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## RESEARCH ARTICLE

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### Special Section:

Major Results From the MAVEN Mission to Mars

### Key Points:

- The composition of the nightside ionosphere of Mars is characterized
- $O_2^+$  is the major nightside ion down to 130 km, below which  $NO^+$  becomes the major ion
- Nightside ion densities can vary by nearly an order of magnitude over monthlong timescales

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## Nightside ionosphere of Mars: Composition, vertical structure, and variability

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**Abstract** We provide an overview of the composition, vertical structure, and variability of the nightside ionosphere of Mars as observed by Mars Atmosphere and Volatile EvolutioN (MAVEN)'s Neutral Gas and Ion Mass Spectrometer (NGIMS) through 19 months of the MAVEN mission. We show that  $O_2^+$  is the most abundant ion down to  $\sim 130$  km at all nightside solar zenith angles (SZA). However, below 130 km  $NO^+$  is the most abundant ion, and  $NO^+$  densities increase with decreasing altitude down to at least 120 km. We also show how the densities of the major ions decrease with SZA across the terminator. At lower altitudes the  $O_2^+$  and  $CO_2^+$  densities decrease more rapidly with SZA than the  $NO^+$  and  $HCO^+$  densities, which changes the composition of the ionosphere from being primarily  $O_2^+$  on the dayside to being a mixture of  $O_2^+$ ,  $NO^+$ , and  $HCO^+$  on the nightside. These variations are in accord with the expected ion-neutral chemistry, because both  $NO^+$  and  $HCO^+$  have long chemical lifetimes. Additionally, we present median ion density profiles from three different nightside SZA ranges, including deep on the nightside at SZAs greater than  $150^\circ$  and discuss how they compare to particle precipitation models. Finally, we show that nightside ion densities can vary by nearly an order of magnitude over monthlong timescales. The largest nightside densities were observed at high northern latitudes during winter and coincided with a major solar energetic particle event.

## 1. Introduction

In the 1970s the Viking Landers obtained the first in situ observations of the dayside ionosphere of Mars. These observations showed that the dayside ionosphere is composed primarily of  $O_2^+$  ions and confirmed that photoionization by solar EUV radiation is the primary source of dayside plasma [Hanson *et al.*, 1977; Chen *et al.*, 1978; Fox *et al.*, 1996; Withers, 2009]. By contrast, in situ observations of the nightside ionosphere were unavailable until 2014 when the Mars Atmosphere and Volatile EvolutioN (MAVEN) mission arrived at Mars [Jakosky *et al.*, 2015a, 2015b]. Consequently, the composition and sources of the nightside ionosphere are not as well understood.

It has been suggested that there are two main sources of plasma in the upper nightside ionosphere. The first being impact ionization from precipitating particles, which are thought mostly to be electrons of solar wind origin [Verigin *et al.*, 1991; Fox *et al.*, 1993; Haider, 1997] but may also include solar wind protons, energetic neutral atoms (ENAs), and dayside photoelectrons [Kallio and Janhunen, 2001; Haider *et al.*, 2013; DiéVal *et al.*, 2013; Xu *et al.*, 2016]. The second source of plasma is thought to be day-to-night ion transport driven by cross-terminator winds [Chaufray *et al.*, 2014; Cui *et al.*, 2015]. However, even in the absence of winds ions can be transported to the nightside, as long as the ionosphere and the planet rotate as a solid body and the ions have long chemical lifetimes [Cui *et al.*, 2009; González-Galindo *et al.*, 2013; Cui *et al.*, 2015].

Before MAVEN, constraints on the nightside ionosphere came primarily from remote sensing observations of the electron density and total electron content by radio occultation experiments on the Mars, Viking, and Mars Express missions, and from the MARSIS radar sounding experiment on Mars Express [Zhang *et al.*, 1990; Mendillo *et al.*, 2003; Gurnett *et al.*, 2008; Duru *et al.*, 2011; Němec *et al.*, 2010; Withers *et al.*, 2012; Cartacci *et al.*, 2013; Diéval *et al.*, 2014; Němec *et al.*, 2014; Cui *et al.*, 2015]. These observations have revealed that the nightside ionosphere is patchy and spatially inhomogeneous with peak densities on the order of a few  $10^3$ – $10^4$   $cm^{-3}$ . They have also shown that nightside densities are larger near regions of vertical crustal magnetic fields [e.g., Safaeinili *et al.*, 2007; Lillis *et al.*, 2011; Němec *et al.*, 2011; Dubinin *et al.*, 2016].

Initial MAVEN observations have provided further constraints on the nightside ionosphere. An analysis of nightside electron density profiles concluded that precipitating energetic electrons are needed to sustain the nightside ionosphere [Fowler *et al.*, 2015]. In addition, observations of electron energy spectra suggest that dayside photoelectrons can be transported across the terminator along closed crustal field loops, then precipitate into the nightside atmosphere [Xu *et al.*, 2016]. This process may be an important nightside ionization source in addition to precipitating electrons of solar wind origin.

Furthermore, the MAVEN Neutral gas and Ion Mass Spectrometer (NGIMS) has provided the first in situ observations of the nightside ion composition. Initial NGIMS observations have shown the general day-to-night variations of several ions and revealed that  $O_2^+$ ,  $NO^+$ , and  $HCO^+$  are the major species in the lower nightside ionosphere [Benna *et al.*, 2015a; Fox *et al.*, 2015]. However, these studies were limited to solar zenith angles less than  $\sim 130^\circ$  and did not focus on the bulk composition of the nightside ionosphere nor its variability.

Our goal in this paper is to describe some of the basic characteristics of the nightside ionosphere by providing an overview of its composition, vertical structure, and variability as observed by NGIMS over the first 19 months of the MAVEN mission. In section 2 we introduce and describe the NGIMS data set; in section 3 we show how the composition of the ionosphere changes from day-to-night across the dawn and dusk terminators; in section 4 we present median ion density profiles from the nightside; in section 5 we show that nightside ion densities from different latitudes and seasons can vary substantially; and in section 6 we summarize our results and present our conclusions.

## 2. NGIMS Data Description

MAVEN began its nominal science mission in November 2014. The 4.5 h orbit of MAVEN is highly elliptical with an apoapsis of  $\sim 6200$  km and a periapsis that is typically  $\sim 150$  km, although there have been several “deep dip” campaigns that lowered the periapsis down to  $\sim 125$  km for short periods of time [Jakosky *et al.*, 2015b, 2015a]. The periapsis of MAVEN precesses slowly so that the spacecraft latitude, local time, and solar zenith angle (SZA) are similar from orbit to orbit, but vary considerably over the course of the mission. This orbit allows NGIMS to determine the composition of the ionosphere over a wide range of conditions. However, during any single orbit, the spacecraft does not travel vertically (radial direction) through the ionosphere. Since NGIMS observations are made along the spacecraft trajectory, vertical ion density profiles are not measured directly. Instead, vertical profiles can only be derived by averaging observations from several orbits [e.g., Benna *et al.*, 2015a; Fowler *et al.*, 2015; Withers *et al.*, 2015]. The resulting vertical profiles, however, represent averages over time, space, and changing underlying conditions (e.g., magnetic topology).

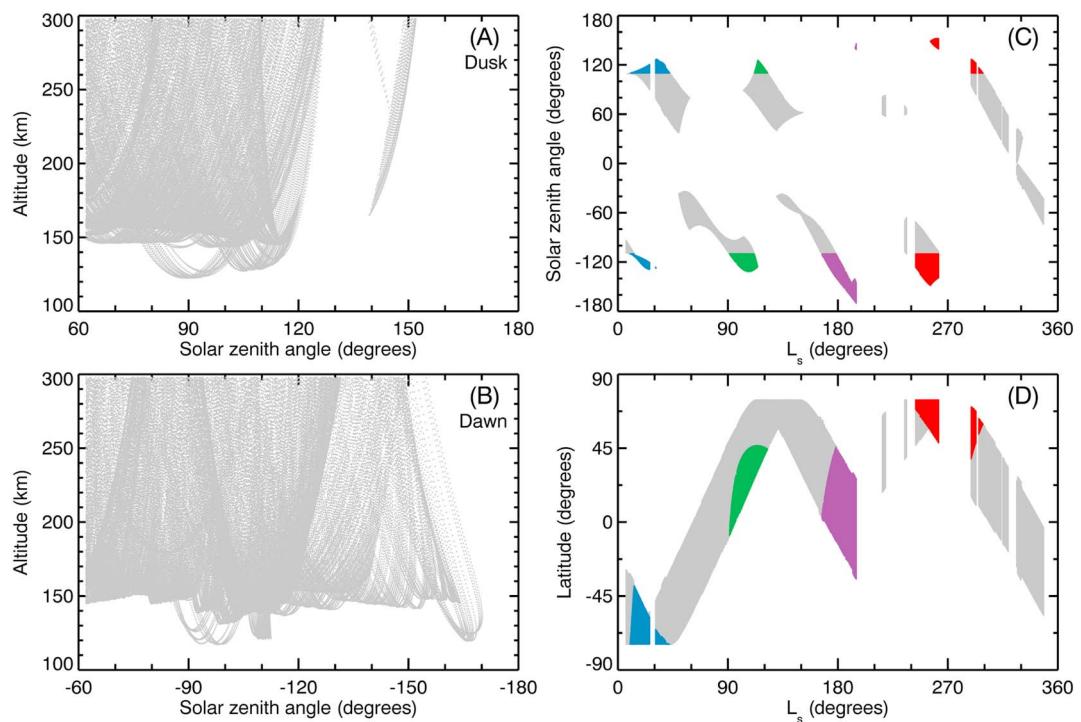
NGIMS has several observing modes that allow it to measure either neutrals or ions. The observing mode is typically alternated so that ion density measurements are collected every other orbit (9 h apart). Detailed descriptions of the NGIMS instrument, data calibration, and initial scientific results have been presented in several publications [Benna *et al.*, 2015b, 2015a; Mahaffy *et al.*, 2015b, 2015a].

Our analysis uses the Level 2 (v06\_r02) NGIMS ion data that were obtained between 18 October 2014 and 30 July 2016. Figure 1 shows the SZA-altitude coverage of the data set along with how the SZA and seasonal coverage have evolved throughout the mission. We adopt the SZA convention such that positive SZAs represent dusk measurements (local times  $> 12$  h) and negative SZAs represent dawn measurements (local times  $< 12$  h).

We focus on observations near the terminator and extending into the nightside, which we define as observations at SZAs greater than  $110^\circ$ . This definition is somewhat arbitrary but was chosen because at this SZA the thermosphere is shaded from the Sun (blocked by solid Mars) at altitudes up to 220 km. We note that at 300 km the thermosphere does not reach the shaded region until a SZA of  $113^\circ$  and that previous studies have defined the nightside using their own SZA conventions [e.g., Němec *et al.*, 2011; Withers *et al.*, 2012].

The NGIMS data set includes 1210 orbits of ion density measurements, 523 of which include nightside observations below 300 km. These nightside observations were obtained during four different time periods throughout the mission. The different latitudes, seasons, and local times (dawn/dusk) covered during each time period are highlighted in Figure 1 and listed in Table 1.

There is a clear bias in the data set with respect to latitude and season. For example, data from high northern latitudes only cover the winter and fall seasons while data from low southern latitudes only cover spring equinox. Additionally, there is a bias in the data set with respect to dawn and dusk. For example, most of the



**Figure 1.** The SZA, altitude, latitude, and solar longitude ( $L_s$ ) distribution of the NGIMS ion data set. (a) The altitude and SZA distribution of the dusk observations (positive SZAs). (b) The altitude and SZA distribution of the dawn observations (negative SZAs). In these two panels each gray dot shows the location of a NGIMS ion observation. For clarity, only half of the observations are shown. (c) The SZA of the NGIMS ion observations below 300 km as a function of  $L_s$ . Gray points show dayside observations and colored points show nightside observations ( $SZA > 110^\circ$ ). The colors highlight the four different time periods of nightside observations within the data set. The red points are from the first period of observations and the blue, green, and purple points are from the second, third, and fourth periods, respectively. (d) Same as Figure 1c but showing latitude versus  $L_s$ .

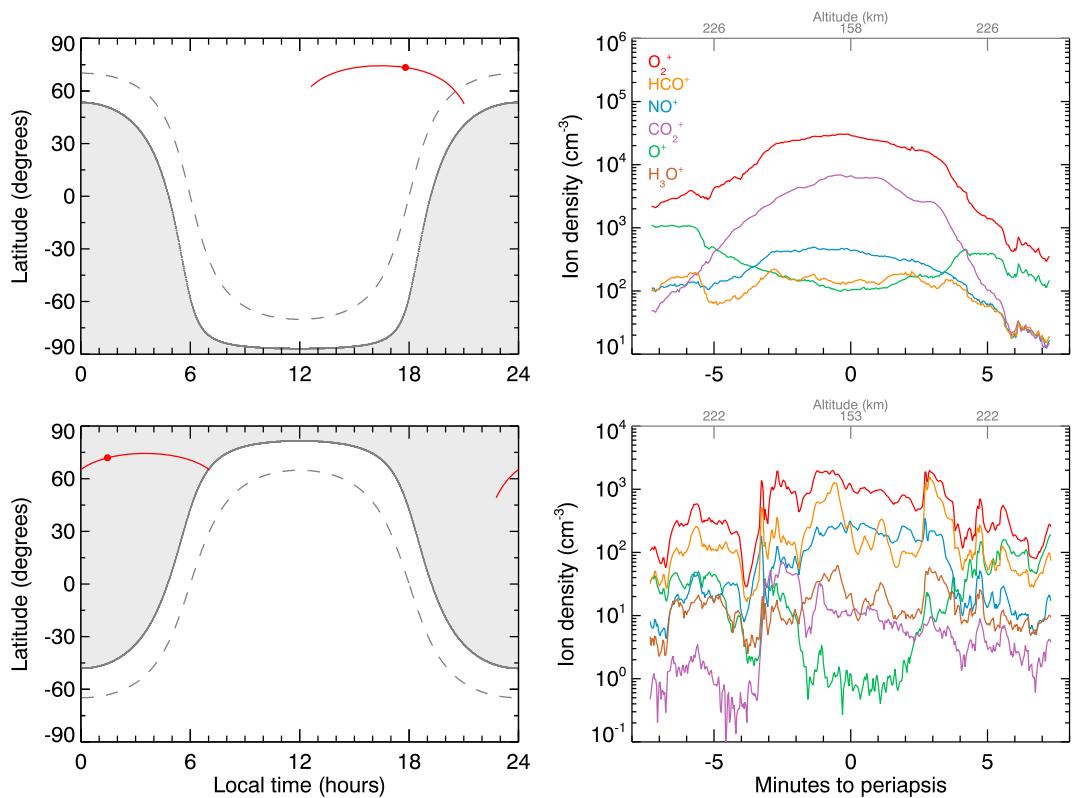
June/July 2016 observations are from dawn while few are from dusk. These biases must be kept in mind when comparing ion densities from the different time periods. Differences between the subsets of data may be caused by variations in the nightside plasma source or by diurnal and seasonal variations in the composition of the neutral atmosphere. The biases make it difficult to distinguish between these two sources of variability.

As Figure 1 shows, the nightside observations extend to SZAs up to  $\sim 170^\circ$ , but the SZA-altitude distribution of the observations are nonuniform (Figures 1a and 1b), with more observations at dawn than dusk, and fewer observations at SZAs greater than  $120^\circ$ . Only in the most recent period of nightside observations did NGIMS sample the ionosphere at SZAs past  $150^\circ$ . These recent observations included a “deep dip” campaign allowing NGIMS to sample the nightside ionosphere down to 120 km near midnight.

The observations were obtained during the declining phase of Solar Cycle 24, corresponding to moderate and minimum solar conditions. Throughout this period the EUV irradiance at Mars changed by a factor of about 2, primarily owing to the varying Mars-Sun distance rather than solar cycle variability. The EUV irradiance was highest during the beginning of the mission, when Mars was near perihelion [Bougher et al., 2017; Lee et al., 2017].

**Table 1.** The Four Different Periods of NGIMS Nightside Ion Measurements Used in This Study ( $SZA > 110^\circ$ )

Dates (mm/dd/yy)	# Dawn Orbits	# Dusk Orbits	$L_s$	Latitudes	Season
11/30/2014 to 2/26/2015	61	60	$245^\circ$ – $300^\circ$	$40^\circ$ N– $75^\circ$ N	Northern winter
7/8/2015 to 9/16/2015	88	141	$10^\circ$ – $40^\circ$	$38^\circ$ S– $74^\circ$ S	Spring equinox
11/6/2016 to 3/14/2016	133	58	$90^\circ$ – $120^\circ$	$8^\circ$ S– $47^\circ$ N	Northern summer
6/11/2016 to 7/30/2016	111	4	$165^\circ$ – $195^\circ$	$34^\circ$ S– $45^\circ$ N	Fall equinox



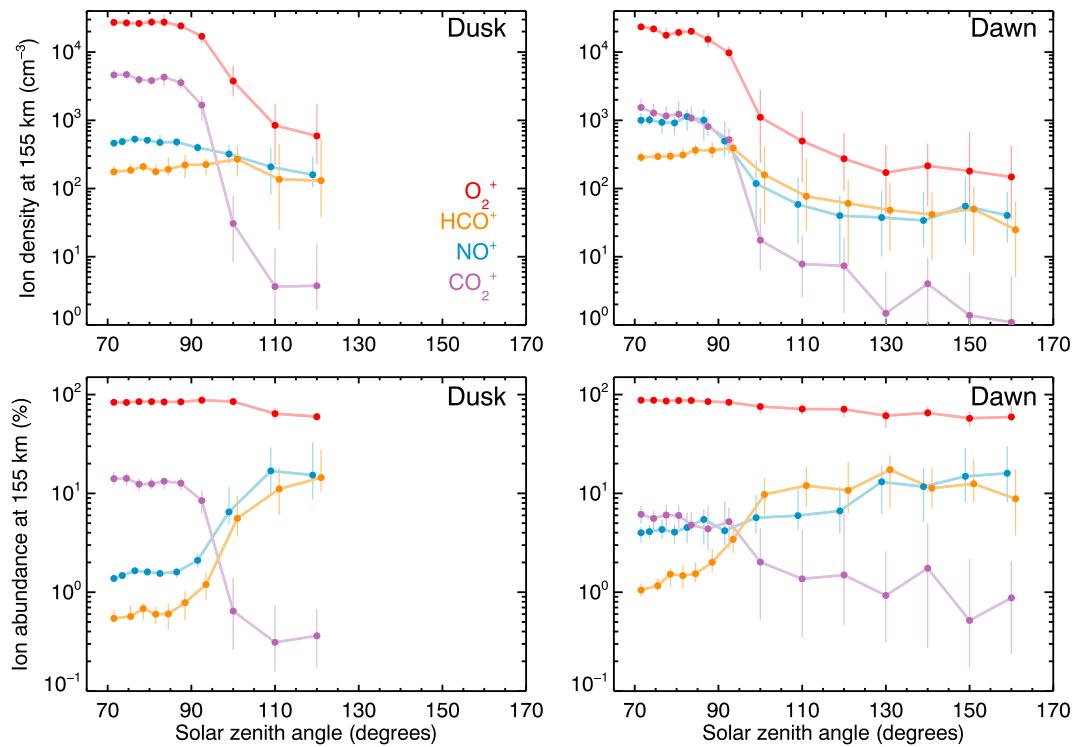
**Figure 2.** Ion densities measured by NGIMS along (top row) one dayside orbit (orbit 2893) and (bottom row) one nightside orbit (orbit 483). (left column) The red line shows the trajectory of MAVEN through latitude and local time during each orbit and the red dot shows the location of periapsis. The dashed line shows where SZA = 90° and the shaded region identifies the nightside (SZA > 110°). (right column) The measured ion densities as a function of time during the orbits. The top axes in these panels indicate the spacecraft altitude. Note that the  $\text{H}_3\text{O}^+$  densities are too small to be visible in the dayside panel.

Although the data set includes many ion species, we focus on those that are the most abundant on either the dayside or the nightside. These include  $\text{O}_2^+$ ,  $\text{CO}_2^+$ ,  $\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{HCO}^+$  [Benna et al., 2015a]. We assume that all mass 29 ions are  $\text{HCO}^+$  even though they cannot be differentiated from other mass 29 ions such as  $\text{N}_2\text{H}^+$  and  $\text{HOC}^+$ . Nevertheless, this is a reasonable assumption because models predict that  $\text{HCO}^+$  is by far the most abundant mass 29 ion [Matta et al., 2013; Fox, 2015; Fox et al., 2015].

We define the total ion density,  $N_{\text{tot}}$ , as the sum of the  $\text{O}_2^+$ ,  $\text{NO}^+$ ,  $\text{CO}_2^+$ ,  $\text{O}^+$ ,  $\text{HCO}^+$ ,  $\text{N}_2^+/\text{CO}^+$ , and  $\text{H}_3\text{O}^+$  densities. This approximation underestimates the true ion density because not every species is included. Nevertheless, it does include the most abundant species on the dayside and the nightside, and results from Benna et al. [2015a] suggest that this approximation underestimates the actual total ion density by less than 5%. We also define the relative ion abundance for a given species as the ion density divided by the total ion density and expressed as a percentage.

Figure 2 shows examples of NGIMS ion observations during a single dayside orbit and a single nightside orbit. The spacecraft trajectory through latitude and local time is shown in the left column and the measured  $\text{O}_2^+$ ,  $\text{CO}_2^+$ ,  $\text{O}^+$ ,  $\text{HCO}^+$ ,  $\text{NO}^+$ , and  $\text{H}_3\text{O}^+$  densities are shown in the right column. There are some striking differences between the dayside and nightside observations. For example, the dayside ion densities vary smoothly along the spacecraft trajectory but the nightside densities vary substantially, demonstrating the patchy nature of the nightside ionosphere.

In addition to the larger variability on the nightside, there is also a difference in the ion composition at lower altitudes. On the dayside  $\text{O}_2^+$  is the dominant ion,  $\text{CO}_2^+$  is the second most abundant ion, and  $\text{NO}^+$  and  $\text{HCO}^+$  are minor components. On the nightside, however, the composition is somewhat different. Although  $\text{O}_2^+$  is still the most abundant ion (although not as dominant),  $\text{CO}_2^+$  is now a minor ion and  $\text{HCO}^+$  and  $\text{NO}^+$  are major components. Additionally,  $\text{H}_3\text{O}^+$ —which is a minor species on dayside—is the fourth most abundant species



**Figure 3.** (top row) Median ion densities at 155 km as a function of SZA across the dusk (left) and dawn (right) terminators. (bottom row) The corresponding relative ion abundances at 155 km. In both panels the circles show the median values after binning in SZA, and the error bars show the 25% and 75% quartiles.

on the nightside. However, as Figure 2 demonstrates, its densities are typically 10–100 times smaller than either  $\text{NO}^+$  or  $\text{HCO}^+$ . Therefore, we exclude  $\text{H}_3\text{O}^+$  in the rest of the paper. A discussion of nightside  $\text{H}_3\text{O}^+$  and its implications for the presence of water in the thermosphere has been presented by Fox *et al.* [2015].

These observations reveal two major features that distinguish the nightside ionosphere from the dayside ionosphere: larger relative abundances of  $\text{NO}^+$  and  $\text{HCO}^+$ , and enhanced variability. In the sections that follow we will further analyze the data by binning observations from multiple orbits in altitude and SZA to obtain a statistical picture of the nightside composition.

### 3. Composition

In section 3.1 we show how the ion composition changes across the dawn and dusk terminators and in section 3.2 we interpret the results in terms of ion chemistry. In both sections the results are obtained by averaging data from the four different time periods of nightside observations (Table 1). As discussed in section 3.2, the four periods cover different latitudes and seasons, which may introduce a bias in the results. Nevertheless, the results presented here will provide a broad overview of how the composition changes across the terminator.

#### 3.1. Changes in Ion Composition Across the Dawn and Dusk Terminators

Figure 3 (top left) shows the median  $\text{O}_2^+$ ,  $\text{HCO}^+$ ,  $\text{NO}^+$ , and  $\text{CO}_2^+$  densities, and their 25%/75% quartiles, at 155 ( $\pm 1$ ) km as a function of SZA across the dusk terminator. This figure includes all the NGIMS ion observations obtained at dusk SZAs greater than  $+70^\circ$ .

The  $\text{CO}_2^+$  and  $\text{O}_2^+$  densities decrease more rapidly with SZA than the  $\text{NO}^+$  and  $\text{HCO}^+$  densities. As a result, nightside  $\text{CO}_2^+$  densities are more than 1000 times smaller than those on the dayside ( $4.0 \times 10^3$  to  $0.5 \times 10^3 \text{ cm}^{-3}$ ) and nightside  $\text{O}_2^+$  densities are  $\sim 50$  times smaller than on the dayside ( $3.0 \times 10^4$  to  $6.0 \times 10^2 \text{ cm}^{-3}$ ). By contrast, nightside  $\text{NO}^+$  densities are only  $\sim 3$  times smaller than on the dayside ( $5.0 \times 10^2$  to  $2.0 \times 10^2 \text{ cm}^{-3}$ ) and nightside  $\text{HCO}^+$  densities are comparable to their dayside values ( $1.0$ – $2.0 \times 10^2 \text{ cm}^{-3}$ ).

Because the four ions have different SZA variations across the terminator, their relative abundances change, leading to a nightside composition that is different than the dayside. This is illustrated in Figure 3 (top right),

which shows the relative ion abundances at 155 km. The most abundant ion at all SZAs is  $O_2^+$ , but its relative abundance decreases from ~85% on the dayside to only ~60% on the nightside. Additionally, although  $CO_2^+$  is the second most abundant species on the dayside with a relative abundance of ~15%, its rapid decay across the terminator leads to a nightside relative abundance of less than 1%. Meanwhile,  $HCO^+$  and  $NO^+$ —which are minor species on the dayside—become the second and third most abundant species on the nightside with relative abundances between 10 and 20% ( $NO^+$  being slightly more abundant).

The densities and relative abundances are also more variable on the nightside than on the dayside. For example, the interquartile ratios (the interquartile range as a percentage of the median) of the  $O_2^+$  densities increase from 1% on the dayside to over 100% on the nightside. A similar trend is seen in the  $O_2^+$  relative abundances where the interquartile ratio increases from 4% on the dayside to more than 20% on the nightside. Thus, at 155 km the dayside ionosphere has a stable composition that is ~85%  $O_2^+$  ions while the nightside ionosphere has variable composition that is only ~60%  $O_2^+$  ions.

Figure 3 (bottom row) also shows median ion densities and relative abundances at 155 km as a function of SZA across the dawn terminator. We calculated the median values using only measurements from the third and fourth periods of nightside observations. Unlike the dusk observations shown in Figure 3, the dawn observations extend to higher nightside SZAs up to 160°.

The SZA variations across the dawn terminator are similar to those across the dusk terminator with  $CO_2^+$  and  $O_2^+$  decreasing more rapidly with SZA than  $HCO^+$  and  $NO^+$ . At SZAs >110° the ion composition at dawn is broadly consistent with the ion composition at dusk with the relative abundance of  $O_2^+$  at ~60% and the relative abundances of  $HCO^+$  and  $NO^+$  between 10 and 20%. There are, however, minor differences in the dawn and dusk ion compositions (e.g., the relative abundance of  $NO^+$  is larger at dusk), but they may be caused by the latitude and seasonal bias in the data set (Table 1) rather than by a true dawn-dusk asymmetry.

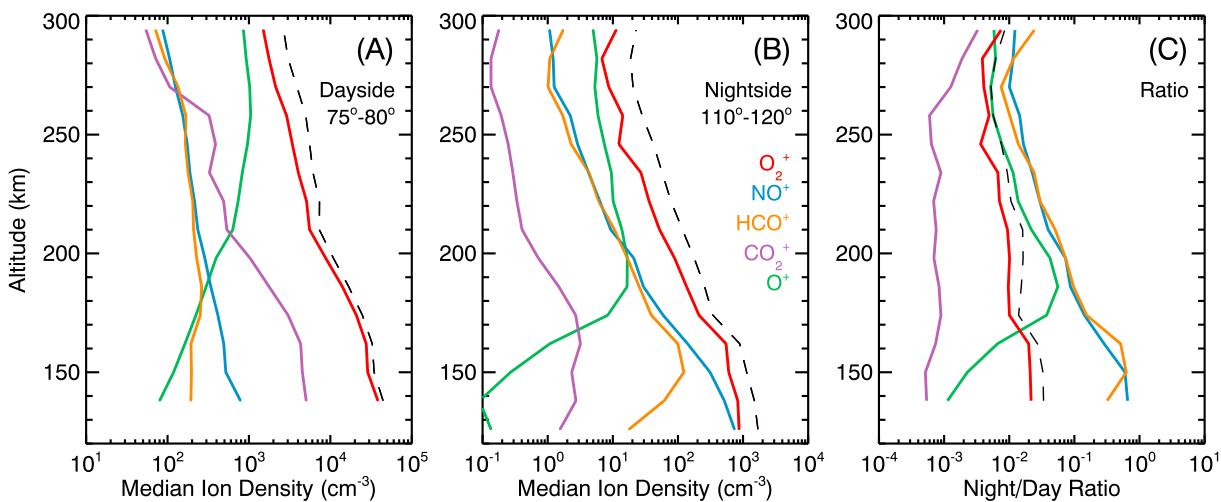
On the dayside near the terminator (SZA = 70–90°) there are differences in the ion composition at dawn and dusk. At dawn  $CO_2^+$  densities are 4 times smaller and  $NO^+$  and  $HCO^+$  densities are 2 times larger. This dawn-dusk asymmetry may also be due to the seasonal bias in the data set. However, this asymmetry is predicted by the Laboratoire de Météorologie Dynamique (LMD) Mars General Circulation Model. It is attributed to a dawn-dusk asymmetry in the composition of the neutral atmosphere (e.g., atomic oxygen) driven by cooler temperatures at dawn than at dusk [González-Galindo *et al.*, 2013; Chaufrey *et al.*, 2014].

Next we show how the composition changes across the dusk terminator at altitudes between 130 and 300 km. We do so by comparing median ion density profiles from the near-terminator dayside (SZA = +75–80°) to median ion density profiles from the near-terminator nightside (SZA = +110–120°). To construct the density profiles, we separated all the nightside data into the specified SZA ranges and into 12 km altitude bins, then calculated the median ion density within each bin. The median profiles and the ratios between the nightside and dayside profiles are shown in Figure 4.

The density profiles in Figure 4a show that  $O_2^+$  is the most abundant ion at all altitudes near the dayside dusk terminator. Above 200 km the topside is a mixture of  $O_2^+$  and  $O^+$ , but below 200 km  $O^+$  becomes a minor species and  $CO_2^+$  becomes the second most abundant ion. Additionally,  $NO^+$  and  $HCO^+$  are minor species at all altitudes. These dayside profiles are consistent with those presented from Viking Lander and early NGIMS observations [Hanson *et al.*, 1977; Benna *et al.*, 2015a; Withers *et al.*, 2015].

The nightside density profiles in Figure 4b show that, like the dayside,  $O_2^+$  is the most abundant ion at all altitudes and the topside is a mixture of  $O_2^+$  and  $O^+$ . However, unlike the dayside,  $CO_2^+$  is a minor species below 200 km where the composition is a mixture of  $O_2^+$ ,  $HCO^+$ , and  $NO^+$ . There is a peak in the  $HCO^+$  density profile near 155 km with a peak density of  $1.2 \times 10^2 \text{ cm}^{-3}$ . There is no distinct peak in the  $O_2^+$ ,  $NO^+$ , or  $N_{\text{tot}}$  density profiles and their maximum densities are at 130 km, the lowest altitude observed. There, the maximum  $N_{\text{tot}}$  density is  $1.7 \times 10^3 \text{ cm}^{-3}$ , the maximum  $O_2^+$  density is  $8.7 \times 10^2 \text{ cm}^{-3}$ , and the maximum  $NO^+$  density is  $7.4 \times 10^2 \text{ cm}^{-3}$ . Hence,  $NO^+$  is a major ion in the nightside ionosphere and if there is a peak at lower altitudes, it will not be dominated by  $O_2^+$ .

The ratios between the night and day profiles in Figure 4c show that the densities of all five species are depleted compared to their dayside values, but the amount in which they are depleted varies with altitude. Above 200 km the night/day ratios of all species, except for  $CO_2^+$ , follow similar altitude trends and the nightside densities are 10–250 times smaller than on the dayside. Alternatively, below 200 km there are substantial differences between the day/night ratios of each species. For example, the  $O_2^+$  and  $CO_2^+$  ratios are nearly



**Figure 4.** (a) Dayside median density profiles from near the dusk terminator at SZAs between  $+75^\circ$  and  $+80^\circ$ . The different colors correspond to different ion species, and the dashed line is the total ion density. (b) Same as Figure 4a but showing nightside median density profiles from dusk SZAs between  $+110^\circ$  and  $+120^\circ$ . (c) The ratios between the nightside and dayside median density profiles, which illustrates how the densities decay across the terminator.

constant with altitude such that the nightside  $O_2^+$  densities are 5–100 times smaller than on the dayside and the nightside  $CO_2^+$  densities are more than 1000 times smaller than on the dayside. Alternatively, the  $O^+$  night/day ratios peak near 180 km then decrease rapidly at lower altitudes. The  $NO^+$  and  $HCO^+$  night/day ratios share similar altitude trends that are different than the other species. Their ratios increase with decreasing altitude and the nightside densities below 180 km are only 1–10 times smaller than on the dayside.

In summary, the ion densities decrease across the terminator with the largest variations occurring between SZAs  $85^\circ$ – $100^\circ$ , the region where EUV radiation diminishes rapidly and photoionization can no longer sustain the ionosphere. The  $O_2^+$  and  $CO_2^+$  densities decrease more rapidly across the terminator than the  $NO^+$  and  $HCO^+$  densities, especially at altitudes below 180 km. This causes the composition below 180 km to change from one that is primarily  $O_2^+$  on the dayside to one that is a variable mixture of  $O_2^+$ ,  $NO^+$ , and  $HCO^+$  on the nightside.

### 3.2. Ion Chemistry and Chemical Lifetimes

The different density variations across the terminator for each ion species can be interpreted in terms of ion chemistry, which controls each species' chemical lifetime and its ability to survive across the terminator [e.g., *Cui et al.*, 2009; *González-Galindo et al.*, 2013; *Fox et al.*, 2015]. In general, ions that are lost through reactions with neutrals will have short chemical lifetimes and ions lost through dissociative recombination (DR) with an electron will have long chemical lifetimes [*Cui et al.*, 2009].

The rapid decay of  $CO_2^+$  across the terminator suggests that it has a short chemical lifetime, which is consistent with model predictions [*Fox et al.*, 1993; *Haider*, 1997; *González-Galindo et al.*, 2013; *Chaufray et al.*, 2014; *Fox*, 2015]. The chemical lifetime of  $CO_2^+$  is short, because it is quickly destroyed by reactions with atomic oxygen that convert it into  $O^+$  and  $O_2^+$ , and a reaction with  $H_2$  that converts it into  $OCOH^+$ . Thus, at SZAs near the terminator and on the nightside where EUV radiation is diminished, there is no longer a photoionization source to replenish the  $CO_2^+$  ions and they quickly become a minor species.

The slow decay of  $NO^+$  and  $HCO^+$  suggests that these ions have long chemical lifetimes, which is also consistent with model predictions [*Haider*, 1997; *Krasnopolsky*, 2002; *González-Galindo et al.*, 2013; *Matta et al.*, 2013; *Chaufray et al.*, 2014; *Fox et al.*, 2015; *Fox*, 2015]. Both  $NO^+$  and  $HCO^+$  are predicted to be terminal ions with long chemical lifetimes, because they are produced by several ion-neutral reactions, but destroyed mainly through DR.  $NO^+$  is a terminal ion, because it has a low ionization potential, it has two major production sources [*Haider*, 1997; *González-Galindo et al.*, 2013]:



**Table 2.** Estimates of the Chemical Lifetimes of Several Species in the Nightside Ionosphere at 155 km and SZA > 130°<sup>a</sup>

Species	Density (10 <sup>2</sup> cm <sup>-3</sup> )	DR Coefficient (cm <sup>3</sup> s <sup>-1</sup> )	Chemical Lifetime (h)
NO <sup>+</sup>	0.5	$4.0 \times 10^{-7} (300/T_e)^{0.5}$	3.0
HCO <sup>+</sup>	0.5	$2.0 \times 10^{-7} (300/T_e)^{1.25}$	2.5
O <sub>2</sub> <sup>+</sup>	2.0	$2.4 \times 10^{-7} (300/T_e)^{0.7}$	2.7
e <sup>-</sup>	3.0		2.7

<sup>a</sup>For each species in column 1, column 2 lists its typical density at 155 km, column 3 its dissociative recombination (DR) coefficient, and column 4 its chemical lifetime. The lifetime for O<sub>2</sub><sup>+</sup> is an upper limit (see text). The DR coefficient for HCO<sup>+</sup> is from Fox [2015] and the others from Schunk and Nagy [2009]. We have adopted a value of  $T_e = 500$  K based on Fowler *et al.* [2015].

The larger night/day ratios of NO<sup>+</sup> below 180 km (Figure 4) are consistent with these production sources because at lower altitudes, O<sub>2</sub><sup>+</sup>, NO, and N densities are larger, making reactions (1) and (2) more efficient. Thus, the decay of NO<sup>+</sup> across the terminator is slow because O<sub>2</sub><sup>+</sup> is continuously being converted into NO<sup>+</sup> through reactions (1) and (2). This behavior is also consistent with the LMD general circulation model, which predicts that NO<sup>+</sup> is a major component of the lower nightside ionosphere, even in the absence of electron precipitation or winds [González-Galindo *et al.*, 2013; Chaufray *et al.*, 2014].

HCO<sup>+</sup> is a terminal ion because its parent neutral, CO, has a large proton affinity. It is produced by several ion-neutral reactions, all of which involve hydrogen-bearing neutral or ion species [Krasnopolsky, 2002; Matta *et al.*, 2013; Fox *et al.*, 2015; Fox, 2015]. Like NO<sup>+</sup>, the HCO<sup>+</sup> night/day ratios are larger at lower altitudes, suggesting that ion-neutral reactions are a production source on the nightside. However, unlike NO<sup>+</sup>, the HCO<sup>+</sup> nightside density profile and night/day ratios peak near 150 km and drop off rapidly below. This may indicate an additional HCO<sup>+</sup> loss process that becomes important below 150 km such as an ion-neutral reaction with atomic carbon [Fox, 2015].

The moderate decay of O<sub>2</sub><sup>+</sup> across the terminator suggests that it has a chemical lifetime that is longer than CO<sub>2</sub><sup>+</sup> but shorter than NO<sup>+</sup> or HCO<sup>+</sup>, which is also consistent with model predictions [Haider, 1997; González-Galindo *et al.*, 2013; Chaufray *et al.*, 2014; Fox *et al.*, 2015]. The two major production sources of O<sub>2</sub><sup>+</sup> are [Haider, 1997; Schunk and Nagy, 2009]



The total production rate of O<sub>2</sub><sup>+</sup> then is proportional to the CO<sub>2</sub><sup>+</sup> and O<sup>+</sup> densities. But on the nightside below 180 km, the CO<sub>2</sub><sup>+</sup> and O<sup>+</sup> densities are less than  $5.0 \times 10^0$  cm<sup>-3</sup> (Figure 4) and chemical production of O<sub>2</sub><sup>+</sup> should be minor. Without a chemical production source, O<sub>2</sub><sup>+</sup> should decrease steadily throughout the night as it is converted into NO<sup>+</sup> and lost through DR [González-Galindo *et al.*, 2013; Chaufray *et al.*, 2014; Fox *et al.*, 2015]. However, Figure 3 shows that O<sub>2</sub><sup>+</sup> densities at 155 km are nearly constant at SZAs between 130° and 160° and are also larger than NO<sup>+</sup> densities. This suggests that there is a source that replenishes nightside O<sub>2</sub><sup>+</sup> or that O<sub>2</sub><sup>+</sup> has a long chemical lifetime.

We can estimate the chemical lifetimes of species that are lost primarily through DR. These include NO<sup>+</sup>, HCO<sup>+</sup>, and electrons. The chemical lifetimes, summarized in Table 2, were estimated using  $t_i = N_i/L_i$ , where  $t_i$  is the lifetime,  $N_i$  is the ion density, and  $L_i$  is the total loss rate [Cravens *et al.*, 2009; Fox, 2009; Cui *et al.*, 2009]. For NO<sup>+</sup> and HCO<sup>+</sup> the total loss rate is given by  $L_i = \alpha_i N_i N_e$ , where  $\alpha_i$  is the DR coefficient listed in Table 2. For electrons, the total loss rate is the sum of the O<sub>2</sub><sup>+</sup>, NO<sup>+</sup>, and HCO<sup>+</sup> DR loss rates. To calculate each lifetime we have adopted typical nightside values of electron and ion densities at 155 km and SZAs > 130° (Figure 3). The typical values are listed in Table 2. Additionally, we have adopted a fixed electron temperature of  $T_e = 500$  K [Fowler *et al.*, 2015].

The chemical lifetimes of NO<sup>+</sup> and HCO<sup>+</sup> are both nearly 3 h. Their long lifetimes suggest that they may be remnants of plasma produced on the dayside rather than a product of electron precipitation or ion winds. If the ionosphere rotates as a solid body with the planet, then the source of nightside NO<sup>+</sup> and HCO<sup>+</sup> would

be the survival of dayside  $\text{NO}^+$  and  $\text{HCO}^+$  with additional production from the chemical conversion of dayside  $\text{CO}_2^+$  and  $\text{O}_2^+$  (from equations (1) and (2)). For  $\text{NO}^+$ , this is consistent with predictions from the LMD general circulation model [González-Galindo *et al.*, 2013].

Table 2 also includes an estimate of the  $\text{O}_2^+$  chemical lifetime which is nearly 3 h. This, however, is an upper limit because it assumes that  $\text{O}_2^+$  is lost only through DR and not through ion-neutral reactions with N and NO (equations (1) and (2)). Since the NGIMS nightside measurements of N and NO are not fully calibrated, we cannot present them here. Nevertheless, we can consider the amount of N or NO needed to significantly reduce the lifetime of  $\text{O}_2^+$ .

The  $\text{O}_2^+$  loss rate due to reaction (1) or (2) is given by  $L_i = k_i N_i n_i$  where  $k_i$  is the rate constant, which is on the order of  $10^{-10}$  ( $\text{cm}^3 \text{s}^{-1}$ ) [Schunk and Nagy, 2009], and  $n_i$  is the neutral density of either N or NO. For the time-scale of this loss process to be 3 h, the N or NO density at 155 km would need to be on the order of  $10^6 \text{ cm}^{-3}$ , which is close to the predicted dayside values at this altitude [Fox, 1993, 2015]. However, nightside N and NO densities may differ significantly than those on the dayside.

What N or NO density is required for the  $\text{O}_2^+$  ion-neutral loss rate to be comparable to the  $\text{O}_2^+$  DR loss rate? This threshold density for N or NO can be estimated by equating the  $\text{O}_2^+$  DR lifetime to the  $\text{O}_2^+$  ion-neutral lifetime, which gives  $n_{\text{thresh}} \approx 10^3 N_e$ . Thus, if N or NO densities exceed the electron density by a factor of  $10^3$  at a given altitude, then both DR and ion-neutral loss of  $\text{O}_2^+$  will be important. In such a scenario the chemical lifetime of  $\text{O}_2^+$  would be cut in half compared to its lifetime due to DR only. At 155 km, the  $\text{O}_2^+$  lifetime would be on the order of an hour. If N or NO densities exceed the electron density by an even greater factor of  $10^4$ , then DR loss of  $\text{O}_2^+$  would be negligible compared to ion-neutral loss. In that scenario the chemical lifetime of  $\text{O}_2^+$  would be 10 times shorter than the lifetime due to DR only. At 155 km the lifetime of  $\text{O}_2^+$  would only be several minutes.

Hence, without measurements of nightside N or NO we cannot be conclusive about the source of nightside  $\text{O}_2^+$  at large SZAs. If nightside N and NO densities are small, then the source of  $\text{O}_2^+$  may be the survival of day-side  $\text{O}_2^+$  with additional production from the chemical conversion of dayside  $\text{O}^+$  and  $\text{CO}_2^+$  (from equations (3) and (4)). Alternatively, if nightside N and NO densities are large, then  $\text{O}_2^+$  densities must be replenished more readily to survive at such large SZAs. This would require a source such as particle precipitation or day-to-night ion winds.

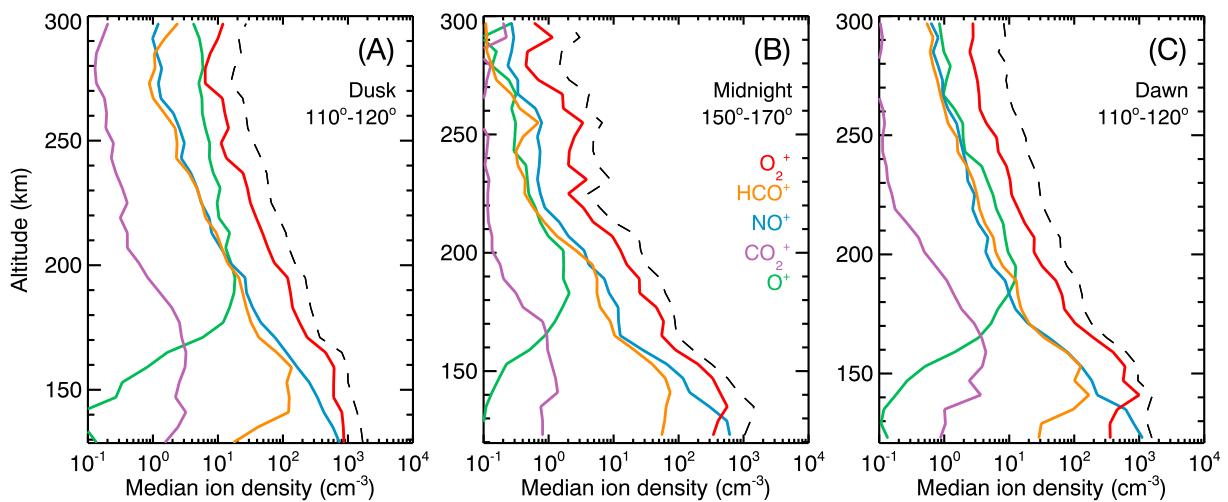
#### 4. Vertical Structure

In this section we present median ion density profiles from three different nightside SZA ranges and compare them to predictions from electron precipitation models. The SZA ranges include near the dusk terminator at SZAs between  $+110^\circ$  and  $+120^\circ$ , near the dawn terminator at SZAs between  $-110^\circ$  and  $-120^\circ$ , and near midnight at SZAs between  $-150^\circ$  and  $-170^\circ$ . In all three cases the median densities were calculated using 6 km altitude bins. The dawn and dusk profiles were constructed using all the data within the given SZA ranges. The midnight profiles were constructed using data from 38 orbits during the fourth set of nightside observations, which included the first NGIMS observations of the nightside composition at SZAs past  $155^\circ$ . These midnight observations were obtained at equatorial latitudes between  $-20^\circ$  and  $+20^\circ$ . The median density profiles for all three cases are shown in Figure 5.

The vertical structure of the density profiles are similar in all three cases. At high altitudes the topside densities decrease exponentially with altitude, but at lower altitudes there are broad peaks in the profiles of all species except for  $\text{NO}^+$ . The  $\text{O}^+$  profile peaks near 200 km while the  $\text{CO}_2^+$  profile peaks lower between 150 and 160 km. The  $\text{O}_2^+$  and  $\text{HCO}^+$  profiles peak even lower altitudes between 130 and 150 km, although the  $\text{O}_2^+$  peak is not distinct in the dusk or midnight profiles.

In all three cases the  $\text{NO}^+$  density profiles have no peak and continue to increase at lower altitudes down to 120 km, which was the lowest altitude observed. In the midnight and dawn profiles the  $\text{NO}^+$  density becomes larger than the  $\text{O}_2^+$  density between 130 and 140 km. In the dusk profile,  $\text{NO}^+$  never overtakes  $\text{O}_2^+$ , but near 120 km their densities are nearly equal and the trend suggests that  $\text{NO}^+$  overtakes  $\text{O}_2^+$  at a lower altitude.

As mentioned in section 3.2, the LMD General Circulation model predicts that  $\text{NO}^+$  is a major component of the lower nightside ionosphere, even in the absence of electron precipitation or winds [González-Galindo *et al.*, 2013; Chaufray *et al.*, 2014]. In the model the source of the nightside  $\text{NO}^+$  is survival of dayside  $\text{NO}^+$  and the chemical conversion of dayside  $\text{CO}_2^+$  and  $\text{O}_2^+$  (equations (1) and (2)).



**Figure 5.** Nightside median density profiles from dawn, dusk, and near midnight. The different colors represent different ion species and the dashed line is the total ion density. (a) Dusk SZAs between  $+110^\circ$  and  $+120^\circ$ . (b) Near-midnight SZAs between  $-150^\circ$  and  $-170^\circ$ . (c) Dawn SZAs between  $-110^\circ$  and  $-120^\circ$ .

Now we discuss how these median density profiles compare to predictions from particle precipitation models. We caution that a direct comparison is limited because our median profiles are derived from observations that cover all longitudes and several latitudes over long periods of time. Thus, they represent temporal and spatial averages over which the precipitation source may vary significantly. Particle precipitation models, however, are often based on single events during which one particle energy spectrum is injected into the atmosphere [e.g., *Fox et al.*, 1993; *Haider*, 1997] or based on particle energy spectra averaged over long periods of time [e.g., *Lillis et al.*, 2011]. Moreover, the energy spectra and neutral atmospheres used in the models may differ from the conditions during the NGIMS observations. Nevertheless, we wish only to compare the major features.

Electron precipitation models predict peaks in the  $O_2^+$  and  $N_{tot}$  density profiles between 140 and 180 km, below which the densities decrease rapidly toward lower altitudes [*Fox et al.*, 1993; *Haider*, 1997; *Fillingim et al.*, 2007; *Lillis et al.*, 2009, 2011; *Haider et al.*, 2013]. These peaks are not distinct in our median profiles. However, our detection of the peak is limited due to the spatial and temporal averaging and because most of the NGIMS observations are from altitudes at and above 150 km where the peak is expected to be. Nevertheless, the  $O_2^+$  profiles do appear to have broad peaks in the predicted altitude range suggesting at least some consistency between the predictions and the observations.

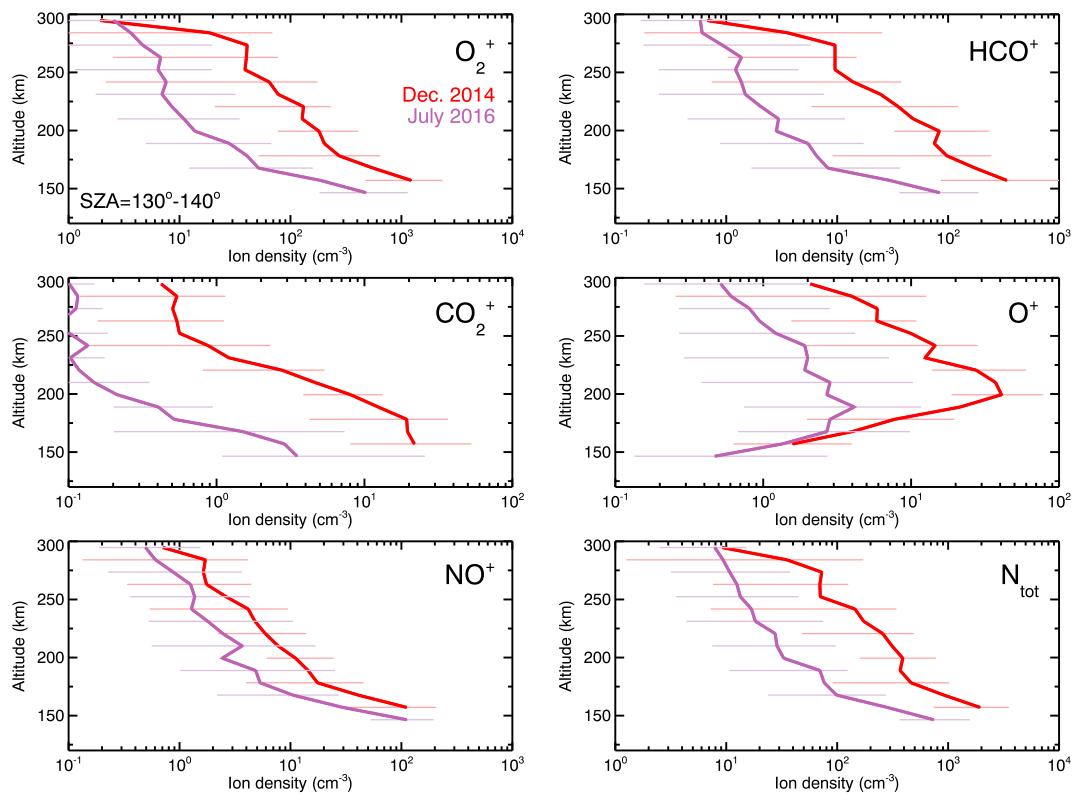
Precipitation models also predict peak  $CO_2^+$  densities on the order of  $10^2 \text{ cm}^{-3}$  near 150 km [*Fox et al.*, 1993; *Haider*, 1997; *Haider et al.*, 2013]. This peak is observed as a broad feature in our median profiles but the peak densities are smaller, on the order of a few  $10^0 \text{ cm}^{-3}$ . The small  $CO_2^+$  peak densities are partly due to our use of medians rather than averages. For example, at 155 km the median  $CO_2^+$  density at midnight is  $\sim 10^0 \text{ cm}^{-3}$  but the average is  $\sim 10^1 \text{ cm}^{-3}$ . Although the average is larger than the median, it is still an order of magnitude smaller than predicted by precipitation models. Such small nightside  $CO_2^+$  densities may suggest that particle precipitation is sporadic.

Electron precipitation models also predict a peak in the  $NO^+$  density profile between 130–150 km [*Fox et al.*, 1993; *Haider*, 1997; *Haider et al.*, 2013]. This peak is absent in our median density profiles where  $NO^+$  densities increase with decreasing altitude down to at least 120 km. Taken as a whole, electron precipitation models fail to predict this behavior, which may suggest that the major source of nightside  $NO^+$  is day-to-night transport.

Precipitation models can still be improved as they typically assume chemical equilibrium and neglect vertical diffusion and transport processes which may be important at these altitudes on the nightside. Precipitation models that include improved constraints based on MAVEN data will be useful for investigating the extent in which particle precipitation can explain the composition of the nightside ionosphere.

## 5. Variability

In this section we show that the nightside ionosphere can vary substantially at different latitudes and seasons. We begin by comparing median ion density profiles from the first and fourth periods of observations.



**Figure 6.** A comparison of the Median ion densities profiles from SZAs  $-130^\circ$  to  $-140^\circ$  during two different periods of nightside observations. The red density profiles are from December 2014 at high northern latitudes. The purple density profiles are from July 2016 at equatorial latitudes. The error bars show the 25% and 75% quartiles.

These periods were chosen because they contain the only measurements made well into the nightside at SZAs greater than  $130^\circ$ . The first set of observations is from high northern latitudes ( $+60^\circ$  to  $+75^\circ$ ) during winter and the second set is from equatorial latitudes ( $-10^\circ$  to  $+30^\circ$ ) during spring equinox (Table 1).

To construct the median density profiles, we grouped the data by observation period, keeping only data with SZAs between  $-130^\circ$  and  $-140^\circ$  to ensure that the altitude-SZA distribution of the two periods were similar. Then we separated the data into 10 km altitude bins and calculated the  $O_2^+$ ,  $HCO^+$ ,  $NO^+$ ,  $CO_2^+$ ,  $O^+$ , and  $N_{tot}$  median densities, as well as the 25%/75% quartiles within each bin. The median density profiles are shown in Figure 6.

The vertical structure of each density profile is similar during both periods of observations, but during the first period the densities are several times larger (red). The total ion densities and  $O_2^+$  densities are  $\sim 8$  times larger, the  $HCO^+$  densities are  $\sim 15$  times larger, and the  $O^+$  peak density is  $\sim 10$  times larger. The  $CO_2^+$  densities are  $10\text{--}40$  times larger and, interestingly,  $NO^+$  densities are only  $\sim 3$  times larger.

There are several possibilities for the larger nightside densities during the first period of observations. During this period the solar EUV irradiance was largest, which may indicate that nightside densities increase with increasing solar activity. Another possibility is that the higher densities are due to polar warming. The first period of observations are from high northern latitudes during winter. Northern polar temperatures are warmer during this season as a result of enhanced interhemispheric circulation [Bougher et al., 2006; Bell et al., 2007; González-Galindo et al., 2009; Bougher et al., 2015]. This enhanced circulation may increase the efficiency of day-to-night ion transport resulting in larger nightside densities.

Alternatively, a more plausible explanation may be that the larger nightside densities were the result of a period of enhanced particle precipitation. The first period of observations covered the full month of December 2014, during which the MAVEN Solar Energetic Particle (SEP) instrument [Larson et al., 2015] detected an extended event of energetic electron fluxes [Lee et al., 2017]. These energetic electrons are expected to produce significant ionization at these altitudes [e.g., Sheel et al., 2012] and MARSIS observations show that

nightside densities are enhanced during SEP events [Némec *et al.*, 2014]. This SEP event also produced the so-called “Christmas Lights” aurora event in the northern hemisphere [Schneider *et al.*, 2015].

As our goal here is to characterize the major features in the nightside ionosphere, we refrain from detailed modeling of the nightside ionosphere during such a SEP event. Nevertheless, we have shown that the median nightside ion densities from monthlong time periods at different latitudes and seasons can vary by nearly an order of magnitude. Additionally, the density variations are not uniform by species. In particular, the  $\text{NO}^+$  densities are only a factor of  $\sim 3$  larger during the first period of observations, which is smaller than all other species. Such a small change in the  $\text{NO}^+$  may be related to variations in neutral N and NO densities since the main source of  $\text{NO}^+$  is through ion-neutral reactions between  $\text{O}_2^+$ , N, and NO (equations (1) and (2)).

## 6. Summary and Conclusions

Using in situ observations from the MAVEN Neutral Gas and Ion Mass Spectrometer we have characterized the composition, vertical structure, and variability of the nightside ionosphere of Mars. We showed that below 200 km the SZA variations of  $\text{CO}_2^+$  and  $\text{O}_2^+$  across the terminator are more rapid than those of  $\text{NO}^+$  and  $\text{HCO}^+$ , which changes the composition from one that is primarily  $\text{O}_2^+$  on the dayside to one that is a variable mixture of  $\text{O}_2^+$ ,  $\text{NO}^+$ , and  $\text{HCO}^+$  on the nightside. This change in the composition is driven by ion-neutral chemistry, which—in the absence of a strong and continuous photoionization source—increases the relative abundances of species with long chemical lifetimes. In the ionosphere of Mars these species are  $\text{NO}^+$  and  $\text{HCO}^+$ .

The composition of the nightside ionosphere is more of a mixture of ions than on the dayside, where below 200 km  $\text{O}_2^+$  is the dominant species with a relative abundance of at least  $\sim 80\%$ . On the nightside above 150 km, however, the relative abundance of  $\text{O}_2^+$  is only  $\sim 60\%$ . Furthermore, on the nightside below  $\sim 130$  km,  $\text{NO}^+$  overtakes  $\text{O}_2^+$  as the most abundant species. Thus, the assumption that the  $\text{O}_2^+$  density is equal to the electron density—which is often employed to simplify calculations—is not justified in the lower nightside ionosphere.

The densities of  $\text{O}_2^+$  are sustained long into the night which may indicate that  $\text{O}_2^+$  is replenished through transport or precipitation. However, the rate at which  $\text{O}_2^+$  needs to be replenished to sustain these densities depends critically on the amount of N and NO in the nightside thermosphere, both of which are poorly constrained by observations. This is because the rate at which  $\text{O}_2^+$  is converted into  $\text{NO}^+$  is proportional to the N and NO densities (equations (1) and (2)). Future constraints on nightside N and NO will be useful for determining the extent in which particle precipitation and day-to-night ion transport supply the nightside ionosphere with  $\text{O}_2^+$ .

The vertical structure of the nightside ionosphere is somewhat consistent with predictions from electron precipitation models. However, the observations show that the  $\text{NO}^+$  density increases with decreasing altitude down to at least 120 km. This behavior presents a challenge to particle precipitation models which predict that the  $\text{NO}^+$  density should peak at higher altitudes and decrease rapidly below [e.g., Fox *et al.*, 1993; Haider, 1997; Fillingim *et al.*, 2007; Haider *et al.*, 2013]. Large  $\text{NO}^+$  densities in the lower nightside ionosphere are predicted, however, by the LMD general circulation model, even without precipitation or winds [González-Galindo *et al.*, 2013; Chaufray *et al.*, 2014]. This suggests that  $\text{NO}^+$ , which has a chemical lifetime of several hours, may be easily transported from the dayside.

We have also shown that nightside ion densities vary by nearly an order of magnitude over small time and spatial scales as well as over monthlong periods. Densities were largest at high northern latitudes during northern winter. Such large densities may be caused by enhanced day-to-night ion circulation associated with polar warming or enhanced electron precipitation due to an extended solar energetic particle event during that time.

In summary, the enhanced relative abundances of  $\text{NO}^+$  and  $\text{HCO}^+$  in the nightside ionosphere are consistent with our knowledge of the ion-neutral chemistry at Mars. However, the contributions from the different nightside ion sources—particle precipitation, day-to-night ion winds, and the chemical survival of dayside plasma—need to be constrained in more detail. Such a task will become attainable as MAVEN continues to monitor the nightside ionosphere under different conditions. Continued monitoring will also be useful for exploring the drivers of the nightside variability which may be linked to crustal magnetic field conditions, ion circulation patterns, thermospheric conditions, and changes in the energetic particle environment.

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