

# First UV satellite observations of mesospheric water vapor

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[1] We report the first UV satellite observations of mesospheric water vapor. The measurements are of nonthermal OH prompt emission between 300–330 nm produced directly from the photodissociation of water vapor by H Lyman- $\alpha$ . This technique is most sensitive to water vapor concentrations between 70–90 km altitude. We present OH data from two limb scanning experiments: the Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) and the Optical Spectrograph and Infra-Red Imager System (OSIRIS). Interpretation of the lower resolution ( $\sim 1$  nm) OSIRIS spectra requires the rotational emission rate factors for OH(1,1) solar fluorescence between 313–318 nm, which we present for the first time herein. Comparison of water vapor concentration profiles with the most coincident profiles from the Halogen Occultation Experiment on the Upper Atmosphere Research Satellite shows agreement to within 30% between 75–80 km for both MAHRSI and OSIRIS. We discuss the benefits of this promising new approach to measuring upper mesospheric water vapor and the need for new laboratory measurements to improve the analysis.

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## 1. Introduction

[2] The measured water vapor distribution in the Earth's upper atmosphere provides important details on global climate processes. Its altitude profile typically results from a balance between vertical transport and photolysis so it is an important tracer for modeling global-scale dynamics [Smith and Brasseur, 1991]. In addition, water vapor is the principal source of hydroxyl (OH) in the mesosphere, which is highly reactive and contributes to the catalytic destruction of ozone (O<sub>3</sub>) [Bates and Nicolet, 1950; Brasseur and Solomon, 1986]. Moreover in the cold polar summer mesosphere water vapor forms mesospheric clouds, which have been used as diagnostics for upper atmospheric variability and for hemispheric asymmetries in climate [Garcia, 1989; Chu et al., 2003; Siskind et al., 2005; Hervig and Siskind, 2006; Stevens et al., 2007].

[3] Despite its significance to these important dynamical, chemical and microphysical processes, satellite observations of mesospheric water vapor have only recently become available [e.g., Harries et al., 1996; Bevilacqua et al., 1996; Pumphrey, 1999; Michelsen et al., 2002; Boone et al., 2005; Milz et al., 2005; Lambert et al., 2007]. Uninterrupted global coverage is still limited, however, and obser-

vations in the vicinity of mesospheric clouds are particularly sparse [Hervig et al., 2003]. Finally, previous satellite observations of mesospheric water vapor have been made at infrared and microwave wavelengths. There have been no UV satellite measurements of mesospheric water vapor to date.

[4] Mesospheric water vapor measurements can be made in the UV near 310 nm by measuring nonthermal OH A<sup>2</sup> $\Sigma^+$  – X<sup>2</sup> $\Pi$  (0,0) emission produced directly by photodissociation [Khaplanov et al., 1996]. Indeed, this OH “prompt” emission has been previously observed from a comet [Bertaux, 1986; Budzien and Feldman, 1991]. We show herein OH prompt emission from the Earth's mesosphere observed by two experiments: The Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) and the Optical Spectrograph and Infra-Red Imaging System (OSIRIS). We invert prompt radiance profiles from each experiment to retrieve volume emission rates and water vapor mixing ratios. We then compare the water vapor mixing ratio profiles from each experiment with the most coincident observations from the HALogen Occultation Experiment (HALOE) [Russell et al., 1993] on NASA's Upper Atmosphere Research Satellite (UARS).

[5] We divide this work into five sections. In section 2 we define the spectral components needed to model the observations between 280–330 nm. This includes the calculation of the OH A<sup>2</sup> $\Sigma^+$  – X<sup>2</sup> $\Pi$  (1,1) rotational emission rate factors (*g* factors) for solar fluorescence as well as the relative intensities of the nonthermal OH(0,0) and (1,1) prompt rotational emission lines. In section 3 we describe the spectral analysis used to infer the OH prompt column emission rate from the MAHRSI and OSIRIS limb spectra.

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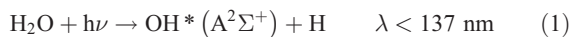
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In section 4 we describe the retrieval of volume emission rates and water vapor mixing ratios from the observed limb radiances. In section 5 we discuss the benefits and current limitations of this new measurement technique.

## 2. Emission Spectrum of OH $A^2\Sigma^+ - X^2\Pi$

[6] When water vapor is photodissociated in the upper mesosphere, most of the OH produced is in the ground electronic state ( $X^2\Pi$ ). However, a small amount is produced in the electronically excited  $A^2\Sigma^+$  state [Terenin and Neujmin, 1934], i.e.



[7] The resultant nonthermal prompt emission appears between 280–330 nm but is most apparent between 300–330 nm [Carrington, 1964; Harich et al., 2000]. With an artificial light source, many have used this technique to obtain in situ measurements of water vapor in both the mesosphere [Khaplanov et al., 1996] and the stratosphere [Bertaux and Delannoy, 1978; Kley et al., 1979; Schwab et al., 1990; Kelly et al., 1993]. However, all of these measurements were made either from a balloon, an aircraft or a rocket and therefore have limited spatial and temporal coverage.

[8] OH prompt emission can also be excited in the Earth's mesosphere by solar H Lyman- $\alpha$  at 121.6 nm. Detection of this OH prompt emission by a satellite experiment poses two challenges. First, there is a bright underlying signal due to Rayleigh scattered sunlight that must be subtracted from the observations. Second, the solar fluorescence of the (0,0) and (1,1) bands are typically brighter than the OH prompt emission and one or both of these bands must also be removed to isolate the overlapping OH prompt lines.

[9] The MAHRSI and OSIRIS data sets require different approaches to the spectral analysis. MAHRSI observes the Earth's limb near 309 nm with a spectral resolution of 0.02 nm [Conway et al., 1999], which is high enough to distinguish three discrete OH(0,0) prompt rotational lines from those due to (0,0) solar resonance fluorescence between 308.52–309.02 nm. The MAHRSI passband used herein is narrow, however, at  $\sim 0.5$  nm so that the observed emission is scaled up to estimate the total OH prompt emission over several hundred OH prompt rotational lines distributed across  $\sim 30$  nm based on our understanding of the intensity distribution. OSIRIS observes the Earth's limb between 280–800 nm with a spectral resolution of  $\sim 1$  nm [Llewellyn et al., 2004; Gattinger et al., 2006, 2008], so in contrast to MAHRSI the entire rotational envelope of the OH(0,0) and (1,1) prompt emission spectrum between 300–330 nm needs to be separated from the blended (0,0) and (1,1) solar fluorescence. For both the MAHRSI and OSIRIS analyses, we require a quantitative understanding of the thermal and nonthermal OH emission lines in the Earth's upper mesosphere between 280–330 nm.

[10] In this section, we focus on the spectroscopy of mesospheric OH between 280–330 nm. We consider four major components to the OH emission spectrum: the (0,0) and (1,1) solar fluorescence bands and the (0,0) and (1,1) prompt bands. The brightest of these by far is (0,0) solar

fluorescence near 309 nm. We express the fluorescence efficiency of each transition with the  $g$  factor, which is the number of solar photons scattered per second per OH molecule. The (0,0) rotational  $g$  factors were presented and compared to MAHRSI observations by Stevens and Conway [1999] and are not reproduced here. We first extend the work of Stevens and Conway by reporting the OH(1,1) rotational  $g$  factors near 314 nm. We then report the relative intensities of the nonthermal (0,0) and (1,1) prompt rotational emission lines used in this study based on previous laboratory work [Carrington, 1964; Crosley and Lengel, 1975].

### 2.1. OH(1, $v''$ ) Solar Fluorescence

[11] The OH  $A^2\Sigma^+ - X^2\Pi$  (1,1) band is observed by OSIRIS between 313–318 nm [Gattinger et al., 2006, 2008]. For solar fluorescence it is stimulated by the solar irradiance near the (1,0) transition at 280 nm. The solar irradiance is spectrally complex in the mid-UV, so that rotational transitions at nearly the same wavelength can be excited by significantly different irradiances. To derive line positions,  $X(0)$  rotational term values were taken from Stark et al. [1994] and  $A(1)$  term values were taken from Coxon [1980]. By invoking the relevant selection rules, rotational line positions for the (1,0) band were calculated and are shown in Table 1. The line positions are listed separately for each of the 12 rotational branches, where  $N'$  represents the angular momentum of the upper state apart from spin, i.e.,  $N' = J' \pm 1/2$ . In Table 1 and all subsequent tables, those branches with  $\Delta J = J'' - J' = 0$  are  $Q$  branches, and those with  $\Delta J = +1$  and  $-1$  are  $P$  and  $R$  branches, respectively. More details of the nomenclature for each branch are provided by Cageao et al. [1997].

[12] For emission,  $X(1)$  rotational levels are taken from Dieke and Crosswhite [1962] and line positions for the (1,1) band are given in Table 2. Although only the first few rotational levels are populated for solar fluorescence in the Earth's mesosphere, we include line positions up to  $N' = 20$  for the (1,1) band because they will be populated in the nonthermal prompt emission spectrum discussed in the next section.

[13] Three important differences arise when extending the OH(0,0)  $g$  factor calculation to the (1, $v''$ ) bands: the band oscillator strength ( $f_{10}$ ), the branching ratio to  $v'' = 1$  ( $\omega_{11}$ ) and the solar irradiance exciting the rotational transitions. Consistent with the recommendations of Schleicher and A'Hearn [1988], we take  $f_{10} = 2.78 \times 10^{-4}$  [Luque and Crosley, 1998] and  $\omega_{11} = 0.63$  [Crosley and Lengel, 1975]. The biggest challenge is the construction of a new solar atlas at superior spectral resolution near 280 nm.

[14] Ideally, a solar atlas with a spectral resolution higher than the Doppler width of a OH rotational line in the Earth's mesosphere ( $\sim 0.001$  nm) is desired to calculate the rotational  $g$  factors, which is not available. To our knowledge, the atlas with the highest spectral resolution in this wavelength range ( $\sim 0.003$  nm) was compiled by Kohl et al. [1978] and we use this as the basis for our calculations. We note that each rotational  $g$  factor is typically derived from many different absorption transitions [Cageao et al., 1997; Stevens and Conway, 1999], effectively averaging the irradiances and reducing the uncertainty arising from the inadequate spectral resolution of the solar atlas. Later in this

**Table 1.** Allowed OH(1,0) Transitions<sup>a</sup>

| $N'$ | $P_{11}$ | $R_{11}$ | $R_{Q_{21}}$ | $Q_{11}$ | $Q_{P_{21}}$ | $S_{R_{21}}$ | $Q_{P_{12}}$ | $Q_{R_{12}}$ | $Q_{22}$ | $P_{Q_{12}}$ | $P_{22}$ | $R_{22}$ |
|------|----------|----------|--------------|----------|--------------|--------------|--------------|--------------|----------|--------------|----------|----------|
| 0    | 282.2532 |          |              |          |              |              | 283.7549     |              |          | 283.2642     |          |          |
| 1    | 282.6630 |          |              | 281.9961 | 281.9986     |              | 284.3109     | 283.0035     | 283.0061 | 283.4966     | 283.4992 |          |
| 2    | 283.0923 | 281.4832 | 281.4875     | 282.1497 | 282.1540     |              | 284.9261     | 282.9766     | 282.9810 | 283.7922     | 283.7965 | 282.4930 |
| 3    | 283.5460 | 281.3807 | 281.3866     | 282.3233 | 282.3293     | 280.7257     | 285.5954     | 283.0136     | 283.0196 | 284.1450     | 284.1511 | 282.2128 |
| 4    | 284.0281 | 281.2983 | 281.3060     | 282.5221 | 282.5298     | 280.3752     | 286.3150     | 283.1089     | 283.1166 | 284.5502     | 284.5580 | 281.9970 |
| 5    | 284.5413 | 281.2414 | 281.2508     | 282.7500 | 282.7595     | 280.0477     | 287.0820     | 283.2575     | 283.2670 | 285.0040     | 285.0136 | 281.8401 |
| 6    | 285.0879 | 281.2143 | 281.2254     | 283.0102 | 283.0214     | 279.7489     | 287.8945     | 283.4560     | 283.4672 | 285.5038     | 285.5152 | 281.7372 |
| 7    | 285.6693 | 281.2204 | 281.2331     | 283.3049 | 283.3178     | 279.4831     | 288.7512     | 283.7018     | 283.7148 | 286.0480     | 286.0612 | 281.6851 |
| 8    | 286.2869 | 281.2621 | 281.2764     | 283.6359 | 283.6505     | 279.2537     | 289.6514     | 283.9936     | 284.0082 | 286.6355     | 286.6506 | 281.6813 |

<sup>a</sup>Units are nm; all wavelengths for vacuum.

section, we will explore the sensitivity of our result to reductions in this spectral resolution. We note that this atlas has previously been used in the calculation of OH(1, $v''$ ) solar fluorescence of cometary OH. Although the rotational population of cometary OH is in fluorescence equilibrium rather than thermal equilibrium, spectra compare favorably to observations that resolve the rotational envelope of the bands [Schleicher and A'Hearn, 1988; Budzien and Feldman, 1991].

[15] In order to obtain the most accurate absolute solar irradiance, we normalize the Kohl *et al.* [1978] atlas to observations by the SOLar STellar InterComparison Experiment (SOLSTICE) [Rottman *et al.*, 1993] on UARS, which has an absolute accuracy of about 3.5% near 280 nm [Woods *et al.*, 1996]. We degrade the Kohl *et al.* [1978] atlas to the spectral resolution of SOLSTICE (0.3 nm) and normalize the Kohl *et al.* [1978] total irradiance between 279–289 nm to that from SOLSTICE. Using this procedure, the Kohl *et al.* [1978] absolute irradiances are adjusted downward by 27%. The result is shown over an important spectral region of excitation in Figure 1. There are some gaps in the atlas over which we interpolate and the regions of these gaps are indicated by symbols at the bottom of the figure. The gaps constitute 16% of the spectrum within the figure. Using this atlas and the transition wavelengths

indicated in Table 1, we determine the solar irradiance at each wavelength and show the results in Table 3.

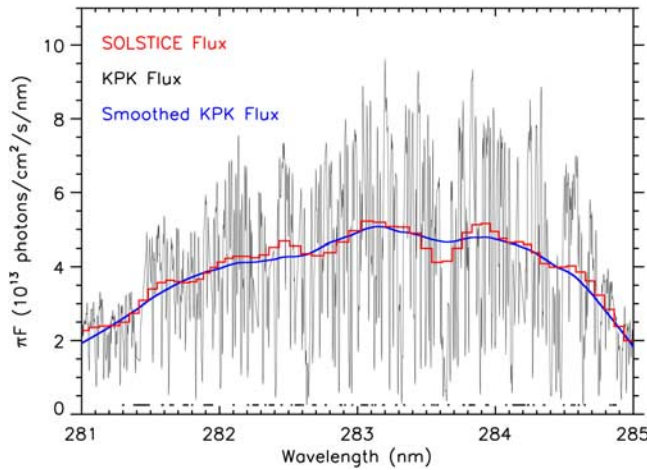
[16] Following the approach described by Stevens and Conway [1999],  $g$  factors at 200 K are calculated from the irradiances in Table 3 and shown in Table 4 for the OH(1,1) band. Boldface entries indicate the brightest ten lines predicted in the (1,1) band. Summing over all rotational transitions, the vibrational band  $g$  factor at 200 K is calculated to be  $5.3 \times 10^{-5} \text{ s}^{-1}$  and in excellent agreement with the estimate by Stevens and Conway [1999] of  $5.2 \times 10^{-5} \text{ s}^{-1}$ . Using their 200 K  $g$  factor for the (0,0) band of  $3.51 \times 10^{-4} \text{ s}^{-1}$ , the calculated (1,1)/(0,0) band ratio for solar fluorescence is therefore 0.15 and in good agreement with airglow observations by OSIRIS [Gattinger *et al.*, 2008].

[17] The predicted brightness of the (1,1) band relative to the (0,0) band is shown in Figure 2, where we have smoothed both bands with the OSIRIS spectral resolution function ( $\sim 1$  nm) to represent the OH solar fluorescence spectrum observed by that instrument. The (1,0) rotational  $g$  factors near 283 nm can be calculated by multiplying the entries in Table 4 by the A(1,0)/A(1,1) ratio measured by Crosley and Lengel [1975] of 0.63 and using the transition wavelengths in Table 1.

**Table 2.** Allowed OH(1,1) Transitions<sup>a</sup>

| $N'$ | $P_{11}$ | $R_{11}$ | $R_{Q_{21}}$ | $Q_{11}$ | $Q_{P_{21}}$ | $S_{R_{21}}$ | $Q_{P_{12}}$ | $Q_{R_{12}}$ | $Q_{22}$ | $P_{Q_{12}}$ | $P_{22}$ | $R_{22}$ |
|------|----------|----------|--------------|----------|--------------|--------------|--------------|--------------|----------|--------------|----------|----------|
| 0    | 313.8646 |          |              |          |              |              | 315.7041     |              |          | 315.1210     |          |          |
| 1    | 314.3424 |          |              | 313.5480 | 313.5511     |              | 316.3512     | 314.7970     | 314.8001 | 315.3839     | 315.3871 |          |
| 2    | 314.8310 | 312.9127 | 312.9180     | 313.7076 | 313.7129     |              | 317.0566     | 314.7410     | 314.7464 | 315.7092     | 315.7146 | 314.1669 |
| 3    | 315.3359 | 312.7574 | 312.7648     | 313.8795 | 313.8869     | 311.9782     | 317.8133     | 314.7459     | 314.7533 | 316.0894     | 316.0969 | 313.7958 |
| 4    | 315.8617 | 312.6138 | 312.6233     | 314.0692 | 314.0787     | 311.5155     | 318.6185     | 314.8080     | 314.8176 | 316.5200     | 316.5297 | 313.4892 |
| 5    | 316.4119 | 312.4882 | 312.4997     | 314.2810 | 314.2927     | 311.0693     | 319.4672     | 314.9208     | 314.9326 | 316.9960     | 317.0079 | 313.2396 |
| 6    | 316.9888 | 312.3857 | 312.3993     | 314.5185 | 314.5324     | 310.6458     | 320.3574     | 315.0819     | 315.0958 | 317.5143     | 317.5284 | 313.0433 |
| 7    | 317.5944 | 312.3108 | 312.3264     | 314.7847 | 314.8007     | 310.2500     | 321.2877     | 315.2869     | 315.3029 | 318.0729     | 318.0892 | 312.8955 |
| 8    | 318.2311 | 312.2660 | 312.2837     | 315.0817 | 315.0997     | 309.8859     | 322.2559     | 315.5344     | 315.5525 | 318.6715     | 318.6904 | 312.7938 |
| 9    | 318.8980 | 312.2541 | 312.2737     | 315.4113 | 315.4322     | 309.5570     | 323.2618     | 315.8233     | 315.8441 | 319.3069     | 319.3283 | 312.7363 |
| 10   | 319.5971 | 312.2775 | 312.3002     | 315.7740 | 315.7972     | 309.2658     | 324.3050     | 316.1522     | 316.1754 | 319.9800     | 320.0038 | 312.7243 |
| 11   | 320.3294 | 312.3365 | 312.3615     | 316.1717 | 316.1973     | 309.0156     | 325.3853     | 316.5215     | 316.5471 | 320.6906     | 320.7169 | 312.7539 |
| 12   | 321.0960 | 312.4335 | 312.4608     | 316.6057 | 316.6337     | 308.8056     | 326.5027     | 316.9313     | 316.9594 | 321.4387     | 321.4676 | 312.8269 |
| 13   | 321.8978 | 312.5700 | 312.5997     | 317.0772 | 317.1077     | 308.6390     | 327.6574     | 317.3821     | 317.4127 | 322.2249     | 322.2564 | 312.9436 |
| 14   | 322.7358 | 312.7474 | 312.7795     | 317.5874 | 317.6204     | 308.5173     | 328.8496     | 317.8744     | 317.9075 | 323.0495     | 323.0838 | 313.1047 |
| 15   | 323.6112 | 312.9673 | 313.0019     | 318.1375 | 318.1733     | 308.4421     | 330.0800     | 318.4090     | 318.4448 | 323.9134     | 323.9505 | 313.3111 |
| 16   | 324.5250 | 313.2311 | 313.2682     | 318.7290 | 318.7675     | 308.4151     | 331.3492     | 318.9868     | 319.0253 | 324.8174     | 324.8574 | 313.5638 |
| 17   | 325.4787 | 313.5403 | 313.5801     | 319.3633 | 319.4045     | 308.4378     | 332.6581     | 319.6090     | 319.6504 | 325.7626     | 325.8056 | 313.8639 |
| 18   | 326.4736 | 313.8968 | 313.9393     | 320.0418 | 320.0860     | 308.5121     | 334.0077     | 320.2769     | 320.3212 | 326.7502     | 326.7963 | 314.2129 |
| 19   | 327.5113 | 314.3022 | 314.3475     | 320.7662 | 320.8134     | 308.6395     | 335.3992     | 320.9919     | 321.0392 | 327.7816     | 327.8309 | 314.6123 |
| 20   | 328.5935 | 314.7584 | 314.8067     | 321.5385 | 321.5888     | 308.8221     | 336.8340     | 321.7557     | 321.8061 | 328.8584     | 328.9110 | 315.0638 |

<sup>a</sup>Units are nm; all wavelengths for vacuum.



**Figure 1.** Solar irradiance used for calculation of OH(1,1)  $g$  factors in this work (black). Symbols at the bottom indicate where the atlas was missing data (16% of the data in the wavelength region shown) and the atlas was interpolated over these regions. The wavelengths are for vacuum and the normalization of the high-resolution spectrum is done so that the integral of the smoothed *Kohl et al.* [1978] (KPK) spectrum (blue) is the same as that of the SOLSTICE spectrum at 0.3 nm resolution (red) between 279–289 nm. The SOLSTICE spectrum was measured on 25 February 1992.

[18] To explore the sensitivity of our results for the (1,1) vibrational band  $g$  factor on the spectral resolution of the solar atlas used, we increasingly degraded our atlas in 12 increments until the spectral resolution was equivalent to that of SOLSTICE (0.3 nm). Results are shown in Figure 3 and indicate that even though our atlas cannot resolve features down to a Doppler width of a rotational line in the Earth's atmosphere, the band  $g$  factor changes by only 6% using an atlas at lower spectral resolution. We take this as evidence that the  $g$  factor calculation is adequate for the analysis of the OSIRIS (1,1) data at 1 nm spectral resolution.

[19] The uncertainty of the OH(1,1) band  $g$  factor is driven primarily by the uncertainty of the A(1,0) Einstein coefficient, from which  $f_{10}$  is directly calculated. On the basis of the available theoretical and experimental work, we estimate this uncertainty to be  $\pm 20\%$  [Rouse and Engleman, 1973; Crosley and Lengel, 1975; Luque and Crosley, 1998].

In addition, we estimate a 6% uncertainty based on our relatively low-resolution solar atlas (Figure 3), 5% for the (1,1) branching ratio [Crosley and Lengel, 1975], 3.5% for the solar flux near 280 nm [Woods et al., 1996] and 3% for the wavelength uncertainty of the solar atlas [Kohl et al., 1978]. The total root-sum-squared 1- $\sigma$  uncertainty for the (1,1) band  $g$  factor is therefore  $\pm 22\%$ . This is significantly larger than the root-sum-squared uncertainty of the (0,0) band  $g$  factor of  $\pm 7\%$  [Conway et al., 1999].

## 2.2. Prompt Emission

[20] As discussed earlier, when water vapor is photo-dissociated by UV light, OH is produced preferentially in the ground state. However, if the photon is energetic enough there is a small but significant quantum yield that produces OH in the  $A^2\Sigma^+$  excited electronic state. The fraction of OH in the excited state depends in part on the wavelength of the photon. In the Earth's upper mesosphere where we observe most of the OH prompt emission, the photodissociation is dominated by H Lyman- $\alpha$  [Nicolet, 1984].

[21] Whereas the OH solar fluorescence spectrum in the mesosphere peaks near rotational states with angular momentum  $N \sim 2$  [Cageao et al., 1997; Stevens and Conway, 1999] the OH prompt spectrum preferentially populates rotational states where  $N \sim 14$ –22, depending on whether the  $A^2\Sigma^+$  state is also vibrationally excited [Carrington, 1964; Vikis, 1978; Okabe, 1980]. It is this difference in the rotational population that allows us to isolate the prompt emission from the solar fluorescence.

[22] The line positions for the OH(0,0) band are shown in Table 5, which is an extension of Table 1 from Stevens and Conway [1999]. Table 5 uses the X(0) and A(0) term values of Stark et al. [1994]. The relative intensities of the rotational lines within the (0,0) and (1,1) bands are taken from Carrington [1964] and are shown in Tables 6 and 7, respectively, where the three lines detected by MAHRSI are highlighted in boldface. The band integrated (0,0)/(1,1) prompt ratio is discussed below.

[23] The relative brightness of the (1,1) and (0,0) prompt emission bands may be written

$$\frac{I(1,1)}{I(0,0)} = \left[ \frac{N(1)}{N(0)} \right] \cdot \left[ \frac{A(1,1)}{A(0,0)} \right] \quad (2)$$

where  $N$  represents the population of the  $v' = 1$  or  $v' = 0$  state and A(1,1) or A(0,0) is the band Einstein coefficient. The ratio of excited state populations  $N(1)/N(0)$  is 0.38 from the work of Lee et al. [1978]. This ratio is reflected in the ratio of the sum of the populations in Tables 6 and 7. Using

**Table 3.** Solar Irradiance Exciting OH( $v' = 1$ )<sup>a</sup>

| $N'$ | $P_{11}$ | $R_{11}$ | $R_{Q_{21}}$ | $Q_{11}$ | $Q_{P_{21}}$ | $S_{R_{21}}$ | $Q_{P_{12}}$ | $Q_{R_{12}}$ | $Q_{22}$ | $P_{Q_{12}}$ | $P_{22}$ | $R_{22}$ |
|------|----------|----------|--------------|----------|--------------|--------------|--------------|--------------|----------|--------------|----------|----------|
| 0    | 3.3      |          |              |          |              |              | 6.9          | 2.2          |          | 5.6          |          |          |
| 1    | 4.5      |          |              | 4.8      | 4.1          |              | 2.1          | 5.9          | 1.8      | 2.1          | 2.6      |          |
| 2    | 8.0      | 3.6      | 4.1          | 5.4      | 3.3          |              | 2.1          | 3.1          | 7.5      | 4.0          | 5.0      | 6.3      |
| 3    | 7.3      | 2.5      | 1.7          | 4.0      | 4.1          | 1.0          | 2.1          | 4.2          | 6.2      | 3.5          | 4.7      | 4.0      |
| 4    | 3.1      | 2.2      | 1.8          | 5.2      | 6.2          | 0.6          | 3.8          | 3.1          | 5.1      | 4.7          | 5.9      | 4.7      |
| 5    | 6.0      | 2.6      | 2.2          | 4.0      | 5.8          | 1.1          | 6.1          | 3.6          | 5.4      | 1.7          | 1.4      | 2.8      |
| 6    | 1.2      | 1.9      | 2.8          | 2.9      | 5.1          | 0.4          | 7.7          | 4.7          | 4.8      | 1.3          | 1.9      | 4.3      |
| 7    | 2.6      | 2.6      | 2.6          | 2.8      | 0.9          | 0.5          | 8.1          | 4.0          | 5.6      | 6.9          | 5.4      | 3.9      |
| 8    | 7.9      | 2.4      | 1.6          | 0.8      | 0.9          | 0.9          | 1.9          | 8.6          | 6.4      | 6.6          | 8.9      | 2.3      |

<sup>a</sup>Units are  $10^{13}$  photons/cm<sup>2</sup>/s/nm.

**Table 4.** OH(1,1)  $g$  Factors at 200 K<sup>a</sup>

| $N'$ | $P_{11}$   | $R_{11}$ | $^R Q_{21}$ | $Q_{11}$   | $^Q P_{21}$ | $^S R_{21}$ | $^O P_{12}$ | $^Q R_{12}$ | $Q_{22}$   | $^P Q_{12}$ | $P_{22}$   | $R_{22}$ |
|------|------------|----------|-------------|------------|-------------|-------------|-------------|-------------|------------|-------------|------------|----------|
| 0    | <b>3.1</b> |          |             |            |             |             | 0.4         |             |            | <b>1.8</b>  |            |          |
| 1    | <b>3.7</b> |          |             | <b>2.6</b> | 1.5         |             | 0.5         | 0.8         | 1.3        | <b>1.7</b>  | 1.0        |          |
| 2    | <b>4.0</b> | 0.6      | 0.9         | <b>4.1</b> | 1.3         |             | 0.4         | 0.9         | <b>2.4</b> | 1.5         | <b>1.9</b> | 0.6      |
| 3    | 1.7        | 0.5      | 0.4         | <b>2.1</b> | 0.4         | 0.1         | 0.1         | 0.4         | 1.5        | 0.5         | 1.0        | 0.5      |
| 4    | 0.8        | 0.3      | 0.2         | 1.0        | 0.2         | 0.0         | 0.0         | 0.1         | 0.8        | 0.2         | 0.6        | 0.3      |
| 5    | 0.2        | 0.1      | 0.0         | 0.4        | 0.0         | 0.0         | 0.0         | 0.0         | 0.3        | 0.0         | 0.2        | 0.1      |
| 6    | 0.0        | 0.0      | 0.0         | 0.1        | 0.0         | 0.0         | 0.0         | 0.0         | 0.1        | 0.0         | 0.1        | 0.0      |
| 7    | 0.0        | 0.0      | 0.0         | 0.0        | 0.0         | 0.0         | 0.0         | 0.0         | 0.0        | 0.0         | 0.0        | 0.0      |
| 8    | 0.0        | 0.0      | 0.0         | 0.0        | 0.0         | 0.0         | 0.0         | 0.0         | 0.0        | 0.0         | 0.0        | 0.0      |

<sup>a</sup>Units are  $10^{-6} \text{ s}^{-1}$ ;  $g_{11} = 5.3 \times 10^{-5} \text{ s}^{-1}$ . The ten brightest rotational lines are in boldface.

the Einstein A coefficients from *Chidsey and Crosley* [1980] we find that  $A(1,1)/A(0,0) = 0.5$ . This is somewhat smaller than that reported by *Crosley and Lengel* [1975] (0.6), which is limited to laboratory observations where  $N' < 6$ . We therefore calculate  $I(1,1)/I(0,0)$  to be 0.2 in Tables 6 and 7.

[24] The modeled OH prompt spectrum between 305–330 nm is shown in Figure 4, where the relative intensities of the (0,0) and (1,1) rotation lines are shown in black and red, respectively. The entire spectrum has been smoothed using the OSIRIS spectral resolution function to simulate the observation by that instrument, analogous to Figure 2 for the solar fluorescence spectrum. The composite spectrum is overplotted as the solid black histogram. We have also indicated (in green) on Figure 4 the narrow spectral region near 309 nm where MAHRSI observes both OH(0,0) solar resonance fluorescence and three OH(0,0) relatively bright prompt emission lines. Since MAHRSI observes only a portion of the OH(0,0) prompt spectrum, we scale the observed intensities upwards to represent the prompt emission for the (0,0) and (1,1) bands. From the results shown in Table 6 and using the MAHRSI spectral resolution function over the passband shown in Figure 4, we calculate this scale factor to be 26.5.

### 3. The Observations

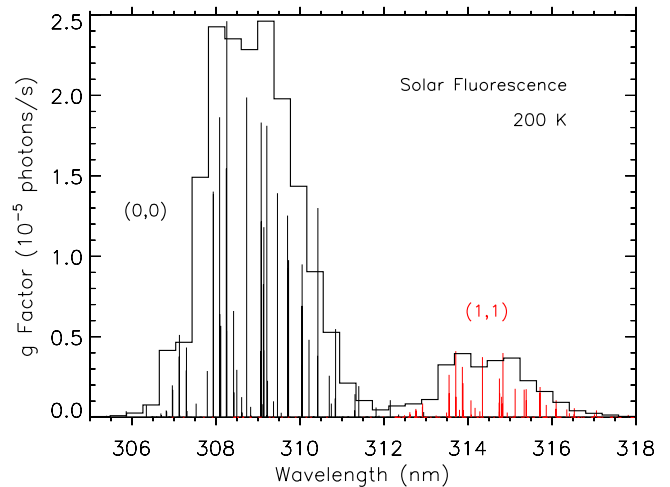
#### 3.1. MAHRSI

[25] MAHRSI flew twice on a satellite deployed and retrieved by the crew of the space shuttle, once in 1994 and again in 1997 [*Conway et al.*, 1999]. The data used for this study are from the second mission and have been presented by *Conway et al.* [2000], who analyzed the OH(0,0) solar resonance fluorescence to retrieve OH densities in the mesosphere and upper stratosphere. We use the observations reported by *Conway et al.* to identify the relatively weak OH prompt emission because they are distinguished by smaller ( $<50^\circ$ ) solar zenith angles (SZAs), which allows for deeper penetration of H Lyman- $\alpha$  and therefore increases the mesospheric OH signal. The data are an average of 34 limb scans collected during six different orbits between 10–15 August 1997. The selected scans were taken from latitudes between  $43\text{--}57^\circ\text{N}$ , where the local solar time ranged between 0930–1430 and the SZA varied between  $33\text{--}49^\circ$ .

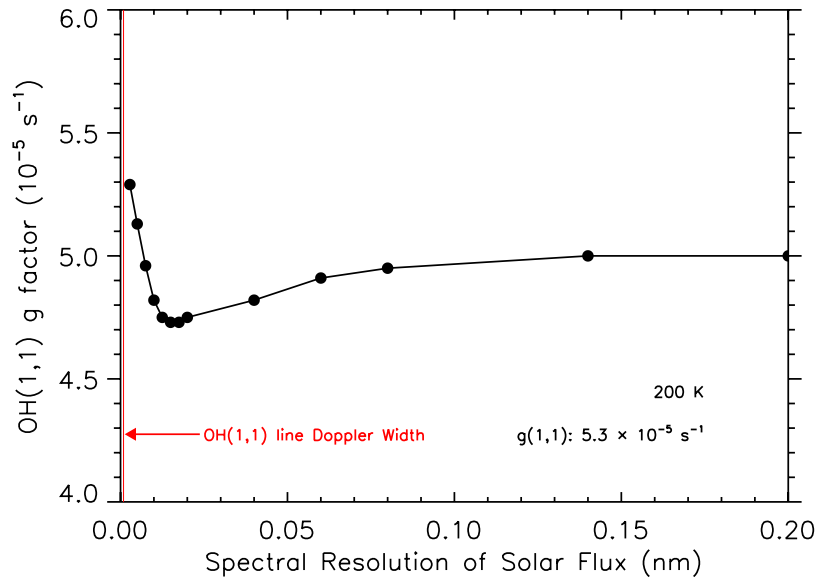
[26] Figure 5a shows these MAHRSI limb data in black, which is an average between 72–79 km altitude near where the OH prompt emission peaks in the mesosphere. Our spectral analysis includes the Rayleigh scattered back-

ground (in blue, top panel), the OH(0,0) solar resonance fluorescence spectrum and the OH(0,0) prompt spectrum. The OH(0,0) prompt spectrum was smoothed with the spectral resolution function of MAHRSI and included in the least squares radiance retrieval procedure discussed by *Conway et al.* [2000]. Excess emission not captured by the (0,0) solar fluorescence spectrum can be seen in the top two panels near 308.58 nm, 308.71 nm, and 309.00 nm.

[27] The effects of ozone on the shape of the background are only important near 65 km and below [*Conway et al.*, 1999], which is below where most of the OH prompt signal originates. In our analysis, we narrow the MAHRSI passband from  $\sim 3$  nm [*Conway et al.*, 2000] to  $\sim 0.5$  nm in Figure 5. Confining the passband to this spectral region reduces the uncertainty arising from imperfections in the background fitting. The passband selected (308.52–309.02 nm) includes three bright OH(0,0) prompt lines as shown in Figure 4. We then use a nonlinear least squares fitting algorithm that includes the Rayleigh scattered back-



**Figure 2.** OH solar resonance fluorescence spectrum between 305–318 nm. The relative intensity of the (0,0) band in black is shown against the (1,1) band in red at 200 K, where the rotational emission rate factors ( $g$  factors) are indicated on the  $y$  axis. Below  $\sim 70$  km, the (0,0)/(1,1) ratio changes due to vibrational energy transfer within the upper electronic state [*Gattinger et al.*, 2008]. The entire spectrum is smoothed using the OSIRIS spectral resolution function with a full-width at half-maximum of  $\sim 1$  nm (scaled arbitrarily).



**Figure 3.** OH(1,1) band  $g$  factor using a solar atlas based on the observations by *Kohl et al.* [1978]. The solar atlas used in the  $g$  factor calculation does not resolve the Doppler width of a OH(1,1) rotational line in the Earth's atmosphere, but the band  $g$  factor calculated at progressively lower spectral resolutions does not change significantly.

ground, the OH(0,0) fluorescence spectrum, the OH(0,0) prompt spectrum and a constant term.

[28] In Figure 5a, the OH(0,0) solar fluorescence spectrum with the Rayleigh background fit to the data is shown in green. The composite model is in red, which includes all components of the fit, including the relatively weak OH(0,0) prompt emission. In Figure 5b the Rayleigh background has been subtracted from the data, leaving only

the OH(0,0) solar resonance fluorescence and OH(0,0) prompt spectrum. The rotational branches and levels of the fluorescence lines are indicated [Stevens and Conway, 1999].

[29] Figure 5c shows the OH(0,0) prompt spectrum after subtracting the (0,0) fluorescence spectrum from the data in Figure 5b. Three different lines originating from high rotational levels ( $N' \geq 20$ ) of the  $R_{22}$  and  $R_{11}$  branches are

**Table 5.** Allowed OH(0,0) Transitions<sup>a</sup>

| $N'$ | $P_{11}$ | $R_{11}$        | $^RQ_{21}$ | $Q_{11}$ | $^OQ_{21}$ | $^S R_{21}$ | $^O P_{12}$ | $^O R_{12}$ | $Q_{22}$ | $^P Q_{12}$ | $P_{22}$ | $R_{22}$        |
|------|----------|-----------------|------------|----------|------------|-------------|-------------|-------------|----------|-------------|----------|-----------------|
| 0    | 308.2560 |                 |            |          |            |             | 310.0479    |             |          | 309.4622    |          |                 |
| 1    | 308.7288 |                 |            | 307.9334 | 307.9366   |             | 310.6957    | 309.1351    | 309.1383 | 309.7236    | 309.7268 |                 |
| 2    | 309.2090 | 307.2903        | 307.2956   | 308.0848 | 308.0902   |             | 311.3981    | 309.0710    | 309.0764 | 310.0442    | 310.0496 | 308.4944        |
| 3    | 309.7023 | 307.1208        | 307.1283   | 308.2442 | 308.2516   | 306.3411    | 312.1488    | 309.0672    | 309.0747 | 310.4170    | 310.4246 | 308.1127        |
| 4    | 310.2131 | 306.9596        | 306.9692   | 308.4174 | 308.4271   | 305.8612    | 312.9431    | 309.1168    | 309.1266 | 310.8360    | 310.8458 | 307.7923        |
| 5    | 310.7448 | 306.8133        | 306.8249   | 308.6095 | 308.6213   | 305.3937    | 313.7774    | 309.2142    | 309.2260 | 311.2966    | 311.3086 | 307.5264        |
| 6    | 311.2996 | 306.6868        | 306.7005   | 308.8239 | 308.8378   | 304.9452    | 314.6491    | 309.3548    | 309.3688 | 311.7956    | 311.8098 | 307.3093        |
| 7    | 311.8794 | 306.5842        | 306.5999   | 309.0633 | 309.0793   | 304.5211    | 315.5563    | 309.5358    | 309.5518 | 312.3308    | 312.3472 | 307.1371        |
| 8    | 312.4851 | 306.5083        | 306.5260   | 309.3295 | 309.3476   | 304.1254    | 316.4980    | 309.7549    | 309.7731 | 312.9005    | 312.9196 | 307.0070        |
| 9    | 313.1184 | 306.4614        | 306.4812   | 309.6239 | 309.6448   | 303.7613    | 317.4731    | 310.0108    | 310.0318 | 313.5042    | 313.5256 | 306.9172        |
| 10   | 313.7799 | 306.4450        | 306.4678   | 309.9483 | 309.9716   | 303.4312    | 318.4812    | 310.3033    | 310.3266 | 314.1411    | 314.1650 | 306.8673        |
| 11   | 314.4704 | 306.4615        | 306.4865   | 310.3038 | 310.3294   | 303.1377    | 319.5219    | 310.6318    | 310.6575 | 314.8111    | 314.8375 | 306.8561        |
| 12   | 315.1907 | 306.5118        | 306.5392   | 310.6912 | 310.7193   | 302.8815    | 320.5950    | 310.9964    | 311.0246 | 315.5141    | 315.5431 | 306.8840        |
| 13   | 315.9416 | 306.5975        | 306.6272   | 311.1117 | 311.1423   | 302.6645    | 321.7004    | 311.3973    | 311.4280 | 316.2503    | 316.2820 | 306.9511        |
| 14   | 316.7239 | 306.7196        | 306.7518   | 311.5663 | 311.5995   | 302.4884    | 322.8384    | 311.8349    | 311.8682 | 317.0201    | 317.0545 | 307.0581        |
| 15   | 317.5385 | 306.8795        | 306.9141   | 312.0560 | 312.0918   | 302.3544    | 324.0092    | 312.3099    | 312.3458 | 317.8240    | 317.8612 | 307.2055        |
| 16   | 318.3862 | 307.0785        | 307.1157   | 312.5819 | 312.6205   | 302.2638    | 325.2133    | 312.8229    | 312.8615 | 318.6626    | 318.7027 | 307.3942        |
| 17   | 319.2682 | 307.3178        | 307.3576   | 313.1452 | 313.1866   | 302.2182    | 326.4511    | 313.3748    | 313.4162 | 319.5366    | 319.5797 | 307.6252        |
| 18   | 320.1854 | 307.5989        | 307.6414   | 313.7471 | 313.7913   | 302.2189    | 327.7234    | 313.9666    | 314.0109 | 320.4471    | 320.4932 | 307.8995        |
| 19   | 321.1391 | 307.9232        | 307.9685   | 314.3889 | 314.4361   | 302.2674    | 329.0309    | 314.5994    | 314.6467 | 321.3949    | 321.4442 | 308.2183        |
| 20   | 322.1306 | 308.2922        | 308.3403   | 315.0720 | 315.1222   | 302.3651    | 330.3747    | 315.2745    | 315.3248 | 322.3813    | 322.4339 | <b>308.5830</b> |
| 21   | 323.1612 | <b>308.7075</b> | 308.7586   | 315.7979 | 315.8513   | 302.5137    | 331.7558    | 315.9932    | 316.0467 | 323.4077    | 323.4637 | <b>308.9950</b> |
| 22   | 324.2327 | 309.1708        | 309.2249   | 316.5682 | 316.6249   | 302.7149    | 333.1756    | 316.7571    | 316.8139 | 324.4754    | 324.5350 | 309.4560        |
| 23   | 325.3467 | 309.6840        | 309.7413   | 317.3848 | 317.4450   | 302.9704    | 334.6356    | 317.5679    | 317.6282 | 325.5863    | 325.6496 | 309.9677        |
| 24   | 326.5051 | 310.2490        | 310.3096   | 318.2495 | 318.3133   | 303.2821    | 336.1373    | 318.4275    | 318.4913 | 326.7420    | 326.8093 | 310.5320        |
| 25   | 327.7101 | 310.8681        | 310.9321   | 319.1646 | 319.2320   | 303.6522    | 337.6829    | 319.3379    | 319.4054 | 327.9448    | 328.0161 | 311.1509        |

<sup>a</sup>Units are nm; all wavelengths for vacuum. OH prompt lines detected by MAHRSI in boldface.

**Table 6.** OH(0,0) Prompt Relative Intensities<sup>a</sup>

| $N'$  | Rel. Pop. | $P_{11}$ | $R_{11}$    | $^RQ_{21}$ | $Q_{11}$ | $^Q P_{21}$ | $^S R_{21}$ | $^O P_{12}$ | $^Q R_{12}$ | $Q_{22}$ | $^P Q_{12}$ | $P_{22}$ | $R_{22}$    |
|-------|-----------|----------|-------------|------------|----------|-------------|-------------|-------------|-------------|----------|-------------|----------|-------------|
| 0     | 0.0000    | 0        |             |            |          |             |             | 0           |             |          | 0           |          |             |
| 1     | 0.0000    | 0        |             |            | 0        | 0           |             | 0           | 0           | 0        | 0           | 0        |             |
| 2     | 0.0088    | 1031     | 167         | 250        | 1074     | 366         |             | 109         | 235         | 689      | 391         | 0        | 167         |
| 3     | 0.0095    | 1034     | 317         | 265        | 1295     | 273         | 38          | 86          | 209         | 924      | 313         | 533      | 290         |
| 4     | 0.0068    | 706      | 299         | 161        | 988      | 142         | 35          | 47          | 120         | 760      | 169         | 650      | 268         |
| 5     | 0.0066    | 666      | 342         | 129        | 1003     | 104         | 33          | 35          | 93          | 811      | 129         | 497      | 308         |
| 6     | 0.0066    | 635      | 372         | 103        | 1007     | 79          | 29          | 27          | 72          | 844      | 100         | 504      | 337         |
| 7     | 0.0066    | 609      | 393         | 83         | 1003     | 62          | 25          | 22          | 58          | 863      | 79          | 505      | 358         |
| 8     | 0.0077    | 692      | 480         | 81         | 1175     | 59          | 24          | 21          | 56          | 1031     | 75          | 502      | 441         |
| 9     | 0.0093    | 805      | 591         | 80         | 1404     | 58          | 24          | 19          | 55          | 1251     | 75          | 586      | 547         |
| 10    | 0.0109    | 918      | 707         | 81         | 1633     | 54          | 24          | 20          | 54          | 1473     | 74          | 696      | 657         |
| 11    | 0.0136    | 1111     | 886         | 84         | 2011     | 58          | 25          | 20          | 56          | 1829     | 76          | 808      | 828         |
| 12    | 0.0163    | 1283     | 1058        | 85         | 2355     | 58          | 27          | 20          | 57          | 2160     | 77          | 988      | 993         |
| 13    | 0.0201    | 1522     | 1291        | 90         | 2828     | 60          | 26          | 21          | 58          | 2615     | 82          | 1154     | 1216        |
| 14    | 0.0238    | 1744     | 1518        | 94         | 3281     | 63          | 27          | 20          | 59          | 3048     | 84          | 1380     | 1430        |
| 15    | 0.0301    | 2128     | 1891        | 102        | 4044     | 68          | 28          | 25          | 62          | 3779     | 93          | 1596     | 1793        |
| 16    | 0.0367    | 2485     | 2251        | 110        | 4721     | 69          | 34          | 23          | 68          | 4446     | 99          | 1957     | 2130        |
| 17    | 0.0539    | 3489     | 3221        | 143        | 6743     | 92          | 41          | 33          | 89          | 6356     | 133         | 2289     | 3066        |
| 18    | 0.0741    | 4593     | 4302        | 168        | 8956     | 112         | 56          | 31          | 107         | 8461     | 153         | 3250     | 4111        |
| 19    | 0.0795    | 4681     | 4468        | 166        | 9215     | 105         | 45          | 33          | 99          | 8727     | 148         | 4280     | 4274        |
| 20    | 0.0883    | 4940     | 4758        | 167        | 9772     | 100         | 50          | 36          | 91          | 9275     | 146         | 4394     | <b>4570</b> |
| 21    | 0.0947    | 5002     | <b>4905</b> | 161        | 9965     | 90          | 36          | 39          | 98          | 9507     | 137         | 4638     | <b>4708</b> |
| 22    | 0.1001    | 5000     | 4938        | 158        | 10000    | 99          | 40          | 41          | 83          | 9982     | 145         | 4727     | 4982        |
| 23    | 0.0159    | 751      | 751         | 23         | 1511     | 13          | 7           | 3           | 13          | 1589     | 20          | 4941     | 796         |
| 24    | 0.0000    | 0        | 0           | 0          | 0        | 0           | 0           | 0           | 0           | 0        | 0           | 783      | 0           |
| 25    | 0.0000    | 0        | 0           | 0          | 0        | 0           | 0           | 0           | 0           | 0        | 0           | 0        | 0           |
| Total | 0.72      |          |             |            |          |             |             |             |             |          |             |          |             |

<sup>a</sup>Relative populations from *Carrington* [1964] and relative rotational lifetimes from *Chidsey and Crosley* [1980]. All intensities normalized to  $Q_{11}(22)$  at 10000. Total (0,0) intensity:  $3.43 \times 10^5$ . OH prompt lines detected by MAHRSI in boldface.

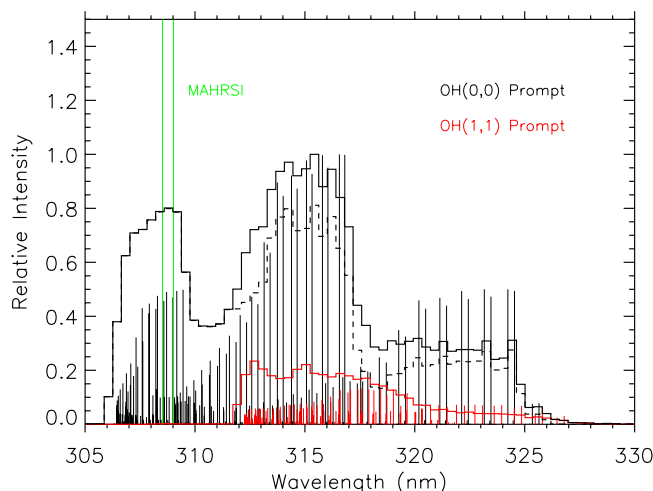
clearly evident and are identified in red using Tables 5 and 6. Weaker OH prompt features originating from much lower rotational levels near 308.61 nm and 308.82 nm are not evident above the noise. The integrated brightness of the prompt radiance within the passband shown is indicated in

the upper right of Figure 5c. Using our scale factor (26.5) derived from results shown in section 2, we find that the total OH(0,0) + (1,1) prompt radiance between 72–79 km is 42 kiloRayleighs (kR), where 1 kR is the apparent emission rate of  $10^9$  photons/cm<sup>2</sup>/s.

**Table 7.** OH(1,1) Prompt Relative Intensities<sup>a</sup>

| $N'$  | Rel. Pop. | $P_{11}$ | $R_{11}$ | $^RQ_{21}$ | $Q_{11}$ | $^Q P_{21}$ | $^S R_{21}$ | $^O P_{12}$ | $^Q R_{12}$ | $Q_{22}$ | $^P Q_{12}$ | $P_{22}$ | $R_{22}$ |
|-------|-----------|----------|----------|------------|----------|-------------|-------------|-------------|-------------|----------|-------------|----------|----------|
| 0     | 0.0000    | 0        |          |            |          |             |             | 0           |             |          | 0           |          |          |
| 1     | 0.0117    | 710      |          |            | 500      | 357         |             | 95          | 147         | 296      | 333         | 242      |          |
| 2     | 0.0115    | 600      | 95       | 148        | 618      | 217         |             | 66          | 135         | 398      | 232         | 308      | 97       |
| 3     | 0.0111    | 526      | 157      | 138        | 650      | 143         | 19          | 45          | 106         | 467      | 164         | 329      | 146      |
| 4     | 0.0113    | 507      | 208      | 119        | 699      | 106         | 25          | 35          | 87          | 540      | 126         | 357      | 189      |
| 5     | 0.0113    | 490      | 243      | 98         | 726      | 80          | 25          | 27          | 70          | 591      | 98          | 372      | 222      |
| 6     | 0.0115    | 474      | 270      | 80         | 739      | 61          | 23          | 22          | 56          | 624      | 77          | 379      | 246      |
| 7     | 0.0117    | 474      | 293      | 68         | 765      | 50          | 19          | 17          | 45          | 664      | 63          | 392      | 271      |
| 8     | 0.0122    | 472      | 315      | 57         | 787      | 42          | 17          | 15          | 38          | 696      | 54          | 402      | 292      |
| 9     | 0.0132    | 491      | 342      | 51         | 835      | 37          | 15          | 12          | 33          | 750      | 47          | 427      | 321      |
| 10    | 0.0143    | 518      | 378      | 47         | 899      | 32          | 14          | 11          | 29          | 820      | 43          | 459      | 357      |
| 11    | 0.0167    | 581      | 436      | 45         | 1020     | 31          | 14          | 11          | 29          | 940      | 42          | 522      | 415      |
| 12    | 0.0213    | 711      | 550      | 49         | 1267     | 33          | 15          | 10          | 30          | 1178     | 44          | 645      | 527      |
| 13    | 0.0226    | 722      | 572      | 47         | 1298     | 30          | 14          | 11          | 25          | 1272     | 39          | 693      | 571      |
| 14    | 0.0237    | 725      | 587      | 43         | 1315     | 29          | 11          | 7           | 22          | 1300     | 34          | 704      | 589      |
| 15    | 0.0237    | 689      | 566      | 38         | 1259     | 23          | 11          | 7           | 19          | 1327     | 30          | 711      | 605      |
| 16    | 0.0217    | 594      | 496      | 34         | 1097     | 19          | 8           | 7           | 14          | 1285     | 24          | 688      | 593      |
| 17    | 0.0143    | 373      | 312      | 25         | 689      | 18          | 7           | 2           | 9           | 1150     | 13          | 613      | 530      |
| 18    | 0.0098    | 243      | 207      | 11         | 452      | 8           | 4           | 2           | 5           | 583      | 8           | 309      | 269      |
| 19    | 0.0035    | 83       | 71       | 3          | 155      | 2           | 1           | 1           | 2           | 156      | 2           | 82       | 72       |
| 20    | 0.0019    | 40       | 34       | 1          | 75       | 1           | 0           | 0           | 1           | 75       | 1           | 40       | 35       |
| Total | 0.28      |          |          |            |          |             |             |             |             |          |             |          |          |

<sup>a</sup>Relative (1,1) rotational population based on *Carrington* [1964].  $v' = 1$  population based on *Lee et al.* [1978] and normalized to populations in Table 6 so that  $N(v' = 1)/N(v' = 0) = 0.38$ . Total OH(1,1) prompt intensity normalized to (0,0) intensity in Table 6 so that  $I(0,0)/I(1,1) = 5.1$ . Rotational Einstein A coefficients from which intensities calculated are from *Chidsey and Crosley* [1980], where  $A(1,1)$  is based on the calculated  $A(1,1)/A(0,0)$  ratio of *Crosley and Lengel* [1975] at lowest rotational levels.



**Figure 4.** OH prompt fluorescence spectrum between 305–330 nm. The relative intensity of the (0,0) rotational spectrum is shown against the (1,1) spectrum. The spectrum is smoothed using the OSIRIS spectral resolution function with a full-width at half-maximum of  $\sim 1$  nm and the resultant (0,0) spectrum is shown as the black dashed histogram, the (1,1) spectrum is shown as the red histogram and the composite of the two is shown as the black solid histogram (arbitrarily scaled). The (0,0) spectrum is a factor of five brighter than the (1,1) spectrum and the region of the OH prompt spectrum observed by MAHRSI is indicated in green.

[30] We employ this procedure at each 2 km altitude step to retrieve the OH(0,0) + (1,1) radiances between 65–85 km and the results are shown as the black curve in the left hand panel of Figure 6. Uncertainties ( $1\sigma$ ) are shown as the darker shaded envelope and do not include systematic uncertainties such as those for the  $g$  factor. We invert these radiances to retrieve the volume emission rates (VERs) as a function of altitude and these are overplotted as the red curve and referenced to the top axis, where the statistical uncertainties are propagated through the inversion and shown as the lighter shaded region beneath the red curve. For this inversion we have included a small amount of extinction by ozone at the lowest altitudes shown [Gattinger *et al.*, 2006] but have assumed that quenching and vibrational energy transfer of the excited state is negligible. We see that the emission increases sharply from 85–75 km due to the increasing water vapor concentrations at these altitudes and then decreases from 75–65 km due to the attenuation of the solar H Lyman- $\alpha$  flux. We will model these processes in section 4.

### 3.2. OSIRIS

[31] OSIRIS was launched aboard the Odin satellite [Murtagh *et al.*, 2002] on 20 February 2001 with an orbital inclination of  $98^\circ$ . Odin is in a sun-synchronous orbit with equator crossing times near 0600 and 1800 local time so that OSIRIS observes the Earth's limb both near sunrise and sunset [Llewellyn *et al.*, 2004]. The instrument measures atmospheric limb scattered solar radiation over the wave-

length range from 274 nm to 810 nm with 1 nm spectral resolution. The vertical field of view is 1 km at the tangent point and the vertical sampling interval is approximately 1.5 km. The on-orbit instrument absolute calibration is based on solar flux data from the Solar Ultraviolet Spectral Irradiance Monitor database [Brueckner *et al.*, 1993] and a multiple scatter atmospheric model.

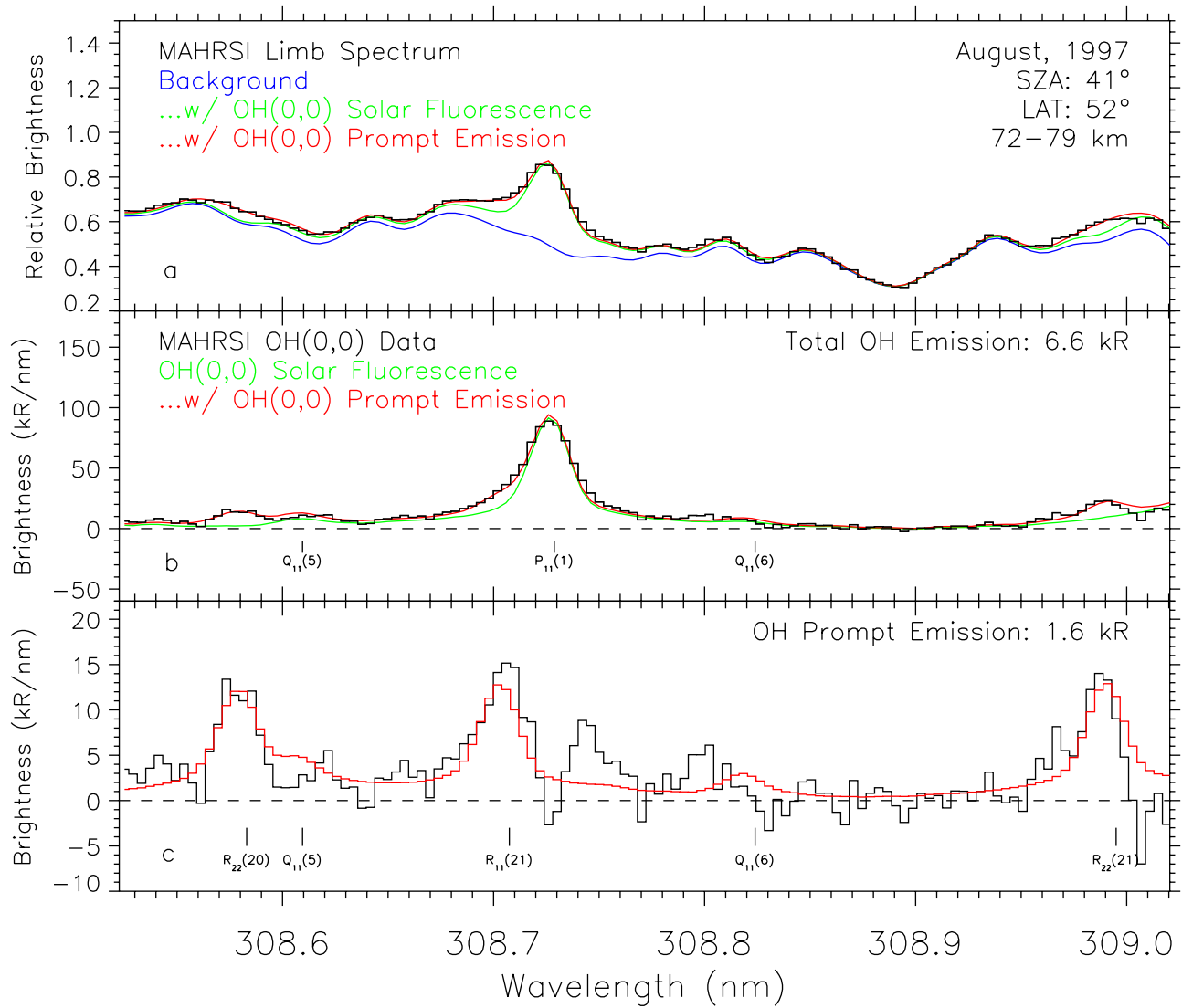
[32] As with the MAHRSI analysis [Conway *et al.*, 1999], an accurate estimate of the atmospheric background spectrum is required to isolate the OH bands [Gattinger *et al.*, 2006]. The procedure adopted here is to first subtract a scaled 60 km Rayleigh scattered atmospheric background spectrum from the upper mesospheric spectra and then to subtract a scaled spectrum above the OH optical emission region, averaged over the 92 to 94 km range, to remove the thermospheric dayglow component [e.g., Cleary *et al.*, 1995] and a weak baffle scatter component present at wavelengths longer than approximately 315 nm.

[33] Since the total OH solar fluorescence is typically much brighter than the prompt emission, we limit our observations to those from the early morning (0700–0800 local time). At this part of the day the OH has not yet accumulated through photodissociation so the OH fluorescence is relatively weak [Gattinger *et al.*, 2006]. Since the OH prompt emission is produced directly by the photodissociation of upper mesospheric water vapor by H Lyman- $\alpha$  we do not expect it to have the strong diurnal dependence of the OH solar fluorescence.

[34] Figure 7a shows an OSIRIS limb spectrum and the estimate of the Rayleigh background spectrum scaled to the data and overplotted in red. The limb spectrum is composed of an average of 42 scans between  $50$ – $70^\circ$ N on 3–4 June 2005. The excess emission near 308 nm and 315 nm is due to OH(0,0) and (1,1) solar fluorescence and prompt emission. Figure 7a serves to illustrate that in general the OH signal is less than 10% of the total limb emission observed at 80 km. The spectrally complex background is fit extremely well away from the OH emission, underscoring its reliability where we infer the signal.

[35] Figure 7b shows the OSIRIS data from Figure 7a with the Rayleigh scattered background removed. Overplotted on the data are the results of a least squares fitting algorithm, which uses the theoretical OH(0,0) and (1,1)  $g$  factors convolved with the OSIRIS spectral resolution function (blue), the OH(0,0) and (1,1) prompt spectrum at OSIRIS resolution (green) and the composite fit to the data (red). The composite fit to the data is excellent and the emission between 320–325 nm demonstrates that OH prompt emission is detected. The total OH(0,0) + (1,1) prompt radiance inferred at 80 km is 43 kR and indicated in green in Figure 7b.

[36] Figure 7 also serves to illustrate that the spectral resolution of OSIRIS ( $\sim 1$  nm) is such that the OH(0,0) and (1,1) fluorescence and prompt components are blended together. Since the uncertainty of the (1,1)  $g$  factor is relatively large at 22% (section 2.1), we considered how the retrieved OH(0,0) + (1,1) prompt emission varied with a 15% reduction in the (1,1)  $g$  factor. We find that the OH prompt intensity increases by only 5–10% near the peak  $\sim 80$  km, which is approximately the statistical uncertainty shown in Figure 6. This is small in the context of our initial



**Figure 5.** (a) MAHRSI limb spectrum from August 1997. The data shown are an average of 34 scans yielding a total integration time of about  $2\frac{1}{2}$  min. The data are shown as a black histogram and the estimated Rayleigh scattered background is scaled to the data and shown in blue. The OH(0,0) solar resonance fluorescence is shown on top of the Rayleigh background in green and the composite fit including the OH(0,0) prompt emission spectrum is shown in red. Average properties of the observation set are shown in the upper right. (b) Same as Figure 5a but with the Rayleigh background subtracted. The most important (0,0) solar resonance fluorescence lines are modeled at 200 K and indicated with the angular momentum of the upper state in parentheses. (c) Same as Figure 5b but with the OH(0,0) solar resonance fluorescence contribution subtracted, revealing the OH prompt emission spectrum.

study, but underscores the need to constrain  $A(1,0)$  in laboratory studies to improve our retrievals.

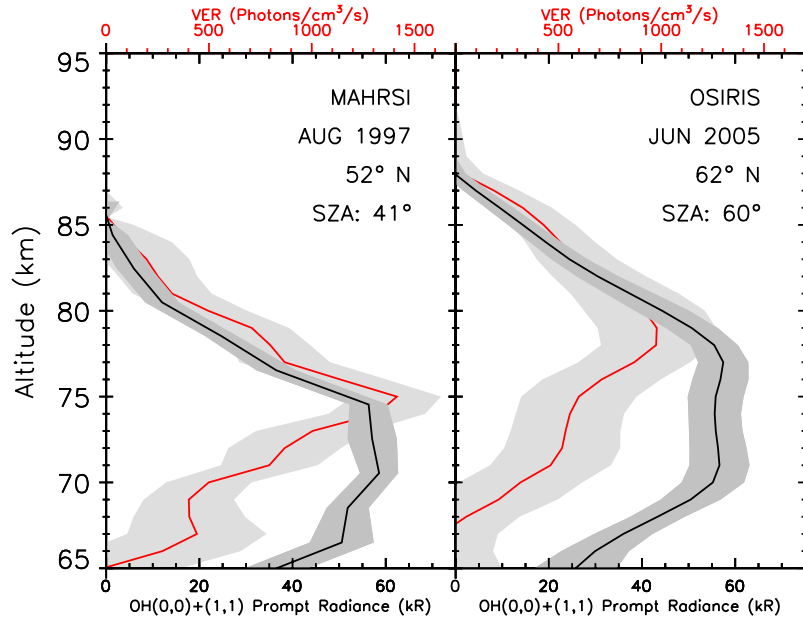
[37] We similarly fit the fluorescence and prompt components of OH to the limb data at other altitudes and infer the OH prompt radiance profile. The results are shown in the right hand panel of Figure 6 in black with the statistical error envelope shaded ( $1\sigma$ ). We invert these radiances to derive VERs, which are overplotted in red and referenced to the top axis. Overall, the OSIRIS VERs are similar to MAHRSI's in the left hand panel. The peak is a slightly higher altitude (near 78 km) compared to MAHRSI (75 km), which is probably due to the larger solar zenith angle for the OSIRIS observations and a different vertical distribution of

water vapor for the conditions indicated. We will explore these differences in the next section.

#### 4. Modeling Approach

[38] We now model the VERs shown in Figure 6 in order to derive the water vapor mixing ratio profiles. We simulate the lighting conditions of each set of observations and use water vapor concentrations inferred from HALOE observations that are as close as possible in time and space to our observations.

[39] For this analysis, we focus on the altitude region between 65–90 km where there is measurable signal from the satellite observations. We also assume that the solar H



**Figure 6.** MAHRSI (left) and OSIRIS (right) OH prompt observations in the upper mesosphere. Black curves indicate the observed OH(0,0) + (1,1) limb radiances with  $1\sigma$  statistical uncertainties indicated. Shown in red are the volume emission rates determined from an inversion of each radiance profile and referenced to the top axis. Solar zenith angles (SZA) for each set of observations are indicated.

Lyman- $\alpha$  flux is the only source of OH prompt emission in the Earth's upper mesosphere. The volume emission rate ( $P$ ) can be expressed as

$$P(z) = \sigma_{\lambda} \cdot \phi \cdot \Psi_{\lambda}(z) \cdot [H_2O(z)] \quad (3)$$

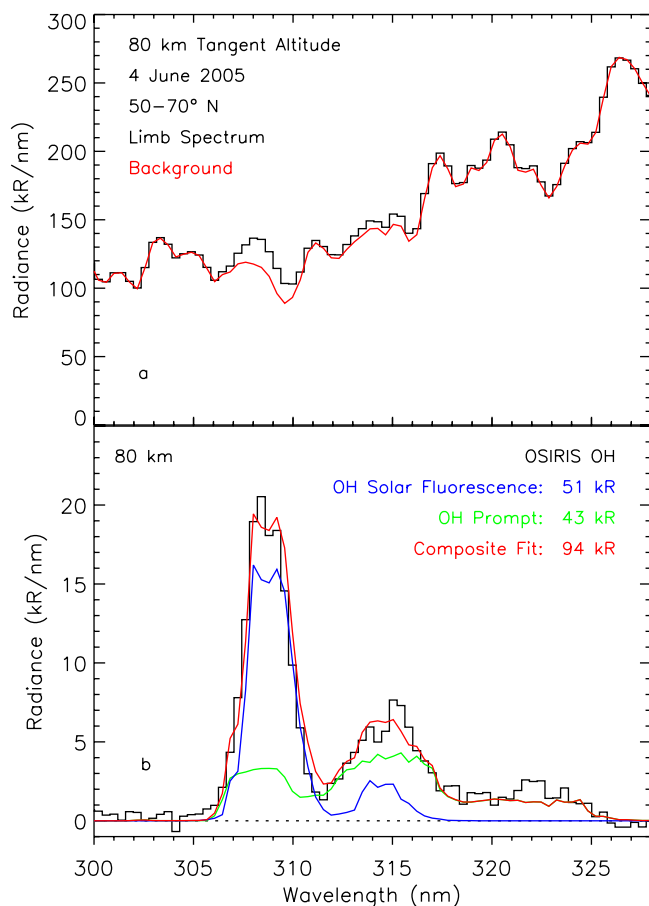
where  $\psi_{\lambda}(z)$  is the H Lyman- $\alpha$  flux at each altitude level,  $\phi$  is the OH(0,0) + (1,1) prompt yield,  $\sigma_{\lambda}$  is the water vapor cross section and  $[H_2O(z)]$  is the water vapor concentration [Gumbel, 1997]. In our modeling approach, we neglect quenching of the  $A^2\Sigma^+$  state as well as vibrational energy transfer (VET) and rotational energy transfer (RET), which become important below  $\sim 65$  km [Conway et al., 1999; Gattinger et al., 2008]. Available laboratory results indicate, moreover, that quenching and RET are less efficient at high rotational levels ( $N' = 16-20$ ) than at low rotational levels ( $N' < 3$ ) [Kaneko et al., 1968; Copeland et al., 1985; Papagiannakopoulos and Fotakis, 1985; Burris et al., 1991; Gumbel, 1997]. As indicated in section 3.1, extinction due to ozone is not important above 65 km [Conway et al., 1999] and is therefore not included in our model simulations. We discuss the inputs to equation (3) in order now.

[40] Although molecular oxygen ( $O_2$ ) controls the attenuation of solar H Lyman- $\alpha$  in the upper mesosphere, the water vapor cross section is required to model the observed OH prompt volume emission rate in equation (3). To determine the average cross section of water vapor,  $\sigma_{\lambda}$ , we model the shape of the solar H Lyman- $\alpha$  line between 121.467–121.667 nm in 0.001 nm increments [Chabrilat and Kockarts, 1997]. We normalize that to unity and integrate over the cross sections as given by Lewis et al. [1983]. This yields an average cross section of  $1.51 \times 10^{-17} \text{ cm}^2$ .

[41] There is currently some ambiguity for the OH prompt yield,  $\phi$ . Carrington [1964] reported a yield of

0.05 with uncertainty of a factor of two to three. Lee and Suto [1986] gave a value of 0.075 near Lyman- $\alpha$  with and uncertainty of 30%. On the other hand, Harich et al. [2000] find that there is an even larger 0.13 yield to OH prompt following photodissociation by H Lyman- $\alpha$ . Given this ambiguity we consider two possible yields: 0.075 and 0.13. From equation (3), the yield directly affects our volume emission rate calculation so we will consider the impact of each on our comparison. We assume that OH prompt emission appears exclusively in the (0,0), (1,1), and (1,0) bands. Since we only model the (0,0) and (1,1) bands herein, we reduce the reported yield slightly to account for the rest of the emission lost to (1,0). We have determined that  $I(1,1)/I(0,0)$  is 0.2 in section 2.2. On the basis of the experimental work of Crosley and Lengel [1975], the  $A(1,0)/A(1,1)$  ratio is 0.63 so that the yields used in our analysis are reduced by 9% to 0.068 and 0.118.

[42] To derive the solar H Lyman- $\alpha$  flux with altitude, we first determine the flux appropriate to the day of the MAHRSI (12 August 1997) and OSIRIS (4 June 2005) observations. This is obtained using the compilation at the LASP Interactive Solar Datacenter (<http://lasp.colorado.edu/LISIRD/>). We find that during the MAHRSI OH observations, the solar H Lyman- $\alpha$  flux was  $3.73 \times 10^{11}$  photon/cm<sup>2</sup>/s whereas for the OSIRIS observations it was  $3.93 \times 10^{11}$  photon/cm<sup>2</sup>/s. We assume that the attenuation of Lyman- $\alpha$  is entirely due to the overhead column of  $O_2$ , which has a well-known window near 121.6 nm allowing for the penetration of H Lyman- $\alpha$  to the upper mesosphere [e.g., Lewis et al., 1983]. We parameterize the absorption following the approach described by Chabrilat and Kockarts [1997, 1998]. For the  $O_2$  column we use the HALOE background atmosphere and the  $O_2$  mixing ratio as a function of altitude from the empirical atmospheric model NRLMSISE-00 [Picone et al., 2002]. As discussed previ-



**Figure 7.** (a) OSIRIS limb spectrum (black) with an estimate of the Rayleigh scattered background brightness fit to the data (red). The data are a 42 scan average from a tangent altitude of 80 km between 50–70°N on 3–4 June 2005. (b) The OSIRIS OH spectrum at 80 km obtained from subtracting the Rayleigh background spectrum from the data in Figure 7a. A least squares fit of OH(0,0) + (1,1) prompt emission (green), OH(0,0) + (1,1) solar fluorescence (blue) and the composite fit (red) to the data are shown with their integrated radiances indicated.

ously, the amount of absorption is sensitive to the solar zenith angle and we use the average zenith angle for each data set in our calculations.

[43] Results are shown in Figure 8a for MAHRSI conditions and Figure 8b for OSIRIS conditions. Note the higher altitudes of extinction for the OSIRIS case, which is due to the larger solar zenith angle indicated in each figure. In general, Figure 8 shows that the OH prompt emission should decrease above 75–80 km because of lower water vapor concentrations and should decrease below these altitudes due to the reduction of available H Lyman- $\alpha$  radiation (see Figure 6).

[44] For comparison against our results we use the HALOE background atmosphere and water vapor profiles most coincident in space and time. For the MAHRSI analysis, we coaverage 59 HALOE profiles from 22–23 July and 2–3 September 1997, which are before and after the MAHRSI observations on 10–15 August. The average latitude of these HALOE scans was 50°N (compared to the

MAHRSI latitude of 52°N) and the uncertainty of the coaveraged profile is indicated by the shaded area in Figure 8a and referenced to the top (red) axis. Above 85 km the HALOE data are highly uncertain so we show this region with a dotted line hereinafter in model calculations.

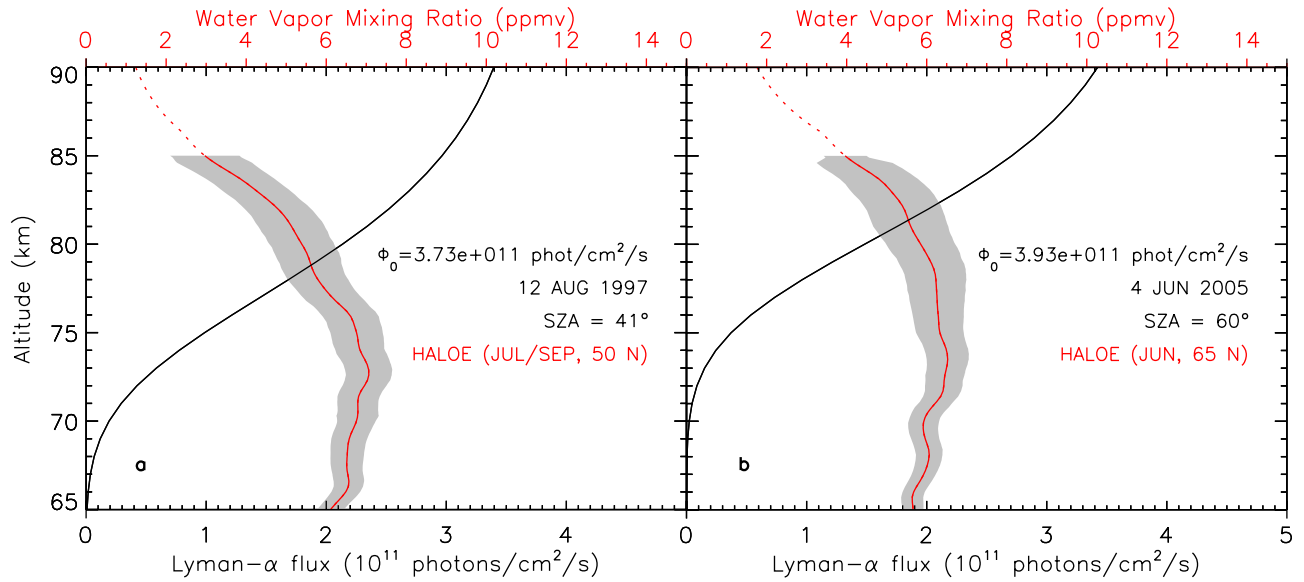
[45] For the OSIRIS analysis, 60 HALOE scans were coaveraged between 4–8 June 2005 near 65°N (compared to OSIRIS at 62°N). PMCs can bias the HALOE water vapor measurements [McHugh *et al.*, 2003], but the PMC signature in the OSIRIS data for these latitudes for this early in the PMC season was very weak. The resultant coaveraged water vapor profile is overplotted with a shaded uncertainty in Figure 8b. Note that the water vapor extends to higher altitudes in Figure 8b compared to Figure 8a, as expected at the higher latitudes during June.

[46] Using the HALOE water vapor concentrations and the H Lyman- $\alpha$  flux shown in Figure 8, we calculate the VERs from equation (3) for two different yields and the results are shown in Figures 9a and 9b. The VERs of MAHRSI and OSIRIS are reproduced from Figure 6 for direct comparison and the model uncertainties are propagated directly from the uncertainties in the HALOE water vapor profiles in Figures 8a and 8b. The agreement for each data set is remarkable, particularly since the HALOE observations are not precisely colocated in space and time with those from either MAHRSI or OSIRIS. Both data sets clearly favor the larger yield of 13% reported by Harich *et al.* [2000].

[47] Using the observed VERs (Figure 9) and the H Lyman- $\alpha$  flux (Figure 8), equation (3) can be solved for the water vapor concentration. By taking the number densities of the background atmosphere from the HALOE measurements in Figure 8, we show the retrieved water vapor mixing ratio profiles in Figure 10. The vertical resolution of the HALOE profiles is 3–5 km [McHugh *et al.*, 2005] and the vertical resolution of both the MAHRSI and OSIRIS water vapor profiles is about 4 km. The MAHRSI results in Figure 10a show excellent agreement with HALOE water vapor, despite the fact that a direct comparison with data from the same month and latitude is not possible. Between 70–80 km, we find that the agreement is within 30% of HALOE observations. Figure 10b shows the comparison between OSIRIS and HALOE and the agreement between 75–85 km is also within 30% of HALOE. Below 74 km the OSIRIS data are well in excess of the HALOE data and are not shown. Inspection of Figure 9b shows that the VERs are systematically higher than the HALOE data and this difference propagates directly to the retrieved mixing ratios. The difficulty in retrieving water vapor by OSIRIS below 74 km is reflected in the uncertainties shown by the shaded area in Figure 9 (right).

## 5. Discussion and Summary

[48] We have reported the first UV satellite observations of water vapor in the Earth's mesosphere. These observations of OH prompt emission near 310 nm come from two separate experiments. The measurement is challenging because the prompt emission is weak compared to both the Rayleigh scattered background and the OH(0,0) and (1,1) solar fluorescence in the spectral region between 300–330 nm. In order to help distinguish between the

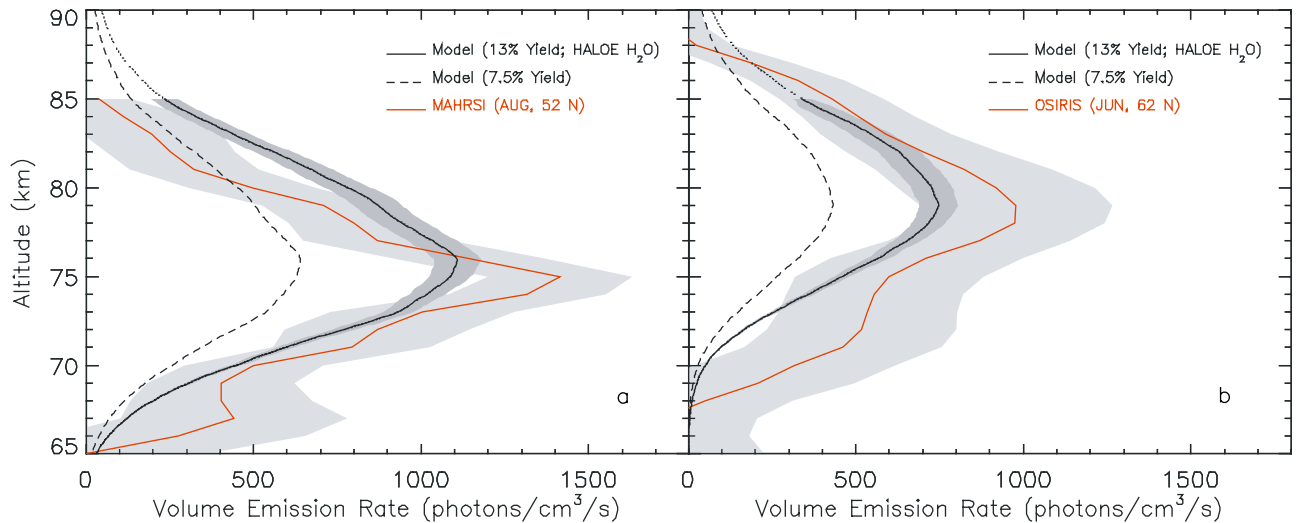


**Figure 8.** Solar Lyman- $\alpha$  fluxes (in black) used for the analysis of (a) MAHRSI and (b) OSIRIS OH prompt emission data. The fluxes at the top of the atmosphere for the indicated dates are shown. Also shown (in red, referenced to the top axis) are averaged HALOE water vapor profiles from July and September 1997 (MAHRSI) and June 2005 (OSIRIS) at latitudes indicated in red. The HALOE profiles are most coincident in space and time with the MAHRSI and OSIRIS results presented herein. The HALOE data above 85 km have large uncertainties and this portion of the profile is shown as a dotted line.

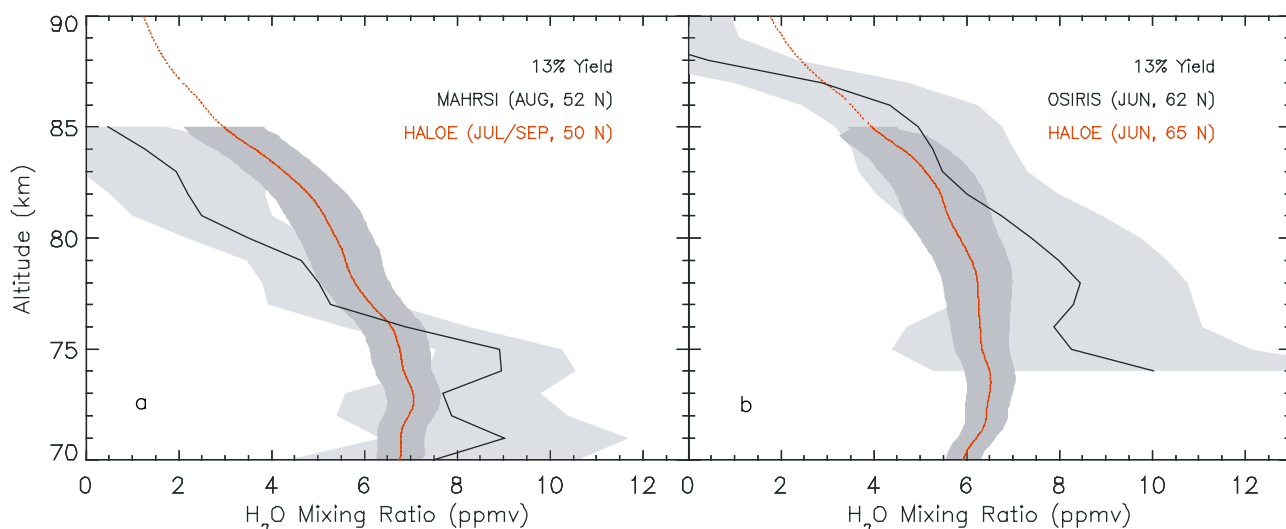
blended emissions within this region, we have calculated the OH(1,1) rotational  $g$  factors for solar fluorescence in the Earth's mesosphere and reported them here for the first time in Tables 2 (line positions) and 4 ( $g$  factors). We have also reported line positions and predicted relative intensities of OH(0,0) and (1,1) prompt rotational emission lines in Tables 2, 5, 6, and 7 on the basis of previous laboratory measurements of the rotational populations [Carrington,

1964] and transition probabilities [Crosley and Lengel, 1975].

[49] Our two data sets offer separate benefits in the analysis and approach. MAHRSI uses higher spectral resolution (0.02 nm) with a narrower passband (0.5 nm) whereas OSIRIS uses lower spectral resolution (1 nm) across a wider passband (more than 30 nm). Because the rotational distribution of the OH prompt emission is non-



**Figure 9.** Calculated OH(0,0) + (1,1) prompt volume emission rates in solid black using a yield of 13% for conditions of (a) MAHRSI and (b) OSIRIS. The error envelope reflects the uncertainty in the HALOE water vapor profiles shown in Figure 8. Model results above 85 km rely on uncertain HALOE water vapor retrievals at these altitudes so these results are shown with a dotted line. The volume emission rates from Figure 6 are overplotted for comparison. Also shown for comparison in dashed black is the model result for a yield of 7.5%. Both data sets are most consistent with a 13% yield.



**Figure 10.** Water vapor retrievals from (a) MAHRSI and (b) OSIRIS in black. HALOE profiles from Figure 8 are overplotted for comparison. For both data sets, agreement is within 30% of HALOE results between 75–80 km altitude using the indicated yield.

thermal and therefore a separate population from solar fluorescence, it is distinguishable either through individual rotational transitions (MAHRSI, Figure 5c) or the shape of the rotational envelope (OSIRIS, Figure 7b).

[50] We show only a limited amount of data herein to emphasize the new approach rather than to provide a database of mesospheric water vapor observations. MAHRSI and OSIRIS observations agree to within 30% of HALOE observations between 75–80 km where the OH prompt radiance peaks. We find that a yield of 13% for OH prompt emission from the photodissociation of water vapor by H Lyman- $\alpha$  [Harich *et al.*, 2000] is most consistent with both the MAHRSI and OSIRIS data. New laboratory work constraining the OH prompt yield following photodissociation by H Lyman- $\alpha$  is needed given the current ambiguity in the literature, where this value varies between 5–13%. In addition, precise measurements of the rotational distribution would benefit high-resolution measurements such as MAHRSI, which has a limited passband so that the analysis relies on a large scaling for the vibrational band intensity. Finally, tighter constraints on the lifetime of the  $v' = 1$  state would benefit measurements at lower resolution such as OSIRIS, which must separate the blended (0,0) and (1,1) fluorescence and prompt components. Nonetheless, the excellent agreement between these two diverse data sets with validated HALOE observations [Harries *et al.*, 1996; McHugh *et al.*, 2005] underscores the reliability of our water vapor retrievals.

[51] It is unlikely that OH prompt emission could provide robust water vapor retrievals below 65 km because not only do quenching and ozone extinction become important below this altitude, but H Lyman- $\alpha$  is attenuated below 75 km and severely reduces the observed prompt emission (Figure 6). Above 75 km, the emission becomes weaker due to the strong decrease of water vapor concentrations with altitude. However, the technique shows promise for quantifying the water budget in the polar summer mesosphere, where concentrations are more elevated and for which few water vapor measurements currently exist.

[52] Since the OH prompt measurement is made from airglow observations rather than occultation, it is more synoptic and could ultimately provide daily global maps of upper mesospheric water vapor. Although MAHRSI was a shuttle payload and will not fly again, OSIRIS continues to collect data up to 82–90° latitude in both hemispheres and work is underway to interpret additional OH data from this valuable data set [Gattinger *et al.*, 2008].

[53] **Acknowledgments.** MHS was supported by the Office of Naval Research. We thank David Siskind and Christoph Englert for helpful discussions and Robert Conway for his leadership during the MAHRSI project. This work benefited from the diligent efforts of the HALOE science and data processing teams, who produced the highest quality water vapor data set possible and shared it with the community.

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