{\text{SS}}(k_{\text{HPMTF}+\text{OH}}[\text{OH}]_{\text{SS}} + k_{\text{wall}} + J_{\text{HPMTF}} + k_{\text{dil}})}{f_{\text{abs}}k_{\text{DMS}+\text{OH}}[\text{DMS}]_{\text{SS}}[\text{OH}]_{\text{SS}}}$$

Table 5.4: Summary of the parameters used to determine the HPMTF calibration factor.

Parameters	Values	References
f_{abs}	0.65	(Barnes et al., 2006)
$k_{\text{DMS}+\text{OH}}$	$6.74 \cdot 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$	(Burkholder et al., 2020)
$k_{\text{HPMTF}+\text{OH}}$	$1.4 (0.24 - 2.4) \cdot 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$	(Jernigan et al., 2022a)
k_{wall}	$0 \cdot 10^{-4} \text{ s}^{-1}$	This work
k_{dil}	$2.7 \cdot 10^{-4} \text{ s}^{-1}$	This work
J_{HPMTF}	$1.2 \cdot 10^{-6} \text{ s}^{-1}$	(Novelli et al., 2022)

The constant C_{HPMTF} can be determined using the parameters listed in Table 5.4, the measured HPMTF and DMS data from the three steady-state conditions (60, 70, and 95 % UV-C lamp opening), and the steady-state OH radical concentrations (as shown in Figure 5.11). Based on this, a value of $C_{\text{HPMTF}} = (3.94 \pm 0.24) \cdot 10^{-7} \text{ ncps} \cdot \text{ppt}^{-1}$ is obtained, assuming the rate coefficient of $k_{\text{HPMTF}+\text{OH}} = 1.4 \cdot 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. The estimated HPMTF sensitivity as a function of the isomerization fraction (f_{isom}) is illustrated in Figure 5.27 for three different values of $k_{\text{HPMTF}+\text{OH}}$, as listed in Table 5.4.

Figure 5.27 illustrates that the estimated HPMTF sensitivity predominantly lies in the range of $(0.5 - 6) \cdot 10^{-6} \text{ ncps} \cdot \text{ppt}^{-1}$. This range is in good agreement with the sensitivity determined for H_2O_2 under dry conditions, which is $4.66 \cdot 10^{-6} \text{ ncps} \cdot \text{ppt}^{-1}$. based on the calibration method described in Crounse et al. (2006). It is assumed, that the high amounts of H_2O_2 do not affect the sensitivity of HPMTF, which is unlikely as e.g. the sensitivity of SO_2 decreases if increasing H_2O_2 (compare Figure 5.7) and the sensitivity of HPMTF changes due to increasing relative humidity (see section 5.5.2).

If the isomerization fraction (f_{isom}) is known, the estimated sensitivity of HPMTF can be derived. To this end, the steady-state concentration of HO_2 ($[\text{HO}_2]_{\text{SS}}$) is estimated. OH is produced via the photolysis of H_2O_2 (see equation 5.1) and can react with either H_2O_2 or O_3 to form HO_2 (see Equations 5.9 and 5.10). While additional HO_2 sources, such as

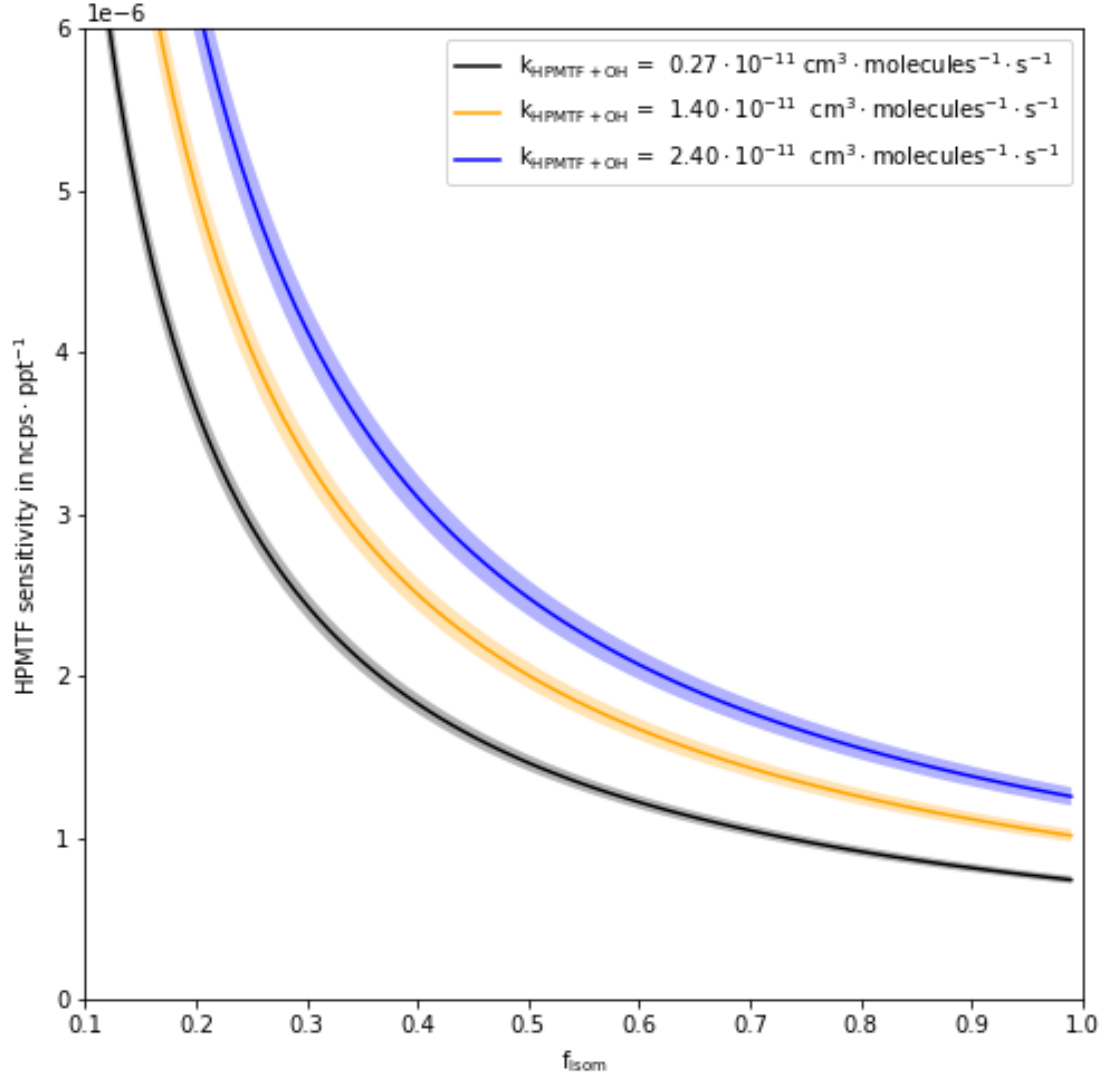


Figure 5.27: Estimated HPMTF sensitivity in $\text{ncps} \cdot \text{ppt}^{-1}$ as function of f_{isom} calculated using three different $k_{\text{HPMTF}+\text{OH}}$ ($0.24 \cdot 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ in black, $1.4 \cdot 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ in orange, and $2.4 \cdot 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ in blue) according to Jernigan et al. (2022a). The shades represents the experimental error using the average of the three steady states.

reactions with trace gases including CO, H₂, formaldehyde (HCHO), and methane (CH₄), are well known, they are excluded from this analysis due to the lack of accurate background measurements. Furthermore, HO₂ production and loss through DMS oxidation are also not considered, in order to keep the estimation straightforward.

In the following, only the two primary HO₂ formation reactions relevant under dry, CO-, NO_x-, and organic-free conditions are considered, as described by the Master Chemical Mechanism (MCM v3.3.1)(Jenkin et al., 1997; Saunders et al., 2003). Photolysis and wall loss of HO₂ are neglected due to a lack of available data. As a result, only HO₂ loss by self-recombination (see Equation 5.11) and its reaction with OH (see Equation 5.12) are considered.

Despite these simplifications, this approach is expected to provide at least the correct order of magnitude for [HO₂]_{ss}. Rate constants at 20 °C are taken from MCM v3.3.1, with the exception of the rate constant for Reaction 5.12, which exhibits considerable variability in the literature ($1 - 11 \cdot 10^{-11} \text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$). Speak et al. (2023) report a lower rate constant of $1 - 1.3 \cdot 10^{-11} \text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, which is approximately a factor of 10 smaller than that used in the MCM.



The same approach as for HPMTF sensitivity calculation is used to estimate the steady-state concentration of HO₂ ([HO₂]_{ss}), utilizing measured steady-state values of [O₃] = 2.5 ppb, [OH] as shown in Figure 5.11, and a range of assumed [H₂O₂]_{ss} values (30, 300, 3000

ppb). In 2023, FunMass measurements indicated approximately 300 ppb of H_2O_2 within the chamber (see Figure 5.8). However, applying the same calibration factor in 2024 led to estimated mixing ratios in the range of 1–2 ppm. The validity of these elevated values remains under investigation and is therefore not used directly in this analysis.

One plausible explanation for the higher apparent H_2O_2 concentrations in 2024 is the enrichment of the aqueous H_2O_2 solution over time due to cumulative bubbling, which would gradually increase the concentration of H_2O_2 delivered to the chamber. To accommodate this uncertainty, a range of H_2O_2 concentrations is employed in the estimation of $[\text{HO}_2]_{\text{SS}}$, allowing for a sensitivity analysis of the derived radical concentrations under plausible chamber conditions.

The resulting $[\text{HO}_2]_{\text{SS}}$ are multiplied by the reaction rate of $1.63 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for the reaction between RO_2 and HO_2 to account for the bimolecular reaction of HPMTF (Jenkin et al., 1997; Saunders et al., 2003). This leads to a bimolecular lifetime τ_{bi} of 3.5 s (30 ppb), 11.2 s (300 ppb), and 35.4 s (3000 ppb).

In Figure 5.28, f_{isom} ($= \frac{k_{\text{isom}}}{k_{\text{isom}} + k_{\text{bi}}}$) is plotted over $[\text{H}_2\text{O}_2]_{\text{SS}}$ for three different k_{isom} (0.04, 0.1, 2.1 s^{-1}) to cover the entire range reported in the literature Wu et al. (2015); Veres et al. (2020); Jernigan et al. (2022a).

The higher the $[\text{H}_2\text{O}_2]_{\text{SS}}$, the greater the formation of HO_2 and, consequently, the more dominant the bimolecular reaction pathway of RO_2 radicals becomes. This increased HO_2 availability shifts the competition away from isomerization toward $\text{RO}_2 + \text{HO}_2$ reaction. However, recent studies suggest that the isomerization rate constant k_{isom} is likely on the lower end of the previously assumed range ($0.04 - 0.1 \text{ s}^{-1}$). As a result, the black and orange circles in Figure 5.27 indicate the more realistic regime, yielding f_{isom} values between 0.15 and 0.8, depending on the actual $[\text{H}_2\text{O}_2]_{\text{SS}}$.

Figure 5.29 presents the estimated gas-phase HPMTF mixing ratios for the dry experiment under three representative f_{isom} values (0.15, 0.4, and 0.8), illustrating the sensitivity of HPMTF quantification to the assumed branching in the MTMP fate. As only values of $k_{\text{HPMTF}+\text{OH}}$ in the range of $1.4\text{--}2.4 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ appear realistic based on current literature and experimental constraints, the mixing ratio calculations were limited to this

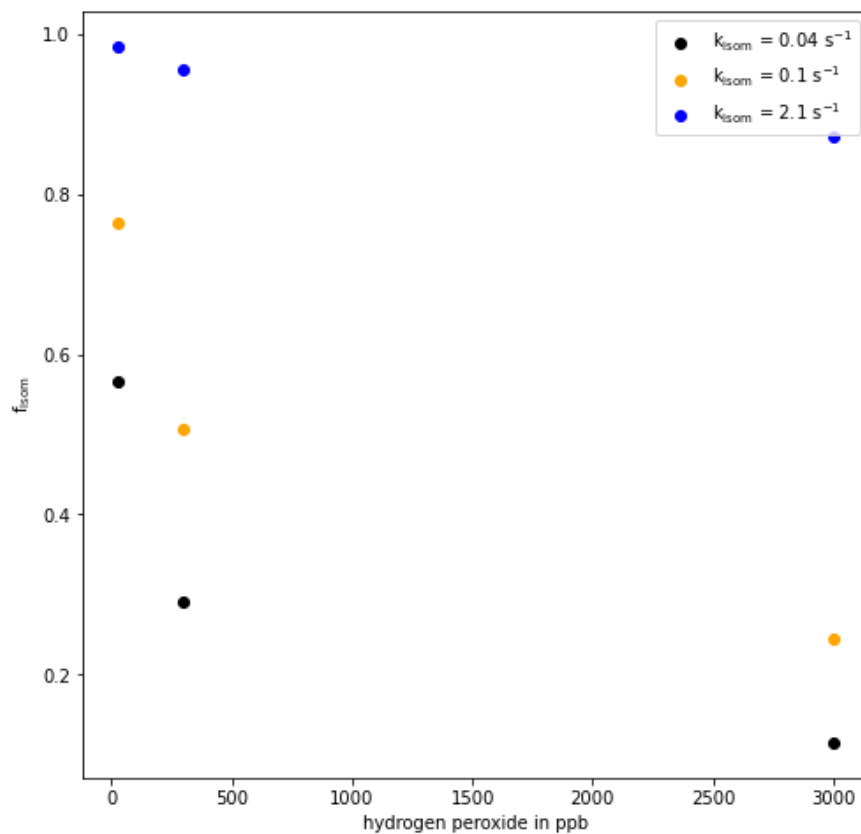


Figure 5.28: Estimation of f_{isom} as a function of the $[\text{H}_2\text{O}_2]_{\text{SS}}$ for several isomerization rate constants (0.04 s^{-1} in black (Assaf et al., 2023; Veres et al., 2020), 0.1 s^{-1} in orange (Jernigan et al., 2022a; Ye et al., 2021), and 2.1 s^{-1} in blue (Wu et al., 2015)) using $k_{\text{HO}_2+\text{OH}} = 1.3 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$.

5.5. RESULTS

range of rate constants. However, these literature values should be treated cautiously as the HPMTF sensitivity, which is still object of ongoing discussion, affects also $k_{\text{HPMTF}+\text{OH}}$.

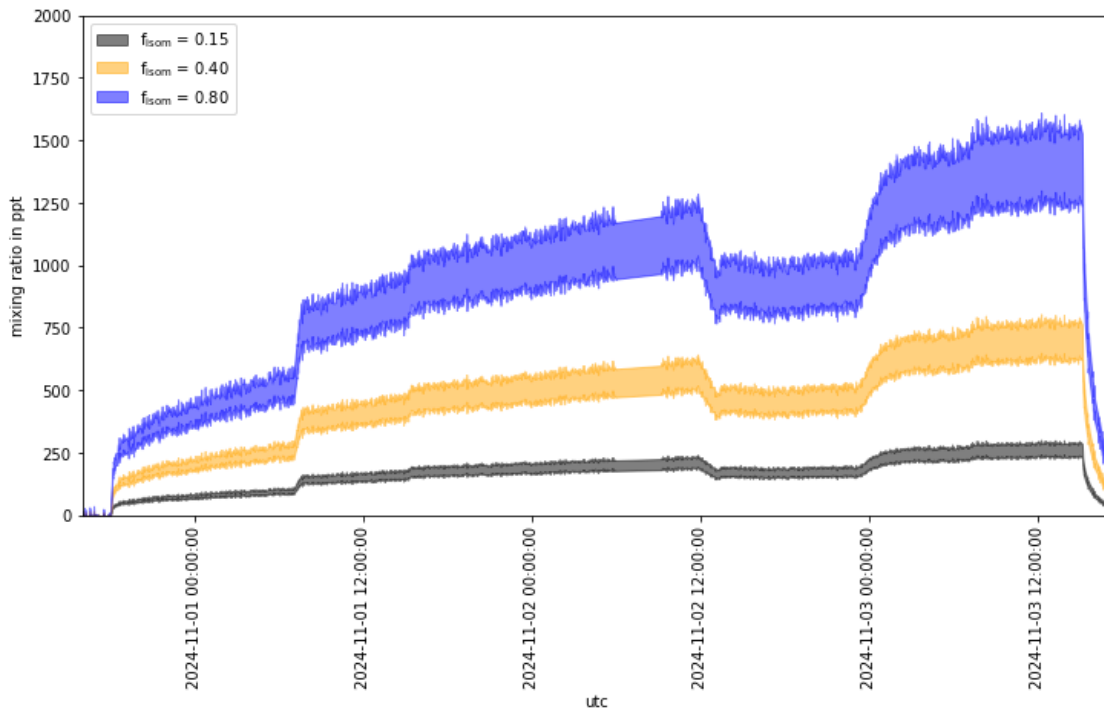


Figure 5.29: Estimation of HPMTF mixing ratio (in ppt) under dry conditions for f_{isom} (0.15 in black, 0.4 in orange, and 0.8 in blue) The lower and upper limit represents $k_{\text{HPMTF}+\text{OH}} = 1.4$ and $2.4 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, respectively.

The final steady-state condition ($\Delta[\text{DMS}] = 4.5 \text{ ppb}$, $[\text{SO}_2] = 1858 \text{ ppt}$, and $[\text{OCS}] = 168 \text{ ppt}$) was utilized to perform a plausibility check of the applied estimation approach. Based on the findings of Barnes et al. (2006), approximately 65 % of the consumed DMS proceeds via the abstraction channel, corresponding to 2.9 ppb. Assuming isomerization fractions (f_{isom}) of 0.15, 0.4, or 0.8, this would theoretically result in 0.4, 1.2, or 2.3 ppb of HPMTF, respectively, neglecting any subsequent loss processes. The upper limit of all three f_{isom} in Figure 5.29 is lower than theoretical calculated maximum of HPMTF neglecting loss processes.

It must be emphasized, however, that this approach is subject to substantial uncertainty. The model is highly simplified, and the relevant measurements carry considerable uncertainty ($\sigma_{\text{SO}_2} = 17 \%$, $\sigma_{\text{HPMTF}} = 17 \%$, $\sigma_{\text{OCS}} = 85 \text{ ppt}$, and $\sigma_{\text{DMS}} \geq 25 \%$). Furthermore, wall losses may be underestimated due to potential sensitivity drifts, and the photolysis rate of HPMTF

remains insufficiently characterized and is currently the focus of active research. Especially, the wall losses strongly affect the results as it could be the major loss process of HPMTF (cf. Figure S6.5). Collectively, these factors introduce uncertainties exceeding 50 %.

Despite these limitations, the approach demonstrates the clear potential of the experimental setup for deriving a calibration factor. Moreover, it highlights the critical need for the calibration of additional species and the implementation of a detailed chemical model to improve the robustness and reliability of the analysis.

Chapter 6

Conclusions and Outlook

The primary objective of this thesis was to modify and improve the Geophysica version of FunMass for deployment aboard the IAGOS-CARIBIC aircraft and to obtain the first atmospheric measurements in the UTLS (targeting 1–2 years of monthly data). However, due to delays in container certification, no flights and thus no atmospheric data could be collected. Consequently, the focus shifted to a more extensive optimization of FunMass and a deeper investigation of its internal ion chemistry. In this context, the influence of various operational parameters (e.g., temperature, pressure) was systematically examined. Furthermore, a preliminary version of FunMass (IMR3) was deployed at SAPHIR-STAR during DMS oxidation experiments, aiming to provide new insights into the DMS oxidation mechanism. The following two subsections summarize these two main research directions.

6.1 FunMass

This work deals with the redesign of FunMass used on the high-altitude research aircraft M55-Geophysica to the version, which will be deployed on the IAGOS-CARIBIC platform. Moreover, the IMR chemistry was characterized and better understood leading to a potential cluster formation mechanism for strong and weak acids.

A complete redesign and optimization of the IMR was carried out, resulting in sensitivities on the order of 10^{-5} ncps · ppt for a wide range of target compounds. These include organic

acids (e.g., HCOOH , CH_3COOH), inorganic acids (e.g., HCN , HCl), and acid anhydrides (e.g., SO_2). The flow and pressure regimes were optimized, and the effect of IMR temperature on sensitivity was systematically investigated within the temperature range expected during IAGOS-CARIBIC flights. These improvements lead to limits of detection (LOD, 2σ , 10 s) ranging from 2 to 9 ppt and a precision (2 s integration time) of 5 ppt while measuring approx. 1 ppb of HCN and SO_2 . These characteristics are state of the art for in-situ instruments and only a few other airborne in-situ instruments are as sensitive and accurate as FunMass measuring SO_2 and HCN .

Since water vapor and O_3 will significantly vary during airborne measurements, the influence on sensitivity and LOD was analyzed in detail. Water vapor primarily affects sensitivity, resulting in increased LODs, particularly for HCOOH . Ozone, in contrast, mainly increases signal noise, especially impacting measurements of the acids HCN and HCOOH . Interestingly, SO_2 is comparatively less affected by O_3 , with smaller impacts on sensitivity.

Isobaric interferences of HCN and SO_2 , two key species measured by FunMass during IAGOS-CARIBIC flights, were quantified. In the presence of water vapor, HCOOH contributes with an equivalent of up to 8 % of its mixing ratio to the SO_2 signal at 83 Th, necessitating correction, particularly in the troposphere, where HCOOH and water vapor levels are elevated and SO_2 can be low. The 45 Th signal (HCOO^-) is suitable and chosen for this correction. While the 45 Th signal has a roughly tenfold lower sensitivity compared to its fluoride cluster, it is less prone to isobaric interference compared to 65Th, providing a more robust correction approach.

This work shows that SO_2 is also the main interfering species for HCN , particularly under high O_3 conditions. Enhanced ozone levels increase the apparent HCN signal due to SO_2 , with interference reaching up to 8 % of the SO_2 mixing ratio, an effect that saturates at high O_3 concentrations. While water vapor has a minor influence on the interference of SO_2 with HCN , the accuracy of the HCN measurement remains highly dependent on precise quantification of SO_2 .

The precise quantification of these isobaric interferences is crucial for the respective analysis of HCN and SO_2 measurement data, e.g. during regular IAGOS-CARIBIC flights. This

work shows that the accurate quantification and the correction of these uncertainties is possible and moreover, ensures that FunMass can provide robust SO₂ and HCN data during field measurements.

The ion chemistry of CF₃O⁻ was further elucidated with the support of theoretical calculations from Jan Meisner’s group at Heinrich Heine University Düsseldorf. While thermodynamic calculations predict CF₃O⁻ cluster formation with nearly all studied species, experimental results revealed that only weak acids (e.g., hydroperoxides) predominantly form CF₃O⁻ clusters. Strong acids (e.g., HCN, HCOOH) tend to protonate CF₃O⁻, leading to its catalytic decomposition into HF and CF₂O. The resulting acid-HF cluster is then detected instead, demonstrating a mechanistic explanation for the observed clustering behavior.

In IAGOS-CARIBIC, a specialized measurement container housing over 20 scientific instruments is installed onboard a Lufthansa A350 long-haul passenger aircraft. FunMass will mainly provide high-resolution and robust data of SO₂ and HCN. However, as this work has shown it is also capable to measure various other (in-)organic acids and hydroperoxides, important for atmospheric chemistry, particle formation and dynamics.

Beginning in 2026, regular monthly flights totaling 50 to 100 flight hours are anticipated. These will primarily sample the upper troposphere and, depending on latitude, parts of the lower stratosphere. The aim is to provide consistent, long-term, and globally representative measurements.

When combined with data from the other onboard instruments, our SO₂ and HCN measurements will help to better understand small-scale processes in the UTLS region — an area known to have significant climate relevance. In particular, we aim to deepen our understanding of aerosol formation in this region, which is likely dominated by sulfate particles.

To date, there is no ongoing global monitoring of background SO₂ in the UTLS. With our high resolution measurements, FunMass will close this critical data gap and contribute significantly to future atmospheric and climate research.

To achieve these goals, the newly designed IMR will undergo a full characterization analogous to the previous version, with the aim of identifying optimal operational parameters (e.g., pressure, flow rates) in the near future. The effects of other trace gases and additional

isobaric interferences will also be reevaluated.

Furthermore, the implementation of a novel scrubber system, based on carbonated nylon wool and a carbonated denuder, as suggested by John Crounse’s group at Caltech, will be tested. These experiments were previously postponed due to measurement campaigns (DMS oxidation campaigns) and instrument development efforts. Accurate background measurements remain essential for both ground and airborne field operations.

Lastly, a new calibration system is currently being developed. This system will allow for the independent calibration of multiple trace gases as well as their interferences and will provide precise control over water vapor and O_3 concentrations. It is based on the established calibration rack and is expected to be operational by early 2026. It will be fully automated and enable calibration series with minimal operator interference. Moreover, it will be portable, which also allows the calibration outside the laboratory.

6.2 DMS Oxidation

As the first IAGOS-CARIBIC flight was postponed over four years (original starting year was 2022), a major planned part of this work (flight data) were not available. However, we were able to participate in two DMS oxidation campaigns in SAPHIR-STAR and to get promising data. These DMS oxidation campaigns conducted in SAPHIR-STAR during 2023 and 2024 provided new insights into the calibration of HPMTF and the DMS oxidation mechanism in general.

Using SAPHIR-STAR with an average residence time of 61 minutes and H_2O_2 as the OH radical precursor resulted in sufficient HPMTF formation to be detected across multiple CIMS techniques. This study demonstrated that four reagent ion schemes, NO_3^- , I^- , Br^- , and CF_3O^- , are capable of detecting HPMTF. Among these, Br^- -CIMS exhibited the highest sensitivity, while NO_3^- -CIMS showed the lowest sensitivity, up to three orders of magnitude lower. Both reagent ion modes were deployed on the same MION API-ToF, enabling a direct and valid comparison. The IMR-based instruments, HToF (I^-) and FunMass (CF_3O^-), showed sensitivities within the same order of magnitude, albeit lower than Br^- -CIMS.

The addition of NO to explore high-NO_x conditions revealed significant discrepancies between the MION (atmospheric pressure) and IMR-based CIMS systems. The IMR-based CIMS instruments tended to overestimate HPMTF formation, while the MION underestimated it. For FunMass, it was demonstrated that N₂O₅ does not interfere with HPMTF measurements, especially when UV lights are active. The MION, however, is more sensitive to NO-induced HNO₃ formation, which suppresses the Br⁻ and likely also the NO₃⁻ mode signals. In 2023, the NO concentration was too low to fully suppress HPMTF formation. Nevertheless, the injection of 20 ppb or more NO showed a measurable effect on net HPMTF formation, consistent with preliminary model simulations (not shown in this work). Thus, this work recommends the use of IMR-based CIMS (operated under low-pressure regimes) over API-ToF MION, especially in Br⁻ and NO₃⁻ modes, for HPMTF measurements.

It was also shown that increased water vapor enhances HPMTF sensitivity for NO₃⁻, I⁻, and CF₃O⁻-CIMS by up to factors of 10, 4, and 3, respectively, at 60 % relative humidity. In contrast, Br⁻ mode is negatively affected, with signal reductions by a factor of 33 under similar humidity conditions. In 2024, this behavior was qualitatively confirmed using FunMass.

A first estimation of the HPMTF calibration factor for FunMass was derived using a steady-state approach (assuming production rate equals loss rate). The resulting factor was on the order of 10⁻⁶ ncps · ppt, comparable to the calibration factor for H₂O₂. However, additional methods will be used to validate and refine this calibration factor estimation.

This study is unique as until now no comparison between several CIMS instruments regarding HPMTF was done. This work shows the advantages and disadvantages of each instruments for HPMTF detection under specific conditions. These results are crucial to better understand and validate field measurements of HPMTF. Moreover, it could be shown that not only I⁻ - CIMS is capable to detect HPMTF but also other reagent ions can be used. This can encourage other groups to reevaluate their existing field data with respect to HPMTF.

Under dry conditions, the observed SO₂ and OCS yields were 28–40 [19–61] %S and 3–5 [1–9] %S, respectively, in good agreement with the literature. Moreover, it was shown that increased photolysis under constant OH exposure leads to reduced net HPMTF formation, while SO₂ production remains unaffected. As the NO additions were insufficient to strongly

influence the chemistry, the product yields remained comparable to those in low- NO_x conditions within uncertainty bounds.

Due to baseline uncertainty in DMS measurements (approximately 3 ppb for values around 4–5 ppb), the influence of water vapor on DMS oxidation could not be quantitatively determined. This uncertainty causes large variability in derived SO_2 and OCS yields. Nonetheless, a decreasing trend in SO_2 yield with increasing humidity was observed, which aligns with the expected formation of H_2SO_4 from SO_2 in the presence of water vapor.

Unfortunately, many datasets, especially those processed by ICE-3—are not yet available (e.g., DMS under NO_3 oxidation, calibrated MSA, DMSO, or H_2SO_4 data). These will be calibrated and analyzed in fall 2025. Once processed, these data will better support the primary objective of quantifying the major sulfur-containing species formed under various oxidation conditions. The sulfur mass balance, i.e., the difference between consumed DMS and quantified sulfur-containing products, will allow better estimation of HPMTF concentrations and corresponding sensitivities under different experimental conditions. These values can be compared to those estimated in this study. Model simulations will also assist in interpreting experimental results and improving mechanistic understanding, ultimately leading to reliable calibration factors for HPMTF that can be applied in field deployments.

Once all data are available this study will be very valuable for the scientific community dealing with the DMS oxidation. Such versatile studies investigating DMS oxidation were barely carried out in the past. Here, almost every major sulfur-containing product was measured quantitatively and many other minor products qualitatively. It can provide new insight in the abstraction channel as various different CIMS techniques and reagent ions were used. Moreover, a calibration factor of HPMTF under various conditions (e.g., water vapor or NO_x addition) can be derived for each CIMS instrument.

Because SAPHIR-STAR experiments are resource-intensive and time-constrained, a dedicated flow tube has been designed and built to increase experimental flexibility, especially for future DMS oxidation studies and beyond. Initial tests indicate a laminar or block flow without unintended turbulence. Unfortunately, further tests had to be temporarily halted due to a broken UV lamp (used for chlorine radical generation). Once the lamp is repaired,

6.2. DMS OXIDATION

these tests will also be resumed.

Appendix

S1 Further Details of the Inlet Motor

For the lab version, an external linear actuator from Nanotec (Nema 6 model LSA141S03-A-TDBA-102 with controller CL3-E-1-0F) is used (shown in figure S1.1). This actuator operates with high resolution (5 $\mu\text{m/s}$) and reliability (no hysteresis), weighing only 30 g with a size of 14 mm. Its maximum speed and force are 20 mm/s and 15.6 N, respectively, while the maximum output power during operation is 0.202 W. These specifications make it ideal for an airborne instrument like FunMass-C (Nanotec[®], 2025).

However, the actuator simply holds its current position during a power failure, preventing the valve from closing. As a result, it cannot be used during CARIBIC flights.

Another option considered was the Amplified Piezo Actuator APA600M from CEDRAT TECHNOLOGIES (illustrated in figure S1.2). While piezo actuators are known for hysteresis (see in figure S1.3), this model offered promising specifications, including a force limit of 16 N and a resolution of 31 nm. Additionally, its compact size (49 mm $\times$ 12 mm $\times$ 13 mm, L $\times$ W $\times$ H) and lightweight design (14 g) made it well-suited for integration into an airborne instrument (CEDRAT, 2025). However, achieving a setup that ensured both leak-tightness and the full required range of motion results in using a solenoid with low power consumption.



Figure S1.1: External linear actuator from Nanotec (Nema 6 model LSA141S03-A-TDBA-102 (Nanotec[®], 2025)).

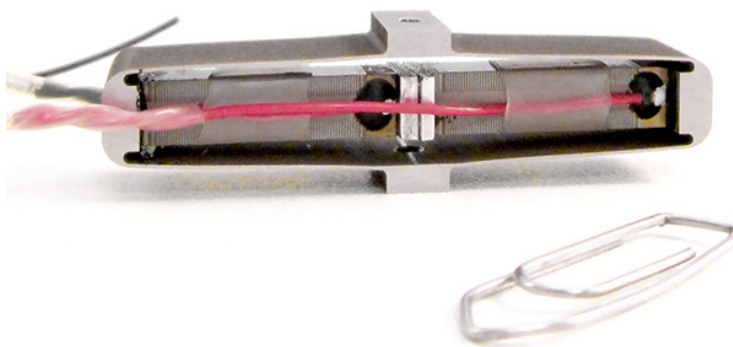


Figure S1.2: Amplified Piezo Actuator APA600M from CEDRAT TECHNOLOGIES (CEDRAT, 2025).

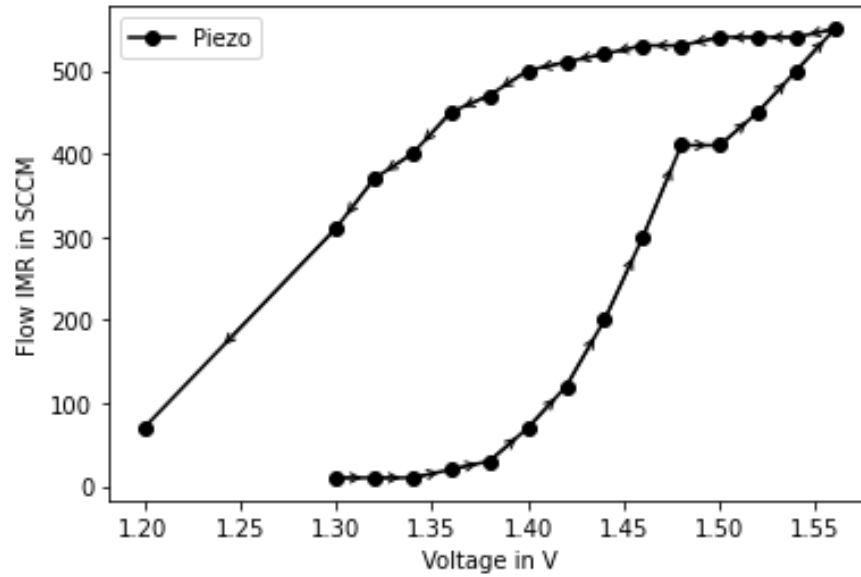


Figure S1.3: Voltage supplied to piezo actuator in V against flow to IMR in SCCM. Source: Sarah Honold.

S2 Further Details of the Scrubber Valve

The Festo AEVC-16-10-A-P short-stroke cylinder offers high speed, requires no electrical power (being pneumatically actuated), and provides a maximum stroke force of 112 N with a spring return force of 5 N. Additionally, its 16 mm piston diameter makes it compact enough for an integration into FunMass-C (FESTO, 2025).

The only drawback is that it requires a pressurized gas source (air or nitrogen) for actuation. However, given the small volume requirements, only a few milliliters from a 200-bar, 20 L nitrogen bottle are needed per switching event. Furthermore, a small, leak-tight, low-power three-way valve is required to control the short-stroke cylinder.



Figure S2.1: Festo AEVC-16-10-A-P short-stroke cylinder used for the scrubber valve of FunMass-C (FESTO, 2025).

S3 Further Details of the IMR

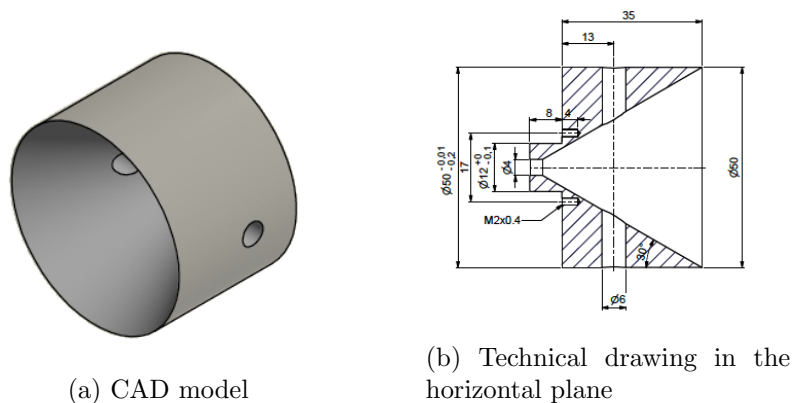


Figure S3.1: IMR1 inset made of PTFE. Source: Jochen Barthel.

The first version of the PTFE inset, shown in Figure S3.1b, had a conical shape with an opening angle of 30° . Its starting diameter was constrained to 4 mm by the small inlet tube and expanded to an inner diameter of 50 mm, resulting in a total length of 43 mm. The cone featured two opposing 6 mm holes, which were singed to maintain the smoothness of the inner wall. These holes allowed the reagent ion flow from the ion source (violet, see Figure 3.17) to enter the IMR1.

Initially, each lamp had a bent stainless steel tube ($45\text{--}60^\circ$) protruding 20–30 cm into the IMR1 to promote smoother mixing of the sampled airflow and reagent ion flow. However, no significant difference was observed between using bent versus straight tubes of the same protrusion length. It was suspected that any potential advantage of improved mixing was negated by turbulence caused by the protruding tubes. To investigate this, a single straight stainless steel tube, which could be moved within the IMR1, was tested. In this experiment, only one vacuum ultraviolet (VUV) lamp was used, along with a customized PTFE inset featuring a single asymmetric hole.

Figure S3.2 presents the main reagent ion CF_3O^- (black) and the background-corrected and normalized to CF_3O^- signal SO_2 signal (orange), both normalized to their respective values at 20 mm, as a function of the tube ending distance from the IMR1. The 0 mm position corresponds to the tube ending at the edge of the cone wall, with negative values indicating

movement away from the IMR1 entry. During calibration, 344 ppt SO₂ was introduced into FunMass. The

As the tube was moved toward the cone wall, an increase in the CF₃O⁻ signal was observed, correlating with the total ion count (TIC). While a higher main reagent ion signal and TIC are generally favorable, an increase in CF₃O⁻ alone is meaningless if it results in decreased sensitivity. To assess this, SO₂ calibrations were performed. Sensitivity increased with distance from the cone wall, reaching a maximum at 20 mm, which is near the center of the IMR1 (approx. 23 mm from the cone wall). Between 10 and 20 mm, sensitivity remained stable within 3 % variation, but it dropped significantly (by almost 40 %) when the tube was moved closer to the cone wall.

These findings suggest that inserting the stainless steel tube at least 10 mm and at most 20 mm into the IMR1 enhances mixing between the two airflows, leading to higher SO₂ sensitivity. However, it remains unclear whether this improvement results from introducing the reagent ion flow closer to the IMR1 center or from turbulence generated by the tube itself. Additionally, better mixing was found to reduce the CF₃O⁻ signal. If the reagent ion flow enters near the cone wall, it mixes with the sampled airflow later, leading to lower sensitivity and a higher CF₃O⁻ signal.

There are two key limitations in the current setup. First, having two tubes inside the IMR1 is not ideal. Second, using straight tubes allows VUV light to enter the IMR1 directly, leading to unintended direct ionization of trace gases in the sampled air. To address the latter issue, several alternatives were tested, but none proved satisfactory.

A T-piece with a perpendicular VUV light source was examined, but the exposure time was too short, significantly reducing the TIC and CF₃O⁻ signal by more than 70 %. Decreasing the flow rate to increase exposure time resulted in greater surface contact, which further worsened performance. Using a larger-diameter VUV lamp or multiple lamps in series was considered but ultimately found unsuitable for FunMass. A bent PFA tube with an approximately 90° angle was also tested; however, its flexibility caused deformations due to instrument vibrations, leading to signal instability. The more the tube was bent, the greater the signal loss, particularly when a kink formed.

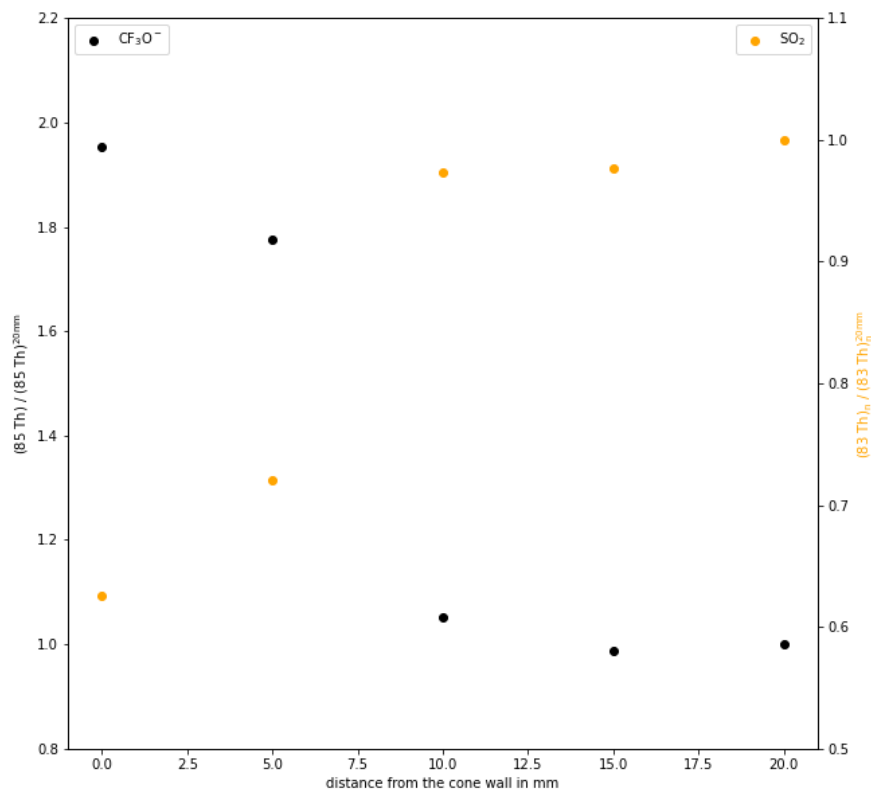


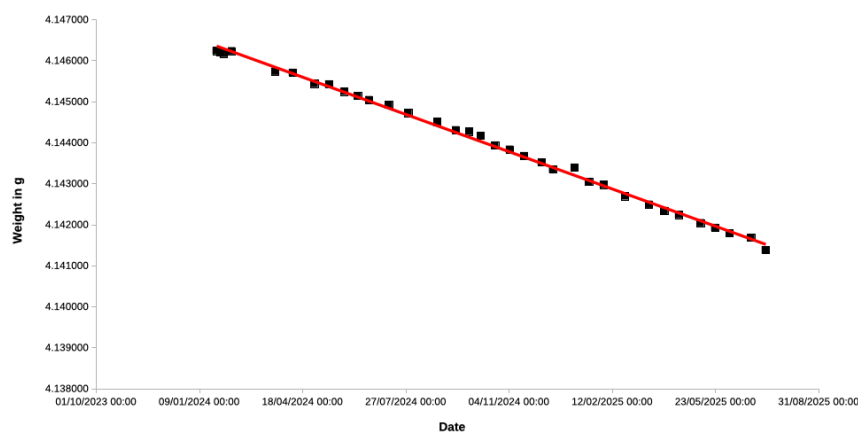
Figure S3.2: The main reagent ion CF_3O^- (85 Th; black) and the background-corrected and to CF_3O^- normalized SO_2 signal (83 Th; orange), both normalized to their respective signals at 20 mm, as a function of the tube ending distance from the IMR1. The position 0 mm corresponds to the tube ending at the edge of the cone wall, with negative values indicating movement toward the cone wall. During the calibration 344 ppt SO_2 was introduced to FunMass.

To improve rigidity, a 90° bent copper tube was used. While this prevented deformation, it led to an 85 % signal loss, likely due to water vapor release from the tube walls despite thorough cleaning. This suggested that copper's high surface activity negatively impacted measurements. To mitigate this issue, a SilcoNert2000®-coated stainless steel tube with a 90° bend was tested. The water vapor signal was significantly reduced, confirming that copper was indeed problematic. However, the overall signal still decreased by 78 %, likely due to turbulence, which increased surface contact and reagent ion loss.

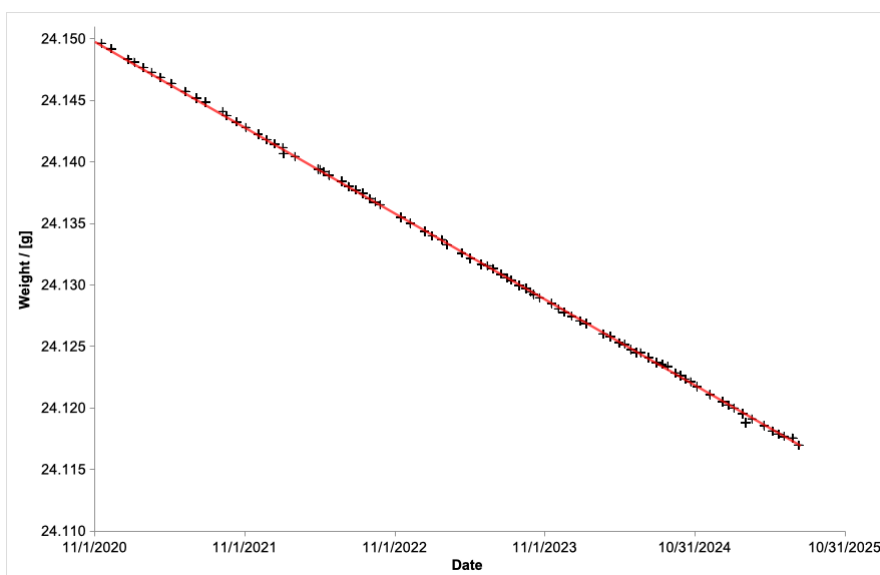
Finally, a capillary with a length of 65 mm and a diameter of 120 μm was tested in both straight and slightly bent configurations. Due to its small diameter, almost no VUV light reached the IMR1. However, the high flow speed caused the reagent ion stream to bypass the

for the ion source were positioned at an angle rather than perpendicular to the IMR2 airflow. However, this presented two major challenges. First, reintroducing VUV light into the IMR2 would again affect the sampled airflow, though this could potentially be mitigated. The second and more critical issue was the limited space available within the instrument. As previously mentioned, space is a highly constrained resource in an aircraft instrument, making it impractical to reposition components freely. The most space-efficient design remains placing the VUV lamps (ion source) perpendicularly to the sampled airflow. Given these constraints, modifying the PTFE inset remains the only viable approach to meet the requirements for the CARIBIC container.

S4 Further Details of Characterization and Calibration of FunMass-C



(a) HCN ($6.32 \pm 0.03 \text{ ng} \cdot \text{min}^{-1}$)



(b) SO₂ ($13.3 \pm 0.0 \text{ ng} \cdot \text{min}^{-1}$)

Figure S4.1: Gravimetric analysis of the permeation tubes

S5 Further Details of IMR Ion Chemistry

Table S5.1: Calculated relative energies for complexes formed between CF_3O^- and various interacting molecules (X). All energies are presented in kcal/mol, based on Coupled Cluster level of theory DLPNO-CCSD(T)/cc-pVQZ // B3LYP/def2-TZVP. “§” indicates bonding via fluorine atoms.

Molecules	$\text{X}(\text{CF}_3\text{O}^-)$	$\text{X} + \text{CF}_3\text{O}^-$	$\text{X}(\text{CF}_3\text{O}^-)^\S$	$\text{X}(\text{F}^-) + \text{CF}_2\text{O}$
HCOOH	-18.27	0	-10.03	-10.09
CH_3COOH	-13.68	0	-10.21	-7.44
HF	-13.74	0	-5.96	5.29
HCl	-17.54	0	-3.15	-14.86
HBr	-22.73	0	-17.92	-21.72
HI	-27.52	0	-22.40	-27.93
HCN	-11.72	0	-6.47	0.44
HNO_3	-20.70	0	-15.04	-19.65
HONO	-11.84	0	-4.62	-6.74
H_2O_2	-10.51	0	-5.14	-15.97
CH_3OOH	-5.89	0	-1.30	13.00
SO_2	-6.52	0	0.49	-1.66

S6 Further Details on DMS oxidation

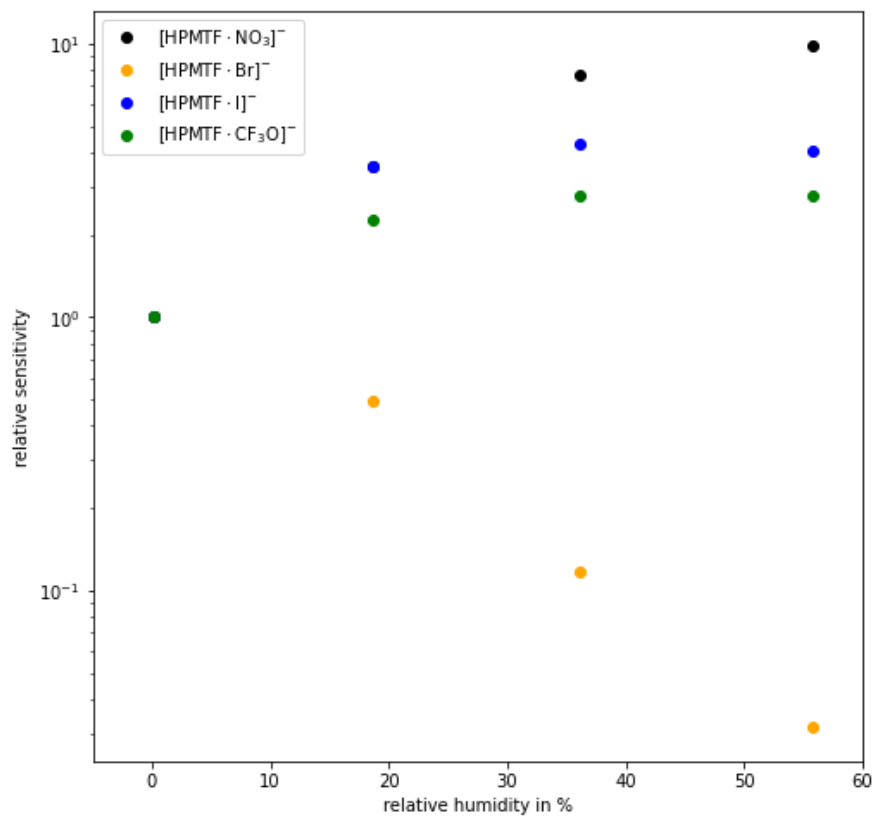


Figure S6.1: The relative sensitivity of HPMTF using the MION NO_3^- mode (in black), MION Br^- mode (in orange), HToF I^- mode (in blue), and FunMass CF_3O^- (in green) as function of the relative humidity in the chamber (in %)

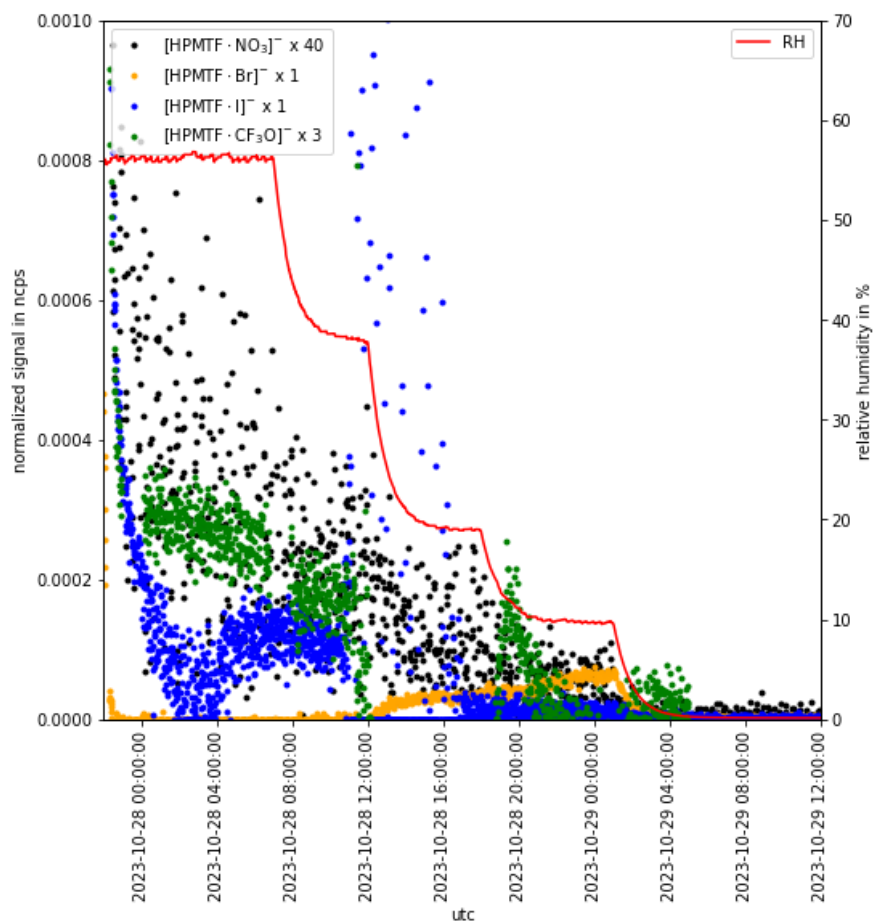


Figure S6.2: The normalized background signal of HPMTF using the MION NO₃⁻ mode (in black; 40 · ncps), MION Br⁻ mode (in orange; ncps), HToF I⁻ mode (in blue; ncps), and FunMass CF₃O⁻ (in green; 3 · ncps). Additionally, the relative humidity (in %) in the chamber is shown in red.

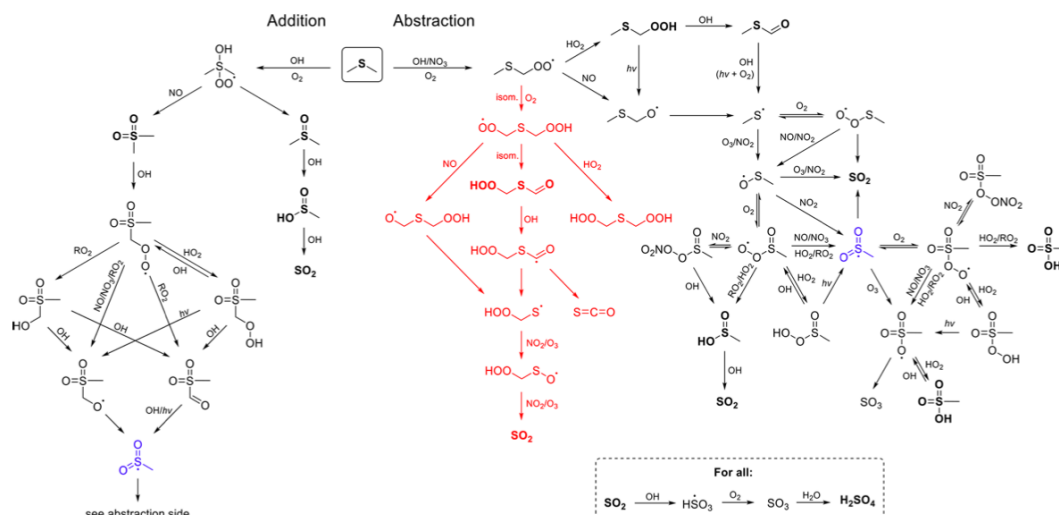


Figure S6.3: Gas-phase DMS + OH oxidation mechanism. Measured closed-shell products are shown in bold. Reactions in black are taken from MCM (Master Chemical Mechanism); reactions in red, related to hydroperoxymethyl thioformate (HPMTF, HOOCH₂SCHO) chemistry, are taken from Wu et al. (2015). Products that do not contain sulfur are not shown. The CH₃SO₂ radical (marked in blue) represents a link between addition and abstraction pathway products. Note that several products are shown multiple times.

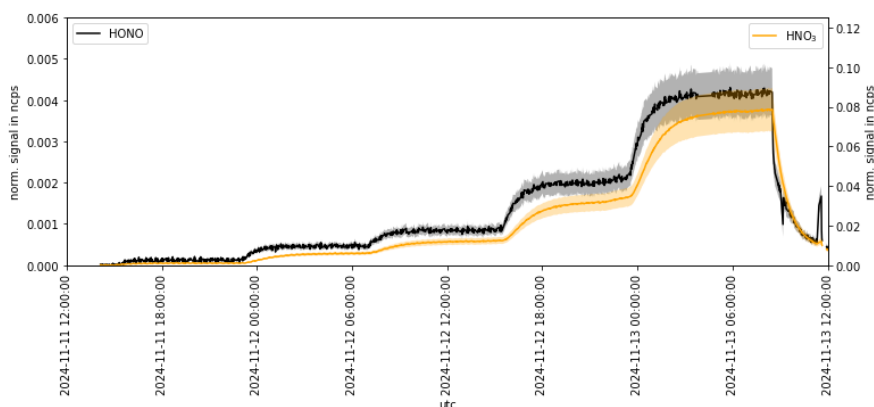


Figure S6.4: Normalized signal of HONO (black) and HNO₃ (orange) in ncps for the NO addition experiment in 2024. The shaded areas corresponds to measurement uncertainty (approx. 17%)

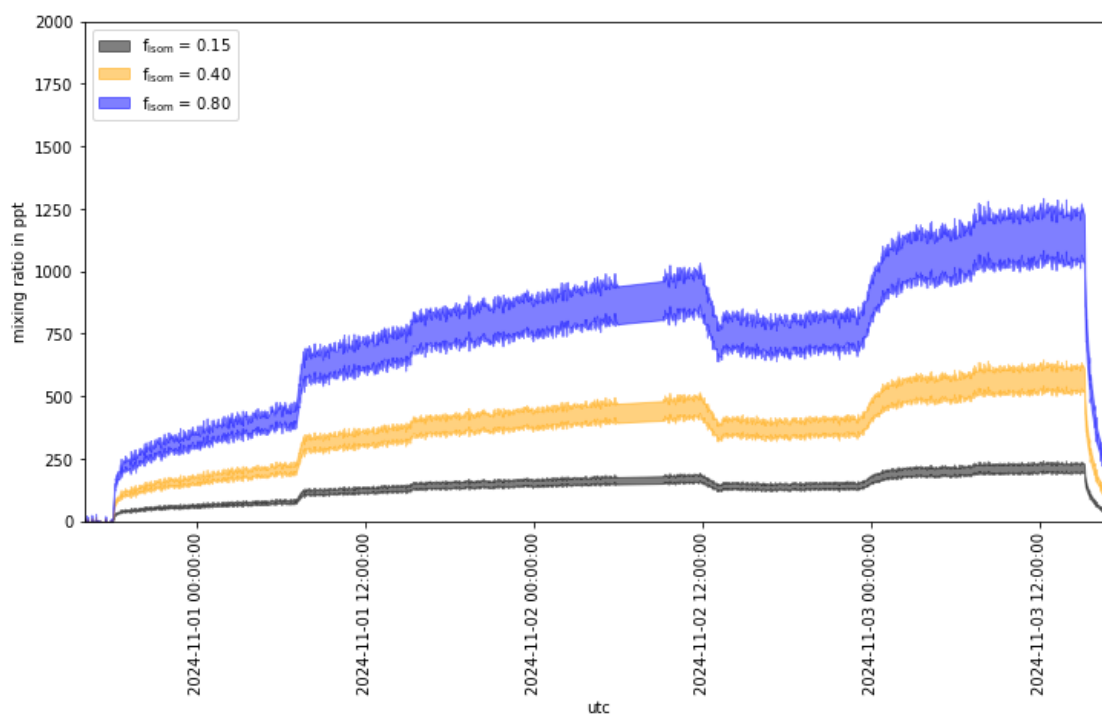


Figure S6.5: Estimation of HPMTF mixing ratio (in ppt) under dry condition for f_{isom} (0.15 in black, 0.4 in orange, and 0.8 in blue) The lower and upper limit represents $k_{\text{HPMTF}+\text{OH}} = 1.4$ and $2.4 \cdot 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, respectively. A wall loss rate of $1.0 \cdot 10^{-4} \text{ s}^{-1}$ was applied instead of the $0 \cdot 10^{-4} \text{ s}^{-1}$

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