1. Introduction

[2] Progress in the study of the radiative and climatic impacts of ozone change requires a quantitative understanding of the formation and loss of ozone in all regions of the atmosphere. Long-term measurements using satellites, balloon sondes and ground-based instruments show two peaks in the vertical profile of ozone loss trends in the northern midlatitudes: one at 40 km with a value of about −6% per decade and one at about 15 km with a value of about −5% per decade [World Meteorological Organization, 2002]. While halogens are mainly responsible for the ozone loss trend at 40 km, above this altitude the major catalytic loss terms are associated with the HOX family. Systematic, long-term measurements of HOX species therefore provide a useful tool for the analysis of ozone trends.

[3] Ground-based ultraviolet spectroscopy has been employed to measure the OH column abundance by observing OH absorption lines in the P1(1) or Q1(2) band at around 32400 cm⁻¹ [Burnett and Burnett, 1981, 1983, 1984; Burnett et al., 1988; Cageao et al., 2001; Iwagami et al., 1995, 1998; Mills et al., 2002, 2003]. Burnett et al. [1988] noted that there is a morning/afternoon asymmetry in the diurnal cycle of the normalized OH column abundance, and called this effect the “AM-PM diurnal asymmetry (AMPMDA)”. The authors analyzed the annual climatology of AMPMDA based on normalized data collected from 1978 to 1986 over the Fritz Peak Observatory (40°N, 105°W), Colorado (FPO) and from 1980 to 1986 over Boca Raton, Florida (26.4°N, 80°W).

[4] Recently, an AMPMDA was reported for measurements of the OH column based on data collected from July 1997 to December 2001 over the Jet Propulsion Laboratory’s Table Mountain Facility (TMF) (34.4°N, 117.7°W) [Mills et al., 2003]. First-order fits of the column abundance vs. the solar zenith angle (SZA) showed a pronounced asymmetry with the OH formation rate in the morning being about 20% larger than the afternoon removal rate for almost all months using solar transit as a reference point. The results were obtained from retrievals that used the P1(1) or Q1(2) lines in the OH spectrum.

[5] Previous modeling studies have noted that HOX concentrations in the upper stratosphere and mesosphere should peak after solar noon [Prather, 1981]. Pickett and Peterson [1996] compared their balloon measurements of the OH vertical profile with the results of a steady-state model. They found that the average PM absolute abundance was larger than the average AM absolute abundance and suggested that the asymmetry could be explained by a 20-min phase lag in the photochemical reactions controlling HOX radicals. The AMPMDA has yet to be explained quantitatively with a fully coupled model constrained by realistic profiles of water vapor and ozone.

[6] This paper focuses on the observational evidence of the AMPMDA from the measurements made at TMF using the Fourier-Transform Ultraviolet Spectrometer (FTUVS) [Cageao et al., 2001]. Our goal was to include multiple OH absorption lines measured simultaneously in our retrieval so as to reduce the statistical uncertainty of the column measurement. We describe a method of analysis using five absorption lines to obtain a weighted average of the OH column abundance over TMF. The result is then used to examine the morning/afternoon diurnal cycle asymmetry in the OH column abundance.
A simple heuristic model is employed to simulate the phenomenon.

2. Observations

[7] The FTUVS has been operated since 1997 under sky conditions which ranged from clear to hazy or partly cloudy. Observations have been made on 342 days from July 1997 through December 2003 and the total number of individual column observations numbered 9576 in this period. Each day in the summer (winter) has about 35–40 (23–27) OH column measurements. The FTUVS has a broad spectral coverage (15600 cm\(^{-1}\) to 37000 cm\(^{-1}\)), high resolving power (540,000) and a high signal-to-noise ratio (about 1700:1 for a 15-minute integration time). This permits observations of lines in the OH A\(\sum\) \(\leftrightarrow\) X\(\Pi\) (0,0) band that have a dynamic range of about a factor of 10. The OH absorption lines observed by FTUVS are optically thin (a few per cent absorption, maximum) and hence the measurement is sensitive to the entire OH column.

[8] The reduction of data has been described previously [Cageao et al., 2001] and is summarized as follows: FTUVS alternately acquires spectra from the east and west solar limbs with an integration time of 15 minutes at each limb. Due to the rotation of the Sun, the east and west limb spectra are Doppler shifted with respect to one another while the telluric OH absorption lines remain fixed. By shifting and ratioing successive east-west spectral pairs, the Fraunhofer features are significantly attenuated. The resulting spectrum is fitted with a reference spectrum derived from a line-by-line forward model calculation that includes the instrument line shape function, Doppler-broadened OH line shape, and the same processing as the measured spectra. For OH column data derived from the P\(_1\)(1) OH line alone, the systematic error, 2\(\sigma_s\), is ±12% and the random error, 2\(\sigma_r\), is ±14% [Cageao et al., 2001].

[9] More than twenty of the strongest OH absorption lines in the A\(\sum\) \(\leftrightarrow\) X\(\Pi\) (0,0) band have been identified in FTUVS solar spectra. Thirteen of these were selected for analysis based on visual inspection of the quality of the spectral fits. The selected lines were further examined to determine their respective spectral fit uncertainties in a large data set. The measurement error at each OH absorption line is taken as the square root of the variance in the residuals between the best spectral fit and the actual measurement, divided by the degrees of freedom. The uncertainty of the fit to each line in the spectrum is estimated from the measurement error by a parabolic expansion of \(\chi^2\) around the \(\chi^2\) minimization of the fit [Bevington and Robinson, 1992]. From a close inspection of the distribution of the spectral fit uncertainty, five absorption lines with relatively low median OH uncertainties were chosen for the present analysis. The line parameters and median spectral fit uncertainties are summarized in Table 1. Four of the five chosen OH lines are among the five lines with the largest effective peak cross sections. Although not in the latter group, the P\(_1\)(3) line was used in the average because it was relatively free from interference from residual solar lines.

3. Results

[10] Previous measurements of OH column abundances have used only the P\(_1\)(1) and Q\(_1\)(2) lines, which are among the strongest [Burnett et al., 1988; Iwagami et al., 1995,

![Figure 1](image-url)
1998; Mills et al., 2002, 2003]. The OH columns derived from somewhat weaker lines may be used to increase the precision of the OH column measurements. To achieve this, the OH columns derived using the five selected absorption lines were averaged with appropriate weighting. For each day of measurement, the diurnal cycle for each absorption line was fitted with a second order polynomial, and the variance between the fit and the \( i \)th absorption line, \( \Delta[OH]/i \), was calculated [see, e.g., Graybill and Iyer, 1994]. The OH column abundance was calculated from an average of the five lines using (\( \Delta[OH]/i \))\(^{-1} \) as the weighting factor for each line.

The diurnal variability of the OH column abundance was quantified by fitting the OH column vs. SHA with a second-order polynomial:

\[
[OH] = a(SHA - b)^2 + c.
\]  

Separate fits were carried out for both summer and winter and the second order diurnal fit parameters are shown in Table 2. As given by the parameter, \( b \), the summer \([OH]_{\text{col}}\) maximum occurs 26.0 ± 0.7 minutes after solar transit. As a comparison, a fourth order polynomial fit is also shown in Figures 1a and 1b. The two fits are almost indistinguishable except near the end points implying higher order fits are unnecessary. A second order fit was also applied to the data collected during November–February in 1998–2003 (Figure 1b). During these months the daily minimum air mass varied from 1.3 to 1.9 at TMF. The second order fit coefficients for the winter data are given in Table 2 and the average daily \([OH]_{\text{col}}\) maximum occurs 36.0 ± 1.8 minutes after transit.

The improvement in precision from the use of five OH lines in the weighted average can be seen by comparing with the results obtained using only the \( P_{1}(1) \) line. The second order fit parameters for summer and winter data of the \( P_{1}(1) \) line are shown in Table 2. The uncertainties from the 5-line weighted averages are a factor of about 1.75–2 smaller than those derived using the \( P_{1}(1) \) line alone.

## Table 2. The Fitting Parameters for the 5-Line Average and \( P_{1}(1) \) in Summer and Winter (Equation (1))

<table>
<thead>
<tr>
<th></th>
<th>a, (10^{12}) cm(^{-2})</th>
<th>b, min.</th>
<th>c, (10^{13}) cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5)-Line Average</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>−1.12 ± 0.01</td>
<td>26.0 ± 0.7</td>
<td>7.14 ± 0.01</td>
</tr>
<tr>
<td>Winter</td>
<td>−1.14 ± 0.03</td>
<td>36.0 ± 1.8</td>
<td>5.04 ± 0.02</td>
</tr>
<tr>
<td>(P_{1}(1))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>−1.13 ± 0.02</td>
<td>28.0 ± 1.4</td>
<td>7.05 ± 0.03</td>
</tr>
<tr>
<td>Winter</td>
<td>−1.19 ± 0.06</td>
<td>34.0 ± 3.1</td>
<td>4.87 ± 0.03</td>
</tr>
</tbody>
</table>

Uncertainties are two standard deviations.

The OH column AMPMDA indices calculated from the FPO data of Burnett et al. [1988] from 1978 to 1986 (open circles) and the TMF data from 1998 through 2003 (filled circles). See text for definition of AMPMDA. The Burnett et al. data were normalized to the diurnal profile from a single year as described in the text. Over the nine-year record, their AMPMDA displays a mean offset of −0.07. The offset has been subtracted from their data for better comparison with the TMF data, which has been normalized to the entire data set and therefore has a mean offset of zero.

### 4. AM-PM Diurnal Asymmetry

In our analysis, the phase shift of the diurnal cycle is given by the polynomial fitting parameters \( b_{\text{av},s} \) and \( b_{\text{av},w} \) from equation (1). It has the same positive sign for both summer and winter, and lies between 26 and 36 minutes. This means that the maximum in the OH diurnal variation always lags SHA = 0 hrs. and explains why the afternoon OH column is larger than the morning column [Mills et al., 2003]. The phase shift can be explained qualitatively by the lengthening of the HO\(_x\) lifetime with increasing altitude in the stratosphere and lower mesosphere [Pickett and Peterson, 1996]. While a detailed analysis lies beyond the scope of this paper the average HO\(_x\) time constant (which controls the diurnal variability of OH) can be estimated using a linear response model with sinusoidal forcing [Camp et al., 2001]:

\[
\frac{dy(t)}{dt} = -\frac{y(t)}{\tau} + F(t); F(t) = A_{0} \sin \omega t, \quad \text{(2)}
\]

where \( y(t) \) is the OH column abundance, \( \tau \) is the HO\(_x\) lifetime, and \( F(t) \) is the photochemical source function of HO\(_x\). The loss of HO\(_x\) is non-linear so this is an approximate description. The source is assumed periodic with a frequency, \( \omega \), approximately equal to one cycle per day. The response function \( F(t) \) is divided by \( \tau \) such that \( A_{0} \) has the same dimension as \( y(t) \). Equation (2) may be solved for \( y(t) \) to obtain:

\[
y(t) = \left( y(0) + \frac{A_{0} \sin \phi}{\sqrt{1 + \omega^2 \tau^2}} \right) e^{-t/\tau} + \frac{A_{0} \sin(\omega t - \phi)}{\sqrt{1 + \omega^2 \tau^2}}, \quad \text{(3)}
\]

where \( y(0) \) is the value of \( y \) at \( t = 0 \), \( \phi = \tan^{-1}(\omega \tau) \) for \( 0 \leq \phi \leq \pi/2 \). The phase shift, \( b_{\text{av}} \), obtained from the diurnal fit is related to \( \tau \) by \( b_{\text{av}} = \phi/\omega = \omega^{-1} \tan^{-1}(\omega \tau) \). Therefore the estimated column averaged lifetime of HO\(_x\)
based on the measurements in summer and winter lies in the range
\[
\tau = \frac{1}{\omega} \tan \omega \theta_n \approx 26 - 36\text{min}.
\]

[15] Burnett et al. [1988] calculated an AMPMDA index by subtracting the monthly average PM normalized abundance from the monthly average normalized AM abundance. The normalization used by Burnett et al. was the average of all data obtained from FPO between July 1981 and June 1982. To enhance the apparent asymmetry, data collected within an hour of local noon were not considered. The index calculated from the FPO data between 1978 and 1986 was consistent from year to year varying from about 0.2 in March to May to about −0.3 in October. The change in the sign of the index in their data indicates that there is a seasonal variation in the asymmetry relative to their normalized profile. In contrast, the asymmetry index, calculated from the TMF OH column data in the same manner, shows no consistent seasonal dependence. This is illustrated in Figure 2 which compares the AMPMDA index from FPO [Burnett et al., 1988] with the data from TMF. It is important to note that since AMPMDA is defined with respect to a normalized temporal profile which is itself symmetric, a value of zero for AMPMDA does not mean that a given profile is symmetric; only that it matches the asymmetry of the reference profile. We conclude that there is a fundamental, unexplained discrepancy between the two data sets. This may be related to an instrumental artifact in one or both instruments, or to differences in dynamical forcing between the measurement sites that affect the transport of OH precursors, such as water vapor, to the stratosphere.

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