JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 101, NO. D6, PAGES 10,077–10,089, APRIL 30, 1996

Diurnal variability of mesospheric ozone as measured by the UARS microwave limb sounder instrument: Theoretical and ground-based validations

P. Ricaud,[1] J. de La Noë,[1] B. J. Connor,[2] L. Froidevaux,[3] J. W. Waters,[3] R. S. Harwood,[4] I. A. MacKenzie,[4] and G. E. Peckham[5]

Abstract. Diurnal variability of mesospheric ozone as measured by the 183-GHz radiometer of the UARS microwave limb sounder (MLS) instrument for the northern midlatitudes in October 1991 and 1992 is compared with theoretical calculations of diurnal amplitudes produced by two photochemical models and with ground-based microwave measurements made from Bordeaux (France, 45°N) in October 1988, 1989, and 1990 and the Table Mountain Facility (California, 35°N) in October 1990. Great care has been taken in comparing all the data sets within the same frame, i.e., interpolating onto the same vertical grid (pressure or altitude), using the same units (concentration or mixing ratio) and degrading the vertical resolution of some data or models (convolution of the vertical profiles with appropriate averaging kernels). MLS diurnal variability generally agrees to within 10% with ground-based and model results at 0.5, 0.2, 0.1, and 0.05 hPa (approximately 55, 60, 65, and 70 km, respectively). Although modeled diurnal changes at 55 ± 8 km are closer to the ground-based Bordeaux measurements than to the MLS data at 45°N, MLS results are closer to ground-based Table Mountain Facility data at 35°N at 0.42 and 0.22 hPa (~55 ± 8 and ~60 ± 8 km, respectively) than to models. At 0.1 and 0.042 hPa, MLS diurnal changes are weaker than ground-based and model variations, but daytime O_3 mixing ratios are found to be in very good agreement for all data sets.

1. Introduction

Mesospheric ozone has been studied over the last 15 years with a wide variety of ground-based microwave radiometers [e.g., *Wilson and Schwartz*, 1981; *Zommerfelds et al.*, 1989]. Despite the poor vertical resolution of ground-based microwave measurements (about 10 to 20 km) the relatively short integration time on one single spectrum (from 1 to 20 min) allowed the study of diurnal and semidiurnal variabilities of mesospheric ozone. In general, our understanding of photochemical processes occurring within the mesosphere can explain to within 5% the variation of O_3 over 24 hours [*Connor et al.*, 1994] and the fine structures that can be detected just after sunrise [*Ricaud et al.*, 1994], although a modeled O_3 deficit is generally found when models are compared to lower-mesospheric measurements [*Froidevaux et al.*, 1985; *Eluszkiewicz and Allen*, 1993]. A general discussion on O_3 diurnal variability can be found in the work of *Allen et al.* [1984].

Since both photochemical models and ground-based microwave measurements have shown their ability for interpreting O_3 diurnal variations, we intend to use them in order to validate recent mesospheric ozone measurements made by the microwave limb sounder (MLS) instrument aboard the Upper Atmosphere Research Satellite (UARS). MLS consists of three radiometers [*Waters et al.*, 1993; *Barath et al.*, 1993] and two of them (the 183- and the 205-GHz radiometers) measure ozone emission lines. Since the 183-GHz radiometer is more sensitive than the 205-GHz radiometer to information coming from mesospheric layers [*Froidevaux et al.*, this issue], we use O_3 measurements obtained by the 183-GHz radiometer.

The MLS mesospheric O_3 measurements are validated by comparison with (1) two photochemical models, one of which is described by *Ricaud et al.* [1994] and the other one is maintained at the University of Edinburgh (Scotland) by R. S. Harwood and I. A. MacKenzie; (2) ground-based measurements taken at the Observatory of Bordeaux, France (45°N), with a radiometer measuring the O_3 emission line at 110 GHz [*Ricaud et*

[1]Bordeaux Observatory, CNRS/INSU, Floirac, France.
[2]NASA Langley Research Center, Hampton, Virginia.
[3]Jet Propulsion Laboratory, Pasadena, California.
[4]Edinburgh University, Edinburgh, Scotland, U.K.
[5]Heriot-Watt University, Edinburgh, Scotland, U.K.

Paper number 95JD02841.
0148-0227/96/95JD-02841$05.00

al., 1991]; and (3) ground-based profiles retrieved at Table Mountain Facility (TMF), California (35°N), with a radiometer measuring the O_3 emission line at 110 GHz [*Connor et al.*, 1994].

We have been careful to take into account the differences in vertical resolution of the measurements and model results. To compare measurements within the same vertical layer, we have used the averaging kernels provided by the MLS team, the Bordeaux team, and the TMF team to convolve either measured or theoretical results onto the appropriate vertical grid, i.e., pressure and mixing ratio for MLS and TMF data and height and concentration for Bordeaux data.

Since the ground-based data are taken at northern midlatitudes, we concentrated the analysis of MLS measurements on zonally averaged data within the two latitude bands 30°N-40°N and 40°N-50°N. Model outputs are set up for the latitude of either 35°N or 45°N. Unfortunately, there is no temporal coincidence between the periods of the MLS measurements (from September 1991, date of the satellite launch, to April 1993, date of the fatal failure of the 183-GHz radiometer) and the periods of ground-based measurements (before September 1991 for both TMF and Bordeaux). We will concentrate our analysis on October 1991 and 1992 for MLS, October 1990 for TMF and October 1988, 1989, and 1990 for Bordeaux Observatory. October was chosen because the atmosphere is rather stable during this month, and there is little year-to-year variation in the measurements.

The first section of this paper presents (1) the data sets used in this validation, i.e., the UARS/MLS O_3 measurements, the two photochemical models, and the two ground-based sets of measurements taken at Bordeaux and at TMF; and (2) the way we convolved/interpolated the measurements to take account of the various vertical resolutions. The second section will deal with comparisons between the various data sets from 0.5 to 0.05 hPa (approximately from 55 to 70 km, respectively) and will present some explanations for differences between diurnal variations calculated by the two photochemical models.

2. Data Sets

2.1. UARS/MLS O_3 Measurements

The MLS instrument samples an area of the atmosphere from 34° on one side of the equator to 80° on the other side, the hemisphere of high-latitude coverage alternating every ~35 days. The orbit of the UARS precesses by a few minutes per orbit, so the local times of the measurements at a given latitude vary by up to 20 min over a 24-hour period.

MLS O_3 mixing ratios are retrieved on constant pressure surfaces $P(i)$ defined as

$$P(i) = 10^{(3-i/3)} \quad (1)$$

hPa with $i = 1, ..., 19$, using the sequential estimation method described by *Rodgers* [1976] and adapted for MLS as by *Froidevaux et al.* [this issue]. MLS ozone measurements of the 183-GHz radiometer have an estimated accuracy of 10% from 0.5 to 0.05 hPa [*Froidevaux et al.*, this issue] and 0.5 ppmv single-profile precision within the same pressure range, using files labeled version V0003 (version 3) in the UARS Center Data Handling Facility (CDHF). Influence of the a priori information on the 183-GHz O_3 retrieved from 0.5 to 0.1 hPa is always less than 50% (this criterion refers to whether the retrieved O_3 amount is significantly contaminated or not by the a priori), but around 0.05 hPa, a third of the measurements used in the monthly average are affected more than 25% by the a priori (i.e., climatology).

We have zonally averaged the MLS data within 10°-wide latitude bands. Since the precession of the satellite orbit is about 20 min per day, it is then possible, when averaging data over a month within a given latitude band, to have the local time of MLS measurements cover essentially 24 hours. MLS data over a north- or south-looking period can then be averaged within 24 one-hour bins in order to display a diurnal variation. For the north-looking October 1991 period, MLS data have been averaged from October 2 to November 2, 1991, while for the north-looking October 1992 period, data measured from September 22 to October 28, 1992, have been used.

Figures 1a, 1b, 1c and 1d show, respectively, for the October 1991 and October 1992 periods, the local time variation of the measurements binned in 1-hour time intervals within a latitude band from 30°N to 40°N and from 40°N to 50°N, as a function of day. Local times are not randomly spread over 24 hours within the 35-day period. As local times vary from 0000 (midnight) to 1200 (noon), MLS data are sampled from the end of the 35-day period (either November 2, 1991, or October 28, 1992) to the beginning (either October 2, 1991, or September 22, 1992) and as local times vary from 1200 (noon) to 2400 (midnight), MLS data are once again sampled from the end of the 35-day period to the beginning. This is particularly important to underline because if trends in the data from 0000 to 1200 are also seen from 1200 to 2400, they may well be induced more by a monthly variation of the sampled data over the 35-day period than by a diurnal effect. Thus we concentrate our analysis on heights where the amplitude of the "diurnal" variation is greater than 10% of the diurnal average, namely, above 0.5 hPa (~55 km).

Averaging kernels A_{183} calculated for 183-GHz O_3 are displayed in Figure 5b of *Froidevaux et al.* [this issue]. They are peaked at each level i of $P(i)$ as defined in equation (1) and have a FWHM of ~5 km for every level. As we concentrated our analysis to lower mesospheric layers, averaging kernels, peaked at 0.46, 0.22, 0.1, and 0.046 hPa (levels i=10-13, respectively), have been used to degrade data sets with better vertical resolution. In our analysis, only model profiles (2-

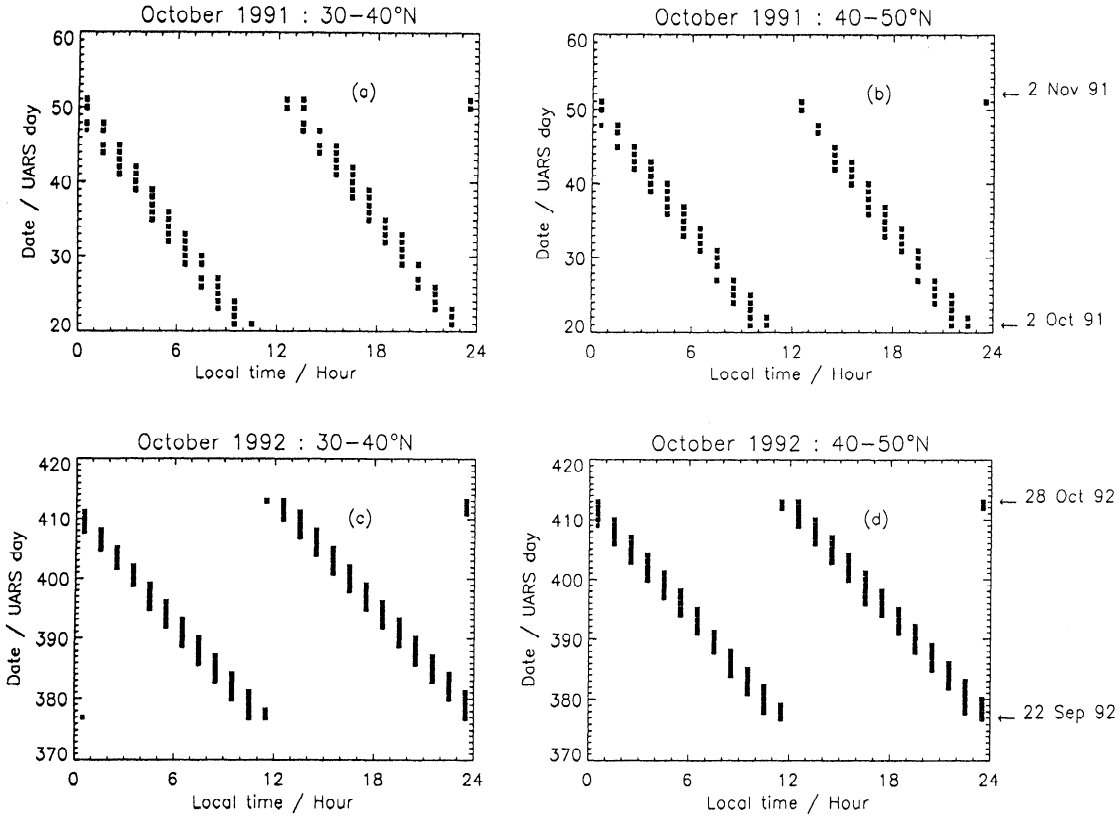

Figure 1. Variation of the local time (hours) of the microwave limb sounder (MLS) measurements, zonally averaged within the 10°-wide latitude bands and binned in 24 bands of 1 hour wide, with respect to the date (UARS day) of the measurements in October 1991: (a) within 30°N-40°N and (b) within 40°N-50°N and in October 1992: (c) within 30°N-40°N and (d) within 40°N-50°N.

to 3.5-km height resolution) have a better vertical resolution than MLS. So model profiles x interpolated onto MLS pressure surfaces have been convolved as

$$\hat{x} = A_{183}x \tag{2}$$

to get the model profiles $\hat{x}$ with the same vertical resolution as MLS.

2.2. Photochemical Models

Two photochemical models are used for the theoretical validation: a zero-dimensional model described by *Ricaud et al.* [1994] that successfully interpreted the O_3 ground-based microwave measurements made at the Bordeaux Observatory, France (45°N), and a zero-dimensional model maintained by R. S. Harwood and I. A. MacKenzie (University of Edinburgh, Scotland). Herein, we will refer to "Bx" and "Ed" models for the models used in Bordeaux and in Edinburgh, respectively.

There are two main differences between the "Bx" model described by *Ricaud et al.* [1994] and the one used in this analysis. First, reaction rate coefficients have been updated in line with *DeMore et al.* [1992] (like the "Ed" model) and, second, the model is initialized with the same profiles as used by the "Ed" model (described below) from the surface to 79 km altitude. We remind readers that the "Bx" model has a 2-km step vertical resolution and a 10-min time step. Transport is ignored. The system of differential equations is solved using the numerical method of *Gear* [1971]. All altitude levels are radiatively coupled, so that a diurnally varying ozone column is used in the calculation of the photolysis rates. Model outputs are set up for October 15, at latitudes of either 35°N or 45°N.

The "Ed" model, an updated version of that described by *Fabian et al.* [1982], has a photochemical time step of 5 min. Initial concentrations of the chemical constituents were taken from daily averaged output of the two-dimensional model of *Kinnersley and Harwood* [1993] and the model run for a few days until repeating diurnal cycles were produced. All absorption cross sections and reaction rates used are from *DeMore et al.* [1992]. The model extends from the surface to $6.5\text{x}10^{-4}$ hPa (~95 km) with a vertical resolution of half a pressure scale height, i.e., 0.5 in $\ln(P/P_0)$, where P is the pressure and P_0 the surface pressure, or approximately 3.5 km. It can be run at latitudes from one pole to the other with a step of $\pi/19$ radians, ~9.5°. Sixty gas phase chemical reactions and 20 photolysis reactions are included. No transport terms are included, but like the "Bx" model, it has a one-dimensional flavor through the radiative coupling of the stack of boxes. In-

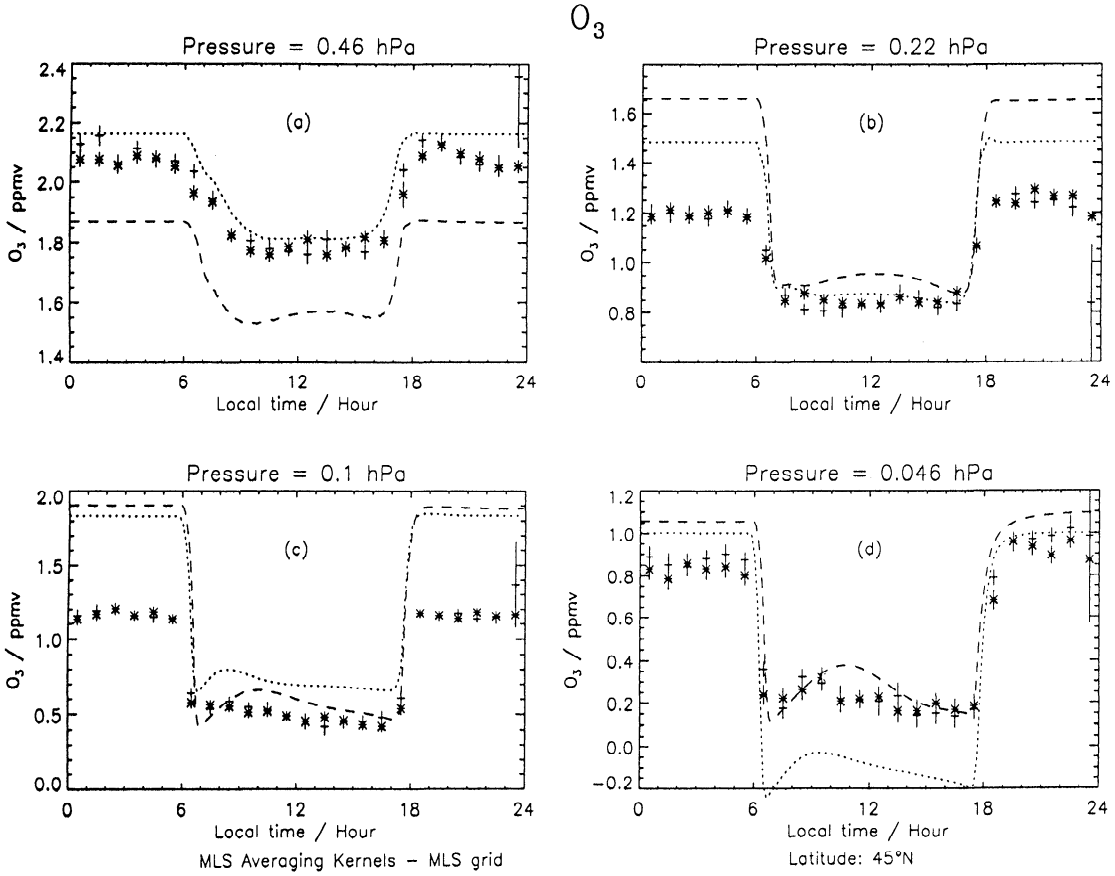

Figure 2. Diurnal variations of ozone mixing ratio (ppmv) as measured by MLS at 45°N in October 1991 (plus) and in October 1992 (asterisk) and calculated by the "Bx" (dotted) and the "Ed" (dashed) photochemical models interpolated onto the MLS pressure surfaces of (a) 0.46 hPa, (b) 0.22 hPa, (c) 0.1 hPa, and (d) 0.046 hPa. Calculations are for October 15, at 45°N and 47°N for the "Bx" and "Ed" models, respectively. Model profiles have been convolved with the 183-GHz ozone averaging kernels.

tegration is by the Numerical Algorithm Group (NAG) routine "DO2EAF" which uses the backward differentiation formulae. Model outputs are set up for October 15, at latitudes of either 37.5°N or 47°N.

2.3. Ground-Based O_3 Radiometers

2.3.1. Bordeaux. The radiometer in Bordeaux, France, is set to the O_3 rotational transition at 110.836 GHz. It was operational from September 1985 to March 1991 but operated sporadically during this period. Ozone concentration was retrieved at 42 ± 4.5 and 55 ± 8 km using the retrieval method of *Backus and Gilbert* [1970]. Some monthly averaged diurnal variations were analyzed by *Ricaud et al.* [1991]. For this comparison we will only use data measured within the upper layer (55 ± 8 km) with a mean precision of about 5% during the following three October periods: October 1988, 1989, and 1990.

Averaging kernels $s(h, h_0)$ peaked at the height of $h_0 = 55$ km and calculated by the Bordeaux team are displayed in Table 1 of *Ricaud et al.* [1991]. As the vertical resolution of both MLS and model O_3 profiles (~2-5 km) is much better than the ground-based resolution of 16 km in Bordeaux, model and MLS profiles $x(h)$ interpolated onto the Bordeaux height grid have been convolved with $s(h, h_0)$ according to [*Ricaud et al.*, 1994]

$$\hat{x}(h_0) = \int_0^H \frac{s(h, h_0)x_0(h_0)}{x_0(h)} x(h)dh \qquad (3)$$

to get MLS and model profiles $\hat{x}(h_0)$ at 55 ± 8 km in concentration units (molecules. cm^{-3}), where $H = 90$ km and $x_0(h)$ is a standard profile taken from *Brillet* [1989].

2.3.2. Table Mountain Facility. Another data set is provided by O_3 diurnal variations measured by a ground-based radiometer at the Table Mountain Facility (TMF) of the Jet Propulsion Laboratory. It observed the 110-GHz emission line of ozone from July 1989 until June 1992 [*Parrish et al.*, 1992]. However, only the data from October 1990 to June 1991 are available in the high time resolution format appropriate for study of the ozone diurnal variation [*Connor et al.*,

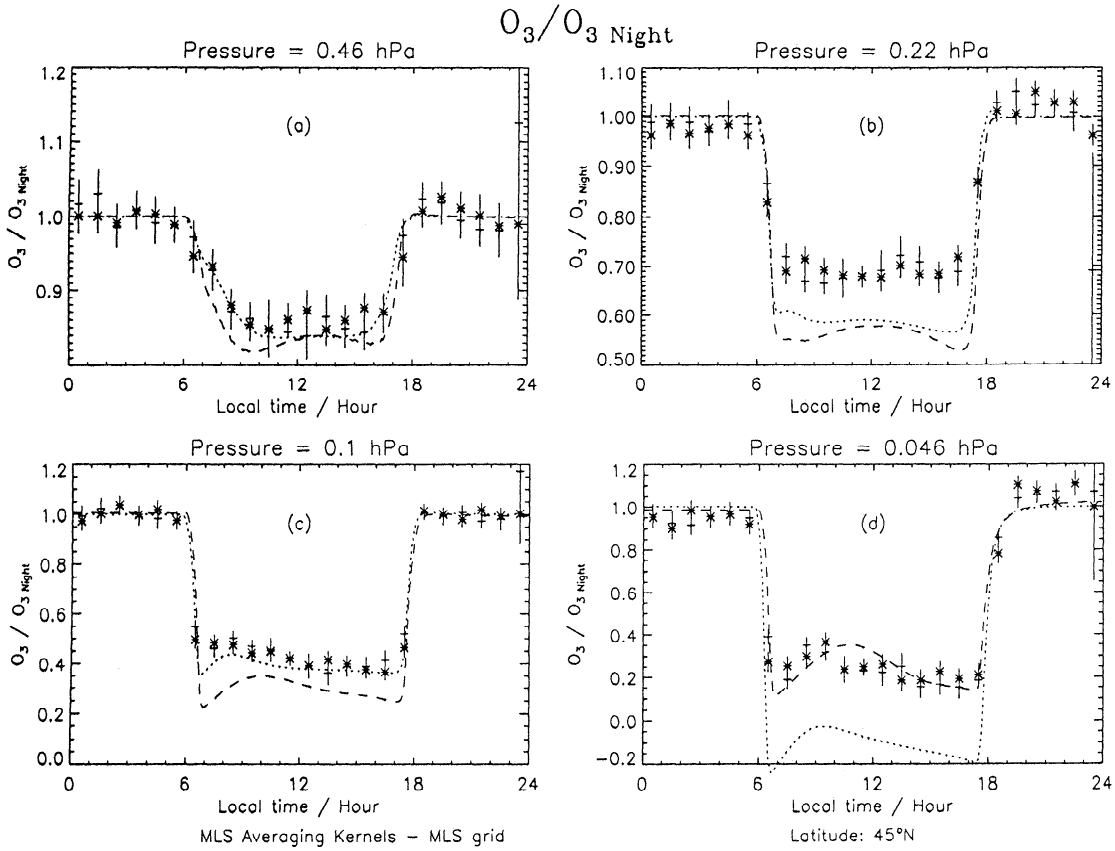

Figure 3. Same as Figure 2 but for the O_3/O_{3night} ratio.

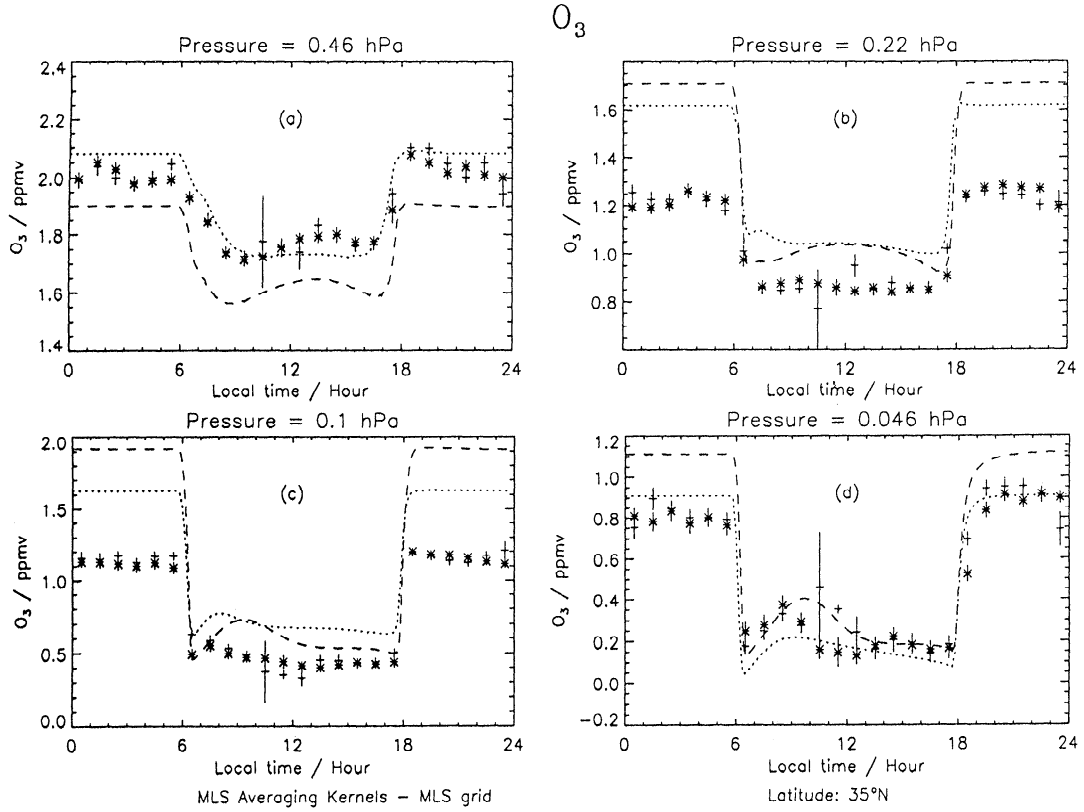

Figure 4. Diurnal variations of ozone mixing ratio (ppmv) as measured by MLS at 35°N in October 1991 (plus) and in October 1992 (asterisk) and calculated by the "Bx" (dotted) and the "Ed" (dashed) photochemical models interpolated onto the MLS pressure surfaces of (a) 0.46 hPa, (b) 0.22 hPa, (c) 0.1 hPa, and (d) 0.046 hPa. Calculations are for October 15, at 35°N and 37.5°N for the "Bx" and "Ed" models, respectively. Model profiles have been convolved with the 183-GHz ozone averaging kernels.

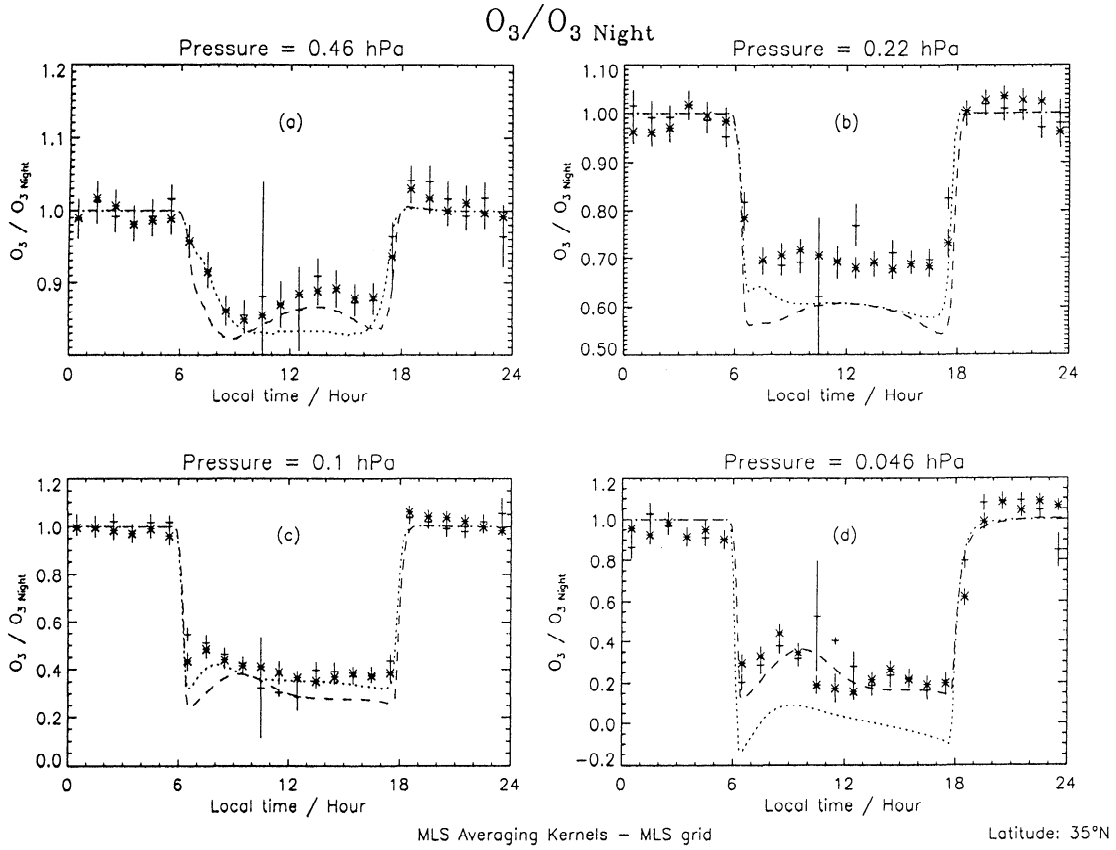

Figure 5. Same as Figure 4 but for the O_3/O_{3night} ratio.

1994]. Therefore for present purposes we have chosen to use the TMF data from October 1990.

Ozone vertical profiles are retrieved at pressure surfaces defined as

$$P(i) = 10^{(i-19/8)} \quad (4)$$

hPa with $i = 0, \ldots, 35$, using the optimal estimation retrieval method of *Rodgers* [1976]. Net accuracy in a single, monthly bin is about 8, 9, 11, and 16% at 0.4, 0.2, 0.1, and 0.04 hPa, respectively, for nighttime measurements, increasing to 15 and 26% at 0.1 and 0.04 hPa, respectively, for daytime measurements, with no change at 0.4 and 0.2 hPa; but when comparing daytime over nighttime measurements, we used day/night ratio errors of 3% at 0.42 and 0.24 hPa, 6% at 0.1 hPa, and 9% at 0.042 hPa, as shown in Table 2 of *Connor et al.* [1994]. Averaging kernels A_{TMF} provided by the TMF team are displayed in Figure 1 of *Connor et al.* [1994]. Vertical resolution of the TMF measurements ranges from ± 5 to ± 8 km, increasing with height from 55 hPa to 0.04 hPa, i.e., poorer than MLS and model vertical resolutions. Therefore model and MLS profiles x interpolated onto the TMF pressure grid have been convolved with A_{TMF} according to

$$\hat{x} = x_a + A_{TMF}(x - x_a) \quad (5)$$

to get MLS and model profiles $\hat{x}$ in mixing ratio with the same vertical resolution as TMF, where x_a is the a priori mixing ratio profile set up for day or night depending upon the local time of the measurements.

3. Validation

3.1. Theoretical Validation at MLS Pressures

Diurnal variations of O_3 mixing ratio calculated with the two photochemical models ("Bx" and "Ed" models) and measured by MLS in October 1991 and in October 1992 within the latitude band 40°N-50°N at MLS pressures of 0.46, 0.22, 0.1, and 0.046 hPa are shown in Figures 2a, 2b, 2c and 2d, respectively. The ratio O_3/O_{3night}, where O_{3night} represents the ozone mixing ratio averaged within the nighttime period, is displayed in Figures 3a, 3b, 3c and 3d for the same pressures. The same analysis done with the MLS data measured within the latitude band 30°N-40°N is represented in Figures 4a, 4b, 4c and 4d for O_3 mixing ratio and in Figures 5a, 5b, 5c and 5d for the ratio O_3/O_{3night}; there is negligible difference between the MLS data recorded in October 1991 and October 1992.

As predicted by both models, as pressure decreases (height increases), the amplitude of the diurnal variation increases; that is, the ratio O_3/O_{3night} decreases

due to the slower recombination of O_3 by the three-body reaction ($O + O_2 + M \longrightarrow O_3 + M$) relative to the rate of O_3 photolysis [see *Allen et al.*, 1984]. MLS and models find a ratio O_{3noon}/O_{3night} of about 0.85-0.90 at 0.46 hPa (~55 km), 0.55-0.70 at 0.22 hPa (~60 km), 0.30-0.40 at 0.1 hPa (~65 km), and about 0.00-0.30 at 0.046 hPa (~70 km) within the two latitude bands. There is little difference between results at 35°N and 45°N except for the shape of the diurnal variation at 0.46 hPa; this shows a daytime maximum at 1400 LT at 35°N for MLS and the "Ed" model, while this maximum occurs at noon for MLS and the "Ed" model at 45°N. The "Bx" model does not predict any daytime maximum at this pressure. This maximum is consistent with the faster photodissociation of O_2 at the lower latitude leading to a higher rate of ozone formation from the three-body reaction of O with O_2 before HO_x catalytic cycles cause O_3 to decrease.

At 0.46 hPa for latitudes of 45°N and 35°N, MLS mixing ratios during the nighttime lie between modeled mixing ratios, while during the daytime period, MLS O_3 is quite close to the "Bx" model outputs; but the amount of O_3 at those heights is very sensitive to the amount of H_2O because the H_2O concentration primarily controls the HO_x-induced O_3 destruction. We find in both models that increasing H_2O from 4.5 to 6.5 ppmv decreases O_3 by about 10% but does not affect the diurnal amplitude itself. Indeed, a 0.3 ppmv night-to-day O_3 decrease is found in both models and in the MLS data. Moreover, MLS and modeled O_{3noon}/O_{3night} ratios (Figures 3a and 5a) are found to be in good agreement (within 5%).

At 0.22 hPa there is a larger disagreement between models and MLS at both latitudes. Daytime O_3 mixing ratios are within 10-15% agreement, but the nighttime values differ strongly, namely, from 1.2 ppmv for MLS, 1.5 ppmv for the "Bx" model, and up to 1.65-1.70 for the "Ed" model (30% discrepancy), the MLS amplitude being weaker (0.70) than the "Bx" and the "Ed" models (0.55-0.60).

At 0.1 hPa at both latitudes, daytime MLS O_3 mixing ratio is close to the models (0.6 ± 0.1 ppmv), but the nighttime amount of ozone is 1.15 ppmv for MLS, (1.6-1.9 ppmv) for the "Bx" model, and 2.0 ppmv for the "Ed" model, i.e., a 40% discrepancy. This mismatch in the daytime and nighttime O_3 mixing ratios is less pronounced in the O_{3noon}/O_{3night} ratio, where we find an MLS amplitude of 0.40, as opposed to 0.35 for the "Bx" model and 0.30 for the "Ed" model.

At 0.046 hPa the daytime MLS O_3 diurnal variation lies between the two modeled variations. At the two latitudes, nighttime MLS ozone is close to the "Bx" model of about 0.80-0.90 ppmv, while for the daytime values, MLS is very close to the "Ed" model of about 0.2 ppmv. We should point out that (1) just after sunrise the "Bx" model ozone mixing ratio is negative because of information coming from heights greater than 70 km ($P <$ 0.046 hPa) where the averaging kernel values are negative [see *Froidevaux et al.*, this issue, Figure 5b] and (2) the "Ed" model O_3/O_{3night} ratio is very close to the MLS one, at both latitudes since daytime O_3 is very low (about 0.2 ppmv), so the ratio will be close to zero independently of the nighttime value. Comparing the local time of the daytime O_3 maximum shows that it occurs at around 0800-0900 LT for MLS, very close to 0800 LT in the "Bx" model and just before 1100 LT in the "Ed" model. This mesospheric maximum at 0.046 hPa, already visible on the modeled variations at 0.22 and 0.1 hPa, comes from the rapid photodissociation of O_2 that is not instantaneously balanced by the destruction rate induced by HO_x, permitting O_3 to slightly increase after the deep sunrise fall [*Ricaud et al.*, 1994]. Early in the morning, at 0.046 hPa the O_2 photodissociation is much greater than the HO_x-induced destruction rate, so the maximum occurs later and its amplitude is greater than at 0.22 hPa. Thus the "Ed"-modeled maximum occurring two hours after the MLS and "Bx"-modeled maxima suggests an insufficient HO_x-induced O_3 destruction within the "Ed" photochemical model and/or a stronger O_2 photolysis in the "Ed" model as compared to the "Bx" model (see section 3.4).

The quasi-systematic difference between measured and modeled amplitudes, as can be seen at 0.22 and 0.1 hPa during the nighttime period, could be also induced by a temperature diurnal variation. Indeed, on a constant pressure surface, variations of O_3 and temperature are anticorrelated [e.g., *Barnett et al.*, 1975; *Froidevaux et al.*, 1989]; but the examination of the diurnal variation of temperature as measured by the MLS 63-GHz radiometer tuned to the O_2 emission line in October 1991 and October 1992 does not show much systematic day-to-night changes at the two pressure levels. Therefore evidence suggests that this difference in O_3 diurnal variations may not be induced by a temperature effect.

3.2. Ground-Based Validation at Bordeaux Latitude and Heights

Comparison of the diurnal variations of the O_3 concentrations (cm^{-3}) at 55 ± 8 km between ground-based measurements in October 1988, October 1989, and October 1990 made at Bordeaux and MLS measurements in October 1991 and October 1992 within the 40°N-50°N latitude band are seen in Figure 6 together with modeled "Bx" and "Ed" outputs. There is no great year-to-year change within the Bordeaux data sets, and as we have already mentioned, this is also true for the MLS data. Yearly averaged MLS and Bordeaux data for the October period and the associated yearly diurnal variations are shown in Figure 7, while Figure 8 displays the O_3/O_{3night} ratio.

The daytime O_3 concentration is found to be about $1.67 \pm 0.02 \times 10^{10}$ cm^{-3} for MLS and about $1.62 \pm 0.05 \times 10^{10}$ cm^{-3} for Bordeaux, an agreement to within 3%, bracketed by the modeled O_3 concentrations of 1.60×10^{10}

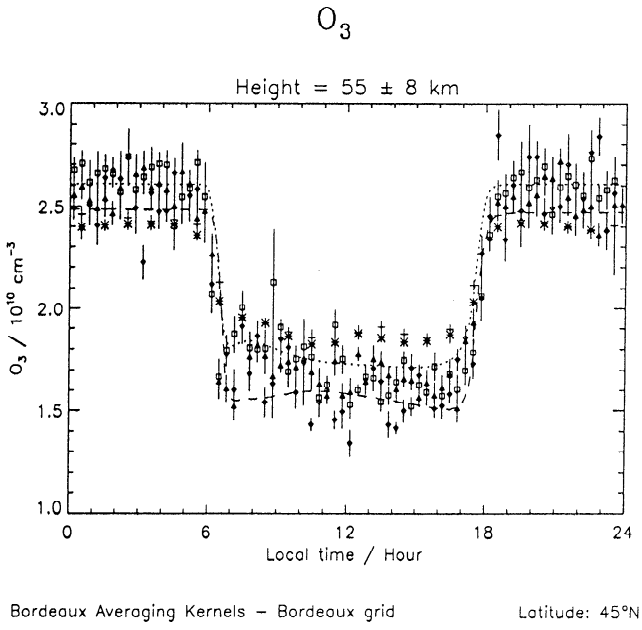

Figure 6. Diurnal variations of ozone concentration (cm^{-3}) as measured by a ground-based radiometer located at Bordeaux (45°N) in October 1988 (diamond), October 1989 (triangle), and October 1990 (square), by MLS at 45°N in October 1991 (plus) and in October 1992 (asterisk) and calculated by the "Bx" (dotted) and the "Ed" (dashed) photochemical models interpolated onto the Bordeaux altitude surface of 55 ± 8 km. Calculations are for October 15, at 45°N and 47°N for the "Bx" and "Ed" models, respectively. MLS and model profiles have been convolved with the averaging kernels provided by the Bordeaux team.

cm^{-3} of the "Ed" model and 1.70×10^{10} cm^{-3} of the "Bx" model. For the nighttime values the data sets differ more. Indeed, in Bordeaux the nighttime average is about $2.57 \pm 0.05 \times 10^{10}$ cm^{-3}, while the MLS O_3 concentration is only $2.25 \pm 0.02 \times 10^{10}$ cm^{-3}, giving agreement only to within 13%. The two model nighttime values are slightly closer to the Bordeaux data (2.48-2.60)$\times 10^{10}$ cm^{-3} than to the MLS data, since the agreement with Bordeaux is within 3.5%, as compared to 9% with MLS. The night-to-day ratio (Figure 8) shows this discrepancy, since O_{3noon}/O_{3night} ratio is close to 0.75 for MLS, while it is 0.65 for Bordeaux, close to the "Ed" model ratio of 0.63 but far from the "Bx" model ratio of 0.70. Once again, as previously mentioned, we must remark that the "Ed" model does show a daytime O_3 maximum around 1100 LT about 3-4 hours later than both the "Bx" and the Bordeaux data, while MLS data do not show this early morning maximum. We will return to this in section 3.4 when we compare model calculations.

3.3. Ground-based Validation at TMF Latitude and Pressures

Diurnal variations expressed in ozone mixing ratio (ppmv) and measured at TMF for October 1990 are plotted for comparison with yearly average (October 1991 and 1992) MLS data in Figures 9a, 9b, 9c and 9d together with modeled variations at TMF pressure levels of 0.42, 0.24, 0.1, and 0.042 hPa, respectively. Figures 10a, 10b, 10c and 10d are as Figure 9 but for the diurnal variation of the O_3/O_{3night} ratio.

At 0.42 hPa we find that the 24-hour average O_3 mixing ratio at TMF (1.67±0.1 ppmv) is slightly lower than for MLS (1.80±0.05 ppmv) but agrees well with the "Ed" model (1.70 ppmv), while the "Bx" model generates greater amounts of about 1.87 ppmv. Night-to-day O_3 decreases of about 0.2 ppmv are found for both TMF and MLS, while the model decrease is calculated to be about twice as large. Indeed, a very good agreement is found in the O_3/O_{3night} ratio diurnal variation of MLS and TMF data (0.90), while the ratio is about 0.80-0.83 for the models. Those O_3/O_{3night} values are rather different from the ones we obtained earlier (Figures 2-4), where there was a good agreement at 0.46 hPa between the MLS and the models. The main reason for this disagreement is certainly not the pressure level considered here (0.42 hPa instead of 0.46 hPa) but may be the vertical resolution, i.e., 5 km for MLS versus 16 km for TMF data. Thus the discrepancy observed earlier be-

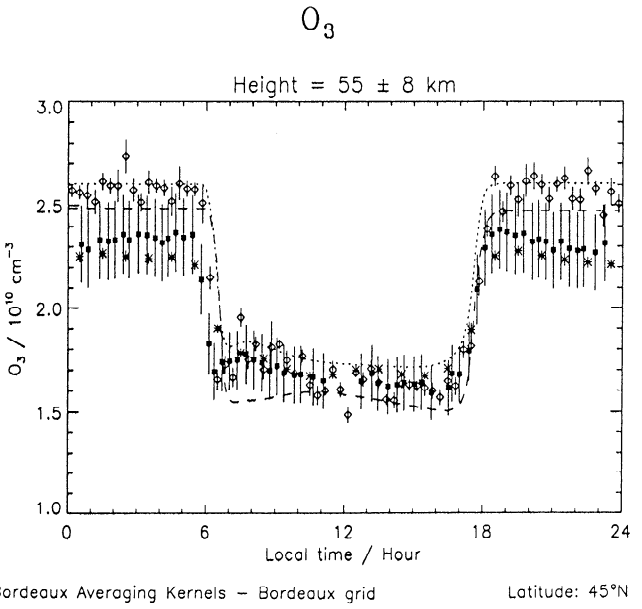

Figure 7. Yearly average diurnal variations of ozone concentration (cm^{-3}) in October as measured by a ground-based radiometer located at Bordeaux, 45°N (diamond), by MLS at 45°N (plus) and calculated by the "Bx" (dotted) and the "Ed" (dashed) photochemical models interpolated onto the Bordeaux altitude surface of 55 ± 8 km. Calculations are for October 15, at 45°N and 47°N for the "Bx" and "Ed" models, respectively. In addition, superimposed are diurnal variations measured at the Table Mountain Facility (solid square) in October at 35°N. MLS, Table Mountain Facility (TMF), and model profiles have been convolved with the averaging kernels provided by the Bordeaux team.

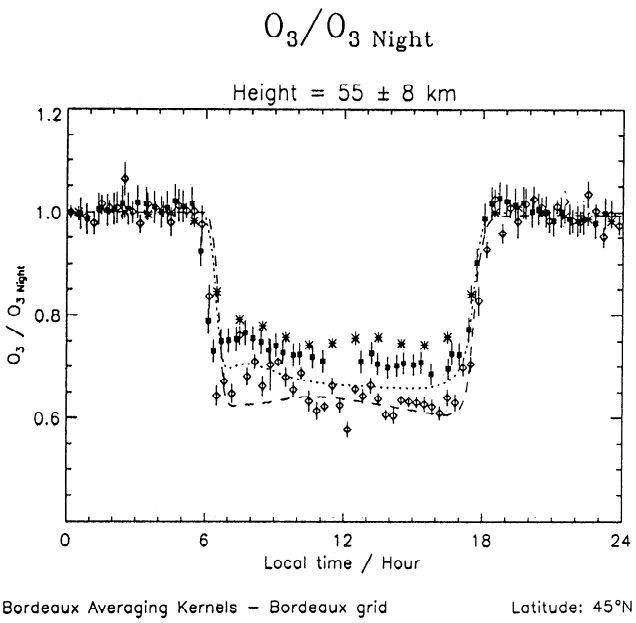

Figure 8. Same as Figure 7 but for the O_3/O_{3night} ratio.

tween MLS and modeled diurnal amplitudes at 0.22 and 0.1 hPa may contaminate the O_3 diurnal amplitude for the 0.46 hPa TMF pressure grid, since we bring information coming from lower pressures (higher altitudes).

Another intriguing feature is the good agreement between MLS and TMF mixing ratios and the slight disagreement with model results at 0.46 hPa TMF grid (~55 ± 8 km) and 35°N, while at 55 ± 8 km Bordeaux grid and 45°N, we found exactly the reverse: agreement between models and Bordeaux concentrations and slight disagreement between MLS and Bordeaux data. We would have expected the TMF data at 0.42 hPa to be very close to the Bordeaux data since they both have the same vertical resolution.

To quantify the differences among MLS, TMF, and Bordeaux data, we have plotted in Figures 7 and 8 the TMF diurnal variations convolved with the Bordeaux averaging kernels using equation (3), i.e., at 55 ± 8 km in concentration unit, regarding TMF, MLS, and modeled data as high-resolution profiles compared to Bordeaux data as low-resolution profiles. We have already noted little year-to-year differences between data sets and also little latitudinal differences between MLS

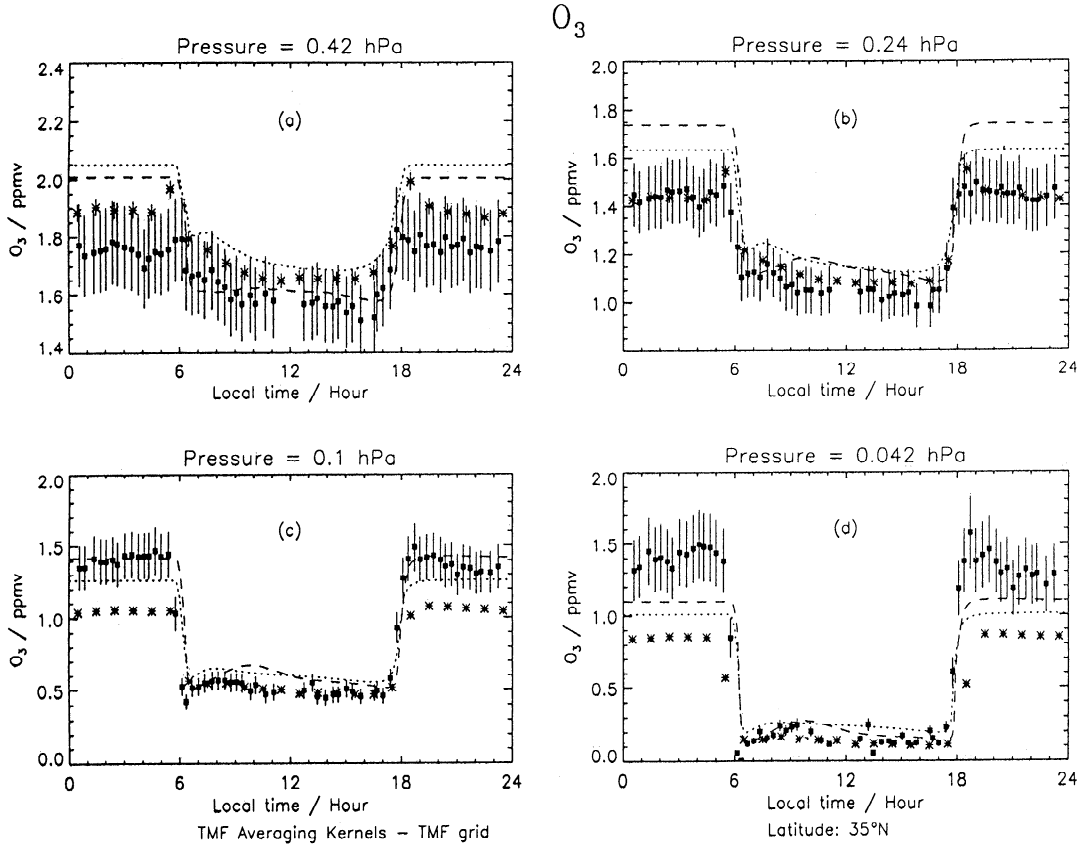

Figure 9. Diurnal variations of ozone mixing ratio (ppmv) as measured by a ground-based radiometer located at the Table Mountain Facility (35°N) in October 1990 (solid square), by MLS at 35°N in October (plus) and calculated by the "Bx" (dotted) and the "Ed" (dashed) photochemical models interpolated onto the TMF pressure surfaces of (a) 0.42 hPa, (b) 0.24 hPa, (c) 0.1 hPa, and (d) 0.042 hPa. Calculations are for October 15, at 35°N and 37.5°N for the "Bx" and "Ed" models, respectively. MLS and model profiles have been convolved with the averaging kernels provided by the TMF team.

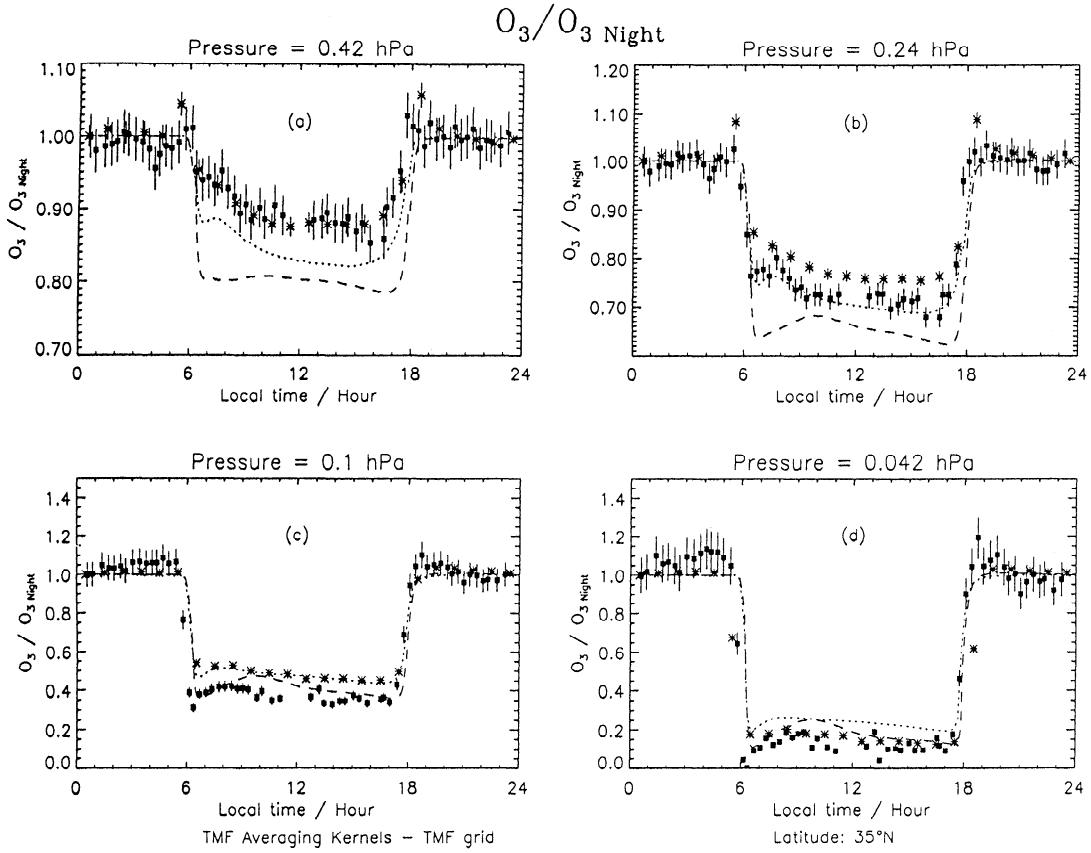

Figure 10. Same as Figure 9 but for the O_3/O_{3night} ratio.

data averaged within 30°N-40°N and 40°N-50°N. By using equation (3) to degrade vertical profiles, averaging kernels are not directly applied to the high-resolution profiles but to a "scaled" profile whose scaling factor is defined by $x_0(h_0)/x_0(h)$. So any profile (high or low resolution) may well be affected by this scaling.

In Figure 7, daytime TMF ozone is in excellent agreement (within 5%) with Bordeaux and MLS data and lies between the two modeled ozone concentrations. The slight bump is clearly visible about one hour and a half after sunrise in agreement with MLS, Bordeaux, and the "Bx" model data; but nighttime TMF concentrations are in good agreement with MLS (within 3%) and significantly smaller by 8-10% than Bordeaux and modeled concentrations. The TMF day/night ratio (~0.72) shown in Figure 8 lies between Bordeaux and MLS day/night ratios with a TMF ratio somewhat closer to MLS data (~0.75) than to other data sets (~0.65). Such a 10% inconsistency between the two ground-based microwave data sets is rather difficult to explain but may be attributable to the way we transform either height to pressure (and vice versa) or mixing ratio to concentration using the hydrostatic approximation.

At 0.24 hPa we have an almost perfect agreement between MLS and TMF nighttime values (~1.45 ppmv) and the daytime MLS mixing ratios are all within the TMF error bars. At this TMF pressure the modeled diurnal amplitude and mixing ratios are greater than measured for both the nighttime (1.65 ppmv for the "Bx" model and 1.75 ppmv for the "Ed" model) and the daytime period (1.2 ppmv for both models). The O_3/O_{3night} TMF ratio is very close to the "Bx" one (0.70), while MLS diurnal amplitude is weaker (ratio of 0.78) and "Ed"-modeled amplitude is greater (ratio of 0.68).

At 0.1 hPa there is good agreement between the "Ed" model and the TMF diurnal variations during the nighttime period (1.4 ppmv). MLS and the "Bx" model values are much lower: 1.25 ppmv and 1.05 ppmv, respectively. For the daytime period, MLS and TMF agree perfectly, while modeled mixing ratios are slightly greater than measured: 0.6 ppmv for the models against 0.5 ppmv for the microwave measurements. The O_3/O_{3night} TMF ratio is this time very close to the "Ed" model ratio (0.37), while the MLS O_3/O_{3night} ratio is perfectly represented by the "Bx" model (0.47).

At 0.042 hPa the daytime O_3 mixing ratio is found to be very weak: about 0.1-0.2 ppmv within all the data sets. The biggest discrepancy comes from the nighttime values that are less than 1 ppmv (0.82 ppmv exactly) for MLS, around 1 ppmv for model results, and much greater than 1 ppmv (1.4 ppmv exactly) for TMF. As mentioned previously, there are no great differences in the O_3/O_{3night} within all the data sets since daytime

mixing ratios are close to zero. We must highlight that this pressure layer of 0.042 hPa corresponds to a height layer from about 62 km to about 78 km. That is to say that (1) MLS vertical profiles above 70 km are more sensitive to a priori information, i.e., climatology, and (2) the limit layers of both photochemical models are going to be reached. Therefore the diurnal variations of O_3 mixing ratios at the TMF pressure of 0.042 hPa must be interpreted with caution.

3.4. Comparison of Models

The results of the two models are generally qualitatively consistent, showing similar diurnal ozone variations which change with height in a similar manner. The actual ozone amounts implied by the models are also in reasonably close agreement. However, some differences have been revealed. The most significant difference is that the daylight ozone maximum seen in the diurnal plots occurs, at all heights, some 2 hours later in the "Ed" model than in the "Bx" model. This difference remains even when the models are run with the same initial trace gas and temperature profiles and the same chemical kinetic parameters. Therefore since neither model includes any transport terms, the origin of the discrepancy must lie in the organization of the photochemical schemes. Both models include all reactions known to be of importance in the mesospheric chemistry of odd oxygen. The "Bx" model treats all the chemical species independently, as does the "Ed" model (in the mesosphere) with the exception of $O(^1D)$ and $O(^3P)$ which are treated as a family and partitioned by assuming photochemical equilibrium. Although different integration schemes are used by the two models, they are both highly accurate methods suited to use in a purely chemical model where speed is not a priority, and they give very similar results.

The major difference between the models lies in the calculation of the photolysis rates. The radiative models used in the "Bx" and "Ed" models are described more fully by *Ricaud et al.* [1994] and *Fabian et al.* [1982], respectively. One notable difference is that the "Bx" scheme includes multiple scattering and surface albedo effects, while the "Ed" scheme does not. The photolysis rates of most relevance to the behavior of odd oxygen in the mesosphere are those for the dissociation of H_2O, O_2, and O_3. The later occurrence of the daylight ozone maximum at 0.046 hPa and the higher ozone amount in the "Ed" compared to the "Bx" model is consistent with there being less destruction of ozone by HO_x in the "Ed" model and/or a higher rate of O_2 photolysis in the "Ed" model. Because the wavelength-dependent attenuation of the incoming solar radiation is somewhat different in the "Bx" and "Ed" models, the rate of photolysis of a given species calculated in one model relative to the rate calculated in the other changes with height in a rather complex manner. Also, the rate of change of photolysis rate with solar zenith angle at a given altitude is not entirely the same in the two models. The effect of these differences at the various heights in the mesophere examined here is further complicated by the fact that from 65 km to 55 km the main source of odd hydrogen changes from being the photodissociation, $H_2O + h\nu \longrightarrow H + OH$, to the reaction: $H_2O + O(^1D) \longrightarrow 2\ OH$ [see *Ricaud et al.*, 1994]. A detailed analysis of the full impact of these effects on the modeled odd oxygen is beyond the scope of this paper, but it does seem that they explain the discrepancies noted in the modeled diurnal ozone variations.

The effect of the differences in the photolysis rates are shown in Figure 11, a plot of the relative differences in the ozone profiles from the two models as a function of height. Data for noon and midnight are presented. It can be seen that the relative ozone amounts in the two models oscillate throughout the mesosphere. At the uppermost levels, there is less daylight ozone in the "Ed" model, but the relative amount increases on descending, surpassing that in the "Bx" model and peaking at around 65 km before declining again. The relative nighttime ozone amount shows a similar vertical structure, but the nighttime mesospheric ozone in the "Ed" model is never significantly less than in the Bordeaux. It is not altogether surprising that two completely independentally developed models should give somewhat different results, and it is noteworthy that despite these differences they both give diurnal ozone variations of a similar magnitude and shape to those which are observed. It may be significant that the "Bx" model which has the more sophisticated photochemical scheme gen-

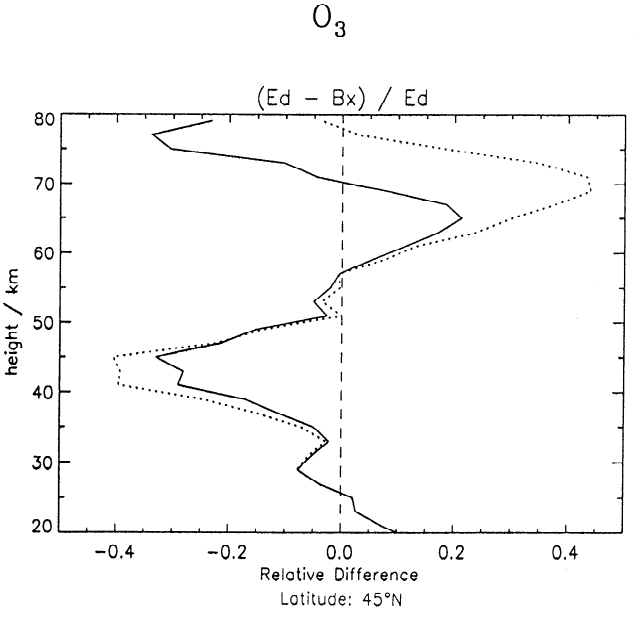

Figure 11. Difference between vertical profiles calculated by the "Bx" model and by the "Ed" model relative to the "Ed" model output at noon (solid curve) and at midnight (dotted) when using the same initialization profiles and the same reaction rates in October at 45°N and 47°N for the "Bx" and "Ed" models, respectively.

erally matches more closely the shape of the diurnal variation observed by MLS.

Throughout the middle and upper stratosphere the "Ed" model underestimates the ozone amount relative to the "Bx" model by a similar amount during both the day and the night. The sharp step which occurs just below 50 km coincides with the height at which the "Ed" model switches between a stratospheric and mesospheric photochemical scheme. The stratospheric scheme incorporates into families many species which are treated individually in the mesophere (e.g., O_3, $O(^1D)$ and $O(^3P)$ become one family) and it includes some extra species and reactions which are not included in the mesopheric scheme or the "Bx" model. Tests have shown that running the mesospheric scheme at stratospheric altitudes gives a stratospheric ozone profile much closer to that from the "Bx" model. In summary then, there appears to be no major conceptual difference between the models, their inequalities being due to differences of detail rather than of theory.

4. Conclusions

Mesospheric ozone measured by the UARS/MLS 183-GHz radiometer in October 1991 and 1992 has been analyzed in order to show its diurnal variability from 0.5 to 0.05 hPa (approximately from 55 to 70 km high). Validation of its diurnal pattern measured in the northern midlatitudes (around 35°N and 45°N) has been performed by comparison with two zero-dimensional photochemical models and by comparison with two ground-based radiometers measuring the O_3 emission line at 110 GHz: one located at the Bordeaux Observatory (France, 45°N) and the other one located at the Table Mountain Facility (California, 35°N). The validation took care to interpolate the data onto the same vertical grid (pressure or altitude), to transform the data into the same units (mixing ratio or concentration) and to degrade the data to the same vertical resolution by convolving the vertical profiles with the appropriate averaging kernels.

MLS mesospheric ozone exhibits a diurnal variability whose amplitude increases with height in general agreement to within 10% with ground-based and model results. Although at 55 ± 8 km for the latitude of 45°N, MLS ozone diurnal variations are generally lower than both the Bordeaux and the model results, at 0.42 hPa ($\sim 55 \pm 8$ km) for the latitude of 35°N, MLS ozone diurnal variations agree very well with the TMF diurnal variations, while modeled amplitudes are greater than measured. At 0.22 hPa, good agreement is found between MLS and TMF, while the modeled amplitude is calculated to be greater than is measured. At 0.1 and 0.042 hPa, MLS daytime O_3 is in very good agreement with TMF and modeled ozone mixing ratios, but nighttime MLS mesospheric values are much lower than TMF and modeled data.

This analysis although restricted to the northern midlatitudes represents the first validation of MLS mesospheric ozone as measured by the 183-GHz radiometer aboard the UARS satellite and shows the need to obtain (1) more data from other ground-based radiometers located around the world and (2) more theoretical results to compare models between themselves and diagnose discrepancies in order to improve our knowledge of photochemical processes occurring in the lower mesosphere.

Acknowledgments. We would like to thank many colleagues who have contributed to the MLS project and in particular to the O_3 measurements done with the 183-GHz radiometer: NASA, the UARS project office; colleagues at JPL (W. G. Read in particular, for ozone averaging kernels), EU, H-WU, and RAL; and J. London for useful discussions on modeling. The work in France was funded by CNES and CNRS/INSU, in the U.K. by SERC and NERC, and in the U.S. by NASA.

References

Allen, M., J. I. Lunine, and Y. L. Yung, The vertical distribution of ozone in the mesosphere and lower thermosphere, *J. Geophys. Res.*, *89*, 4841-4872, 1984.

Backus, G., and F. Gilbert, Uniqueness in the inversion of inaccurate gross Earth data, *Philos. Trans. R. Soc. London*, *266*, 123-192, 1970.

Barath, F., et al., The Upper Atmosphere Research Satellite microwave limb sounder instrument, *J. Geophys. Res.*, *98*, 10,751-10,762, 1993.

Barnett, J. J., J. T. Houghton, and J. A. Pyle, The temperature dependence of the ozone concentration near the stratopause, *Q. J. R. Meteor. Soc.*, *101*, 245-257, 1975.

Brillet, J., A theoretical study of ozone measurements made with ground-based microwave sensors, *J. Geophys. Res.*, *94*, 12,833-12,850, 1989.

Connor, B. J., D. E. Siskind, J. J. Tsou, A. Parrish, and E. E. Remsberg, Ground-based microwave observations of ozone in the upper stratosphere and mesosphere, *J. Geophys. Res.*, *99*, 16,757-16,770, 1994.

DeMore, W. B., et al., Chemical kinetics and photochemical data for use in stratospheric modeling, in *Evaluation 10, JPL Publ. 92-90*, Jet Propul. Lab., Pasadena, Calif., 1992.

Eluszkiewicz, J., and M. Allen, A global analysis of the ozone deficit in the upper stratosphere and lower mesosphere, *J. Geophys. Res.*, *98*, 1069-1082, 1993.

Fabian, P., J. A. Pyle, and R. J. Wells, Diurnal variations of minor constituents in the stratosphere modeled as a function of latitude and season, *J. Geophys. Res.*, *87*, 4981-5000, 1982.

Froidevaux, L., M. Allen, and Y. L. Yung, A critical analysis of ClO and O_3 in the midlatitude stratosphere, *J. Geophys. Res.*, *90*, 12,999-13,029, 1985.

Froidevaux, L., M. Allen, S. Berman, and A. Daughton, The mean ozone profile and its temperature sensitivity in the upper stratosphere and lower mesosphere: An analysis of LIMS observations, *J. Geophys. Res.*, *94*, 6389-6417, 1989.

Froidevaux, L., et al., Validation of UARS microwave limb sounder ozone measurements, *J. Geophys. Res.*, this issue.

Gear, C. W., Numerical Initial Value Problems in Ordinary Differential Equations, Prentice Hall, Englewood Cliffs, N. J., 1971.

Kinnersley, J. S., and R. S. Harwood, An isentropic two-dimensional model with an interactive parameterisation of dynamical and chemical planetary wave fluxes, *Q. J. R. Meteorol. Soc.*, *119*, 1167-1194, 1993.

Parrish, A., B. J. Connor, J. J. Tsou, I. S. McDermid, and W. P. Chu, Ground-based microwave monitoring of stratospheric ozone, *J. Geophys. Res.*, *97*, 2541-2546, 1992.

Ricaud, P., J. Brillet, J. de La Noë, and J.-P. Parisot, Diurnal and seasonal variations of stratomesospheric ozone: Analysis of ground-based microwave measurements in Bordeaux, France, *J. Geophys. Res.*, *96*, 18,617-18,629, 1991.

Ricaud, P., G. Brasseur, J. Brillet, J. de La Noë, J.-P. Parisot, and M. Pirre, Theoretical validation of ground-based microwave ozone observations, *Ann. Geophys.*, *12*, 664-673, 1994.

Rodgers, C. D., Retrieval of atmospheric temperature and composition from remote measurements of thermal radiation, *Rev. Geophys.*, *1*, 609-624, 1976.

Waters, J. W., Microwave limb sounding, in *Atmospheric Remote Sensing by Microwave Radiometry*, edited by M. A. Janssen, chap. 8, John Wiley, New York, 1993.

Wilson, W. J., and P. R. Schwartz, Diurnal variations of mesospheric ozone using millimeter wave measurements, *J. Geophys. Res.*, *86*, 7535-7538, 1981.

Zommerfelds, W. C., K. Künzi, M. E. Summers, R. M. Bevilacqua, D. F. Strobel, M. Allen, and W. J. Sawchuck, Diurnal variations of mesospheric ozone obtained by ground-based microwave radiometry, *J. Geophys. Res.*, *94*, 12,819-12,832, 1989.

B. J. Connor, Atmospheric Sciences Division, Mail Stop 401B, NASA Langley Research Center, Hampton, VA 23681-0001.

J. de La Noë and P. Ricaud (corresponding author), Bordeaux Observatory, CNRS/INSU, BP 89, 33270, Floirac, France.

L. Froidevaux and J. W. Waters, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

R. S. Harwood and I. A. MacKenzie, Department of Meteorology, Edinburgh University, Scotland UK EH9 3JZ.

G. E. Peckham, Department of Physics, Heriot-Watt University, Scotland UK EH14 4AS.

(Received November 16, 1994; revised September 2, 1995; accepted September 4, 1995.)