



The chemistry of protonated species in the martian ionosphere



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ARTICLE INFO

Article history:

Received 1 July 2014

Revised 9 November 2014

Accepted 13 January 2015

Available online 29 January 2015

Keywords:

Mars, atmosphere

Ionospheres

Aeronomy

Abundances, atmospheres

ABSTRACT

The Mars Atmosphere and Volatile Evolution Mission (MAVEN) spacecraft entered orbit around Mars on 22 September 2014. The Neutral Gas Ion Mass Spectrometer (NGIMS) instrument on this spacecraft will measure the ion densities with unprecedented sensitivity of $\sim 1 \text{ cm}^{-3}$ above the nominal periapsis altitude $\sim 150 \text{ km}$. The upper region of the martian ionosphere consists of a suite of ions that have been modeled many times, and several protonated species, for which there are fewer models. We model here the density profiles for 14 major ions that have been modeled previously and 10 additional protonated species, which include the most important 4 species, HCO^+ , OCOH^+ , OH^+ , and N_2H^+ , with smaller densities of several minor species, including H_2^+ , H_3^+ , HO_2^+ , HNO^+ , ArH^+ , and CH^+ . To the ~ 220 reactions that were already in our ionospheric models, we add ~ 75 reactions that are of relevance to protonated species, including ion–molecule reactions and dissociative recombination reactions. These reactions also largely complete the chemistry of thermospheric H and H_2 , which we also show. We first discuss the chemistry of protonated species in general, and then we justify our choices for the rate coefficients of the reactions that we add here. We then describe the major production and loss mechanisms for the four major protonated species. Finally we present density profiles for all 10 protonated species that we consider here for low and high solar activity models, and show that most of their peak densities are anticorrelated with solar activity. This will confer an advantage to the MAVEN mission, which will enter the ionosphere during a period of declining solar activity. We compare our model to two previous models, and show that there are significant differences between them. The results presented here will provide a guide for the mass settings on the NGIMS instrument.

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1. Introduction

That even a small abundance of H_2 in the thermosphere of Mars can have a profound effect on the density profiles of the major ions, and therefore on atmospheric evolution processes was shown by Fox (2001). The abundance of H_2 at the time of the presentation by Fox (2001) and the submission of the manuscript of Fox (2003) had been determined only by models, and the predicted abundances in the lower thermosphere varied from 7.5 ppm to 56 ppm (e.g., Kong and McElroy, 1977; Anderson, 1974; Rodrigo et al., 1990; Krasnopolsky, 1993; Nair et al., 1994; Krasnopolsky et al., 1998). As we will show, however, some of these models were based on assumptions that are no longer valid. The most recent model of the H_2 mixing ratio at the time was that of Krasnopolsky et al. (1998), who computed an abundance of 40 ppm. Fox (2001, 2003) showed that the O^+ density profile measured by the Retarding Potential Analyzer (RPA) on the Viking 1 lander (Hanson et al., 1977) could not be reproduced with such large H_2 mixing ratios.

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On 12 July 2001, Krasnopolsky and Feldman (2001a) reported measurements of the intensities of 14 emission lines of the $\text{H}_2(B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+)$ Lyman band system from Mars in spectra taken by the Far Ultraviolet Spectroscopic Explorer (FUSE). These measurements were made on 12 May 2001, a time of moderate solar activity, when $F_{10.7}$ at Earth was 141, and, since the Mars–Sun–Earth angle at the time was $\sim 16^\circ$, Mars and Earth faced nearly the same side of the Sun. The FUSE instrument, which was used to observe various emission sources over the spectral range 905–1187 Å with 0.2 Å resolution, has been described in detail by Moos et al. (2000). The H_2 mixing ratio derived from the measurements was initially reported as 20 ppm (Krasnopolsky and Feldman, 2001a), but was later revised to 15 ± 5 ppm (Krasnopolsky and Feldman, 2001b). Fox (2003) constructed models of the martian thermosphere/ionosphere for mixing ratios of H_2 of 4, 10, 15, 40 and 100 ppm at the lower boundary of the models, which was at 80 km. We showed that several of the major ions, including O^+ , CO_2^+ , CO^+ , and N_2^+ , react with H_2 to form the protonated species OH^+ , OCOH^+ , HCO^+ , and N_2H^+ , respectively. In fact, ten of the fourteen ions in our models react with H_2 , and the

density profiles of these ions are affected by reactions with H₂. The densities of the protonated species that are produced in these reactions are therefore dependent upon the assumed abundance of H₂. Fox (2003) suggested that with the solar fluxes and chemistry then included in our model, the Viking O⁺ density profiles (Hanson et al., 1977) were best reproduced with H₂ mixing ratios of 4 ppm or less.

The density profiles of protonated species are important for interpretation of the measurements of ion densities to be made by the Neutral Gas and Ion Mass Spectrometer (NGIMS) on the Mars Atmosphere Volatile and Evolution (MAVEN) mission. The spacecraft was inserted into orbit around Mars on 22 September 2014. The NGIMS instrument is capable of measuring ions with an unprecedented sensitivity of $\sim 1 \text{ cm}^{-3}$. It is important, therefore, to predict the density profiles of ions, including protonated species, to guide the instrument mass settings. The nominal mission, which lasts one year, will be during a period of declining solar activity.

We here model the density profiles of the 14 ions that were in our model previously, and we add 10 protonated species. We include 12 neutrals in the background thermosphere, 5 of which are computed self-consistently in the model. We here predict density profiles for a total of 24 ions and 9 minor neutral species from 80 to 400 km. About 75 rate coefficients for reactions that produce and destroy protonated species are added to the ~ 220 reactions that are already in the model. These additional reactions will be explained in detail in the text that follows. The chemical reactions involving protonated species largely completes the photochemistry of H and H₂ in the model. We find that density profiles of the 14 ions that we have previously included do not change much. This is because we had included loss of the major ions by reactions with H₂ previously; we did not, however, track the products of these reactions. We here identify the most important protonated species and their production and loss mechanisms.

Previous work on this topic includes the models of Krasnopolsky (2002) and Matta et al. (2013). Krasnopolsky (2002) constructed models of the martian thermosphere/ionosphere for low, medium, and high solar activities. Among the ions included were ten “primary ions” and eight “secondary ions”. The “primary ions” included those that are produced by direct ionization and dissociative ionization in interactions of photons and photoelectrons with the neutral species in the background thermosphere. The background model included CO₂, N₂, Ar, O, CO, NO, He, H, D, H₂, and HD. The density profiles for the latter four neutrals were computed self-consistently in the models. The “secondary ions” were those formed via photochemical reactions of the primary ions, and included O₂⁺, NO⁺ and six protonated species that are produced by photochemistry. These ions were coupled via a total of 54 photochemical reactions. Predicted density profiles of the protonated species HCO⁺, OCOH⁺, OH⁺, and N₂H⁺ were shown for low, moderate, and high solar activity. The dominant protonated species was found to be HCO⁺, with peak densities that were anticorrelated with solar activity, and ranged from $\sim 2.3 \times 10^3 \text{ cm}^{-3}$ at solar minimum to slightly less than 10^3 cm^{-3} at solar maximum. The computed peak density of O⁺ in the low solar activity model was slightly larger than $\sim 100 \text{ cm}^{-3}$, a factor of ~ 6 less than that measured by the Viking Retarding Potential Analyzer (RPA) (Hanson et al., 1977). Since Krasnopolsky used the measured H₂ abundance from the FUSE observations of 15 ppm at 80 km, uncertainty in the H₂ abundance was not considered as a reason for this discrepancy. Although Krasnopolsky included altitude profiles for D and HD among the neutrals, no density profiles were presented for deuterium ions or molecular ions containing deuterium.

More recently Matta et al. (2013) have constructed several models of the martian thermosphere/ionosphere for solar minimum conditions, in which they have included seven neutral species in the background atmosphere. The density profiles of CO₂, N₂, O, CO, and

Ar, which were mostly taken from the Mars Climate Database MCD (e.g., Forget et al., 1999; website: www-mars.lmd.jussieu.fr), were held fixed in the models. The atomic hydrogen abundance at the bottom of the model was chosen to reproduce the high altitude densities derived from remote sensing. In order to explore the role of H₂ on the ion density profiles, the H₂ mixing ratio was treated as a free parameter, and varied from 1.6 to 16 ppm at 80 km. The density profiles of H and H₂ were computed using eddy and molecular diffusion, and then held fixed in the various models. The variation of the ion density profiles of seven “primary” ions, including CO₂⁺, N₂⁺, O⁺, CO⁺, Ar⁺, H₂⁺ and H⁺, and nine “secondary” ions, including O₂⁺, NO⁺, H₃⁺, OH⁺, HCO⁺, ArH⁺, N₂H⁺, OCOH⁺ and HOC⁺ were investigated, with emphasis on the topside ionosphere. The simplified chemical scheme for all the ions included 52 ion–molecule reactions with rate coefficients greater than $10^{-12} \text{ cm}^3 \text{ s}^{-1}$, and 18 recombination reactions. The results of the models of Krasnopolsky (2002) and Matta et al. (2013) will be discussed below in more detail when we compare our predictions to previous work.

2. Modeling approach

To facilitate comparison with our previous Mars thermosphere/ionosphere models we have adopted background major neutral density and temperature profiles that are similar to the standard models that we have used in the past. The neutral background thermospheric models consist of 12 species, including CO₂, Ar, N₂, O, CO, O₂, N, C, NO, He, H₂, and H, the altitude profiles for which are shown in Fig. 1. Although the top altitude for the calculated ions and minor neutrals is at 400 km, the neutral density profiles were extended to 700 km on a 1 km grid for the photoabsorption calculations, using the assumption that the scale heights are constant from 400 to 700 km. The low solar activity neutral thermospheric model is based on the Viking 1 neutral density profiles (e.g., Nier and McElroy, 1977), and the high solar activity models is based on a vertical cut through the Mars Thermospheric General Circulation Model (MTGCM) of Bougher et al. (2000, 2009, and private communication), with the O density doubled so that its mixing ratio is slightly larger than that at low solar activity.

Both the low and high solar activity models are characterized by solar zenith angles (SZAs) of 60°, and an average Sun–Mars distance of 1.524 AU. The solar fluxes for low and high solar activities were adopted from the Solar2000 (S2K) v1.24 models of Tobiska (2004, also private communication) for day 200 of 1976 (76200) and day 178 of 1999 (99178) when the $F_{10.7}$ indices adjusted to 1 AU were 68 and 214, respectively. The solar fluxes from 18 to 2000 Å were adopted in “Hinteregger format”, that is, as delta functions at the strong solar lines, and at 1 Å resolution in the continua; we also added fluxes in 1 Å bins from 1 to 17 Å as given by Ayres (1997). The models were characterized by exospheric temperatures of 200 K and 300 K for low and high solar activities, respectively (e.g., Bougher et al., 2009).

The background neutral species that are computed self-consistently in the models include N, C, NO, H₂, and H. In addition to photochemistry, both molecular diffusion and eddy diffusion were included in the computations. The eddy diffusion coefficient in units of $\text{cm}^2 \text{ s}^{-1}$ was adopted in the usual form $K(z) = A/n^{1/2}$, where n is the total number density in units of cm^{-3} at a given altitude z ; the parameter A has been found to be near $1.4 \times 10^{13} \text{ cm}^{1/2} \text{ s}^{-1}$ in the lower thermospheres of Venus, Mars and the Earth (e.g., Krasnopolsky, 1986; von Zahn et al., 1980). We adopt this value for our low solar activity model. For high solar activity, we assume that the eddy diffusion coefficient is larger and the parameter A takes on the somewhat arbitrary value $2 \times 10^{13} \text{ cm}^{1/2} \text{ s}^{-1}$. The maximum value of the eddy diffusion coefficient is taken to

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