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ClO AND O_3 STRATOSPHERIC PROFILES: BALLOON MICROWAVE MEASUREMENTS

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Abstract. Stratospheric ClO and O_3 vertical profiles were measured at 32° N in May 1985 and October 1986. The ClO profiles and diurnal variation are in general agreement with theory, but have somewhat less midday ClO near 34 km. Measured 35-45 km O_3 is larger than theory and no stratospheric O_3 diurnal variation was observed, as expected. HNO_3 was detected, and an H_2O_2 upper limit obtained.

Introduction

This paper reports stratospheric ClO and O_3 measurements with the Balloon Microwave Limb Sounder (BMLS). The BMLS measures thermal millimeter wavelength molecular emission spectra as its field of view (FOV) is step-scanned through the stratosphere. The FOV width is 0.3°, corresponding to ≤3 km vertical extent for stratosphere limb observations from balloon. The instrument simultaneously measures 105 filter spectral channels near 205 GHz. These cover the 204.352 GHz ClO lines, 206.132 GHz O_3 line, and weaker HNO_3, ^{18}OOO, and H_2O_2 lines. Waters et al. [1984] describe the instrument and technique. Previous measurements are in Waters et al. [1981], Froidevaux et al. [1985], and Robbins et al. [1988].

Measurements were made during two flights from the National Scientific Balloon Facility in Palestine, Texas (32° N): from ~noon on 9 May to mid-afternoon on 10 May 1985, and from ~midnight to mid-afternoon on 11 October 1986. These were the first flights with the BMLS liquid-nitrogen cooled radiometer. This radiometer receives equal energy from two spectral bands centered 1.2 and 2.9 GHz on both sides of the 203.267 GHz local oscillator. Its input is chopped between limb and 50° elevation FOVs. An additional subtraction of 2° and 4° elevation spectra was done before ClO and HNO_3 retrievals to remove residual instrumental effects. Each 45 minute limb scan included calibration measurements of a blackbody target, 16 stratospheric observation paths with tangent heights separated by ~1 km, and tropopause scans of the sharp onset of H_2O continuum emission for pointing.

Profiles were retrieved using both least-squares fitting and sequential estimation [Rodgers, 1976]. The two methods gave equivalent results, as they should. Vertical mixing ratio profiles were modeled as piece-wise linear and retrieved from a full limb scan measurements. Only radiance spectral variation was used, eliminating effects of any spectrally flat stray radiation. Temperature profiles from radiosondes near the balloon track were used in the retrievals, and spectral line frequencies and strengths from the JPL catalog [Poynter and Pickett, 1985]. Uncertainties in these spectroscopic parameters, and in temperature, contribute negligibly to uncertainty in results. Radiometric calibration error is ≤5% based on instrument tests and comparison between measured and calculated tropospheric radiance. Information on pointing in the vertical plane was obtained from the 206.132 GHz O_3 linewidth, tropopause scans, and instrument alignment. We found O_3 linewidth to be the best indicator, allowing correction to ~0.05° of small pointing changes due to ballast drops. We used 2.1 MHz/mb for the O_3 pressure-broadening parameter at 300K (from laboratory measurements with ~5% uncertainty by E.A. Cohen at JPL) and $T^{-0.7}$ temperature dependence. The O_3 broadening parameter retrieved from BMLS flight data, using pointing from tropopause scans and instrument alignment, is 2.3±0.2 MHz/mb at 300K, consistent with the lab value.

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ClO

Figure 1 shows May 1985 ClO band midday spectra for 27, 33, and 37 km tangent height observation paths. These are only 3 of ~15 paths used in each profile re-

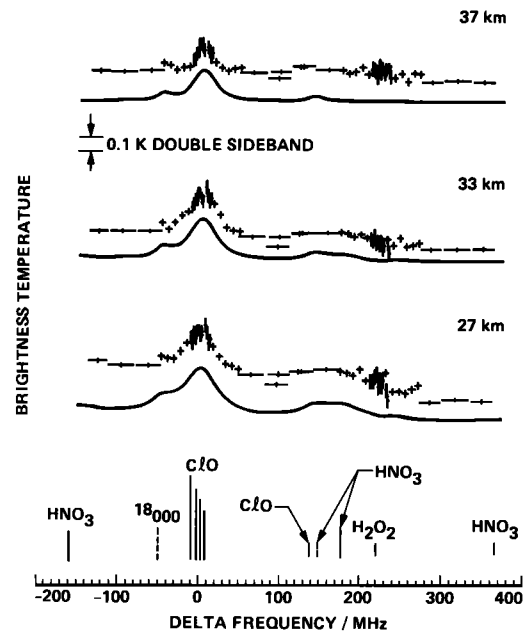

Figure 1. BMLS ClO band midday spectra. Calculated spectra are offset. Spectral lines are identified at bottom; dashed indicates line is in the radiometer lower sideband.

trieval. Measurements are crosses whose heights are predicted $\pm 1\sigma$ noise and widths are filter widths; these are averages from 10 limb scans and have 15 minutes total integration time. Smooth curves are calculated using retrieved ClO, HNO_3, and O_3 profiles, with 4.08×10^{-3} relative isotopic abundance of ^{18}OOO (2.04×10^{-3} $^{18}O/^{16}O$ abundance [Nier, 1950] increased 2× for the two available ^{18}O positions), and a theoretical H_2O_2 profile [WMO report 16, p. 456, 1985]. The assumed ^{18}OOO and H_2O_2 have negligible effect on retrieved ClO: channels in the immediate vicinity of these lines were not used in ClO retrievals. The ClO pressure broadening parameters of Pickett et al. [1981] were used.

Although measured and calculated spectra generally agree well, the measured has more slope at lower tangent heights than the calculated. This could be due to wing emission from strong lines outside the instrument range or to FOV characteristics not adequately modeled in the calculation. These effects were removed before ClO retrievals by subtracting a spectrum composed of smoothed and averaged late-night data. The smoothing was sufficiently broad to not affect the narrow night ClO line.

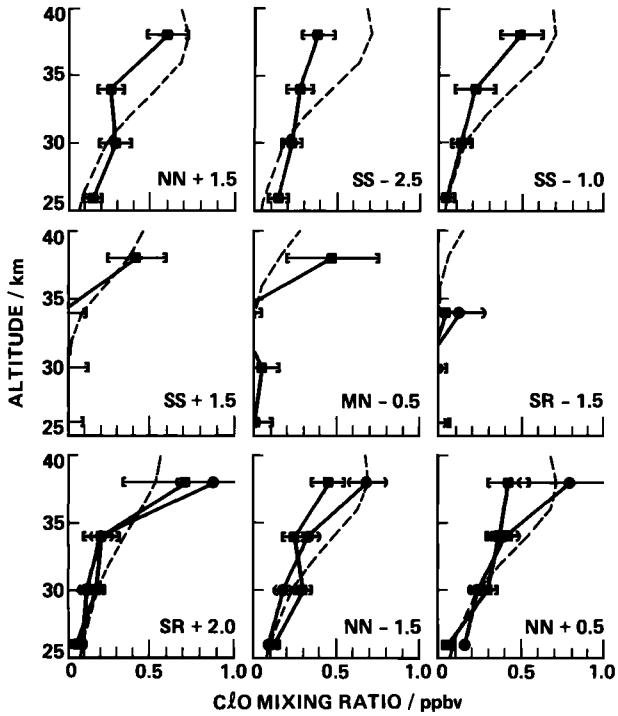

Figure 2. ClO profiles on 9-10 May 1985 (▪) and 11 October 1986 (•). Time in hours relative to local noon (NN), sunset (SS), midnight (MN), and sunrise (SR) is indicated. The 38 km measurement is noisier at MN-0.5, and missing at SR-1.5, due to lower balloon height during these times. Dashed lines are from the LLNL model.

Measured ClO profiles are shown in Figure 2. Each is the average of 3 separate limb scan profiles around the indicated time; horizontal bars show $\pm 1\sigma$ variation of values included in the average. We believe systematic errors are $\leq$0.1 ppbv. An additional point at 42 km was retrieved to prevent contamination of the 38 km value by effects from higher altitude, but was too noisy to be significant. Figure 2 also shows LLNL 1-D model equinox profiles (D.J. Wuebbles, private communication). Similar theoretical profiles are obtained by others [e.g., Froidevaux et al., 1985; Ko and Sze, 1984]. Our data show that within 1.5 hours of sunset the ClO between 26 km (the lowest altitude of useful measurements) and 34 km virtually disappears, whereas 38 km ClO changes little. This is an important confirmation of theoretical predictions, and consistent with results of Solomon et al. [1984]. Our data suggest that 38 km ClO may not decrease as fast at night as predicted and that stratospheric ClO may have unpredicted short-term variations, but instrument sensitivity is inadequate for a definitive statement (we plan to improve sensitivity 10×). The slow morning rise of 28-34 km ClO seen in our May 1981 data [Froidevaux et al., 1985] is not so evident, nor is the slow morning rise of ClO column above ~30 km seen in the average of 12 days' 19°N mountaintop October/December 1982 microwave observations [Solomon et al., 1984]. The ATMOS 30°N May 1985 sunset ClO upper limit from infrared absorption [Raper et al., 1987] is consistent with our results.

Figure 3 compares measured midday ClO with other midday measurements and with model predictions. BMLS measurements are in general agreement with others. At 26-30 km our measured ClO is in the mid-range of models. At 34 km it is somewhat less, but error bars overlap predictions. The average of May 1985 and October 1986 38 km measurements is also in the mid-range of models. The differences between May 1985 and October 1986 measurements of both the ClO abundance at 38 km and its 34-38 km gradient agree well with the 30°N differences between summer and winter predicted by Solomon and Garcia [1984], although our measured absolute ClO values are somewhat lower. This model ClO difference is due largely to CH_4 (CH_4 converts Cl_x to HCl), whose variations could explain some of the observed ClO variations [Solomon and Garcia, 1984]. SAMS monthly-averaged 32°N data [Jones, 1984] show more 38 km CH_4 in October than April 1979/1981, but slightly less in October than April 1980. This suggests that consistent spring/fall variations might not be expected in 32°N 38 km ClO. Comparison of in-situ and BMLS measurements in Figure 3 also suggest this: BMLS measured more ClO in fall 1986 than in spring 1985, whereas in-situ measured more ClO in spring 1986 than in fall 1984. It is interesting to note that these four measurements show 38 km ClO increasing between 1984 and 1986. Increasing ClO is expected due to industrial chlorocarbon releases, but this effect cannot be isolated from ClO variations due to other causes such as CH_4. Early in-situ measurements [Anderson et al., 1977, 1980; Weinstock et al., 1981] reported large ClO variations and occasional ClO abundances much larger than those shown in Figure 3. Understanding stratospheric ClO and its variation are essential for assessing

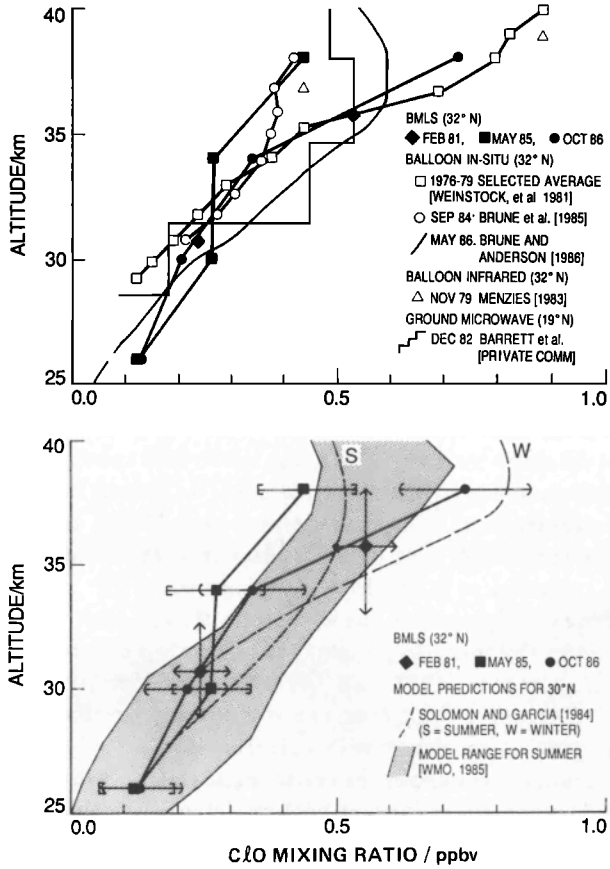

Figure 3. BMLS midday ClO profiles compared with other measurements (top) and with model predictions (bottom). BMLS profiles shown here are averages which include only measurements made between 2 hours before noon and 3 hours after noon, in which diurnal variation is negligible. The other measurements are from WMO report no. 16, p. 606 [1985], with those of Brune et al. [1985] and Brune and Anderson [1986] added; error bars are omitted in the top panel for clarity. Note that the Solomon and Garcia [1984] model predictions are for both summer and winter, whereas the model range from WMO report no. 16, p. 706 [1985] is for summer only.

the depletion of stratospheric O_3 by chlorine from industrial products. Other measurements, in addition to O_3 and CH_4, which are simultaneously needed in order to critically test theoretical predictions of ClO and its variation include OH, O, HCl, $ClONO_2$, HOCl, NO and NO_2. Simultaneous ClO measurements by different techniques are also needed to test measurement techniques.

O_3

Figure 4 shows measured O_3 profiles. O_3 retrievals were performed the same as for ClO, except that the 100× stronger O_3 signal made it unnecessary to subtract up-looking or smoothed reference spectra. We estimate the overall systematic errors in retrieved profiles are ≤10%.

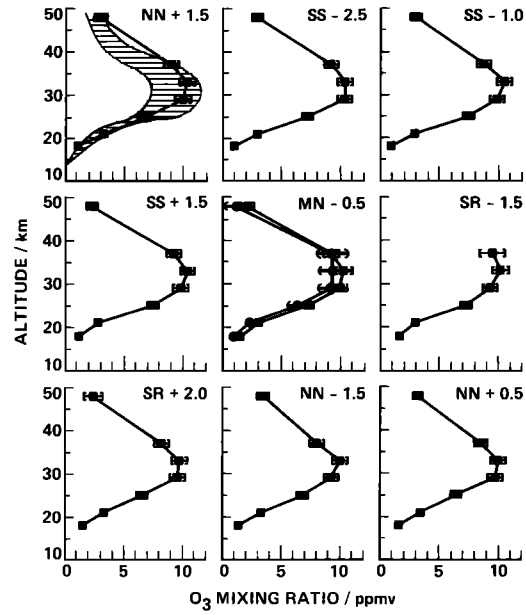

Figure 4. O_3 profiles. Format is same as Figure 2. Shaded is range of 2-D model predictions for 30°N summer [WMO report no. 16, p. 710, 1985].

No stratospheric O_3 diurnal variation was observed on the May 1985 flight with an upper limit of ~ ±5%, consistent with theory. O_3 measurements were obtained only during the first three hours of the October 1986 flight (around midnight) due to a component failure. Figure 5 compares measured upper stratosphere O_3 with theoretical model predictions. As previously found [e.g., Froidevaux et al., 1985; WMO report no. 16, p. 425, 1985; Robbins et al., 1988], measured upper stratosphere O_3 is larger than theory. This is disturbing because theoretical models should

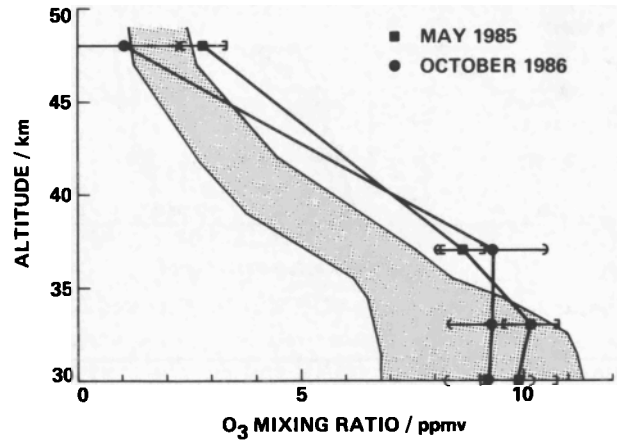

Figure 5. Upper stratosphere O_3 profiles. The May 1985 measurement is an average of 24 hours data equally distributed over a diurnal cycle, whereas the October 1986 measurement is for 3 hours around midnight. Shaded is range of 2-D model summer and winter 30°N results [WMO report 16, p. 425, 1985].

be more reliable in the upper stratosphere where it is thought that photochemical equilibrium is a better approximation and chemistry is less complex than at lower altitudes. Clearly, simultaneous measurements of O_3 and quantities which determine its upper stratospheric abundance (e.g., NO_2, ClO, HO_2, O, and J_{O_2}) are needed.

HNO_3 and H_2O_2

The broad low-altitude HNO_3 line at 180 MHz, and wings of HNO_3 lines at −160 and 370 MHz, are covered by the instrument as shown in Figure 1. An HNO_3 profile was retrieved from flight-average measurements which agrees, to within large error bars, with other measurements at 32°N [WMO report 16, p. 518, 1985].

Spectra were also analyzed for H_2O_2, whose 204.574 GHz line is covered by the instrument. Results give 0.5 ppbv upper limit averaged over 26-38 km, consistent with findings of Chance and Traub [1987], and de Zafra et al. [1985]. These do not confirm our earlier tentative measurement of 1.1 ppbv H_2O_2 at 27-35 km which was made with a less sensitive instrument [Waters et al., 1981].

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