

**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

Measurement of low-ppm mixing ratios of water vapor in the upper troposphere and lower stratosphere using chemical ionization mass spectrometry

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

A chemical ionization mass spectrometer (CIMS) instrument has been developed for the fast, precise, and accurate measurement of water vapor (H_2O) at low mixing ratios in the upper troposphere and lower stratosphere (UT/LS). A low-pressure flow of sample air passes through an ionization volume containing an α -particle radiation source, resulting in a cascade of ion-molecule reactions that produce hydronium ions (H_3O^+) from ambient H_2O . The production of H_3O^+ ions from ambient H_2O depends on pressure and flow through the ion source, which were tightly controlled in order to maintain the measurement sensitivity independent of changes in the airborne sampling environment. The instrument was calibrated every 45 min in flight by introducing a series of H_2O mixing ratios between 0.5 and 153 parts per million (ppm) generated by Pt-catalyzed oxidation of H_2 standards while overflowing the inlet with dry synthetic air. The CIMS H_2O instrument was deployed in an unpressurized payload area aboard the NASA WB-57 high altitude research aircraft during the Mid-latitude Airborne Cirrus Properties Experiment (MACPEX) mission in March and April 2011. The instrument performed successfully during seven flights, measuring H_2O mixing ratios below 5 ppm in the lower stratosphere at altitudes up to 17.7 km, and as low as 3.5 ppm near the tropopause. Data were acquired at 10 Hz and reported as 1-s averages. In-flight calibrations demonstrated a typical sensitivity of 2000 Hz ppm^{-1} at 3 ppm with a signal to noise ratio (2σ , 1-s) greater than 32. The total measurement uncertainty was 9 to 11 %, derived from the uncertainty in the in situ calibrations.

1 Introduction

Water vapor in the lower stratosphere (LS) plays significant roles in both stratospheric photochemistry and Earth's radiation budget (Forster and Shine, 2002; Brasseur and Solomon, 2005; Trenberth et al., 2007; Solomon et al., 2010) despite dehydration processes in the upper troposphere (UT) that reduce H_2O mixing ratios to low part per

AMTD

6, 381–422, 2013

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



million (ppm) levels. Over the past several decades there has been considerable systematic disagreement among in situ H₂O measurements made by different instruments at the low mixing ratios found in the UT/LS. These discrepancies have limited our understanding of the microphysics related to cirrus cloud particle nucleation and growth which underlies the dehydration processes in the tropical UT that regulate H₂O transport across the tropopause (Jensen et al., 2005, 2008; Peter et al., 2006; Krämer et al., 2009), and which in turn limits our ability to determine and predict the effect of climate changes on the radiatively important feedback from UT/LS H₂O (Solomon et al., 2010; Maycock et al., 2011).

H₂O in the UT/LS is measured from aircraft and balloons using a variety of in situ techniques including Lyman- α photofragment fluorescence (e.g. Weinstock et al., 1994; Zöger et al., 1999), tunable diode laser absorption spectrometry (e.g. May, 1998), and chilled mirror hygrometry (e.g. Vömel et al., 2007). UT/LS H₂O is also measured remotely using Raman lidar from the ground (Leblanc et al., 2012) and differential absorption lidar (DIAL) from aircraft (Kiemle et al., 2008), and by satellite instruments such as the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on EnviSat (Milz et al., 2005) and the Microwave Limb Sounder (MLS) on Aura (Read et al., 2001). One commonality among all current UT/LS H₂O instruments is a lack of in situ calibration. Instruments are typically calibrated on the ground before and after missions or between individual flights, or by comparison to a reference method (e.g. direct absorption) at lower altitudes with higher mixing ratios, and rely on assumed consistency of instrumental background and sensitivity to apply the calibrations to flight conditions in the UT/LS.

Significant effort has been expended to assess the accuracy of UT/LS H₂O measurements (Weinstock et al., 1994, 2009; Hintsa et al., 1999; Kley et al., 2000; Fahey et al., 2009). Both in-flight and laboratory comparisons have demonstrated persistent differences among instruments at mixing ratios below 10 ppm, with significantly larger differences observed in the UT/LS than in the laboratory. The in-flight differences have

typically been much greater than the combined instrumental uncertainties, and indicate the presence of unrecognized artifacts in some or all of the instruments.

To address these issues related to the accuracy of UT/LS H₂O measurements, we have developed a sensitive and specific chemical ionization mass spectrometry (CIMS) technique for the measurement of H₂O at low-ppm mixing ratios. We have adapted an existing CIMS instrument capable of operating on high-altitude research aircraft to make measurements of UT/LS H₂O. The instrument conducts in situ calibration procedures during flight using two separate sources to ensure the accuracy of in-flight measurements. The instrument has been successfully operated in the UT/LS aboard the NASA WB-57 high-altitude research aircraft.

2 Instrument description

2.1 General description

A schematic of the CIMS H₂O instrument, including the principal components of the sampling and calibration flow systems, is shown in Fig. 1. The instrument is a modification of the CIMS instrument described by Neuman et al. (2000) previously used to measure nitric acid (HNO₃) and hydrochloric acid (HCl) in the UT/LS. Minor changes were made to the quadrupole mass spectrometer electronics to convert the instrument from measuring negative ions to positive ions, the control software was rewritten to allow greater flexibility in the autonomous operation sequence, the long flow tube was replaced with a compact, custom ion source, and one of the four turbomolecular pumps was removed and replaced with a second molecular drag pump to provide low pressure pumping for the ion source. Only one channel of the two-channel instrument was converted for H₂O measurements and the other channel was not operated. The NOAA CIMS instrument was designed to function in the unpressurized and unheated fuselage payload bay of the NASA WB-57F aircraft. A design principle of the instrument is to utilize highly regulated internal temperatures, pressures, and flows in order to produce an

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



analytical measurement that is independent of changes in the sampling environment during flight. The instrument operates and is calibrated identically in flight and in the laboratory.

2.2 Inlet system

5 The CIMS H₂O sampling point was located at the bottom of a pylon extending 40 cm below the aircraft fuselage pallet. The pylon is indicated in the schematic in Fig. 1, and a drawing of the pylon showing the inlet flow control valve, zero air and calibration valves, and the ion source appears in Fig. 2. This location places the sampling point outside the aircraft boundary layer, which avoids possible contamination (i.e. artifact)
10 from outgassing of H₂O from aircraft surfaces. Sample air is drawn through a 0.32 cm orifice at the tip of the inlet line, which consists of 0.46 cm ID electropolished stainless steel tubing (WinTech 10, Winter Technologies). The ambient air flow past the sampling point is set by a flow straightener and, hence, is perpendicular to the flow into the inlet line, allowing for sampling of H₂O vapor while rejecting cloud droplets and ice
15 crystals (Popp et al., 2004). The tip of the inlet is heated to ~ 45 °C in order to prevent condensation on the inlet.

The first 5 cm length of the inlet line is enclosed in a heating mantle which heats the ambient sample flow to 45 °C and the air within the pylon was maintained near 30 °C in flight in order to keep all non-heated components near normal room temperatures. Dur-
20 ing calibration, dry synthetic air (zero air) is added to the inlet 3 cm from the sampling point through a 0.2 cm ID stainless steel tube brazed into the inlet tube. Calibration gas is added through a second 0.2 cm ID tube brazed into the inlet tube 15 cm downstream of the inlet tip. This arrangement ensures that all of the calibration gas sent to the inlet flows into the instrument and allows for standard addition of H₂O to the ambient air
25 sample as well as zero air.

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.2.1 Flow and pressure control

An essential feature of the inlet sample flow control is to maintain the pressure and flow conditions in the ion source constant over a wide range of ambient pressures. To achieve this control, three custom butterfly valves are used to hold the pressures constant at the ion source inlet and within the ion source chamber. The valves are of a design similar to that described in Gao et al. (1999) that were developed for the HNO₃ CIMS instrument (Neuman et al., 2000). The new valves are constructed of stainless steel instead of the original Teflon[®] to minimize H₂O adsorption on the valve surfaces. The first butterfly valve (BV1, Fig. 1) controls the inlet flow to 1460 standard cubic centimeters per minute (sccm) using the signal from a mass flow meter (Model AWM5101, Honeywell) located in the main inlet flow downstream of the pylon structure (MFM1, Fig. 1). The second butterfly valve (BV2), located downstream of the pylon and the ion source inlet, is servo controlled to maintain constant pressure in the inlet using the signal from the main flow pressure transducer (P1). The ion source pressure is controlled by the third butterfly valve (BV3) that is servo controlled by the ion-source chamber pressure and pumped directly by a molecular drag pump (Drag Pump 2). The pressure in the main inlet was controlled to 18.5 ± 0.04 hPa while that in the ion source was maintained at 1.6 ± 0.01 hPa. This pressure difference produced a constant flow near 60 sccm through an 18 cm long, 0.18 cm ID electropolished stainless steel capillary into the ion source. The pressures inside the inlet system and ion source were held constant to within their respective tolerances during flights while the aircraft operated over a wide range of ambient pressures (600–80 hPa) and temperatures (280–195 K).

Minimizing the residence time of the ambient sample in the instrument inlet before it reaches the ion source chamber also minimizes the response time of the instrument to rapid variations in ambient H₂O. The near-ambient pressure region of the inlet from the sampling point to the flow control valve (BV1) had a volume of 4.7 cm³ and presented the dominant source of sample residence time. At the inlet sample flow rate (main

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



flow + ion source flow) of 1520 sccm, the resulting sample residence time was < 0.1 s at ambient pressures below 500 hPa.

2.2.2 Materials

Laboratory studies were performed using a prototype of the CIMS H₂O instrument to characterize different inlet line materials for their H₂O desorption properties. A fast solenoid valve controlling H₂O addition to the CIMS H₂O sampling line was used to create a sharp transition from ~ 50 ppm to less than 1 ppm. The resulting decays were reasonably well represented by a triple exponential function. Only small differences were observed in the desorption time constants for 500 sccm flows through 50 cm lengths of 0.64 cm OD electropolished stainless steel, fluoropolymer-coated (Fluoropel 504A-FS, Cytonix Corp.) stainless steel, borosilicate glass, PFA Teflon[®], and Synflex 1300 (Eaton Corp.) tubing. The Teflon[®] tubing was observed to allow measurable H₂O permeation and is therefore not a suitable material for measuring low ppm mixing ratios of H₂O. With the additional considerations of ease and flexibility of manufacturing and minimization of trapped volume, the wetted inlet components were all constructed of electropolished stainless steel.

2.3 Ion source

In contrast to typical chemical ionization techniques for the measurement of atmospheric trace species (e.g. Huey, 2007), no separate reagent ion flow was used for detection of H₂O in the new CIMS technique. Instead, a flow of sample air was directed through the ion source chamber and exposed directly to α particles emitted from a radioactive source. The resulting cascade of ion-molecule reactions produced protonated water ions (H₃O⁺) as a stable end product, with the number of H₃O⁺ ions monotonically related to the H₂O mixing ratio. Optimization of the ion source pressure to achieve a balance between dynamic range and sensitivity (Hz ppm⁻¹) to H₂O required operation at low pressure. The source pressure of less than a few hPa, required

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to prevent saturation of the H_3O^+ signal at a low H_2O mixing ratio, is lower than is typically used in CIMS instruments for atmospheric measurements (Huey, 2007). Standard ^{210}Po ionization sources (Nuclecel, NRD Static Control, Inc.) that are often used in CIMS instruments are designed to work at much higher pressures and flow rates than optimal for the new CIMS design. To address this issue, a custom ion source was designed and constructed.

The custom ion source chamber, shown in Fig. 3, is a cylinder 3.2 cm long and 3.1 cm ID with a $3.2\text{ cm} \times 9.6\text{ cm}$ ^{241}Am foil (NRD Static Control, Inc.) mounted on the inner surface. The total activity of the ^{241}Am foil is 7.2 mCi, of which approximately 15 % is emitted into the ion source volume (NRD Static Control, Inc., personal communication). The end cap of the ion source is comprised of two metal discs with circular openings, separated by a thin insulating disk of plastic (Kel-F[®]). The inner disc is at the same potential as the body of the ion source, while the outer disc is biased at a lower potential to provide an attractive potential for the efficient extraction of positive ions from the ion source chamber. The ion source housing was machined from a tungsten alloy to provide adequate shielding from the gamma rays co-emitted from the ^{241}Am foil, and then gold plated for inertness prior to installation of the foil.

In order to improve ion extraction from the ion source chamber, transmission of ions into the mass spectrometer, and ion declustering, the ion source body and extraction lens were maintained at positive potentials relative to the mass spectrometer entrance nosecone, which was held at ground potential. The ion source body was held at +140 V relative to the nosecone and the extraction lens was held at +90 V. These voltages produced a -50 V attractive potential to extract positive ions from the ion source and a 70 V cm^{-1} field to accelerate the ions to the entrance to the mass spectrometer.

The custom ^{241}Am ion source yielded a factor of 2 increase in total ion current over a 20 mCi commercial ^{210}Po source when operating at pressures below 2 hPa and a flow of 1000 sccm. This improved signal was maintained while operating with flows as low as 30 sccm, for which almost no H_3O^+ signal was observed using the commercial ^{210}Po source.

2.3.1 Ionization mechanism

The α particles emitted by the ^{241}Am foil are energetic enough to ionize any molecule they encounter on their passage across the ion source chamber, so the bulk of the ions are initially formed from interaction with N_2 and O_2 (Takebe, 1974)



The N_2^+ , N^+ and O^+ ions are rapidly converted to O_2^+ with minor branches producing stable NO^+ ions. A small fraction of the N_2^+ ions react with H_2O to produce N_2H^+ ions, which can subsequently react with an additional H_2O molecule to produce H_3O^+ . The dominant channel for producing H_3O^+ is through a series of reactions beginning with the association of O_2^+ with H_2O (R3) or with another O_2 molecule to form O_4^+ (R4), which can then form H_3O^+ clusters in a series of reactions involving multiple H_2O molecules (Fehsenfeld et al., 1971; Anicich, 2003):



25 This ion chemistry is similar to that occurring in the D region of the ionosphere (Ferguson, 1974). The multi-step and multi- H_2O nature of the reaction mechanism results in a non-linear relationship between the H_2O mixing ratio and number of H_3O^+ ions

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



produced. The important role of three-body reactions (R3, R4, R5) in the ionization mechanism leads to a large pressure dependence of the H_3O^+ product ion yield. Maintaining a constant ion source pressure is thus critical in order to produce a consistent measurement sensitivity.

5 The ion-molecule clusters are all dissociated by energetic ion-molecule collisions induced by the strong electric field used to accelerate the ions from the ion source into the mass spectrometer, thereby converting all of the $\text{H}_3\text{O}^+ \cdot \text{OH}$ and $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ into H_3O^+ . The observed mass spectra for two example mixing ratios of H_2O are shown in Fig. 4. The well-defined H_3O^+ signal at mass-to-charge ratio (m/z) 19 is used to
10 quantify the H_2O in the sample flow. The largely H_2O -independent NO^+ signal at m/z 30 serves as a useful diagnostic for tracking the stability of the ion source and mass spectrometer and the O_2^+ signal at m/z 32 represents the majority of the ion current at low H_2O mixing ratios. The effective declustering of ions prior to entering the mass spectrometer is demonstrated by the absence of any signal from $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ at m/z
15 37.

2.3.2 Interferences

Due to the relatively high abundance of H_2O compared to most other atmospheric trace gases in the UT/LS (especially those containing hydrogen atoms), significant chemical interferences are not expected in the ionization scheme producing H_3O^+ as outlined
20 above. To quantify the potential effects on the H_3O^+ signal from the most abundant atmospheric trace species, laboratory experiments were conducted by adding O_3 , CO_2 and CH_4 along with H_2O to dry (~ 0.5 ppm H_2O) synthetic zero air (Ultra Zero Air, Scott-Marrin, Inc.). These mixtures were introduced into the CIMS H_2O instrument and the
25 H_3O^+ signal response to H_2O mixing ratio was observed as the mixing ratios of the other species were varied. O_3 at mixing ratios up to several ppm was found to have no effect on the measured H_2O sensitivity. CH_4 in the sample flow produced an H_3O^+ signal with approximately 1% of the sensitivity to H_2O . Adding 380 ppm CO_2 to the zero air resulted in a decrease in sensitivity to H_2O of $\sim 10\%$.

Zero air containing mixing ratios of CO₂ and CH₄ similar to current ambient values, 380 ppmv and 1.8 ppmv, respectively, was found to yield a sensitivity to H₂O indistinguishable from that obtained using a desiccated ambient air standard prepared by the NOAA Earth System Research Lab Global Monitoring Division. To account for the CO₂ and CH₄ effects, the synthetic zero air used in the laboratory and in flight contained 380 (± 8) ppmv CO₂ and 1.78 (± 0.04) ppmv CH₄ (Scott-Marrin, Inc.) to simulate ambient air concentrations.

2.4 Calibration system

Calibration of the CIMS H₂O instrument in flight and in the laboratory was accomplished using two separate H₂O sources. The primary calibration source was quantitative oxidation of H₂ in zero air over a Pt catalyst to produce known mixing ratios of H₂O. The development and evaluation of this calibration source is described in detail by Rollins et al. (2011). For calibration of the CIMS instrument, flows (0–20 sccm each) from three H₂ standards of different mixing ratios (303 ppm, 2588 ppm, and 2.069 %, Scott-Marrin, Inc.) were combined with a 50 sccm flow of zero air and passed through a Pt catalyst. The catalyst was located in the inlet pylon so that the H₂ was converted to H₂O immediately prior to the calibration flow being added to the sample flow. The catalyst consisted of a 14 cm long, 0.22 cm ID Pt tube with two 2.5 cm × 5 cm pieces of 100 mesh Pt gauze (Sigma-Aldrich) rolled up and packed loosely inside. A 10 cm long copper block containing a cartridge heater was clamped around the Pt tube and the assembly insulated with rigid silica foam. The catalyst was maintained at a constant temperature of 180 °C, which results in quantitative oxidation (> 99 %) of the H₂ in the flow to H₂O (Rollins et al., 2011). A 100 μm orifice at the exit of the catalyst tube maintained the pressure in the catalyst at greater than 1000 hPa, independent of the lower sample line pressure. In the primary procedure for instrument calibration in flight and in the laboratory, the calibration flow from the catalyst containing H₂O was added to a sample flow of zero air with known residual H₂O, thereby producing accurately known H₂O mixing ratios in the instrument.

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The secondary calibration source was a gravimetrically-prepared H₂O-in-zero-air standard. The cylinder zero air balance gas contained CO₂ and CH₄ as described above for the sample-flow zero air. The H₂O standard was stored in a 34 L electropolished stainless steel cylinder (Essex Industries) in which low H₂O mixing ratios have been shown in NOAA tests to be stable to within a few percent for periods of up to several years. A subsample from this cylinder was transferred to a 4.5 L electropolished stainless steel cylinder (Essex Industries) in the instrument for use during flight. A 2500 sccm flow from this standard was delivered to the inlet line using valve V2 in Fig. 1 in place of zero air or ambient sample, thereby producing an independent, absolute, single calibration point that could be used to confirm the accuracy of the multipoint dynamic-dilution H₂ catalyst calibration in flight.

In order to maintain flow through the calibration system while not adding calibration gas to the inlet, and to minimize dead volume and wetted surface area in the calibration line, the H₂/Pt H₂O calibration flow is diverted from the inlet to the instrument vacuum pump by means of a tee and 2-way valve (V3) when it is not needed. The diverted calibration flow passes through a mass flow controller, which is set to also take a small amount (< 50 sccm) of air from the sample line to ensure complete diversion of the calibration flow. Switching this valve allows the calibration gas to be rapidly added or removed from the sample flow.

The calibration flows were controlled using Bronkhorst EL-Flow thermal mass flow controllers (Bronkhorst High-Tech B.V., The Netherlands). Previous experience with thermal mass flow controllers aboard unpressurized high altitude aircraft has indicated that errors in the reported flow could result from operation at low ambient pressure external to the flow controller. In laboratory tests, the Bronkhorst flow controllers used in the CIMS instrument were found to be insensitive (< -1 % deviation) to external ambient pressure at pressures down to 80 hPa, which was the lowest pressure reached in the WB-57 payload bay. At lower pressures, larger errors in the reported flow were observed, reaching -10 % at 22.5 hPa and -25 % at the lowest pressure tested of 17 hPa.

3 Instrument performance

3.1 Laboratory evaluation

3.1.1 Sensitivity

The multiple reaction paths and multiple steps in the ionization mechanism leading to the production of H_3O^+ result in a non-linear response to H_2O in the CIMS instrument (Fig. 5). At low mixing ratios (< 10 ppm), H_2O is the limiting reagent in multiple steps in the ionization mechanism and, thus, the sensitivity is greater than first order in H_2O . At higher mixing ratios (> 10 ppm), the availability of O_2^+ becomes limiting and the sensitivity begins to decrease with increasing H_2O . The combination of these two effects leads to an overall sigmoidal shape to the instrument sensitivity function. The ionization mechanism also involves three-body reactions and therefore the sensitivity is a strong function of the ion source pressure. With the active control of the pressure in the ion source to within ± 0.01 hPa, no sensitivity changes due to pressure variations could be detected.

Due to the non-linearity of the instrument response, the calibration of instrument sensitivity to H_2O requires the addition of multiple H_2O mixing ratios spanning the measurement range of interest in the ambient atmosphere. Further, a means of interpolating between the individual calibration points is necessary to provide a smooth function of the sensitivity over the mixing ratio range. Several different interpolation approaches were considered, including linear and spline interpolation and curve fitting using a number of different equations. The shape of the response curve suggested the use of a sigmoidal function, and the best results, as measured by fit residual to omitted data points, were achieved using overlapping, piecewise fitting with Hill's equation to the lower and upper portions of the curve. The formulation of Hill's equation used is

$$y(x) = y_0 + (y_{\max} - y_0) \left[1 + (x_{\text{half}}/x)^\rho \right]^{-1} \quad (1)$$

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

and time constant of the decaying signal would be a function of the H₂O in the sample flow. Hence, adding desiccated air is not necessarily an effectual approach for determining the contribution to the instrument signal from desorbing H₂O at ambient H₂O values. For our CIMS inlet system, we argue that a better and more effective approach is to conduct a multi-point calibration with at least one calibration point at a mixing ratio lower than the lowest expected ambient value. In this way, any background artifact contributes to the H₃O⁺ signal during the calibration process in the same manner as it does when sampling ambient air. Thus, a background artifact is automatically accounted for in the CIMS H₂O sensitivity calculation without explicit knowledge of the artifact value. For the CIMS H₂O measurement, the lowest calibration mixing ratio was that of the zero air, with a value between 0.5 and 0.8 ppm. At these mixing ratios, a stable H₃O⁺ signal could be achieved in a reasonable time (< 60 s), even starting from mixing ratios of several hundred ppm.

3.1.3 Accuracy

The primary standard used to evaluate the accuracy of the CIMS H₂O measurement was a NIST-traceable, reference chilled mirror hygrometer (model 373LX, MBW Calibration Ltd.). The MBW model 373LX (MBW hereafter) has a lower limit frost point temperature of −95 °C and a stated accuracy of ± 0.1 °C. At 1 atm pressure this translates to a minimum detectable mixing ratio of less than 0.04 ppm, and an uncertainty of ± 0.08 ppm (< 2 %) at 5 ppm. The MBW was used to show routinely in the laboratory that the two calibration sources used in flight, namely, Pt-catalyzed H₂ oxidation and the single-point H₂O standard, were accurate to within a few percent.

In practice, the ultimate accuracy of the CIMS H₂O measurement was evaluated in the laboratory by simultaneous measurement of a range of H₂O mixing ratios with the MBW and CIMS sampling from a common manifold. During these intercomparisons, the CIMS instrument was operated and calibrated using the same calibration and data reduction procedures as used in flight. The CIMS measurement exhibited agreement better than 3 % over a wide mixing ratio range, as is shown in an example in Fig. 7.

3.1.4 Precision

The precision of the CIMS measurement was evaluated by comparing the observed standard deviation in the H_3O^+ signal while sampling a flow with constant H_2O mixing ratio to the value expected from Poisson statistics for pulse-counting noise in the mass spectrometer electron multiplier. The observed ratio was < 1.2 , indicating that there were no significant additional sources of instrument noise. The observed instrument precision (2σ , 1 s) at 3 ppm was < 0.07 ppm, or $\sim 2\%$. Precision contributed only slightly to the overall measurement uncertainty.

3.1.5 Uncertainty

The uncertainty of the CIMS measurement of H_2O mixing ratio is tied directly to the accuracy of the H_2O amounts delivered to the instrument during a calibration. The factors that contribute to the overall measurement uncertainty include the uncertainty in the measured calibration and sample flows, the uncertainty in the mixing ratios of H_2 and H_2O in the calibration flow and zero air, the uncertainty in the efficiency of the Pt catalyst in converting H_2 to H_2O , the error in the curve fit representation of the calibration data, and the uncertainty arising from interpolating the sensitivity between calibrations.

3.2 Operation on the NASA WB-57 during MACPEX

During the Mid-latitude Airborne Cirrus Properties Experiment (MACPEX) campaign, the CIMS instrument was flown in the fourth (aft-most) pallet position on the WB-57. The instrument operated fully autonomously following instrument power-on from the cockpit. The instrument pumps were turned on to begin instrument flow and pump-down of the vacuum chamber when the aircraft passed a pressure level of 600 hPa (approximately 4 km) during initial ascent. Data acquisition began as soon as the vacuum chamber reached operating pressure for the electron multiplier ($< 10^{-5}$ hPa). The

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



instrument operated throughout the flight following a programmed measurement and calibration sequence and shut down when the aircraft descended past 600 hPa. The quadrupole mass filter was set to transmit H_3O^+ ions for 9 s, followed by NO^+ and O_2^+ for 0.5 s each. Data were acquired at a rate of 10 Hz and reported as 1 s averages.

3.2.1 In-flight calibration

During MACPEX flights, the CIMS H_2O instrument was calibrated at mixing ratios ranging from 0.5–0.8 ppm (the H_2O content of the zero air) to 153 ppm using the Pt-catalyzed H_2 oxidation system. Calibrations were automatically performed every 42–46 minutes during a 4.5–6 h flight. Additional single point calibrations using the H_2O in zero air standard were conducted during every other calibration sequence. Figure 8 shows a typical in-flight calibration sequence including a calibration from the single-point H_2O standard. During a calibration sequence, a 2500 sccm flow of zero air was added to the inlet, providing ~ 1000 sccm overflow from the inlet opening to insure no ambient air was sampled. After 30 s, a mass scan from m/z 16 to m/z 43.5 was recorded to allow an assessment of the stability of peak shape and position in the mass spectrum. After 90 s, the flow of zero air was replaced with a 2500 sccm flow from the H_2O cylinder for 120 s in order to ensure a stable signal. Following the H_2O standard measurement, the zero air flow to the inlet was resumed. 60 s later, the calibration flow diversion valve (V3 in Fig. 1) was closed so that flow from the H_2 oxidation system was added to the zero air in the sample flow. The H_2 calibration standard flows were adjusted in a series of 11 steps in order to generate increasing mixing ratios from 0.8 (zero air only) to ~ 153 ppm. In each step, the new mixing ratio was stable after 20 s and then averaged for 10 s for a total of 30 s per step. Following the final calibration step, the calibration diversion valve was opened and after 10 s the zero air flow was stopped, returning the instrument to ambient sampling. The entire calibration sequence required 640 s to complete; the calibration sequence without the single-point H_2O standard required 495 s. The resulting calibration curve from the calibration shown in Fig. 8, including the single-point gravimetric standard, appears in Fig. 9. The calibration curves

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



determined by the in-flight calibrations were indistinguishable from those measured in calibrations on the ground (e.g. Fig. 5).

Ambient H₂O mixing ratios were calculated using a linear interpolation of the measured sensitivity curves between adjacent calibrations. The contribution of this interpolation to the uncertainty in the calculated mixing ratio at a given point in time was estimated from the difference between the mixing ratios calculated at that point using the preceding and subsequent calibrations, weighted by the inverse of the time interval from each calibration. This results in a maximum contribution to the uncertainty from the interpolation at the midpoint between calibrations.

In order to verify that there were no unexpected differences between the sensitivity measured using zero air and the sensitivity in ambient air, a standard addition test was conducted following every calibration sequence by adding the H₂ Pt/H₂O calibration flow directly to the ambient air sample in quantities to that produced H₂O mixing ratio increases of 1.2 ppm and 3.6 ppm. When the variance in ambient mixing ratios was sufficiently low for the added H₂O amounts to be reliably measured, the observed mixing ratio increase agreed with the expected value to within 5%, indicating no systematic bias in the sensitivity due to calibrating in zero air.

The mixing ratios of H₂O in the zero air and single-point H₂O cylinders were measured before and after each flight using the MBW. The pre- and post-flight values in all cases were consistent within ± 0.1 ppm.

3.2.2 Instrumental artifact

Since the H₂O concentrations at the surface are so much greater than in the UT/LS, an artifact H₃O⁺ signal caused by residual parasitic H₂O in the instrument during flight is always a concern. As a consequence, effort was expended to minimize exposure of the internal surfaces of the instrument to ambient air when the instrument was not in flight. Overnight prior to a flight, the main inlet line was purged (see Fig. 1) with a small (~25 sccm) flow of zero air from an external cylinder in order to reduce exposure of the instrument flow system to ambient H₂O. This purge flow was maintained using the

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

on-board zero air cylinder during installation and pre-flight, until the instrument received power on the aircraft, at which point the 2.5 slpm zero air flow to the inlet began and continued through the instrument startup sequence. These efforts were only partially successful in preventing infiltration of ambient H₂O into the instrument calibration and zero air flow paths. H₂O contamination in the zero air and calibration lines caused the actual H₂O amount delivered to the inlet line during the first and second calibrations to be higher than the calculated value, resulting in an overestimate of the sensitivity and leading to a negative bias in the calculated H₂O mixing ratio. As a result, H₂O mixing ratios could not be accurately calculated for the first ~ 45 min of a flight due to uncertainty in the absolute value of the calibration mixing ratios. The magnitude of this potential bias during subsequent portions of a flight was assessed by comparing the mixing ratios observed in-flight for the H₂O standard to the values determined pre- and post-flight with the MBW. The excellent agreement (better than 5 %) found between the in-flight value measured by the CIMS and the MBW determination indicated that there was not a significant bias in the CIMS measurement from H₂O contamination in the zero air and calibration lines after the first hour of flight.

3.2.3 In-flight performance

The CIMS H₂O instrument operated successfully on seven science flights during the MACPEX campaign. A summary of the typical performance metrics for the instrument is shown in Table 1. The overall duty cycle of the measurement, accounting for calibrations, was 0.68. Propagation of uncertainties from all factors contributing to the calculation of H₂O mixing ratios (see Table 2) in flight yields a total measurement uncertainty ranging from 9 to 11 %. Statistically determined uncertainties were estimated at the 2 σ level, and where the individual uncertainties are independent, the uncertainties were combined in quadrature.

One issue with sampling H₂O through an inlet line is the potential effect on the measurement response time of H₂O adsorption on inlet surfaces. The in situ calibrations of the CIMS instrument provide an opportunity to directly assess the inlet response time.

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The observed H_3O^+ signals exhibit exponential decay behavior following sharp transitions in H_2O in the instrument inlet from addition of zero air or diversion of calibration gas away from the inlet. Analysis of these transitions reveals that the time required to reach 95 % of the decay to the final value (3 e-folding times) is less than 3 s following an approximate step change of several ppm in H_2O at mixing ratios of a few ppm. The response time becomes significantly shorter with increasing mixing ratio and equilibration to step increases in H_2O is generally faster than to similar decreases.

The time series of H_2O mixing ratios measured by CIMS during the MACPEX science flight on 25 April 2011 is shown in Fig. 10 along with the ambient pressure (inverted scale). On this flight, the mixing ratios during the in-cloud measurement legs in the middle of the flight were below the upper end of the CIMS calibration range (~ 150 ppm) and therefore could be quantified. During the final high-altitude leg on the return to Ellington field, H_2O reached its minimum value near 4.3 ppm just prior to final descent. Two features observed during this flight highlight the capabilities of the CIMS H_2O measurement and are shown in greater detail in Figs. 11 and 12. First, the averaged 1 s data and the raw 10 Hz data during a short in-cloud segment of this flight are shown in Fig. 11. Significant structure in H_2O on small scales is clearly visible in the 10 Hz data (which corresponds to ~ 20 m spatial scale at aircraft speeds) that is not fully represented in the 1 s average values. This additional structure demonstrates the fast response time of the instrument to ambient H_2O fluctuations at timescales of less than 1 s. The inlet response time determined from step changes in zero air and calibration flows, discussed above, is a conservative estimate of the actual response time to ambient fluctuations since rapid variations don't have time to saturate or deplete the H_2O adsorbed to inlet surfaces (Li and Dylla, 1994). Second, measured H_2O mixing ratios from the final high-altitude segment of the flight are plotted in Fig. 12 along with O_3 mixing ratios measured by the NOAA O_3 instrument (Gao et al., 2012). Over the period shown, the aircraft ascended from 13.9 km to 16.9 km and descended back 13.9 km. The high precision of the CIMS H_2O measurement (< 0.1 ppm) allows the correlation in the structure between the H_2O and O_3 mixing ratios to be clearly observed.

4 Discussion

A number of attempts have been made during the last decade to determine the source(s) of the significant discrepancies observed among in situ UT/LS H₂O measurements. Ground-based comparisons and comparisons of laboratory calibration standards have generally yielded better agreement than is observed in flight. These results indicate that there are unrecognized errors that arise in the measurements by some or all of these instruments under the sampling conditions they experience in the UT/LS. A complication in determining the sources of these errors is the lack of representative, in situ, calibration and background determinations by any of the instruments under in-flight UT/LS sampling conditions.

The success of the MACPEX deployment of the CIMS H₂O instrument demonstrates the power of applying this calibrated technique for the measurement of low H₂O mixing ratios the UT/LS. The excellent agreement demonstrated here between two in situ calibration sources for H₂O measurements below 10 ppm in the UT/LS has no precedent, and combined with the consistency of the calibrations between laboratory and flight environments provides significant confidence in the measurements. These results show that in situ calibration flows of H₂O can be accurately and routinely provided in a physically challenging aircraft environment. We note that other in situ techniques incorporating extractive sampling (e.g. Lyman- α photofragment fluorescence, tunable diode laser absorption, and chilled mirror) could potentially adopt the CIMS calibration system. The calibration system that has been developed and deployed with the new CIMS H₂O instrument should provide a useful tool for addressing issues of measurement accuracy and consistency from flight to flight.

The CIMS H₂O technique has a number of further advantages and some disadvantages. A primary advantage is the potential for higher signal-to-noise (S/N) than is achieved with any other existing H₂O measurement technique. During the first aircraft flights the ionization source pressure was adjusted to achieve S/N while maintaining a useful dynamic range for the UT/LS region (1–150 ppm). An increase in S/N

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**T. D. Thornberry et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

by a factor of 3 or more is easily achievable if reduced dynamic range is acceptable. Higher S/N could be useful for investigating extremely dry regions of the atmosphere. Secondly, the ability to operate the detector under low-pressure conditions offers a significant advantage over other analytical techniques because it provides the basis for a short response time and minimizes the potential for outgassing artifact to influence the measurements. Thirdly, because the mass spectrometer detection region is downstream and at significantly lower pressure than the ion source chamber, outgassing into this region does not produce H_3O^+ ions to interfere with the measurement. Thus, H_2O leaks into most of the instrument are not expected to result in an artifact response.

A potential disadvantage of the current CIMS instrument is its large size, weight, and power requirement, which preclude its operation on many platforms, in particular many unmanned aircraft. With current technology and optimization of the instrument design for H_2O measurements, these values could be reduced substantially. A disadvantage of the CIMS technique for H_2O measurements described here is the non-linearity of the sensitivity, which is a fundamental aspect of the ion-molecule chemistry arising from the direct ionization of the ambient sample. This aspect necessitates multipoint calibrations across the entire range of mixing ratios to be quantified in order to maintain uniform accuracy. Adjustments to the geometry and operating potentials of the ion source can have significant effects on the shape of the sensitivity curve, and might yield simpler functional forms (e.g. power law) across the measurement range of interest. It may also be possible that the sensitivity of CIMS to H_2O could be rendered linear over the range of interest with a different source geometry and operating parameters, or by using a typical CIMS ionization scheme in which reagent ions are generated and added to the sample flow instead of passing ambient flow through the ion source.

5 Conclusions

A new CIMS technique has been successfully developed for the measurement of low-ppm mixing ratios of H_2O . Ambient sample air flow is directly exposed to α -particle

**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

radiation in a custom ion source and the resulting H_3O^+ ions are used to quantify the H_2O mixing ratio. This technique has been implemented in a CIMS instrument capable of operating in unpressurized payload spaces on a high-altitude research aircraft. Critical pressures and flows are tightly controlled to allow the instrument to operate identically in flight and on the ground. The new CIMS is unique among current UT/LS H_2O instruments in that it includes a calibration system and conducts in-flight calibration with standard addition of known H_2O amounts. The consistency of in-flight and laboratory calibrations demonstrates that the CIMS H_2O measurements in the UT/LS were not subject to significant artifacts.

The CIMS instrument flew on board the NASA WB-57 during the 2011 MACPEX campaign and measured H_2O mixing ratios as low as 3.5 ppm in the mid-latitude UT/LS. The instrument demonstrated excellent precision ($< 2\%$) and high accuracy ($\sim 10\%$) across its total calibrated measurement range of < 1 to 150 ppm. Data were acquired at 10 Hz and averaged to 1 s. The high precision and fast time response allow use of the 10 Hz data to resolve H_2O fluctuations at scales down to 20 m at typical aircraft speeds.

Using the new CIMS H_2O instrument for UT/LS measurements is expected to contribute to resolving the issues of differences among measurements in multiple instrument intercomparisons by providing high precision measurements that are directly calibrated in flight under UT/LS conditions.

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- 30

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. Summary of typical H₂O CIMS performance metrics during the MACPEX campaign.

Sensitivity ^a	~ 2000 Hz ppm ⁻¹ (at 3 ppm)
Signal to noise ^a	32 (1 s, 2σ, at 3 ppm)
Detection limit	0.5–0.8 ppm (lowest calibration point)
Data rate	10 Hz, averaged to 1 s
Total uncertainty	9–11 %
Response time ^b	< 3 s
Calibrated range	0.5–153 ppm
Weight	220 kg
Power	2.2 kW

^a Average over seven UT/LS flights in the MACPEX campaign. For the last two flights, re-optimization of the ion transmission optics in the mass spectrometer resulted in a factor of 1.9 increase in sensitivity and 1.4 increase in signal to noise over the values observed during the first five flights.

^b Time required to reach 95 % (3 e-folding times) of the decay to the final value following a step change down in mixing ratio at low-ppm mixing ratios.

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Table 2. Summary of components of uncertainty for the H₂O CIMS measurement during the MACPEX campaign.

Source of uncertainty	Uncertainty
H ₂ standards	< ± 2 %
Zero air H ₂ O content	< ± 0.1 ppm
Flow controller accuracy	< ± 3 %
H ₂ catalytic conversion efficiency	< −1 %
Calibration curve fitting	< ± 2 %
Zero artifact	< +0.1 ppm
Interferences	< ± 0.5 %
Interpolation between calibrations	< ± 4 %

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

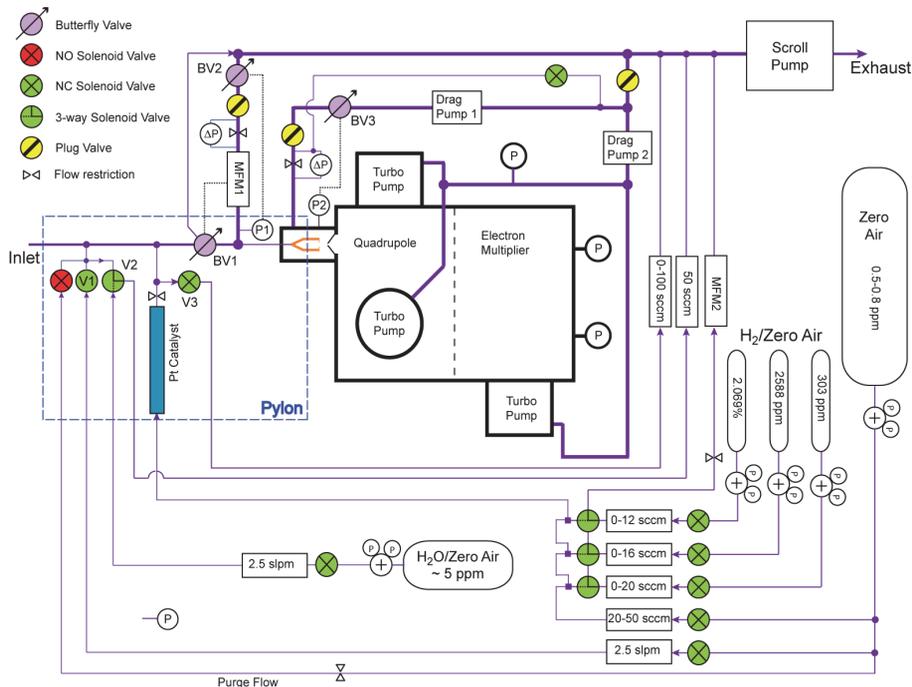


Fig. 1. Schematic of the CIMS instrument showing the principal components of the flow and calibration systems. A custom butterfly valve (BV1) controls the inlet sample mass flow measured by mass flow meter MFM1. BV2 regulates the main inlet pressure (P1) and BV3 regulates the ion source pressure (P2). Solenoid valve V1 is the zero air delivery valve, V2 is the H₂O standard delivery valve, and V3 is the H₂/Pt-H₂O calibration diversion valve. Mass flow controller flows or flow ranges during operation are specified. NO and NC denote normally open and normally closed solenoid valves.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

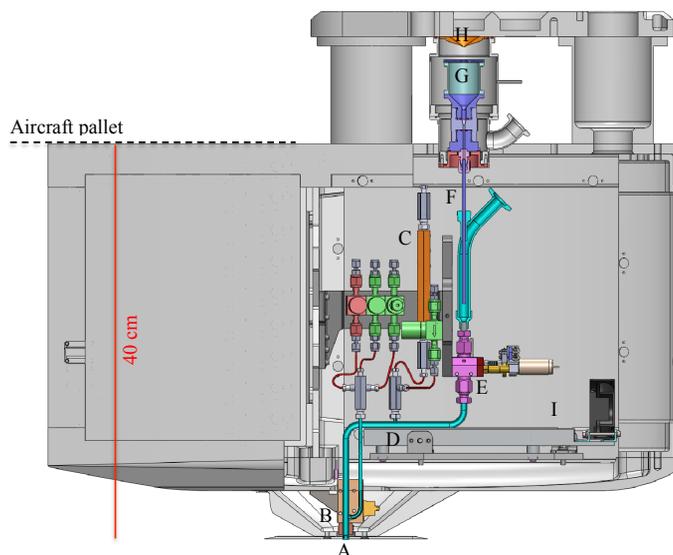


Fig. 2. Model of the CIMS H₂O inlet pylon showing the inlet geometry and components of the flow and calibration system. Ambient air enters the instrument through the sample point (A) in the center of the thin flow straightener plate at the bottom of the pylon. The zero air addition point (B) is located 3 cm downstream of the sample point. The principal calibration source is H₂O produced by H₂ oxidation in a Pt catalyst (C), which is added to the inlet flow (D) 15 cm from the sample point. A custom butterfly valve (E) maintains a constant mass flow through the inlet independent of the ambient pressure. A small fraction of the sample flow is extracted through a stainless steel capillary (F) and flows into the ion source (G). Ions produced in the ion source enter the mass spectrometer (not shown) through the entrance nosecone (H). A fan and heater (I) are used to heat the interior of the pylon to near 30 °C during flight.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



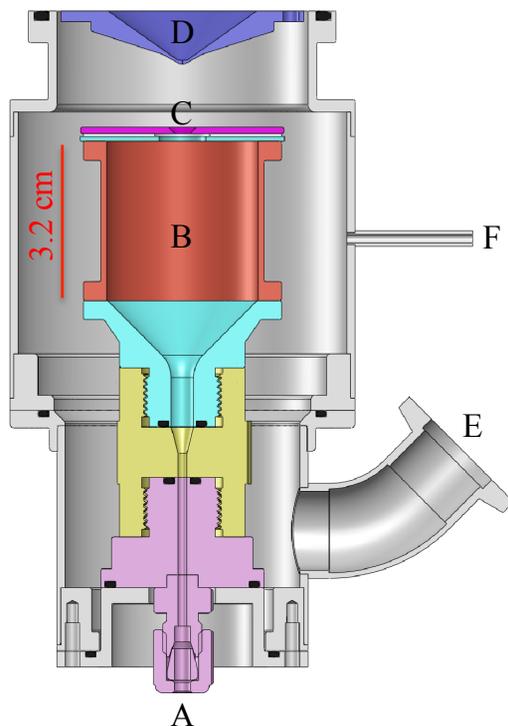


Fig. 3. Custom ion source for the CIMS H₂O measurement. Air enters the ion source chamber through a capillary connected to the fitting (A) at the bottom. The ²⁴¹Am foil is located on the inside of the ion source chamber (B), which is held at a +140 V potential with respect to ground. Positive ions formed inside the chamber are extracted through the exit lens (C) by applying a +90 V potential to the lens (−50 V relative to the chamber). The ions exit the chamber directly in front of the entrance nosecone of the mass spectrometer (D), which is held near ground potential. Air flowing through the ion source chamber is pumped away through port (E) on the vacuum can, while the pressure is monitored through a smaller port (F).

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

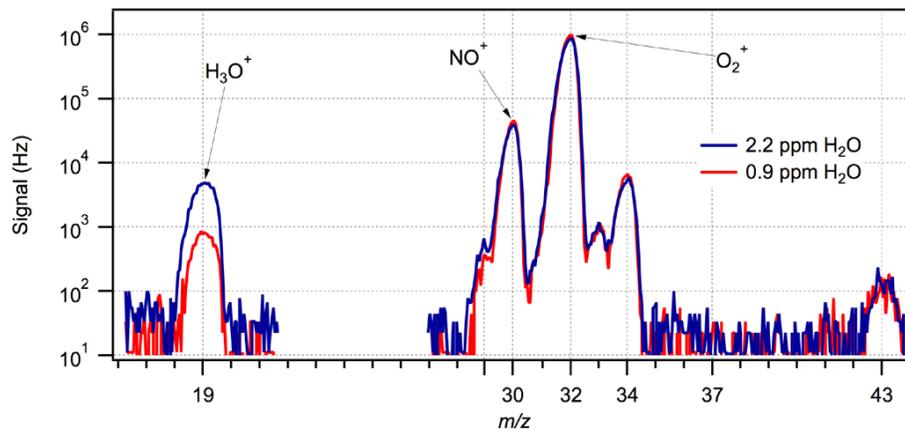


Fig. 4. Observed mass spectra with 0.9 (red) and 2.2 (blue) ppm H₂O in the sample flow. The complete declustering of ions entering the mass spectrometer is demonstrated by the absence of a peak corresponding to H₃O⁺ · H₂O at *m/z* 37.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



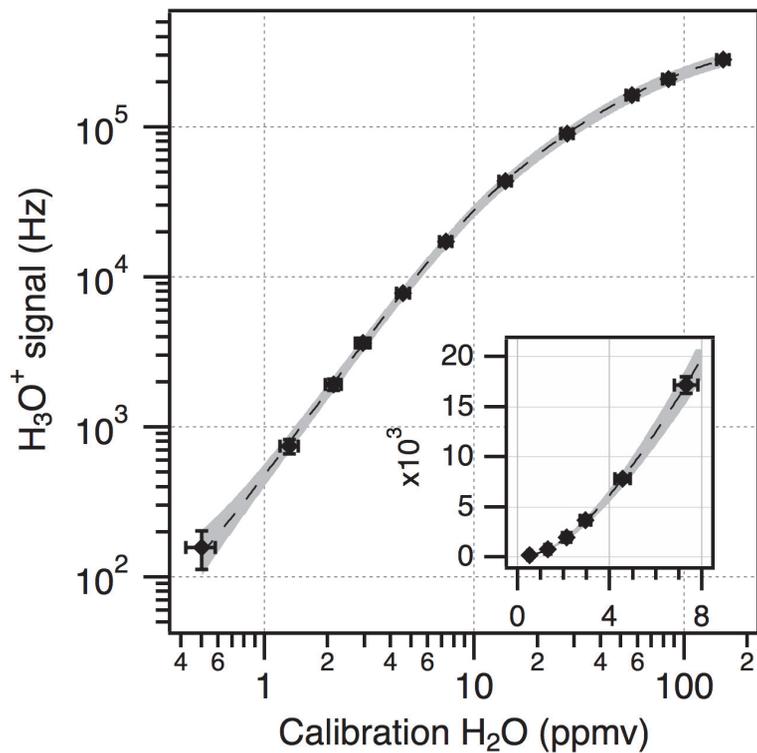


Fig. 5. CIMS calibration curve showing the non-linearity of the response to H₂O. The data are fit piecewise using two overlapping Hill equation (sigmoidal) curves, one for the lower 7 data points and one for the upper 7 data points. The grey shaded region represents the experimental uncertainty in the fit.

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

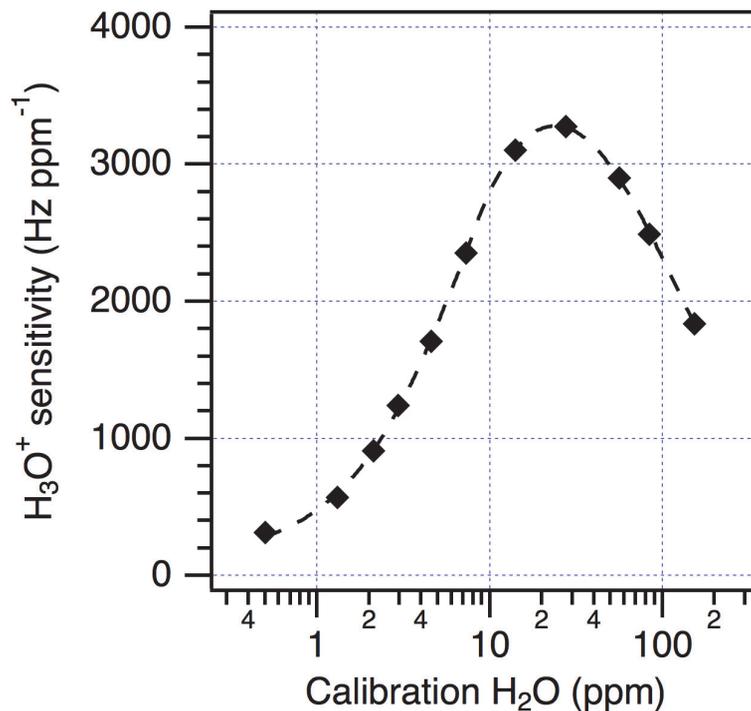


Fig. 6. The sensitivity of the CIMS measurement as a function of the H₂O mixing ratio from the calibration shown in Fig. 6. The diamonds are the values from the individual calibration points and the dashed line is the curve fit.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

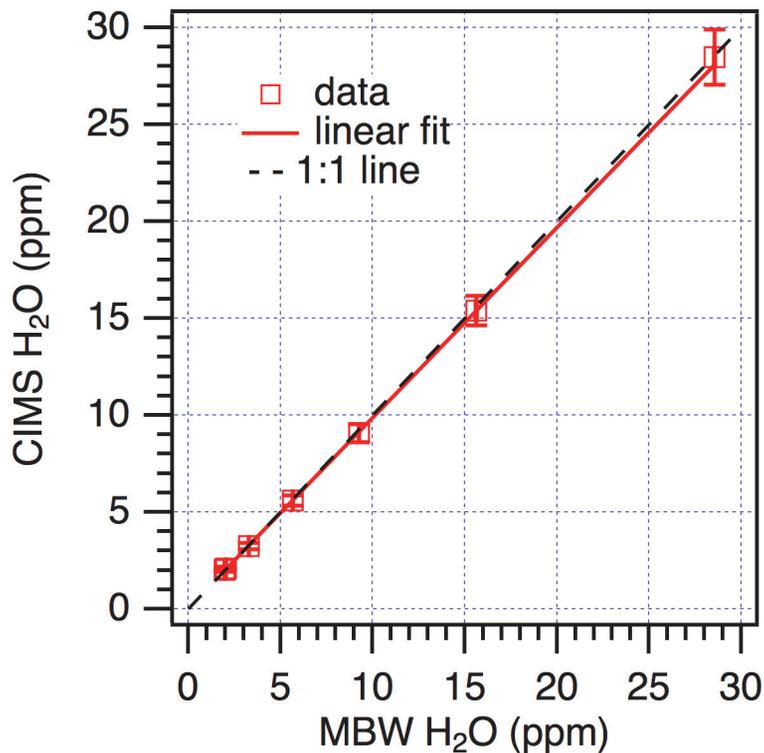


Fig. 7. Comparison of CIMS measured H₂O mixing ratios to MBW measured mixing ratios in a laboratory experiment. The black dashed line is the 1 : 1 line and the weighted, orthogonal linear regression fit to the data (red line) is $\text{CIMS} = 0.06 (\pm 0.05) + 0.98 (\pm 0.01) \times \text{MBW}$.

Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

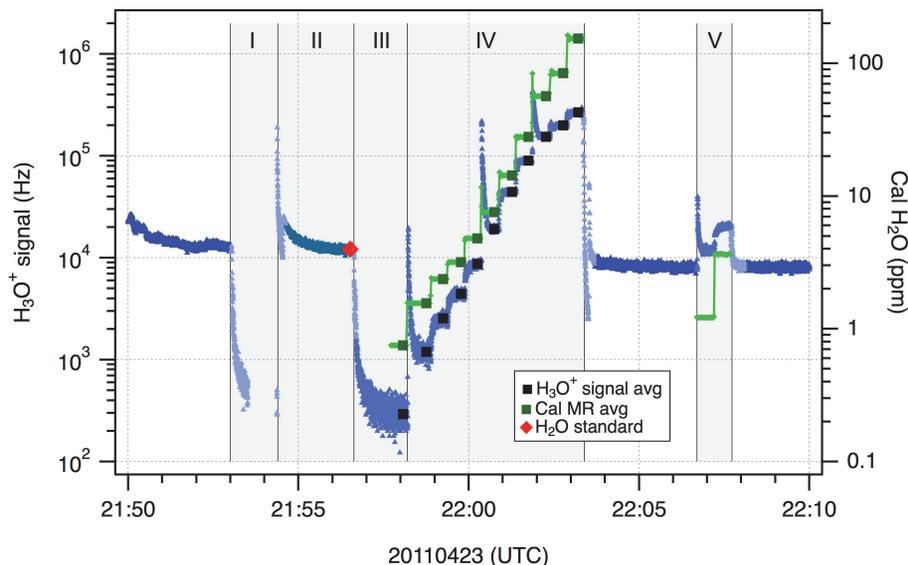


Fig. 8. In-flight calibration sequence from the flight on 23 April 2011. The small blue symbols are the H_3O^+ signal and the green trace is the H_2 -generated H_2O calibration mixing ratio. The shaded regions in the plot denote zero air and calibration gas flow to the inlet. Regions I and III are zero air alone, region II is the H_2O standard, region IV is zero air plus $\text{H}_2/\text{Pt H}_2\text{O}$ calibration flow, and region V region is the $\text{H}_2/\text{Pt H}_2\text{O}$ standard addition to ambient air. The red diamond denotes the average H_3O^+ signal during the last 10 s of the H_2O standard, the black squares are the average H_3O^+ signal during the last 10 s of each $\text{H}_2/\text{Pt-H}_2\text{O}$ calibration step, and the green squares are the calculated absolute H_2O mixing ratios for the last 10 s of each calibration step. The mass scan performed during the calibration resulted in the apparent data gap in region I.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Measurement of low-ppm mixing ratios of water vapor

T. D. Thornberry et al.

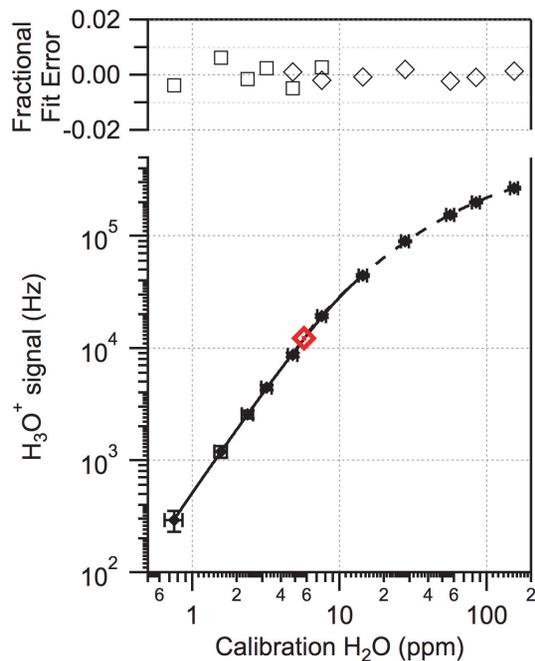


Fig. 9. H_3O^+ signal from the calibration sequence shown in Fig. 8. The solid squares are 10 s average values of the signal plotted against the H_2O mixing ratio calculated for the calibration steps. The open squares are the fractional residual from the lower Hill equation fit (solid line) and the open diamonds are the fractional residuals from the upper Hill equation fit (dashed line). The red diamond is the calibration point from the gravimetric H_2O standard, demonstrating the excellent agreement between the gravimetric and H_2 calibrations.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

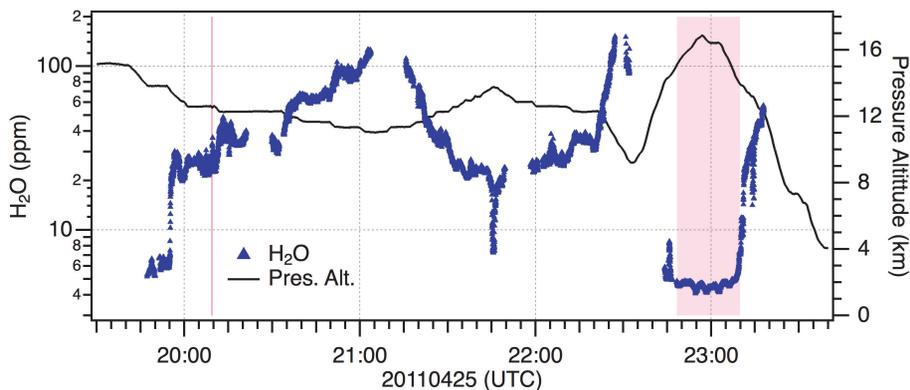


Fig. 10. Time series of H₂O mixing ratios (blue) measured by the CIMS instrument and aircraft pressure altitude (black) from the MACPEX science flight on 25 April 2011. The highlighted sections correspond to the segments shown in greater detail in Figs. 11 and 12.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

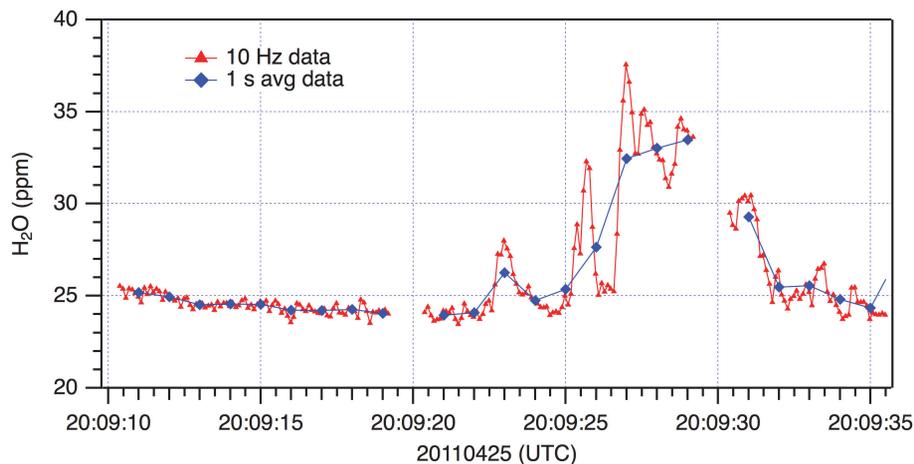


Fig. 11. Time series of CIMS H₂O 10 Hz data (red triangles) and corresponding 1 s averages (blue diamonds) during sampling within a cirrus cloud on the flight on 25 April 2011. The 10 Hz data reveal additional structure in the H₂O mixing ratio on smaller spatial scales (~20 m) than those resolved with the 1 s data (~200 m).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Measurement of
low-ppm mixing
ratios of water vapor**

T. D. Thornberry et al.

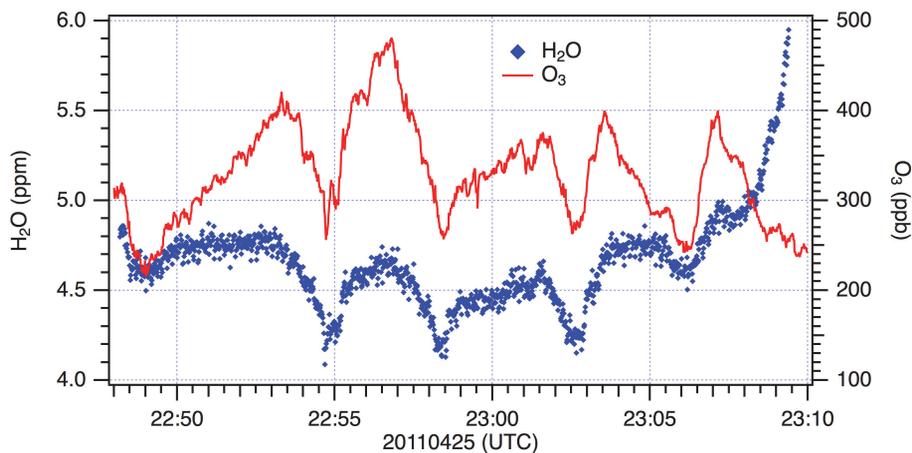


Fig. 12. Measured H_2O mixing ratios (blue) on the flight on 25 April 2011 in the lower stratosphere (13.9–16.9 km) showing the excellent measurement precision at low mixing ratios. Also shown are coincident O_3 mixing ratios (red) measured by the NOAA O_3 instrument that display a correlated structure to that observed in H_2O .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

