THOMAS 2.5 THz Measurements of Middle Atmospheric OH: Comparison With MAHRSI Observations and Model Results

Christoph R. Englert[1],
Birger A. Schimpf[2], Manfred Birk[2], Franz Schreier[2]

Institut für Optoelektronik, Deutsches Zentrum für Luft- und Raumfahrt e.V., Oberpfaffenhofen, Germany

Robert R. Conway, Michael H. Stevens, Michael E. Summers

E. O. Hulburt Center for Space Research, Naval Research Laboratory, Washington DC

In this work OH observations of the middle atmosphere performed by the improved 2.5 THz heterodyne spectrometer THOMAS (Tera Hertz OH Measurement Airborne Sounder) during the 1997 THOMAS/MAHRSI (Middle Atmosphere High Resolution Spectrograph Investigation) campaign are presented. Results of the THOMAS OH measurements are compared to simultaneous MAHRSI OH observations and to photochemical model calculations using both standard HO_x chemistry and a recently proposed change in HO_x chemistry. The 40 km – 90 km OH column densities measured by THOMAS and MAHRSI show excellent agreement, the 50 km – 90 km OH column densities agree well within the measurement uncertainties throughout the diurnal cycle. The comparison of the observed and modeled OH column densities in the upper stratosphere and mesosphere suggests that neither model is capable of simultaneously reproducing the measurements in both regions.

1. INTRODUCTION

Chemical reactions involving the HO_x family (H, OH, and HO_2) play a significant role in middle atmospheric ozone chemistry. However, recent measurements of HO_x in the upper stratosphere and mesosphere present an inconsistent picture, indicating either measurement errors or deficiencies in our understanding of atmospheric odd hydrogen. Up to now, measurements of middle atmospheric OH could not be compared directly because they were carried out at different locations, at different times, or covered altitude regions that do not overlap. For instance, retrievals from the 1994 space borne observations of mesospheric OH by MAHRSI [*Conway et al.*, 1996, *Summers et al.*, 1997, *Conway et al.*, 1999] extend down to 50 km, whereas the measurement of stratospheric OH profiles by a balloon borne instrument (FIRS–2) covers altitudes below 50 km [*Jucks et al.*, 1998]. For the balloon borne meas-

[1]Now at Upper Atmospheric Physics Branch, Space Science Division, Code 7641, E. O. Hulburt Center for Space Research, Naval Research Laboratory, Washington, D.C., 20375–5352.

[2]Now at Remote Sensing Technology Institute, Deutsches Zentrum für Luft- und Raumfahrt e.V., Oberpfaffenhofen, D–82230 Weßling, Germany.

Atmospheric Science Across the Stratopause
Geophysical Monograph 123
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urement, the reported OH concentrations at 50 km are in agreement with the standard chemistry prediction, while the 1994 MAHRSI results were found to be 30 % – 40 % lower than the calculated model values at 50 km [*WMO*, 1998]. To resolve these problems, coordinated atmospheric measurements with different measurement techniques and overlapping altitude regions are desirable in order to rule out potential unknown systematic errors.

OH measurements covering the middle and upper stratosphere and the mesosphere were performed in August 1997 with the improved airborne 2.5 THz heterodyne spectrometer THOMAS. These measurements were coordinated in space and time with measurements of mesospheric and upper stratospheric OH from the second MAHRSI flight. In the following, we give a brief overview of the THOMAS instrument, the inversion technique and the method applied to compare THOMAS observations to MAHRSI results. Finally, the results of the THOMAS OH measurements are presented and compared to MAHRSI measurements as well as to photochemical model calculations.

2. EXPERIMENT

2.1. Instrument

The THOMAS instrument is a further development of a 2.5 THz heterodyne spectrometer for extraterrestrial observations that was built at the Max–Planck–Institute for Radio Astronomy in Bonn, Germany [*Röser*, 1991]. At DLR (German Aerospace Center, Oberpfaffenhofen), the instrument design was modified to allow the observation of OH thermal emission lines in earth's atmosphere from the DLR research aircraft FALCON, using an up–looking geometry. The operation of THOMAS above the tropopause is desirable because of the significant signal absorption due to water vapor in the far–infrared at lower altitudes. The first measurement flights were performed in 1994/95, proving the airworthiness of the instrument [*Titz et al.*, 1995a; *Titz et al.*, 1995b]. Between these flights and the 1997 THOMAS measurements, the spectrometer was significantly improved and a new aircraft window was built [*Englert et al.*, 1999a; *Englert et al.*, 1999b; *Englert*, 1999].

The instrumental modifications increased the signal to noise ratio by more than a factor of five, while improving the spectral resolution by about a factor of two. Figure 1 shows a typical spectrum measured by THOMAS after the improvements. A strong water vapor line and the OH triplet (two strong and one weak line near 83.869 cm^{-1}) can clearly be recognized.

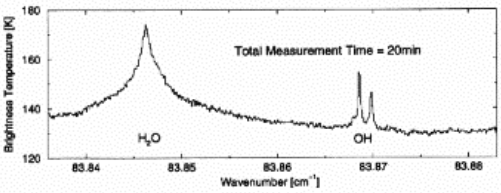

Figure 1. Calibrated spectrum measured during the THOMAS/MAHRSI campaign in August 1997.

The photometric accuracy of THOMAS was investigated using laboratory measurements of methanol emission lines and was included in the error budget.

2.2. Measurement Geometry and Time Coverage

The measurement locations and timing were selected to achieve nearly zero miss distance and zero miss time with respect to the MAHRSI observations for the upper stratosphere and mesosphere. Due to the different viewing geometries of the instruments (THOMAS: up–looking, 70° – 85° from zenith, MAHRSI: limb viewing, tangent heights between about 35 km and 90 km) a perfect match of the probed air volume is not possible. However, since the upper stratospheric and mesospheric OH column amount is dominated by OH between 40 km and 60 km, the FALCON flight route was planned in a way that the air volume observed by THOMAS at 50 km coincided with the tangent point track of MAHRSI, whenever possible. Plate 1 shows the measurement geometry for August 15, 1997. The two lines indicating the layer entrance and exit points of a virtual MAHRSI 50 km tangent height line of sight (layer thickness: 5 km) were added to the plate to illustrate the extent of the air volume measured by MAHRSI. Minimal miss distance and time was achieved for ten MAHRSI overflights on 4 days between August 10, and August 15, 1997. The coordinated measurements range over a local solar time (LST) interval between about 7 am and 5 pm. An additional sunset flight was performed with THOMAS to extend the time coverage to about 8 pm LST.

3. DATA ANALYSIS

3.1. Inversion

A best fit of a radiative transfer calculation to the measured spectrum is used to determine OH concentration profiles from the up–looking thermal emission spectra. The information about the vertical distribution of OH is contained in the pressure dependent line

width (OH line parameters were adopted from Park et al. [1996] (pressure broadening and temperature exponent) and the HITRAN data base (line position and strength)). The inversion of concentration profiles from atmospheric emission data is generally known to be an ill–posed problem. Regularization, i.e. the introduction of additional constraints, is necessary to get a numerically stable and physically meaningful solution.

The THOMAS spectra have been processed using Phillips–Tikhonov regularization (PTR) as developed by *Hansen* [1992] and first applied to atmospheric retrieval by *Schimpf and Schreier* [1997]. In contrast to optimal estimation [*Rodgers,* 1976] PTR does not require specification of an a priori profile and its covariance matrix. Instead, PTR stabilizes the solution of the least squares problem by adding a smoothness constraint, and Hansen's L–curve criterion is used to automatically determine the optimal smoothing, allowing the extraction of as much information as possible from the measurement [*Schimpf*, 1999, *Englert et al. manuscript in preparation*].

In addition to the OH concentration profile, the inversion algorithm also calculates the averaging kernel matrix. In theory, the inverted spectrum is the product of the averaging kernel matrix and the true concentration profile, which means that the averaging kernel matrix rows determine the sensitivity of the retrieved OH concentration at a particular altitude to the OH concentration at other altitudes. Due to the smoothing of the inverted profile by the averaging kernel, it is commonly used to characterize the altitude resolution of the retrieved profile. The middle panel of Plate 2 shows typical THOMAS averaging kernel rows, illustrating how the resulting profile is smoothed on the altitude grid of the inversion. In the middle and upper stratosphere, the averaging kernel rows are strongly peaked and the typical full width at half maximum of the rows is around 25 km. In the mesosphere however, the averaging kernel rows are not strongly peaked, showing that in this region no height information is available from the spectrum. This behavior is a consequence of the fact that in the mesosphere the line shape of OH thermal emission is no longer dominated by pressure broadening, but by temperature broadening, which results in a nearly altitude independent line shape in the mesosphere.

3.2. Determination of Weighted Column Densities

Due to the substantial smoothing of the OH profiles inverted from THOMAS data, a direct comparison to high vertical resolution MAHRSI OH profiles or photochemical model results is not possible. Multiplication of the high vertical resolution profiles with a THOMAS averaging kernel can be used to match the vertical resolution of the profiles to be compared. The comparisons presented here utilize *weighted column densities*, defined as the atmospheric OH profile smoothed by a THOMAS averaging kernel and integrated over altitude as illustrated in Plate 2. The left panel of Plate 2 shows two photochemical model OH profiles representing the standard odd hydrogen chemistry [*DeMore et al.*, 1997] (henceforth referred to as Model A) and revised odd hydrogen chemistry (henceforth referred to as Model B) after *Summers et al.* [1997]. In the right panel the same profiles are shown after smoothing with the averaging kernel which is depicted in the middle panel. In addition to the model profiles, a THOMAS measured profile is included in the right panel of Plate 2. The shaded area illustrates the 40 km – 90 km weighted OH column density. The smoothing of the OH profiles prior to the integration makes the weighted column densities dependent on OH below the lower limit of integration. For the 50 km to 90 km weighted OH column, the sensitivity to OH at lower altitudes is about 20 % whereas it is about 15 % for the 40 km to 90 km weighted OH column.

The different altitude coverage of THOMAS and MAHRSI further complicates the comparison of the results of the two experiments. OH profiles inverted from individual MAHRSI limb scans, that are used for the minimum miss time and distance comparisons, cover the altitude region between about 50 km and 90 km. In order to smooth the single scan MAHRSI profiles using a THOMAS averaging kernel, the MAHRSI profiles have to be extended into the stratosphere. The extension into the upper stratosphere was performed based on averaged MAHRSI limb scan data [*Conway et al.*, 2000] that allowed a reliable inversion of OH concentrations down to about 38 km. Below 38 km the extension was made using standard photochemistry results (Model A) that show reasonable agreement with MAHRSI results at 38 km [*Conway et al.*, 2000]. Using this technique, 50 km to 90 km weighted OH column densities have been derived from single MAHRSI limb scans. 40 km to 90 km weighted column densities have been derived from averaged MAHRSI limb scans extended by Model A results below 38 km.

3.3. Error Assessment

The assessment of possible errors in the THOMAS weighted OH column amounts was performed using a typical noise contaminated synthetic spectrum. The synthetic spectrum has been inverted including perturbations due to assumed error sources, in order to estimate the effects on the weighted OH column density.

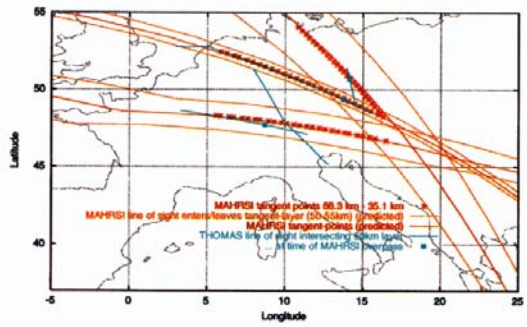

Plate 1. Measurement geometry of August 15, 1997. The 'predicted' data is the result from initial calculations.

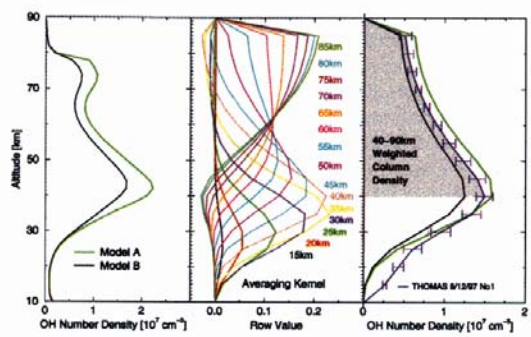

Plate 2. Left panel: Model OH profiles using the standard (Model A) and a revised chemistry (Model B). Center panel: typical THOMAS averaging kernel representing the mapping of the high resolution model profiles to the low resolution domain of THOMAS retrieval results. The rows correspond to fifteen altitude layers of equal spacing between 15 km and 85 km. Right panel: Both model profiles, smoothed with the averaging kernel so that they can be compared directly to the corresponding profile retrieved from a THOMAS measurement (LST $\approx$ 13:00). (Error bars illustrate the statistical error only.) The shaded area represents the weighted column density between 40 km and 90 km.

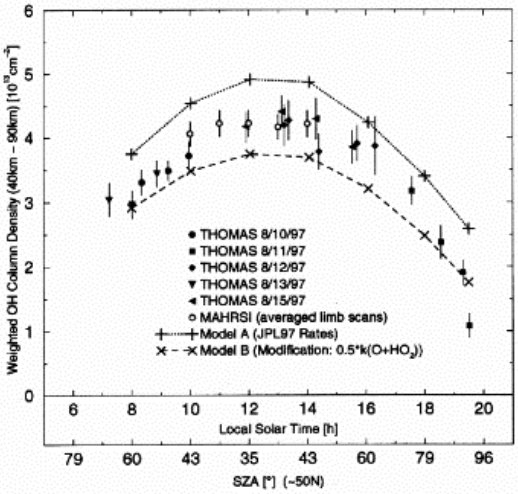

Figure 2. Comparison of 40 km – 90 km weighted OH column densities derived from THOMAS observations, MAHRSI results from averaged limb scans, and two photochemical model calculations. The MAHRSI profiles from averaged limb scans cover the 38 km – 90 km altitude region. Model A uses standard odd hydrogen chemistry [*DeMore et al.*, 1997], model B uses a 50 % reduction in the rate coefficient for $O+HO_2 \rightarrow OH+O_2$ as discussed in *Summers et al.*, [1997].

For the 1997 THOMAS measurements, eighteen systematic error sources are investigated this way and the total systematic error for the 40 km – 90 km as well as the 50 km – 90 km weighted OH column density is found to be on the order of ±15 %. The error sources regarded here include instrumental errors, uncertainties in atmospheric pressure and temperature, variations in interfering gas concentrations and uncertainties in spectral line and continuum data. The statistical error of the inversion is typically in the range of ±7 %.

4. RESULTS

Figure 2 shows 40 km – 90 km weighted column densities as a function of LST that were derived from THOMAS data, averaged MAHRSI limb scans and from photochemical model results. Model A uses standard odd hydrogen chemistry whereas Model B incorporates a 50 % decrease in the key OH/HO_2 partitioning reaction ($O+HO_2 \rightarrow OH + O_2$) as discussed by *Summers et al.*, [1997]. The comparison of the 40 km to 90 km weighted OH column densities shows excellent agreement of THOMAS and MAHRSI observations. The upper stratospheric and mesospheric OH column abundances observed by both instruments are about 15 % lower than the model prediction using the standard odd hydrogen chemistry (Model A). The model results using the revised chemistry are about 10 % lower than the experimental values.

Figure 3 shows 50 km – 90 km weighted OH column densities derived from THOMAS observations, MAHRSI single scan observations coinciding in space and time with the THOMAS observations and photochemical model results as a function of LST. The 50 km – 90 km weighted OH column densities measured by THOMAS are about 15 % lower than Model A results and about 15 % greater than predicted by Model B. The values derived from coincident MAHRSI single limb scans show agreement with THOMAS to better than about 10 %, but are generally lower than the THOMAS observations.

The overall shape of the diurnal variation of the OH weighted column densities depicted in Figures 2 and 3 is in agreement with model predictions. This shows, that neither local variations in OH, nor changes between the days of observation have been significant regarding the statistical error of the presented experimental data.

The error bars depicted in Figures 2 and 3 represent the statistical errors due to measurement noise only. As

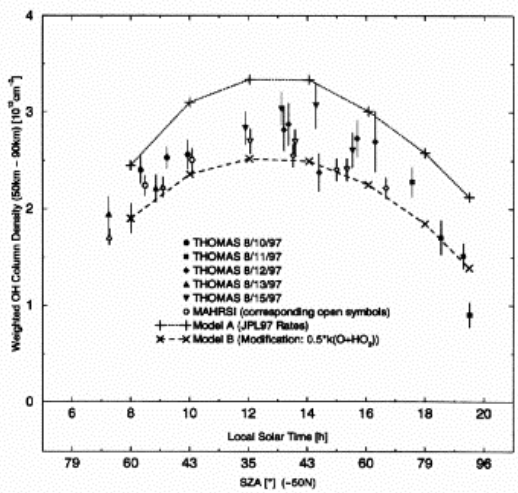

Figure 3. Comparison of 50 km – 90 km weighted OH column densities, derived from THOMAS observations, single limb scan MAHRSI results, and two photochemical model calculations. The single limb scan MAHRSI profiles cover the 50 km – 90 km altitude region and coincide in space and time with the respective THOMAS measurements. The denotation of the model results is analogous to Figure 2.

discussed in Section 3.3, the maximum systematic error for the OH column amounts observed by THOMAS is approximately 15 %. The total systematic errors of the MAHRSI measurements are estimated to be +12.0/-15.5 % for the 50 km – 90 km column and +19.0/-22.5 % for the 40 km – 90 km column density (see also [*Conway et al.*, 1999]).

5. CONCLUSIONS

The results of this first joint upper stratospheric and mesospheric OH measurement campaign, using two entirely different measurement techniques (different geometry of observation and different spectral regions), show that measurements of mesospheric OH are generally lower than expected from standard photochemical theory. This conclusion brings into question our understanding of the upper stratospheric HO_x chemistry, since the same HO_x chemical reactions dominate OH/HO_2 partitioning in both regions. In view of the latest balloon observations by *Jucks et al.* [1998], long term column measurements by *Burnett et al.* [1998] and the 1994/97 MAHRSI results, it seems unlikely that a rate change of a single reaction rate in HO_x chemistry will lead to agreement between HO_x models and measurements throughout the middle atmosphere.

Acknowledgment. The authors would like to thank R. Titz, M. Krocka, R. Nitsche, T. Weber and the CRISTA group (University of Wuppertal, Germany) for their support. C.R. Englert and B.A. Schimpf would like to thank Prof. K. Künzi for the supervision of their doctoral theses which largely contributed to this work. This work was partially supported by the Office of Naval Research, NASA OES Atmospheric Chemistry and Modeling and Analysis Program (ACMAP), NASA OSS Ionosphere, Thermosphere, and Mesosphere (ITM) Program, and DARA/DLR (Bonn).

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C. R. Englert[1], B. A. Schimpf[2], M. Birk[2], F. G. Schreier[2], Institut für Optoelektronik, Deutsches Zentrum für Luft– und Raumfahrt e.V. (DLR), Oberpfaffenhofen, 82234 Weßling, Germany. (e-mail: englert@-uap2.nrl.navy.mil)

R. R. Conway, M. H. Stevens, M. E. Summers, Upper Atmospheric Physics Branch, Space Science Division, Code 7640, E. O. Hulburt Center for Space Research, Naval Research Laboratory, Washington, D.C., 20375–5352.