Abnormal Dawn–Dusk Asymmetry of Protonated Ions in the Martian Ionosphere

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Abstract

Normally, the Martian ionosphere displays a dusk enhancement due to continuous depletion of plasma via recombination during day-to-night transport. Using the extensive measurements made by the Neutral Gas and Ion Mass Spectrometer on board the Mars Atmosphere and Volatile Evolution spacecraft, we show that several species, including H2, OH+, H2O+, and NH+, present instead an abnormal dawn enhancement above the exobase where they are mainly produced by ion-neutral reactions involving H2. Such a peculiarity is indicative of a dawn bulge of H2 present in the Martian upper atmosphere and corona, which is driven by subsidence in regions of horizontal wind convergence and the subsequent buildup of minor atmospheric species with large vertical scale heights. A similar dynamical process is also known to occur in the upper atmospheres of other solar system bodies such as the Earth, Venus, and Titan. Interestingly, despite that the diurnal variations of O and N are subject to the same dynamical effect, a dawn enhancement is not seen for O+ and N+, possibly due to the nonthermal production of their parent atoms in the ambient atmosphere via processes such as photodissociation and dissociative recombination. The H2 distribution inferred in this study is important for a thorough understanding of hydrogen escape and climate evolution on Mars.

Unified Astronomy Thesaurus concepts: Solar system astronomy (1529); Solar system planets (1260); Solar system (1528); Inner planets (797); Mars (1007); Atmospheric variability (2119); Atmospheric composition (2120); Upper atmosphere (1748); Aeronomy (22); Atmospheric science (116); Planetary science (1255); Planetary atmospheres (1244)

1. Introduction

Each planet with a substantial atmosphere also contains an ionosphere composed of equal amounts of free ions and electrons (Witasse et al. 2008, and references therein). On the dayside, the Martian ionosphere contains a well-defined primary layer and a low-altitude secondary layer, which are mainly produced by solar extreme ultraviolet and X-ray ionization along with impact ionization by photoelectrons and their secondaries (Withers 2009; Haider & Mahajan 2014, and references therein). Near the primary peak, it is reasonably described by the idealistic Chapman theory under photochemical equilibrium (e.g., Mendillo et al. 2015, 2017). On the nightside, the Martian ionosphere is highly variable and generally thought to be contributed by either solar wind electron precipitation or day-to-night plasma transport (e.g., GirAZian et al. 2017a, 2017b; Cui et al. 2019a).

Previous studies of the Martian ionosphere largely relied on the electron density profiles extracted from the Mars Advanced Radar for Subsurface and Ionospheric Sounding measurements made by the Mars Express (MEs; Gurnett et al. 2008) and the Radio Occultation measurements made by both the Mars Global Surveyor (Tyler et al. 2001) and the MEs (Pätzold et al. 2016). Knowledge of the ion composition and distribution was generally not available except for several ion density profiles measured by the Viking Retarding Potential Analyzer on the dayside of Mars (Hanson et al. 1977). This situation has been significantly improved by the Mars Atmosphere and Volatile Evolution (MAVEN) mission (Jakosky et al. 2015) with its Neutral Gas and Ion Mass Spectrometer (NGIMS) providing, in the Open Source Ion (OSI) mode, a wealth of information on the densities of many important species of the Martian ionosphere covering a broad mass range of 2–150 Da (Mahaffy et al. 2015b).

The full coverage of the available NGIMS data set allows the diurnal variation of the Martian ionosphere to be explored in detail. Of particular interest is the discovery of an enhanced dusk ionosphere over the dawn one (GirAZian et al. 2017b), which could be interpreted as the continuous depletion of ionospheric plasma via recombination as Mars rotates into the darkness. Such a day-to-night transport scenario was further supported by a more pronounced dusk enhancement for long-lived ions such as NO+ as compared to short-lived ones such as CO2+ (GirAZian et al. 2017b), quite analogous to the situation occurring in the ionosphere of Titan (Cui et al. 2009). The dawn–dusk asymmetry has also been shown to be modulated by the ambient magnetic field configuration (Cao et al. 2019).

In this study, we show further that the dawn–dusk asymmetry first reported by GirAZian et al. (2017b) is not necessarily a general feature of the Martian ionosphere and that several protonated ion species present instead an abnormal dawn enhancement. The observations reported here provide important clues to the variability of H2 in the Martian upper atmosphere and corona, of which available measurements are extremely limited (e.g., Krasnopolsky & Feldman 2001).
2. Observations of Dawn–Dusk Asymmetry in the Ionosphere

Our analysis relies exclusively on the NGIMS OSI data accumulated from the arrival of MAVEN at Mars on 2014 September 21 to 2019 May 14, covering mostly low to moderate solar activity conditions. Benna et al. (2015) reported the detection of dozens of species in the Martian ionosphere, from O₂⁺ and O⁺ as the two most abundant species to trace species such as He⁺ and ArH⁺. The diurnal variations of 12 selected species are compared in Figure 1, covering the altitude range of 150–400 km. For a better view of the dawn–dusk asymmetry, we show further in Figure 2 the density variations of the same species as a function of local time and at different altitudes, either 300 km (solid) or 180 km (dashed) depending on whether a distinctive layer structure is observable over the altitude range examined in this study. A strong dawn enhancement is observed for each species in the middle panel. Note that the HNO⁺ density has been everywhere divided by 100 to improve visibility.

Figure 1. Density variations of 12 selected species in the Martian ionosphere as a function of local time, over the altitude range of 150–400 km based on the available MAVEN NGIMS measurements. A strong dawn enhancement is observed for each species in the middle row, in contrast to the normal dusk enhancement expected by the continuous depletion of ionospheric ions during day-to-night transport (Girazian et al. 2017b).

Figure 2. Density variations of the same species as in Figure 1 as a function of local time and at fixed altitudes, either 300 km (solid) or 180 km (dashed) depending on whether a distinctive layer structure is observable over the altitude range examined in this study. A strong dawn enhancement is observed for each species in the middle panel. Note that the HNO⁺ density has been everywhere divided by 100 to improve visibility.
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Withers et al. 2019; Wu et al. 2019), will not be considered in this study.

The four species in the top row of Figure 1 or the left panel of Figure 2, including O_2, O^+, NO^+, and N^+, present a normal dawn–dusk asymmetry analogous to the one reported by Girazian et al. (2017b), in that the observed ion distribution extends further into the darkness at the dusk terminator as compared to the dawn terminator. In contrast, the four species in the middle row of Figure 1 or the middle panel of Figure 2, including OH^+, H_2O^+, NH^+, and H_3^+, present an opposite pattern of dawn–dusk asymmetry in the form of a distinctive density bulge early in the morning. Note that the distribution of H_3^+ witnesses a secondary peak near 160 km, a feature that has also been predicted by existing photochemical models (e.g., Fox et al. 2015). The dawn bulge in this species is actually seen near both peaks.

According to Figure 1, the abnormal dawn enhancement in ion density appears to be restricted to the high-altitude regions only. However, there are also exceptions such as O^+ and N^+ in that their vertical distributions are both peaked at around 300 km (e.g., Girazian et al. 2019) but their diurnal variations are still characterized by the normal dusk enhancement. In addition, we note that all species in the middle row of Figure 1 are protonated, to be distinguished from those in the top row. For further demonstration, we show in the bottom row of the same figure several additional protonated species, including HCO^+/N_2H^+, OCCHO^+, HO_2^+, and HNO^+. Note that HCO^+ and N_2H^+ cannot be distinguished by the NGIMS due to their equality in mass per charge (ignoring HOC^+ due to its greater heat of formation). Interestingly, the diurnal variations of these additional protonated species are still characterized by the normal dusk enhancement as the unprotonated ones. However, they are to be distinguished from the protonated species with clear dawn enhancement in that these ions are primarily distributed at relatively low altitudes and their density peaks are located below 150 km.

Combining the above observations, we may draw the tentative conclusion that any species with a clear dawn enhancement in the Martian ionosphere should be protonated and at the same time should have a vertical distribution peaked well above the exobase.

3. Inference of a Dawn Bulge of H_2 in the Upper Atmosphere and Corona

The normal dusk enhancement reported by Girazian et al. (2017b) in the Martian ionosphere, which has also been discovered on Titan (Cui et al. 2009), is a natural result of continuous depletion of ionspheric plasma as Mars rotates into the darkness. Such an enhancement is more prominent for long-lived ion species such as NO^+ due to its replenishment via the reactions of O_2 with odd N species during day-to-night transport (González-Galindo et al. 2013). Related observations have been extensively discussed in Girazian et al. (2017b) and Cao et al. (2019). We focus here on the interpretation of the abnormal dawn enhancement.

The observation of dawn enhancement is persistent to protonated species peaked at high altitudes, motivating us to connect it to the possible existence of a dawn bulge of H_2 in the Martian upper atmosphere and corona. The chemistry of protonated species in the Martian ionosphere is well documented by Fox et al. (2015). Near and above 300 km, the Martian atmosphere is dominated by H_2 due to diffusive separation despite that its distribution has not been accurately characterized (e.g., Krasnopolsky & Feldman 2001). At such altitudes, the formation of the four protonated species in Figure 1 with clear dawn enhancement occurs mainly via proton transfer reactions:

\[ O^+ + H_2 \rightarrow OH^+ + H_2, \]  
\[ OH^+ + H_2 \rightarrow H_2O^+ + H_2, \]

and

\[ N^+ + H_2 \rightarrow NH^+ + H, \]

as well as H_2 photoionization for H_3^+ production. In all cases, the diurnal variation of H_2 controls the diurnal variations of the protonated ion species. Enhanced chemical loss of these species, which also occurs via reactions with H_2, does not necessarily counterbalance the effect of enhanced production, because within such tenuous regions of the Martian atmosphere, diffusion becomes more important than chemical loss (e.g., Mendillo et al. 2011; Cravens et al. 2017; Wu et al. 2019). Following the above line of reasoning, several other protonated species such as H_3^+, H_2O^+, ArH^+, and CH^+ (Benna et al. 2015), which are also peaked at high altitudes, may display a similar dawn enhancement. Unfortunately, the abundances of these species are typically too low to allow a rigorous determination of their diurnal variations.

At relatively low altitudes, the Martian atmosphere is dominated by CO_2 and O rather than by H_2 (Mahaffy et al. 2015a). Because the dominant production channels of many protonated ion species, including those in the bottom row of Figure 1, are ion-neutral reactions involving CO_2 and O, the diurnal variations of these species are not sensitive to the H_2 distribution. Instead their diurnal variations should be characterized by the normal dusk enhancement driven by the continuous depletion of ionspheric plasma during day-to-night transport (Girazian et al. 2017b), as indeed revealed by the NGIMS data. Special concern should be placed on H_3^+, which shows a significant dawn enhancement at both low and high altitudes in Figure 1. This must be due to its production via H_2 photoionization at all altitudes displayed in the figure, implying a persistent impact of H_2 distribution on the dawn–dusk asymmetry of H_3^+.

Finally, we caution that H_2O^+ and OH^+ could also be produced from the photoionization of H_2O in the Martian upper atmosphere and corona. Historically, atmospheric H_2O is thought to be confined to low altitudes by cold trapping at the hygropause, but recent observations suggest that H_2O is able to reach the middle and upper atmosphere, especially during planet-encircling dust storms (e.g., Vandevele et al. 2019). Despite this, the H_2O abundance is probably too low to produce a substantial amount of water group ions at the altitudes investigated here (e.g., Fox et al. 2015).

4. Discussions

It is well known that in the terrestrial upper atmosphere, horizontal winds due to pressure gradients drive subsidence in regions of convergence and buildup of light species due to their large vertical scale heights (e.g., Reber & Hays 1973). Similar structures have also been observed beyond the Earth, such as the He and H enhancements at the nighttime of Venus (e.g., Brinton et al. 1980; Chaufray et al. 2015a), the CH_4 and H_2 enhancements in the polar regions of Titan (Müller-Wodarg
et al. 2008), and more recently the He enhancement both at the nighttime and in the polar regions of Mars (Elrod et al. 2017). Motivated by the diurnal variation of neutral temperature reported by Stone et al. (2018, see their Figure 15), we propose that a similar dynamical process is responsible for the inferred H$_2$ enhancement early in the morning.

On Mars, H$_2$ is produced by the reaction of H with the minor species HO$_2$ in the middle atmosphere (Krasnopolsky 1993), followed by diffusion into the upper atmosphere where it affects substantially the ionospheric chemistry and composition (e.g., Fox 2003; Matta et al. 2013). The H$_2$ distribution in the Martian upper atmosphere and corona has been calculated by Chaufray et al. (2015b) using a sophisticated three-dimensional atmosphere–exosphere coupling model. Their calculation indeed reveals the presence of a substantial dawn bulge of H$_2$, especially during the equinoxes. An improved model by the same authors that self-consistently accounts for lateral transport above the Martian exobase essentially reproduces the earlier results, though the modeled diurnal variation is somewhat reduced (Chaufray et al. 2018).

Our analysis presented so far does not distinguish between different seasons. For further demonstration, we show in Figure 3 the diurnal variation of H$_2^+$ as a proxy of the diurnal variation of H$_2$, for different ranges of solar longitude, $L_s$. Regions containing less than 10 individual NGIMS measurements are deemed as statistically unreliable and are color coded by black.

![Figure 3. Density variation of H$_2^+$ in the Martian ionosphere as a function of local time and over the altitude range of 150–400 km, for four different ranges of solar longitude, $L_s$. Regions containing less than 10 individual NGIMS measurements are deemed as statistically unreliable and are color coded by black.](image)

Distinctive features of H$_2$ distribution suggested by both NGIMS data analysis and model calculation include (1) a pronounced dawn enhancement during the northern spring equinox, (2) a more symmetric distribution during the northern summer solstice, and (3) the extension of the bulge into the midnight during the northern winter solstice. The H$_2$ distribution during the northern fall equinox is presently unconstrained due to limited data coverage.

As expected by the aforementioned dynamical process, an extra ion species that likely displays a dawn enhancement is He$^+$, which is produced by He photoionization and obviously linked to the observation of a dawn bulge of He in the Martian upper atmosphere and corona (Elrod et al. 2017, see their Figure 1). The diurnal variation of He$^+$ is presented in Figure 4 based on the available NGIMS measurements, confirming our expectation.

In contrast, both O$^+$ and N$^+$ in Figure 1 show the normal dusk enhancement expected by continuous depletion during day-to-night transport (Girazian et al. 2017b; Cao et al. 2019). This is apparently in conflict with a similar dawn enhancement of their parent atoms, also formed in response to subsidence in regions of horizontal flow convergence (e.g., Valeille et al. 2009a, 2009b, 2010; Yagi et al. 2012). Such a conflict could be resolved by noting that with increasing altitude above the exobase, the O and N densities should have an increasing contribution from hot neutrals produced by nonthermal
processes such as dissociative recombination (DR) or photodissociation (e.g., Lillis et al. 2017; Cui et al. 2019b). For instance, the model calculation of Valeille et al. (2010) predicts that hot O atoms from O$_2^+$ DR become more abundant than the cold ones above 350–400 km. At these altitudes, the diurnal variation of O$^+$ should more closely follow the diurnal variation of O$_2^+$ rather than the dynamically controlled variation of cold O. As for H$_2$ and He, we may further expect that their corona structures on Mars are likely well described by a single cold component. It is of relevance to remind that the presence of a hot component in the Martian H corona has not been confirmed by the Lyman $\beta$ observation carried on board the Rosetta (Feldman et al. 2011).

5. Concluding Remarks

The distribution of hydrogen in the Martian upper atmosphere and corona, in the form of both H and H$_2$, is crucial to a proper understanding of climate evolution on the planet from a warm, wet early state to a cold, arid present state (e.g., Chaffin et al. 2014, 2017). Direct measurements of these species are limited and provide column integrated abundances only (e.g., Krasnopolsky & Feldman 2001; Chaufray et al. 2008; Chaffin et al. 2015). Accordingly, the density trends of H and H$_2$ have been indirectly derived from observations of X-ray emission (e.g., Dennerl 2002), energetic neutral particles (Galli et al. 2008), and cyclotron waves (Bertucci et al. 2013). We show in this study that the ionospheric distribution of several protonated species could also be used to infer the ambient hydrogen distribution.

Based on the available MAVEN NGIMS measurements of a large number of ionospheric species, we present a systematic investigation of their diurnal variations, in terms of the dawn–dusk asymmetry, over the altitude range of 150–400 km. The normal dusk enhancement is observed for the majority of ion species, analogous to the asymmetry reported by Girazian et al. (2017b) and interpreted as a natural result of continuous depletion of ionospheric plasma during day-to-night transport. However, a number of species, including H$_3^+$, OH$^+$, H$_2$O$^+$, and NH$^+$, show clear evidence for an abnormal dusk enhancement.

At the altitudes where the dawn enhancement is witnessed, these protonated species are mainly produced from ion-neutral reactions involving H$_2$, implying that their diurnal variations are likely linked to the presence of a substantial dawn bulge of H$_2$ in the Martian upper atmosphere and corona as predicted by existing model calculations (Chaufray et al. 2015b, 2018). In contrast, heavier protonated species, such as HCO$^+$ and HNO$^+$, are peaked at low altitudes where they are mainly produced from ion-neutral reactions involving CO$_2$ or O. The diurnal variations of these species are hence not sensitive to the ambient H$_2$ distribution and present the normal dusk enhancement.

Motivated by similar phenomena on other terrestrial bodies (e.g., Reber & Hays 1973; Brinton et al. 1980; Müller-Wodarg et al. 2008; Chaufray et al. 2015a), the inferred H$_2$ bulge could be interpreted as a result of subsidence in regions of horizontal flow convergence, which causes the buildup of minor species with large vertical scale heights. An analogous dawn enhancement is also seen for He$^+$, consistent with the observation of a dawn bulge of parent He in the Martian upper atmosphere and corona (Elrod et al. 2017). However, the O and N densities in the Martian corona have a substantial contribution from hot neutrals produced by DR and photodissociation, indicating that the diurnal variations of O$^+$ and N$^+$ do not follow closely the dynamically controlled variations of cold O and N (Valeille et al. 2009a, 2009b, 2010).

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References
Benna, M., Mahaffy, P. R., Grebowsky, J. M., et al. 2015, GeoRL, 42, 8958
Bertucci, C., Romanelli, N., Chaufray, J. Y., et al. 2013, GeoRL, 40, 3809
Brinton, H. C., Taylor, H. A., Niemann, H. B., et al. 1980, GeoRL, 7, 865
Cao, Y. T., Cui, J., Wu, X. S., Guo, J. P., & Wei, Y. 2019, JGRE, 124, 1495
Chaffin, M. S., Chaufray, J. Y., Deighan, J., et al. 2015, GeoRL, 42, 9001
Chaffin, M. S., Chaufray, J.-Y., Stewart, I., et al. 2014, GeoRL, 41, 314
Chaffin, M. S., Deighan, J., Schneider, N. M., & Stewart, A. I. F. 2017, NatGe, 10, 174
Chaufray, J. Y., Bertaux, J. L., Leblanc, F., & Quémerais, E. 2008, Icar, 195, 598
Chaufray, J. Y., Bertaux, J. L., Quémerais, E., Leblanc, F., & Sulis, S. 2015a, Icar, 262, 1
Chaufray, J. Y., Gonzalez-Galindo, F., Forget, F., et al. 2015b, Icar, 245, 282
Chaufray, J. Y., Yelle, R. V., Gonzalez-Galindo, F., et al. 2018, JGRA, 123, 2441
Cravens, T. E., Hamil, O., Houston, S., et al. 2017, JGRA, 122, 10626
Cui, J., Cao, Y. T., Wu, X. S., et al. 2019a, ApJL, 876, L12
Cui, J., Galand, M., Yelle, R. V., et al. 2009, JGRA, 114, A06310
Cui, J., Wu, X. S., Gu, H., Jiang, F. Y., & Wei, Y. 2019b, A&A, 621, A23
Dennerl, K. 2002, A&A, 394, 1119
Elrod, M. K., Bougher, S., Bell, J., et al. 2017, JGRA, 122, 2564
Feldman, P. D., Steffl, A. J., Parker, J. W., et al. 2011, Icar, 214, 394
