

## Retrieval of CO<sub>2</sub> and N<sub>2</sub> in the Martian thermosphere using dayglow observations by IUVS on MAVEN

J. Scott Evans, Michael H. Stevens, Jerry D. Lumpe, Nick M. Schneider, A.  
Ian F. Stewart, Justin Deighan, Sonal K. Jain, Michael S. Chaffin, Matteo  
Crismani, Arnaud Stiepen, et al.

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## RESEARCH LETTER

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## Special Section:

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## Key Points:

- Retrieved CO<sub>2</sub> densities at 170 km vary by a factor of about 2.5
- On average, N<sub>2</sub>/CO<sub>2</sub> increases from 4% at 130 km to 12% at 200 km
- Mean Martian upper atmospheric temperature over the sampled time frame is 324 (±) 22 K

## Supporting Information:

- Figures S1–S3

## Correspondence to:

J. S. Evans,  
evans@cpi.com

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Retrieval of CO<sub>2</sub> and N<sub>2</sub> in the Martian thermosphere using dayglow observations by IUVS on MAVENJ. S. Evans<sup>1</sup>, M. H. Stevens<sup>2</sup>, J. D. Lumpe<sup>1</sup>, N. M. Schneider<sup>3</sup>, A. I. F. Stewart<sup>3</sup>, J. Deighan<sup>3</sup>, S. K. Jain<sup>3</sup>, M. S. Chaffin<sup>3</sup>, M. Crismani<sup>3</sup>, A. Stiepen<sup>3</sup>, W. E. McClintock<sup>3</sup>, G. M. Holsclaw<sup>3</sup>, F. Lefèvre<sup>4</sup>, D. Y. Lo<sup>5</sup>, J. T. Clarke<sup>6</sup>, F. G. Eparvier<sup>3</sup>, E. M. B. Thiemann<sup>3</sup>, P. C. Chamberlin<sup>7</sup>, S. W. Bougher<sup>8</sup>, J. M. Bell<sup>9</sup>, and B. M. Jakosky<sup>3</sup>

<sup>1</sup>Computational Physics, Inc., Springfield, Virginia, USA, <sup>2</sup>Naval Research Laboratory, Washington, District of Columbia, USA, <sup>3</sup>Laboratory for Atmospheric and Space Physics, University of Colorado Boulder, Boulder, Colorado, USA, <sup>4</sup>LATMOS, CNRS, Paris, France, <sup>5</sup>Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona, USA, <sup>6</sup>Center for Space Physics, Boston University, Boston, Massachusetts, USA, <sup>7</sup>NASA Goddard Space Flight Center, Greenbelt, Maryland, USA, <sup>8</sup>Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, Ann Arbor, Michigan, USA, <sup>9</sup>National Institute of Aerospace, Hampton, Virginia, USA

**Abstract** We present direct number density retrievals of carbon dioxide (CO<sub>2</sub>) and molecular nitrogen (N<sub>2</sub>) for the upper atmosphere of Mars using limb scan observations during October and November 2014 by the Imaging Ultraviolet Spectrograph on board NASA's Mars Atmosphere and Volatile Evolution (MAVEN) spacecraft. We use retrieved CO<sub>2</sub> densities to derive temperature variability between 170 and 220 km. Analysis of the data shows (1) low-mid latitude northern hemisphere CO<sub>2</sub> densities at 170 km vary by a factor of about 2.5, (2) on average, the N<sub>2</sub>/CO<sub>2</sub> increases from 0.042 ± 0.017 at 130 km to 0.12 ± 0.06 at 200 km, and (3) the mean upper atmospheric temperature is 324 ± 22 K for local times near 14:00.

## 1. Introduction

Ultraviolet emissions from the Martian atmosphere provide an important means of inferring atmospheric composition [Meier, 1991; Paxton and Anderson, 1992]. The Martian UV airglow was first observed by the Mariner 6 and 7 missions in 1969 and subsequently by Mariner 9 in 1971–1972 [Barth et al., 1969, 1971; Stewart, 1972; Strickland et al., 1972; Stewart et al., 1972; Barth et al., 1972; Strickland et al., 1973]. From these early missions, excitation processes resulting in UV emissions were found to include photolysis, electron impact, dissociative recombination, and solar resonant fluorescent scattering [Barth et al., 1971, 1972; Fox and Dalgarno, 1979].

More recently, the Spectroscopy for the Investigation of the Characteristics of the Atmosphere of Mars spectrometer on board Mars Express has made important UV airglow observations. These include the discovery of emission due to solar energetic particles [Bertaux et al., 2005a; Leblanc et al., 2006a; Brain et al., 2006; Leblanc et al., 2008; Dubinin et al., 2009; Ip, 2012] and chemiluminescence [Bertaux et al., 2005b, 2005c; Cox et al., 2008]. More detailed analyses have obtained N<sub>2</sub> emissions [Leblanc et al., 2006b; Jain and Bhardwaj, 2011] and ozone global climatology [Perrier et al., 2006].

NASA's Mars Atmosphere and Volatile Evolution (MAVEN) spacecraft was launched on 18 November 2013 and arrived at Mars on 22 September 2014. The primary goal of the MAVEN mission is to quantify the diurnal, latitudinal, seasonal, and solar activity variations in the Martian atmosphere and to use that knowledge to determine the present and historical rates of escape of the Martian atmosphere [Jakosky et al., 2015]. To that end, we present a first attempt to directly retrieve CO<sub>2</sub> and N<sub>2</sub> densities in the Martian thermosphere from the mid-ultraviolet (MUV) dayglow. We use limb observations from 130 to 200 km tangent altitude by the Imaging Ultraviolet Spectrograph (IUVS) [McClintock et al., 2014] on board MAVEN. We compare our retrievals to results from the Mars-Global Ionosphere-Thermosphere Model (M-GITM) [Bougher et al., 2015], as well as in situ measurements by Vikings 1 and 2 [Nier and McElroy, 1977], and quantify the differences throughout the altitude region of interest.

We first discuss IUVS limb scan observations and the associated geographic and temporal coverage followed by a discussion of the forward model and optimal estimation techniques used herein. We then present the methodology used for direct retrievals of CO<sub>2</sub> and N<sub>2</sub> densities and deriving temperatures from CO<sub>2</sub> density profiles. We also explore the implications of forward model and calibration systematic uncertainties on density retrievals. In the final section, we summarize the most significant results of this study.

## 2. Observations

IUVS is designed to provide global 3-D maps of major molecules, atoms, and ions in the atmosphere [McClintock *et al.*, 2014; Jakosky *et al.*, 2015]. The instrument is a UV imaging spectrograph with a  $10 \times 0.06^\circ$  slit and occultation apertures at each end. The MAVEN orbit is elliptical with apoapsis at  $\sim 6200$  km and periapsis nominally at an altitude of  $\sim 175$  km. Nadir viewing allows for disk maps near apoapsis, while limb viewing allows for scans near periapsis [Jain *et al.*, 2015]. IUVS measures the far ultraviolet (FUV) airglow on Mars between 110 and 190 nm at  $\sim 0.6$  nm resolution and the MUV airglow between 180 and 340 nm at  $\sim 1.2$  nm resolution. The vertical resolution is 5 km [McClintock *et al.*, 2014].

We use 82 dayglow limb scan observations constrained to solar zenith angles (SZAs)  $< 60^\circ$  made by IUVS during MAVEN orbits 109–128 on 18–22 October 2014 and orbits 261–269 on 16–18 November 2014. These observations span northern hemisphere latitudes from  $-5^\circ$  to  $35^\circ$  and all longitudes. Local times cluster near 14:00 and 11:00 for orbits 109–128 and 261–269, respectively; SZAs range from  $30^\circ$  to  $60^\circ$ . We use two types of MUV emission for our retrievals: the  $\text{CO}_2^+$  Ultraviolet Doublet (UVD, 288–289 nm) produced primarily by photoionization and the  $\text{N}_2$  Vegard-Kaplan bands (VK, 258 – 287 nm) produced exclusively by photoelectron excitation. Limb profiles of these blended emission features are extracted from calibrated data using multiple linear regression (MLR) techniques described by Stevens *et al.* [2015a].

## 3. Forward Model

The Atmospheric Ultraviolet Radiance Integrated Code (AURIC) software package was developed for upper atmospheric radiance modeling from the FUV to the near-infrared [Strickland *et al.*, 1999]. AURIC has been used to study the extreme ultraviolet (EUV) dayglow from the Earth [Bishop *et al.*, 2007], Titan [Strobel *et al.*, 1991, 1992; Stevens *et al.*, 2015b], Triton [Strobel *et al.*, 1991; Stevens, 2002], and Pluto [Schindhelm *et al.*, 2015].

The molecular states associated with the emissions of  $\text{CO}_2$  and  $\text{N}_2$  that are of interest here are produced by processes related to energetic solar irradiance: photoelectron excitation, photodissociative excitation and photodissociative ionization [Meier, 1991; Samson *et al.*, 1991; Bishop and Feldman, 2003]. The starting point for these processes is the unattenuated solar flux as a function of wavelength  $\lambda$ ,  $\pi F_o(\lambda_i)$ , where  $\lambda_i$  refers to the  $i$ th solar irradiance wavelength in photons  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ . The wavelength range of interest for nonresonant excitation is from  $\sim 100$  nm down to 1 nm. Solar energy at shorter wavelengths is deposited below  $\sim 100$  km and is insignificant except under extreme solar activity [Fox, 2004b].

The flux at altitude  $z$  and for  $\mu_s = \cos(\text{SZA})$  is related to the unattenuated flux by

$$\pi F(\lambda_i, z, \mu_s) = \pi F_o(\lambda_i) \exp[-\tau(\lambda_i, z, \mu_s)]. \quad (1)$$

The optical depth,  $\tau$ , is given by

$$\tau(\lambda_i, z, \mu_s) = \sum_l \tau_l(\lambda_i, z, \mu_s) = \sum_{lk} \sigma_{lk}^{\text{photo}}(\lambda_i) \int n_l(s) ds \quad (2)$$

where  $n_l$  is the density of the  $l$ th species and  $\sigma_{lk}^{\text{photo}}(\lambda_i)$  is the wavelength-dependent photoabsorption cross section for channel  $k$  of species  $l$ . The integration in equation (2) is from the top of the atmosphere to altitude  $z$  along a slant path defined by  $\mu_s$ . Although AURIC performs multistream photoelectron transport calculations, application of the model to limb scan retrievals is restricted to SZAs less than  $60^\circ$ , since anisotropy effects become increasingly important near the terminator. The photoabsorption cross sections (dissociation and ionization) in equation (2) come from the compilation of Conway [1988] for  $\text{N}_2$  and molecular oxygen ( $\text{O}_2$ ); from Bell and Stafford [1992] for atomic oxygen; and from Gronoff *et al.* [2012a] for  $\text{CO}_2$ , carbon monoxide, argon, molecular hydrogen, helium, and atomic hydrogen.

The production of ionic or neutral states by absorption of photons from the solar flux  $\pi F(\lambda_i, z, \mu_s)$  is given by

$$\delta p_{lki}(z, \mu_s) = n_l(z) \pi F(\lambda_i, z, \mu_s) \sigma_{lk}^{\text{photo}}(\lambda_i). \quad (3)$$

The accompanying expression for production of photoelectrons is

$$\delta p_{S_{lki}}(z, \mu_s, h\nu_i - I_{lk}) = n_l(z) \pi F(\lambda_i, z, \mu_s) \sigma_{lk}^{\text{photo}}(\lambda_i) \quad (4)$$

where  $h\nu_i - I_{jk}$  is the energy of the photoelectron. Treatment of K-shell ionization and production of Auger electrons is explicitly included, as described by *Strickland et al.* [1999]. The total production rate summed over all solar lines capable of producing a specified state is

$$p_{jk}(z) = n_l(z) \sum_i \pi F(\lambda_i, z) \sigma_{jk}^{\text{photo}}(\lambda_i) \text{ cm}^{-3} \text{ s}^{-1}. \quad (5)$$

Production by electron impact is given by

$$p_{e,jk}(z) = n_l(z) \int_{W_{jk}}^{E_{\text{max}}} \sigma_{jk}(E) \phi(z, E) dE \text{ cm}^{-3} \text{ s}^{-1}, \quad (6)$$

where  $\sigma_{jk}(E)$  is the electron impact cross section producing state  $k$  of species  $l$  by electrons at energy  $E$ ,  $\phi(z, E)$  is the spherically integrated photoelectron flux ( $\text{cm}^{-2} \text{ s}^{-1} \text{ eV}^{-1}$ ), and  $W_{jk}$  is the threshold (eV).

We use a representative level 3 solar irradiance (energy flux of  $1.9 \text{ ergs cm}^{-2} \text{ s}^{-1}$  over 1–45 nm) measured on 19 October 2014 by the Extreme UltraViolet Monitor (EUVM) on board MAVEN as reported by *Eparvier* [2015]. The level 3 product is a 1 nm modeled solar spectrum from 0.5–190.5 nm derived using three calibrated solar irradiance bands measured by EUVM. The solar irradiance is rebinned to a finer wavelength grid (equal apportionment of energy flux across subbins using 0.05 nm resolution from 1–10 nm and 0.1 nm from 10–105 nm) for use in our forward model calculations. Our analysis is not sensitive to the rebinning scheme as long as total energy flux within each EUVM bin is conserved in the rebinned spectrum. During the observations considered here, the Sun was moderately active producing one coronal mass ejection and multiple flares, including an X1.1 flare on 19 October 2014.

The  $\text{CO}_2^+$  UVD ( $\text{B } ^2\Pi_u^+ \rightarrow \text{X } ^2\Pi_g$ ) transition is allowed and the main sources are photoionization and electron impact ionization of  $\text{CO}_2$ . Equation (5) is used to calculate the photoionization production rate, whereas equation (6) is used to calculate the electron impact ionization production rate. Photoionization of  $\text{CO}_2$  is by far the dominant source of UVD at altitudes below  $\sim 240 \text{ km}$  [*Fox and Dalgarno*, 1979; *Jain and Bhardwaj*, 2012]. We omit fluorescent scattering of sunlight by  $\text{CO}_2^+$ , since it contributes less than 10% to the total UVD emission at altitudes below  $\sim 200 \text{ km}$  [*Fox and Dalgarno*, 1979; *Fox*, 2004a, 2004b; *Jain and Bhardwaj*, 2012; *Stiepen et al.*, 2015]. Because UVD is emitted at 288–289 nm in a region of negligible pure absorption, accurate modeling of this transition is achievable to within the combined uncertainties of the relevant photoabsorption and photoionization cross sections and the assumed solar irradiance.

The volume production rate of the  $\text{N}_2$  VK ( $\text{A } ^3\Sigma_u^+ \rightarrow \text{X } ^3\Sigma_g^+$ ) transition, which derives exclusively from photoelectron impact excitation, is obtained from equation (6). However, the  $\text{N}_2$  A state undergoes radiative cascade, intrasystem cascading, and electronic quenching [*Trajmar et al.*, 1983; *Morrill and Benesch*, 1996; *Jain and Bhardwaj*, 2011]. For modeling  $\text{N}_2$  VK emission, we adopt the quenching parameters of *Gronoff et al.* [2012b]. Previous terrestrial work using AURIC showed that modeled  $\text{N}_2$  VK emission is in good agreement with observations [*Strickland et al.*, 1999]. Analyses of Titan dayglow data using AURIC shows that observed  $\text{N}_2$  VK emissions are in excellent agreement with model results in retrievals constrained only by photofragmented features [*Stevens et al.*, 2015b].

We use a spectral model of  $\text{CO}_2^+$  UVD in AURIC to retrieve brightness profiles from IUVS observations [see *Stevens et al.*, 2015a]. In our model, we assume the  $\text{B}(0,0,0)^2\Sigma_u^+ \rightarrow \text{X}(0,0,0)^2\Pi_g$  transition is the dominant contributor to the spectrum and that rovibrational effects due to perturbations by other vibronic states can be ignored. We use rotational term value parameters reported by *Farley and Cattolica* [1996] and Hönl-London factors from *Earls* [1935]. For modeling  $\text{N}_2$  VK emission spectra, we use the band model described in *Stevens et al.* [2015a]. Vibrational populations of the  $\text{N}_2$  ( $\text{A } ^3\Sigma_u^+$ ) state for progressions  $v' = 0\text{--}10$  are adopted from *Strickland et al.* [1999]. Relative populations are those reported by *Morrill and Benesch* [1996]. For the  $\text{N}_2$  VK electron impact emission cross section, we use a sum of direct production cross sections of *Cartwright et al.* [1977] as discussed by *Daniell and Strickland* [1986].

#### 4. Retrieval Algorithm

We infer atmospheric composition from IUVS measurements using the Generalized Retrieval and Analysis Tool. This tool merges AURIC with OPTimal estimation (hereafter OPT) retrieval algorithms [*Lumpe et al.*, 1997, 2002, 2007] and has already been applied to dayglow observations of Titan for the retrieval of  $\text{N}_2$  and methane ( $\text{CH}_4$ ) [*Stevens et al.*, 2015b]. We herein adapt the Titan algorithm to the Martian dayglow.

In the spectral dimension we convolve AURIC model spectra at 0.1 nm resolution for each tangent altitude with an IUVS point spread function as well as a slit function. We sum over all AURIC model spectral bins associated with chosen passbands for CO<sub>2</sub><sup>+</sup> UVD and N<sub>2</sub> VK molecular band systems. For vertical smoothing we use a box car average, which yields an effective resolution of ~5 km and is consistent with the vertical resolution of the observations. Our forward model calculations assume that the atmosphere is spherically symmetric along the line of sight, which is a safe approximation at Mars for solar zenith angles below 60°.

The forward model problem is stated in general form as  $y = F(x)$ , where  $y$  represents the measurement vector of limb radiance profiles,  $x$  is the atmospheric state vector to be retrieved, and the full forward model  $F$  is defined by the combination of AURIC and an IUVS instrument model. This nonlinear equation is solved using the optimal estimation technique [Rodgers, 2000], with the solution vector  $\hat{x}$  obtained by iterating from the a priori vector  $x_a$  according to

$$\hat{x}_{n+1} = x_a + S_a K_n^T (K_n S_a K_n^T + S_y)^{-1} [y - y_n + K_n (\hat{x}_n - x_a)] \quad (7)$$

In equation (7)  $y_n = F(x_n)$ ,  $S_y$  and  $S_a$  are the data and a priori covariance matrices, respectively, and the kernel matrix  $K_n$  is the derivative of the forward model with respect to the state parameters

$$K_n \equiv \left. \frac{\partial F}{\partial x} \right|_{x=x_n} \quad (8)$$

The covariance of the solution is a weighted sum of uncertainties from the a priori contribution and direct inversion of the data

$$\hat{S} = (S_a^{-1} + K^T S_y^{-1} K)^{-1} \quad (9)$$

The 1- $\sigma$  retrieval uncertainties reported here are the diagonal elements of the retrieval covariance matrix:  $\sigma_i \sim \sqrt{\hat{S}_{ii}}$ . Since this approach is strictly formal uncertainty propagation, it may underestimate the true errors, which must be derived through a detailed uncertainty analysis using simulations to quantify individual uncertainty components.

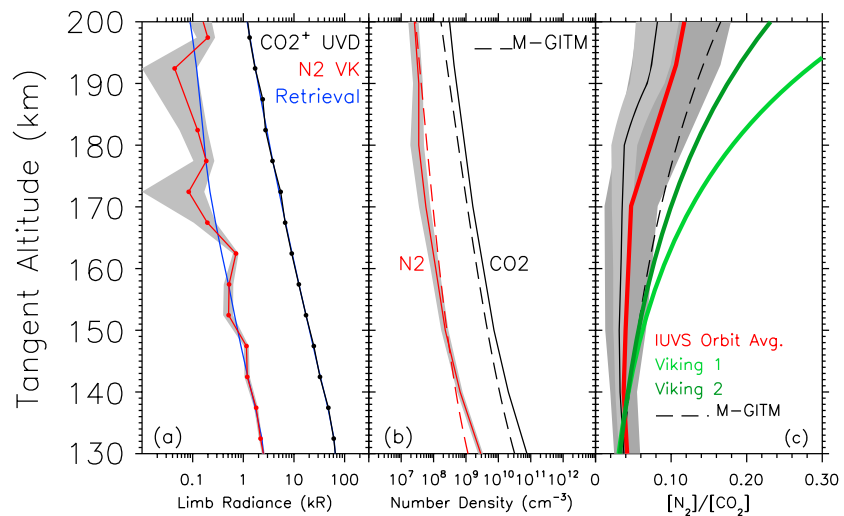
## 5. Results

### 5.1. Density Profile Retrievals

The algorithms used in this analysis sequentially retrieve CO<sub>2</sub> and N<sub>2</sub> density profiles by fitting IUVS limb scan data. The density retrievals use a total of 20 (16) parameters for each CO<sub>2</sub><sup>+</sup> UVD (N<sub>2</sub> VK) limb scan: constituent densities on a fixed altitude grid (19 grid points for CO<sub>2</sub> and 15 points for N<sub>2</sub>) and a forward model brightness scale factor. The retrieval altitude grid uses equally spaced increments of 10 km from 80 to 150 km for CO<sub>2</sub> and 80 to 190 km for N<sub>2</sub> and an exponential grid up to 600 km. We find that the forward model is insensitive to variations in CO<sub>2</sub> and N<sub>2</sub> densities below the peak of volume production (nominally ~130 km for SZA < 60°) and above ~220 km.

As shown by Picone [2008], the influence of systematic biases on compositional retrievals from UV airglow is mitigated by scale factors. Forward model brightness scale factors are used to compensate for systematic biases between observed brightness profiles and values calculated by AURIC. These biases primarily arise from uncertainties in instrument calibration, cross sections used in AURIC, and solar XUV irradiance. IUVS MUV calibration uncertainties are estimated to be  $\pm 30\%$ , cross section uncertainties are reported to be  $\pm 25\%$  [Avakyan et al., 1998; Majeed and Strickland, 1997], and EUVM level 3 daily irradiance uncertainties are  $\pm 32\%$  [Eparvier, 2015]. We find that the retrieved CO<sub>2</sub><sup>+</sup> UVD forward model scale factor has a mean value of  $0.6 \pm 0.1$ , whereas the retrieved N<sub>2</sub> VK scale factor has a mean value of  $1.02 \pm 0.24$ . These are both within the combined systematic uncertainties of the biases listed above (see section 5.3).

Retrieved forward model brightness profiles are calculated from CO<sub>2</sub> and N<sub>2</sub> densities obtained by modifying an a priori guess until a best fit solution is found. We use a priori values of 1.0 with a variance of 0.2 for the CO<sub>2</sub><sup>+</sup> UVD and N<sub>2</sub> VK brightness scale factors. For observations with high signal-to-noise, scaling the variance up or down by a factor of 2 changes the retrieved CO<sub>2</sub> by at most a factor of 1.6 and N<sub>2</sub> by less than a factor of 1.4. A priori CO<sub>2</sub> and N<sub>2</sub> abundances for the density retrievals reported here are



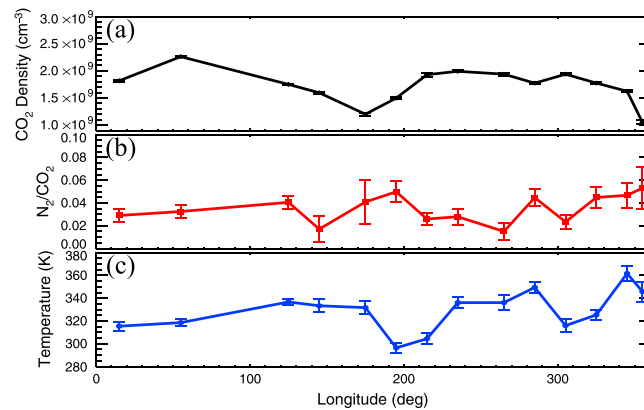
**Figure 1.** (a)  $\text{CO}_2^+$  UVD (black) and the  $\text{N}_2$  VK (red) brightness profiles observed by IUVS on 18 October 2014 at 16:44 UT during the tenth scan of MAVEN orbit 109 compared with retrieved forward model fits (blue). The mean satellite altitude for the scan was 319.4 km and the SZA was  $42.5^\circ$ . The shaded region designates a  $1\text{-}\sigma$  standard deviation for the observation. (b) Retrieved  $\text{CO}_2$  (black) and  $\text{N}_2$  (red) density profiles compared to corresponding density profiles predicted by M-GITM for  $L_s = 180$  (dashed). Random uncertainties for the retrieved densities are shown in the shaded region. (c) Retrieved  $\text{N}_2/\text{CO}_2$  profile (solid black) compared with corresponding values predicted by M-GITM (dashed), Viking 1 (light green), Viking 2 (dark green), and the ensemble average of IUVS retrieved  $\text{N}_2/\text{CO}_2$  for all scans considered herein (red). Shaded regions designate  $1\text{-}\sigma$  standard deviations for single scan (light grey) and ensemble average (dark grey).

the mean of density profiles taken from the Mars Climate Database [Millour *et al.*, 2014] sampled over a full Martian year. Since  $\text{CO}_2$  is the dominant source of photoelectrons in the Martian thermosphere, we perform  $\text{CO}_2$  retrievals first and then use the retrieved density in the a priori atmosphere for  $\text{N}_2$  retrievals (all other a priori species are unchanged). We find that scaling the a priori density up or down by a factor of 2 changes the retrieved  $\text{CO}_2$  by a factor of 1.4 and  $\text{N}_2$  by a factor of 1.2, where the retrievals are most sensitive to changes in density (130–220 km).

Figure 1a shows brightness profiles of  $\text{CO}_2^+$  UVD and  $\text{N}_2$  VK observed by IUVS on 18 October 2014 during the tenth scan of MAVEN orbit 109 (SZA =  $44^\circ$ ; UT = 16:44;  $F_{10.7} = 65$ ; latitude =  $12^\circ\text{N}$ ; longitude =  $131^\circ\text{E}$ ; s/c altitude = 320 km). The shaded region designates a  $1\text{-}\sigma$  standard deviation for the observation. The MLR technique used to unblend and extract emission features from calibrated data is described in detail by Stevens *et al.* [2015a]. Comparisons of measured spectra with MLR retrieved composite synthetic spectra for the tenth scan of orbit 109 are illustrated in the supporting information in Figures S2 and S3. The overall agreement between retrieved forward model  $\text{CO}_2^+$  UVD limb radiance profile and the data is better than 25% for tangent altitudes below 200 km. The ratio of forward model  $\text{N}_2$  VK limb brightness to the observed brightness increases from a factor of 1.2 below 150 km to a factor of 2 at 200 km.

Figure 1b shows retrieved  $\text{CO}_2$  and  $\text{N}_2$  density profiles compared to corresponding density profiles predicted by M-GITM (dashed) [Bougher *et al.*, 2015] for  $L_s$ ,  $F_{10.7}$ , latitude, and local solar time values of  $180^\circ$ , 130,  $12.5^\circ$ , and 14.2 h, respectively. The shaded region represents  $1\text{-}\sigma$  retrieval uncertainties.  $\text{CO}_2$  densities are in excess of model predictions by factors of 2 to 3 between 200 and 130 km, whereas a direct comparison of  $\text{N}_2$  densities shows an overestimation by the model at and above 150 km and an underestimation below.

The quantity  $\text{N}_2/\text{CO}_2$  can be used to assess the strength of vertical mixing in the Martian upper atmosphere, and the comparison of  $\text{N}_2/\text{CO}_2$  with M-GITM-predicted values in Figure 1c contrasts with the separate comparison of  $\text{N}_2$  and  $\text{CO}_2$  densities in Figure 1b. The comparison of retrieved  $\text{N}_2/\text{CO}_2$  with M-GITM results in Figure 1c clarifies the differences, indicating good agreement at 130 km, but an overestimation from the model by a factor of  $\sim 2$  at 200 km. The increase in mean  $\text{N}_2/\text{CO}_2$  with altitude reflects the fact that  $\text{N}_2$  is in the diffusively separated region of the Martian atmosphere.



**Figure 2.** (a) Retrieved  $\text{CO}_2$  density at an altitude of 170 km for 23 (out of 82) limb scans from orbit 109 on 18 October 2014 to orbit 269 on 18 November 2014 binned by latitude from  $-5^\circ$  to  $10^\circ$  and by longitude every  $10^\circ$ . All points falling within each bin are averaged together with uncertainties rigorously propagated to derive the error bars shown in the figure. (b) Retrieved  $\text{N}_2/\text{CO}_2$  binned by latitude and longitude. (c) Upper atmospheric temperature derived from fits to retrieved  $\text{CO}_2$  density profiles over altitudes from 170 to 220 km binned by latitude and longitude (see text).

To determine if the single scan considered here is representative of overall behavior, we include in Figure 1c the ensemble average of  $\text{N}_2/\text{CO}_2$  from 82 limb scans. Figure 1c shows that our sample  $\text{N}_2/\text{CO}_2$  profile from orbit 109 is lower than the ensemble average, but nearly within the  $1\text{-}\sigma$  standard deviation of the geophysical variability. We find good agreement between the ensemble average and M-GITM predictions at 130 and 200 km, but an overall difference in the shape of the profiles, with a maximum difference of a factor of  $\sim 1.8$  near 170 km.

Given the current state of analyses and data product generation, it is beyond the scope of this paper to conduct a detailed comparison of IUVS results with (nearly) coincident in situ data from the Neutral

Gas Ionizing Mass Spectrometer (NGIMS) [Mahaffy *et al.*, 2014] on board MAVEN. However, we can make qualitative comparisons of our results with previous in situ composition measurements by the Vikings 1 and 2 entry probes in 1976 [Nier and McElroy, 1977], which extended from  $\sim 200$  km down to  $\sim 120$  km. These data are included in Figure 1c as least squares fits to  $\text{N}_2/\text{CO}_2$  (assuming the ratio varies exponentially with altitude). The Viking data suggest that the homopause should be located between 120 and 130 km. However, the data also suggest that the atmosphere sampled by Viking 1 was statically more stable than that sampled by Viking 2; thus, the homopause sampled by Viking 2 was higher than that seen by Viking 1. The ensemble data presented here indicate that the mean atmosphere sampled by IUVS is well mixed to slightly higher levels than predicted by M-GITM, but consistent with the differences observed by Vikings 1 and 2, although this result should be examined with a larger MAVEN data set.

The recently revised  $\text{N}_2$  mixing ratio at the Martian surface as measured by the Sample Analysis at Mars (SAM) experiment on the Curiosity rover of the Mars Science Laboratory mission is  $0.0203 \pm 0.0003$  [Franz *et al.*, 2015]. Mahaffy *et al.* [2015] report that at altitudes near  $\sim 125$  km  $\text{N}_2/\text{CO}_2$  measured by NGIMS approaches the bulk atmospheric mixing ratio established by the SAM experiment. In contrast, both the IUVS and M-GITM  $\text{N}_2/\text{CO}_2$  values near that altitude are about a factor of 2 higher than the surface value. More specifically, we find that the mean  $\text{N}_2/\text{CO}_2$  increases from  $0.042 \pm 0.017$  at 130 km to  $0.12 \pm 0.06$  at 200 km. NGIMS values near the same altitudes are approximately 0.02 and 0.12, respectively [Mahaffy *et al.*, Figure 6]. It should be mentioned that the M-GITM results used here reflect assumed boundary conditions in the lower atmosphere. Thus, differences in M-GITM predictions with other measurements (Viking, NGIMS, or IUVS) require further study with a larger MAVEN data set.

Using an ensemble of retrievals for 23 (out of 82) limb scans, we can investigate the spatial variability of densities in the equatorial region covered by the available observations. In Figure 2a we show retrieved  $\text{CO}_2$  densities corresponding to an altitude of 170 km as a function of longitude. The retrievals have been averaged over northern hemisphere latitudes from  $-5^\circ$  to  $35^\circ$  and in  $10^\circ$  longitude bins. The  $\text{CO}_2$  densities vary by over a factor of 2 ranging from  $1 \times 10^9$  to  $2.3 \times 10^9 \text{ cm}^{-3}$ . Longitudinal structure in the densities is evident with maxima centered near  $50^\circ$  and  $280^\circ$ . If the dayglow at Mars has small temporal variations over the month of observations shown in Figure 2, this longitudinal structure may be a signature of tides in the Martian thermosphere [Lo *et al.*, 2015]. A similar degree of variability is evident in the ratio of retrieved  $\text{N}_2$  and  $\text{CO}_2$  shown in Figure 2b.

### 5.2. Temperature Retrievals

Following the approach of *Westlake et al.* [2011], we retrieve upper atmospheric temperatures at Mars by inferring scale heights from retrieved CO<sub>2</sub> density profiles between 170 and 220 km. We use a geopotential altitude to account for changes in gravitational acceleration with altitude. Considering all scans, we find a mean Martian temperature (reference altitude of 170 km) of 324 K with a 1- $\sigma$  standard deviation of 22 K. Figure 2c shows spatially binned upper atmospheric temperatures as a function of longitude. The observed variation of  $\sim 60$  K in temperature is considerable but consistent with values derived from previous observations [*Stewart, 1972; Stewart et al., 1972; Leblanc et al., 2006b; Stiepen et al., 2015*] and climate model predictions [*Bougher et al., 2009, 2015*]. We note that the mean temperature from our analysis agrees within the respective uncertainties with a temperature of  $285.1 \pm 21.7$  K determined from changes in the density scale height of Argon (Ar) measured by NGIMS over the same time frame (see Figure S1 in the supporting information).

### 5.3. Systematic Uncertainty Analysis

It is evident from equations (5) and (6) that the main sources of forward model uncertainty are solar irradiance (energy input), total photoabsorption cross sections (attenuation), photoionization cross sections (ion and photoelectron production), and finally elastic and inelastic electron impact cross sections (ion production and energy loss). Additional uncertainties unrelated to the forward model include instrument pointing and calibration.

Through simulated retrievals we determined that the sensitivity of CO<sub>2</sub> densities to nonflare solar variability is negligible at and above the CO<sub>2</sub><sup>+</sup> UVD emission peak, whereas the impact on N<sub>2</sub> retrievals is at most  $\sim 25\%$ . To quantify the sensitivity of density retrievals to more active solar conditions, we repeated the retrievals shown in Figure 1 with an alternative solar irradiance spectrum measured by EUVM 45 min after the X1.1 flare occurring on 19 October 2014 [*Thiemann et al., 2015*], with an energy flux 1.6 times the value from the representative solar irradiance used in this study that was measured by EUVM on 18 October 2014. We find that retrieved densities based on the postflare solar spectrum are reduced relative to preflare densities by at most a factor of 1.4 at altitudes above 140 km, with an increased effect at lower altitudes. The overall reduction in retrieved densities using the postflare solar spectrum compensates for the increased energy in the solar spectrum. The increased effect at lower altitudes is due to soft X-ray solar photons penetrating deeper in the atmosphere, thereby changing the shape of forward model emission profiles near and below the emission peak. While not critical, it is best to use a solar irradiance that is appropriate for the solar activity during which dayglow observations are made.

IUVS was calibrated against UV-bright stars and scaled by instrument geometric factors appropriate for extended source observations. The MUV systematic uncertainty estimated from these stellar calibrations is  $\pm 30\%$ . We find that a 30% reduction in the absolute calibration has a negligible impact on the retrieval of CO<sub>2</sub> densities but leads to a 30% reduction in retrieved N<sub>2</sub> densities. In the former case, it is the altitude distribution of the observed CO<sub>2</sub><sup>+</sup> UVD limb brightness profile, rather than the magnitude, that is directly diagnostic of the CO<sub>2</sub> density profile. Specifically, the height of the peak of emission corresponds to an absolute CO<sub>2</sub> density, and the relative shape of the CO<sub>2</sub><sup>+</sup> UVD limb profile above the peak describes the CO<sub>2</sub> scale height. This behavior is expected when considering the expression for volume production of CO<sub>2</sub><sup>+</sup> UVD given by equation (5). The estimated pointing accuracy of MAVEN is 5 km on the limb [*McClintock et al., 2014*]. This corresponds to a factor of 2 uncertainty in retrieved CO<sub>2</sub> densities due to the direct relationship between CO<sub>2</sub><sup>+</sup> UVD emission peak altitude and absolute density at the emission peak. We therefore conclude that the dominant uncertainty in retrieved CO<sub>2</sub> densities is pointing accuracy.

In contrast, equation (6) suggests that the 30% instrument calibration uncertainty propagates directly to N<sub>2</sub> retrievals since there is a linear relationship between the N<sub>2</sub> density and the N<sub>2</sub> VK brightness. This is because VK is produced exclusively by photoelectrons exciting N<sub>2</sub> that result predominately from photoionization of CO<sub>2</sub>. The total systematic uncertainty in the retrieved N<sub>2</sub> densities is a combination of instrument calibration, solar irradiance, and cross sections, although the total N<sub>2</sub> uncertainty is mitigated by a scale factor used in the retrieval [*Stevens et al., 2015b*]. A complete uncertainty analysis of the IUVS limb scan retrieval data products will be presented in a forthcoming algorithm paper.



## 6. Conclusions

We have presented the first direct retrievals of CO<sub>2</sub> and N<sub>2</sub> number densities in Mars' upper atmosphere using MUV dayglow observations from 130 to 200 km. We use two MUV emission features observed by IUVS on MAVEN for our retrievals: CO<sub>2</sub><sup>+</sup> UVD and N<sub>2</sub> VK. The dominant source of UVD is photoionization of CO<sub>2</sub>, and so the emission is directly diagnostic of CO<sub>2</sub> density variations. Similarly, N<sub>2</sub> VK emission is produced exclusively by photoelectron impact and is diagnostic of N<sub>2</sub> density variations. It is worth noting that neither of the selected emission features is affected by pure absorption over the range of tangent altitudes reported here.

Key findings in this study are

1. CO<sub>2</sub> densities at 170 km vary by a factor of about 2.5 over a month of observations in October and November 2014.
2. The N<sub>2</sub>/CO<sub>2</sub> indicates that N<sub>2</sub> is in the diffusively separated region of the Martian atmosphere with a mean ratio that increases from  $0.042 \pm 0.017$  at 130 km to  $0.12 \pm 0.06$  at 200 km.
3. The mean Martian upper atmospheric temperature over the sampled time frame is  $324 \pm 22$  K.

We also find that CO<sub>2</sub> and N<sub>2</sub> density retrievals from MUV limb scan observations at Mars are insensitive to quiet time variability in solar irradiance, but care must be taken to use appropriate flare spectra during active times. Finally, CO<sub>2</sub> density retrievals from MUV limb scan observations at Mars are insensitive to instrument calibration and instead are primarily sensitive to the accuracy of the pointing, while instrument calibration errors propagate directly to errors in N<sub>2</sub> retrievals. Observed densities that are a factor of 3 less than predictions as suggested by some previous studies [e.g., *Leblanc et al.*, 2007; *Simon et al.*, 2009; *Jain and Bhardwaj*, 2011] are not supported by the comparisons presented herein [see also *Stevens et al.*, 2015a].

IUVS observations over additional months will provide valuable insight to seasonal variations of CO<sub>2</sub> and N<sub>2</sub> in the Martian upper atmosphere. In addition, a variety of other emissions [*Jain et al.*, 2015] will be used to quantify spatial and temporal variations of composition in the Martian upper atmosphere.

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