Chemistry of the dayside ionosphere of Mars

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The density calculations for nine ions CO⁺, N⁺, O⁺, O₂⁺, NO⁺, N₂⁺, H⁺ and C⁺ are made to study the chemistry of the dayside ionosphere of Mars using analytical yield spectrum approach and coupled continuity equation for the steady state condition. Among these ions, O₂⁺, NO⁺ and CO₂⁺ are major, while others are minor. The density of NO⁺ is directly related to its parent density. The ionization and dissociative ionization of CO₂ produce large amount of CO₂⁺ and O⁺, respectively, which are lost by dissociative recombination and atomic oxygen to form O₂⁺ as a dominant ion in the dayside ionosphere of Mars. The ionization and dissociative ionization of N₂ are also important processes for the production of N₂⁺ and N⁺, respectively. The ions H⁺, CO⁺ and C⁺ are entirely destroyed by CO₂. These ions are mainly produced by photoionization of atomic hydrogen and photodissociative ionization of CO₂. In the calculation, the loss of ions due to horizontal transport along Martian magnetic field line is also included by solving a simplified horizontal momentum equation for ion-neutral and ion-electron collisions. It is found that the horizontal plasma transport is an important loss process for all ions above 150 km. Below this altitude, the ionosphere of Mars is controlled by photochemical equilibrium condition. The calculated electron density is in good agreement with the measurements made by radio occultation experiment on Mariner-4 and retarding potential analyzer experiments on Viking-1 and 2.

1 Introduction

The ground-based observations of Mars are difficult to make because of perturbing effects of the earth’s atmosphere. Some composition and temperature data have been obtained from a stellar occultation in the visible as well as from infrared spectroscopic observations. However, the latter generally pertains to the lower atmosphere below 100 km. Some composition data have also been obtained from planetary ultraviolet airglow observations made from sounding rocket platforms. The techniques for observing Martian ionosphere near earth are non-existent. Therefore, our knowledge of the Martian ionosphere, by and large, comes from the instrumented spacecraft launched to the vicinity of the planet. Mariner-4 (Refs 1, 2) in 1965, Mariner-6 and 7 (Ref. 3) in 1969, Mars-2 (Ref. 4) in 1971, Mariner-9 (Refs 5, 6) in 1971-72 and Mars-4 and 6 (Refs 7, 8) in 1974 have contributed much data which helped to define the structure and properties of the dayside ionosphere at low and high solar activity. Finally, during the period of low solar activity in 1976, Viking-1 and 2 (Ref. 9) have provided a detailed information of the ionosphere from in situ measurements taken over an entire Martian year. Almost thirteen years after the launch of Viking spacecraft, the next phase of Mars exploration began in 1988 with the launch of Phobos-2 (Ref. 10), which did not contribute to the knowledge of Martian ionosphere (the ionospheric experiments were not aboard on Phobos-2).

There have been many attempts to describe the dayside ionosphere of Mars. The ionospheric composition was first reported11,12 on the basis of dayglow and radio occultation measurements from Mariner-6 and 7. Later Chen et al.13 and Fox and Dalgarno14 have calculated ion densities in low solar activity for the dayside Martian ionosphere by solving coupled continuity equation. They have compared their ion profiles with retarding potential analyzer (RPA) experiment onboard Viking-1 and 2. Recently, Shinagawa and Cravens15 have used MHD model to study the effect of induced/intrinsic magnetic field in the Martian ionosphere. This calculation was also made at low solar activity and was compared with Viking-1 and 2 RPA experiment. They15 did not study the chemical processes which govern the balance of ionization in the dayside ionosphere.

The objective of this paper is to study the chemistry of the dayside ionosphere of Mars for solar minimum condition. The chemistry in the Martian ionosphere is driven by different physical and chemical processes. The solar extreme ultraviolet (EUV) radiation penetrates Martian atmosphere leading to photoionization and
photodissociative ionization of the atmospheric species. The photoelectrons thus produced by photoionization cause secondary ionization and dissociative ionization by impact process. The electron dissociative recombination is another important process in which the electron recombines with molecular ions which subsequently dissociates. Because of the long range nature of the Coulomb interaction this process has a large cross-section and the rate varies as \( T_e^{-1/2} \), \( T_e \) being the electron temperature. The chemical reactions including positive ion-atom interchange and positive ion charge transfer compose a large part of the chemical network and are also responsible for the formation of the Martian ionosphere.

Our knowledge of Martian magnetic field is not enough. Actual determination of the characteristics of the Martian magnetic field whether it is induced or intrinsic, however, needs further magnetic field observations. From the available data of magnetic field measurements onboard Mariner-4, Mars-2, 3 and 5, and Phobos-2, several workers\(^{16-25}\) have reported that Mars has an intrinsic magnetic field of dipole nature. Others\(^{26-30}\) have indicated that magnetic field in the Martian magnetotail is correlated with the upstream interplanetary magnetic field which suggests that Martian magnetotail is induced. If there is an influence of the intrinsic planetary magnetic field on the magnetotail of Mars, that influence is weak. Vaisberg and Smirnov\(^{31}\) and Axford\(^{32}\) suggested hybrid magnetosphere of Mars which is the combination of intrinsic magnetic field emanating from the pole of a weak dipole and Venus-like draped interplanetary field supplying in the neighbourhood of the magnetic equator. If Mars has such a weak dipole magnetosphere, the magnetic field lines would be horizontal throughout most of the dayside ionosphere, except in the vicinity of magnetic poles. In such a field, the horizontal plasma transport along the magnetic field lines is an important loss process of ions\(^{15}\). The loss of ions due to vertical transport by ambipolar diffusion is negligible in most of the Martian ionosphere because the chemical loss time is very less than the diffusion time below 220 km (Refs 14, 33). All these processes are included in the present chemical model to study the chemistry of the dayside Martian ionosphere at low solar activity.

### 2 Sources of ionization

#### 2.1 Photoionization / photodissociative ionization rates

The primary photoelectron production rate due to absorption of solar EUV radiation at altitude \( Z \) and solar zenith angle \( \chi \) is given below

\[
Q(Z,E) = \sum_i n_i(Z) \sum_{\lambda} \sigma_i^\lambda(\lambda) I(\lambda, \chi) \times \delta\left(\frac{hc}{\lambda} - E - W_i\right) \times \exp\left[-\text{ch}(-\chi) \sum_i \sigma_i^\lambda(\lambda) \int n_i(Z) dZ\right]
\]

where \( \sigma_i^\lambda(\lambda) \) and \( \sigma_i^\lambda(\lambda) \) are, respectively, the photoionization and photoabsorption cross-sections of gas \( i \) at wavelength \( \lambda \), \( \text{ch}(\chi) \) is the Chapman function, \( n_i(Z) \) the neutral density of gas \( i \) at altitude \( Z \), \( I(\lambda, \chi) \) the incident solar photon flux at the top of the Martian atmosphere, \( \delta[(hc/\lambda) - E - W_i] \) is the delta function in which \( hc/\lambda \) is the incident photon energy, \( W_i \) the ionization potential of \( i \)th constituent and \( E \) the energy of the ejected electron. It is assumed that the photoelectrons are ejected isotropically. To calculate the primary photoelectron production rates we employed Hinteregger's AE R74113 EUV reference spectrum\(^{34}\). The R74113 reference spectrum refers to the condition of solar minimum appropriate for Mars exploration in 1965 and 1976 by Mariner-4 and Viking-1 and 2, respectively. This solar flux is scaled to Mars' heliocentric distance. We have used the model atmosphere of eight gases \( \text{CO}_2, \text{N}_2, \text{O}_2, \text{O}, \text{CO}, \text{NO}, \text{H} \) and \( \text{N} \) in the calculation. The photoabsorption and photoionization cross-sections of \( \text{N}_2, \text{O}_2 \) and \( \text{O} \) were taken from Torr and Torr\(^{34}\). The photoabsorption cross-sections of \( \text{CO}_2 \) for \( \lambda \) greater than 900 \( \text{Å} \) and in the range 480-600 \( \text{Å} \) were taken from Cairns and Samson\(^{35}\) and in the range 600-797 \( \text{Å} \) from Cook \textit{et al.}\(^{36}\). In the wavelength range 180-480 \( \text{Å} \), we have adopted the cross-sections measured by Lee \textit{et al.}\(^{37}\). The photoionization cross-section of \( \text{CO}_2 \) in the wavelength range 600-900 \( \text{Å} \) were taken from McCulloh\(^{38}\) and Cook \textit{et al.}\(^{36}\). For shorter wavelength we assume photoionization yield equal to 1. The photoabsorption and photoionization cross-sections of \( \text{CO} \) have been taken from Cairns and Samson.\(^{35}\) Various branching ratios for \( \text{N}_2, \text{O}_2, \) and \( \text{O} \) have also been
taken from Torr and Torr. The branching ratio for CO₂ is obtained from Gustaffson et al., and Samson and Gardner and that for CO from Gardner and Samson. The calculations are made at solar zenith angle of 45°. The photoionization rates of CO₂, N₂, O₂, O⁺ and CO⁺ are obtained by integrating Eq (1) over energy. The photoionization rates of other ions, i.e. NO⁺, H⁺ and N⁺ are calculated using frequencies given by Schmidt et al. The photodissociative ionization of CO₂, N₂, O₂, CO and NO are also calculated using frequencies given by Schmidt et al. For these calculations the attenuation of solar radiation in the Martian atmosphere is taken into account. The densities of CO₂, N₂, O₂, O, NO and CO are taken from Nier and McElroy. The densities of atomic hydrogen and nitrogen are taken from Anderson and Fox, respectively.

Figure (1) shows the calculation of primary photoelectron production rates for energies 1-100 eV at different altitudes starting from 115 to 240 km in the height interval of 5 km. To save the computational time for the calculation of photoelectron-impact ionization rate we have chosen the energy grids of width 2 eV between 0 and 10 eV and 2.5 eV width between 10 and 100 eV. The prominent spectral features in the energy range 20-30 eV are due to strong He-II Ly-α line at 304 Å. A closer inspection indicates that these features are located at 22-24 eV as indicated by Mantas and Hanson and Fox and Dalgarno. The other major peak which was noted by these workers at 27 eV is not found in the present calculation due to our choice of energy intervals of 2.5 eV above 9 eV. The primary photoelectron energy spectrum falls off by an order of magnitude due to rapid decrease of solar flux and photoionization cross-sections at shorter wavelengths.

The absorption of photons with wavelength of less than 110 Å produces photoelectrons of energies greater than 100 eV. To include these electrons without expanding the energy range of the calculations, we have resorted to electron splitting in the calculation of primary photoelectron energy spectra. Thus, when an electron is produced with energy E > 100 eV, it is assumed that N (equal to integral part of E/100) electrons are produced with energy of 100 eV and an additional one with the remainder. In this manner, all the energy of R74113 solar EUV reference spectrum can be included in the calculations without expanding the energy above 100 eV. This procedure distorts, somewhat, the shape of the primary photoelectron energy spectra at lower altitudes below ~ 130 km. The distortion is not, however, very large and it is preferable to neglect this effect altogether in the calculation.

2.2 Photoelectron-impact ionization/dissociative ionization rates

Several theoretical models have been developed since last 30 years for photoelectron energy degradation in planetary atmospheres. These include the continuous slowing down approximation, the diffusion approach, two-stream method, Monte Carlo approach and so forth. In the present paper, we have used an analytical yield spectrum approach based on Monte Carlo method. In this method, monoenergetic electrons of energy E₀ are introduced in a gas medium. The energy of secondary or tertiary electrons and their positions are calculated at that time when the primary electrons excite/ionize the atmospheric constituents. In this way, yield spectrum function was generated for the calculation of the yield of any state in the mixture of gases. The function was fitted analytically later. The yield spectra are presented in terms of two, three, four and five-dimensional functions. We have used two-dimensional yield spectra for the calculations of
photoelectron flux and photoelectron-impact ionization / dissociative ionization rates in the Martian atmosphere. The two-dimensional yield spectra $U(E, E_0)$ (in unit eV$^{-1}$) is defined as

$$U(E, E_0) = \sigma_T(E) f(E, E_0) = \frac{N(E)}{\Delta E} \quad \ldots (2)$$

where, $\sigma_T(E)$ is the total inelastic cross-section, $N(E)$ the number of electrons in the bin centered at $E$ after the bin has been emptied and before the next lower non-empty bin of width $\Delta E$ centered at $E$ is considered, and $f(E, E_0)$ the equilibrium flux or degradation spectrum$^{56}$. The two-dimensional yield spectra are useful in the Martian ionosphere where magnetic field lines are horizontal and the photoelectrons lose their energy at the same height where they are produced$^{57,58}$. The analytical form of Eq. (2) is given as

$$U(E, E_0) = C_0 + C_1 X + C_2 X^2 \quad \ldots (3)$$

where

$$X = \frac{(E_0/1000)^{0.585}}{E + 1} \quad \ldots (4)$$

and $C_0$, $C_1$, $C_2$ are adjustable parameters$^{54}$ for CO$_2$, N$_2$, O$_2$, O and CO. For mixture of gases the composite yield spectra $U^C(E, E_0)$ are obtained by weighting$^{59,60}$ the component of yield spectra $U(E, E_0)$ as

$$U^C(E, E_0) = \sum f_i U_i(E, E_0) \quad \ldots (5)$$

In Eq. (5), $f_i$ is given by

$$f_i = \frac{S_i n_i}{\sum S_j n_j} \quad \ldots (6)$$

where, $S_i/S_j$ is the average value of $\sigma_T/E_0$ between $E_{\text{min}}$ (= 2 eV) and $E_0$, $\sigma_T$ and $\sigma_f$ being the total (elastic + inelastic) cross-sections of the gas $i$ and $j$, respectively. The elastic and inelastic cross-sections for CO$_2$, N$_2$, O$_2$, O and CO are taken from Porter and Jump$^{61}$ and Jackman$^{62}$, respectively.

The primary photoelectron production rate $Q(Z, E_0)$ and two-dimensional composite yield spectra $U^C(E, E_0)$ are used to calculate the photoelectron flux $\phi(Z, E)$, as follows$^{57}$

$$\phi(Z, E) = \int_{E_0}^{100} Q(Z, E) U^C(E, E_0) \frac{dE_0}{\Delta E} \quad \ldots (7)$$

The photoelectron-impact ionization/dissociative ionization rates are calculated as

$$J_i(Z) = n_i(Z) \int \phi(Z, E) \sigma_i(E) dE \quad \ldots (8)$$

where, $W_i$ is the ionization/dissociative ionization energy of gas $i$ and $\sigma_i(E)$ is the electron-impact ionization/dissociative ionization cross-sections of gas $i$. Furthermore, $\sigma_i(E)$ between $E_{\text{min}}$ (= 2 eV) and $E_0$, $\sigma_f$ being the total (elastic + inelastic) cross-sections of the gas $i$. The photoelectron-impact ionization rates for other ions NO$^+$, H$^+$ and N$^+$ are calculated using frequencies given by Schmidt$^{42}$. The calculations for ions CO$^+$, O$^+$ and C$^+$ due to photoelectron dissociation of CO$_2$ and CO, respectively, are made using the cross-sections of Orient and Srivastava$^{65}$. The production rates of NO$^+$ due to photoelectron impact on N$_2$ and O$_2$ are calculated taking the cross-sections given by Krishnakumar and Srivastava$^{66}$ and Tawara and Katoh$^{67}$, respectively. The photoelectron dissociative ionization rates of NO$^+$ due to photoelectron dissociation of CO$_2$ and CO, respectively, are made using the cross-sections of Orient and Srivastava$^{65}$. The production rates of NO$^+$ due to photoelectron impact on N$_2$ and O$_2$ are calculated taking the cross-sections given by Krishnakumar and Srivastava$^{66}$ and Tawara and Katoh$^{67}$, respectively. The photoelectron dissociative ionization rates of NO$^+$ due to photoelectron dissociation of CO$_2$ and CO, respectively, are made using the cross-sections of Orient and Srivastava$^{65}$. The production rates of NO$^+$ due to photoelectron impact on N$_2$ and O$_2$ are calculated taking the cross-sections given by Krishnakumar and Srivastava$^{66}$ and Tawara and Katoh$^{67}$, respectively.

Figure 2 shows the photoelectron fluxes at the same energies and altitudes as plotted in Fig. 1. It is found that there is a general exponential decrease in photoelectron fluxes with increasing energy. The peak near 25 eV in photoelectron spectra is due to the peak located in Fig. 1. The signature of vibrational excitation of the ground state of CO$_2$ near 3.5 eV found in the calculation of Mantas and Hanson$^{46}$ is not seen in the present calculation due to the choice of a coarser energy grid with intervals of 2 eV in the range 1-9 eV. Above 9 eV we have chosen the energy intervals of 2.5 eV. Therefore, the second peak obtained by Mantas and Hanson$^{46}$ is also absent in the present calculation.

3 Chemistry of dayside ionosphere

In Sec. 1 we have discussed that the magnetic field lines are horizontal in the dayside Martian
Fig. 2—Photoelectron fluxes at different altitudes

In the presence of horizontal magnetic field, Shinagawa and Cravens have found that the horizontal transport is an important loss process of ions. For the calculation of ion densities in the Martian ionosphere, we have solved steady state continuity and ion momentum equations for horizontal plasma flow in presence of intrinsic magnetic field as follows:

\[
\frac{\partial n_i}{\partial t} = -P_i n_i \frac{\partial (n_i w_i)}{\partial z} - n_i C \frac{\partial v_i}{\partial y} \quad \ldots (9)
\]

where, \( n_i(Z) \) and \( P_i(Z) \) are the density and production rate of \( i \)th ion at altitude \( Z \), \( l_i \) the loss coefficient of gas \( i \) at altitude \( Z \), \( w_i \) the vertical velocity of the \( i \)th ion, \( v_i \) the horizontal velocity of \( i \)th ion in \( y \) direction and \( C \) a constant correction factor. The calculations are made below 240 km where ambipolar diffusion is not important in most of the ionosphere of Mars. Therefore, term \( \partial(n_i w_i)/\partial z \) is neglected in this calculation. For steady state condition, \( \partial n_i/\partial t = 0 \). For \( C = 0 \), the horizontal plasma transport is zero and Eq. (9) calculates the ion densities for steady state photochemical equilibrium condition. For \( C = 1.0 \), the horizontal transport is maximum which reduces the electron densities by an order of magnitude above 160 km. For close agreement between calculation and measurements, we have used correction factor of 12% of total horizontal transport. Several assumptions were made in deriving the horizontal divergence term used in Eq. (9), e.g. (i) the time derivative term in horizontal momentum equation is negligible (i.e. steady state condition; \( \partial v_i/\partial t = 0 \)), (ii) the magnetic field varies as \( \cos^2 \theta \) in the horizontal direction (where \( \theta \) is the solar zenith angle); the plasma pressure has no solar zenith angle dependence, (iii) the viscosity term is zero, (iv) the horizontal ion velocity is zero at sub-solar point (\( \theta = 0 \)), (v) the influence of the vertical velocity on horizontal velocity is negligible (i.e. the term \( w_i \partial v_i/\partial z \) in the momentum equation is negligible) and (vi) the ion production term in momentum equation is negligible. The \( y \) component of the steady state ion momentum equation without viscosity term can be written as

\[
\frac{\partial v_i}{\partial y} = -\frac{1}{\rho_i} \frac{\partial P_i}{\partial y} - \frac{1}{\rho_i} v_i v_m \quad \ldots (10)
\]

where, \( v_{in} = K_{in} n_i \) is the ion-neutral and ion-electron collision frequencies which are calculated from reaction rates \( K \) and densities as used in chemical scheme; \( \rho \) is the mass density (\( \rho = mn \)) and \( P_i \) is the total pressure as given by

\[
P_i = P_{b_0} \cos^2 \theta + P_0 \quad \ldots (11)
\]

where, \( P_{b_0} \) is a magnetic pressure at sub-solar point and \( P_0 \) is plasma pressure (constant with \( \theta \)). In spherical co-ordinates, Eq. (10) is written as

\[
v_i \frac{\partial v_i}{\partial \theta} + \frac{1}{R} \frac{\partial P_i}{\partial \theta} + \frac{1}{\rho_i R} v_{in} v_i = 0 \quad \ldots (12)
\]

where \( R \) is the distance from the centre of Mars (i.e., Martian radius \( \sim 3390 \) km + atmospheric altitude \( Z \)). Substituting Eq. (11) into Eq. (12) we get

\[
v_i \frac{\partial v_i}{\partial \theta} \frac{P_{b_0}}{R} \sin 2\theta + \frac{1}{\rho_i R} v_{in} v_i = 0 \quad \ldots (13)
\]

Dividing Eq. (13) by \( v_i \) we have

\[
\frac{1}{R} \frac{\partial P_i}{\partial \theta} \frac{P_{b_0}}{\rho_i R} \sin 2\theta + v_{in} = 0 \quad \ldots (14)
\]
A smoothed version of the ion temperature profile was presented by Fox and Dalgarno\textsuperscript{4}. From a comparison of model and measured ion densities, they inferred an electron temperature profile in which it rose to a limiting value of \( \sim 350 \) K at about 180 km and was lower than the measured ion temperature at altitudes higher than 200 km. Chen \textit{et al.}\textsuperscript{13} and Rohrbaugh \textit{et al.}\textsuperscript{70} computed much larger electron temperatures assuming a heat source flowing at the top of the Martian ionosphere to get the agreement between calculation and measurement. Their computed values below 200 km differed from each other by a factor of 4. In the later ionospheric model\textsuperscript{71} the electron temperature was assumed to be equal to the ion temperature. Recently, Hanson and Mantas\textsuperscript{72} have used the Viking RPA data to derive the electron temperatures in the Martian ionosphere. Their profiles are highly variable. It varies from 2500 K to 30000 K above 200 km. Chen \textit{et al.}\textsuperscript{13} suggested that the variation of electron temperature is associated with the solar wind interaction on the topside Martian ionosphere. This idea seems to be incorrect because Phobos-2 during 56 circular orbits revealed a clear and strong dependence of location of the magnetopause at large distance from the ionosphere. In presence of intrinsic magnetic field the Martian ionosphere would not be affected by the solar wind directly as observed in the ionosphere of Venus. Thus, electron temperature in the Martian ionosphere is uncertain. The electron density shown in Fig. 3 is calculated using the ion temperature equal to electron temperature as Fox\textsuperscript{4} assumed in her calculation (Fox\textsuperscript{4} has revised this calculation using assumed electron temperature profile which was similar to that calculated by Rohrbaugh \textit{et al.}\textsuperscript{70}). This shows close agreement with the observations. We have also made calculations using electron temperatures computed by Chen \textit{et al.}\textsuperscript{13} and Rohrbaugh \textit{et al.}\textsuperscript{70} and measured by RPA experiment\textsuperscript{72}. These calculations are not shown in this paper. The use of electron temperature profiles either from Rohrbaugh \textit{et al.}\textsuperscript{70} or Fox\textsuperscript{4} produces more electron densities (by factor of \( \sim 1.2 \) from the measurements). The electron density also increases due to the use of electron temperature as calculated by Chen \textit{et al.}\textsuperscript{13} and measured by RPA experiment\textsuperscript{72}. Thus, computed and measured electron density profiles can be brought into agreement if the electron temperature is smaller than that from the RPA.
measurements and approximately equal to ion temperature.

In Fig. 4 we have shown the density profiles of nine ions CO2+, N+, O2+, O+, H+, NO+, CO+, C+ and N+. Among them O2+, NO+ and CO2+ are major ions, while others are minor. The chemistry of these ions has been discussed later. Viking-1 and 2 measured the densities of three ions O2+, CO2+ and O+ only in the dayside ionosphere of Mars (no other observations for ion densities are available on Mars). The present calculations of ion densities agree well with these measurements. The calculated densities are also in reasonable agreement with other calculations with some minor differences which can be incorporated by an appropriate choice of collision cross-sections and the densities of minor ions.

3.1 Chemistry of major ions

The production and loss of ions CO2+ and O2+ are shown in Figs. 5 and 6, respectively. The most important sources of CO2+ are photoionization and photoelectron-impact ionization rates at all altitudes with peak values of ~ 4.0 x 10^3 and 1.4 x 10^3 cm^-3s^-1, respectively. The charge exchange reactions

(R1) : \[ N_2^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + N_2 \]

(R2) : \[ \text{CO}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{CO} \]

and

(R3) : \[ \text{N}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{N} \]

are important sources of CO2+. The rate coefficients for (R1), (R2) and (R3) are taken as 3.0 x 10^-10, 1.0 x 10^-9 and 1.1 x 10^-9 cm^3 s^-1, respectively. Among the five loss processes of CO2+, the following three reactions

(R4a) : \[ \text{CO}_2^+ + \text{O} \rightarrow \text{O}_2^+ + \text{CO} \]

(R4b) : \[ \text{CO}_2^+ + \text{O} \rightarrow \text{O}^+ + \text{CO}_2 \]

and

Fig. 5—Production and loss rates for CO2+ in the dayside ionosphere of Mars

Fig. 4—The density profiles for CO2+, N2+, O2+, O+, C+, N+, H+, C+ and NO+ ions in the dayside ionosphere of Mars [Viking-1 data: \( \bullet \) O2+, \( \blacksquare \) O+, \( \bigtriangleup \) CO2+; Viking-2 data: \( \circ \) O2+, \( \square \) O+, \( \bigtriangledown \) CO2+]

Fig. 6—Production and loss rates for O2+ in the dayside ionosphere of Mars
are very important. The rate coefficients for reactions (R4) \( \sim 1.12 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) [sum of rate coefficients (R4a) and (R4b)] and (R5) \( \sim 3.80 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \) are taken from Fehsenfeld et al.\(^{76}\) and Weller and Biondi\(^{77}\), respectively. The maximum loss rates due to these reactions are found to be 2-3\( \times 10^{3} \) cm\(^{-3} \) s\(^{-1} \) at altitude 135 km. The other minor loss processes of CO\(_2^+\) are obtained from following reactions:

\[(R6a) : \quad \text{CO}_2^+ + \text{N}(^2\text{D}) \rightarrow \text{NO}^+ + \text{CO} \]
\[(R6b) : \quad \text{CO}_2^+ + \text{N}(^2\text{D}) \rightarrow \text{CO}^+ + \text{NO} \]
\[(R7) : \quad \text{CO}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}_2 \]
\[(R8) : \quad \text{CO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{CO}_2 \]

These reactions are not important in the chemistry of CO\(_2^+\). The rate coefficients for these loss processes are taken from Fehsenfeld et al.\(^{76}\) Thus, most of the CO\(_2^+\) ions produced by the photoionization and photoelectron-impact ionization processes are converted to O\(_2^+\) by the reaction (R4a) only. Using simplified reaction scheme the density of CO\(_2^+\) can be obtained as follows:

\[
\left[ \text{CO}_2^+ \right] = \frac{\text{[photoionization rate]}}{\left( K_4[O] + K_5[n_e] \right)}
\]

\[\ldots (17)\]

where \( K_4 \) and \( K_5 \) are the rate constants for (R4) and (R5), respectively. There are three destruction processes of O\(_2^+\) ions, namely, dissociative recombination

\[(R9) : \quad \text{O}_2^+ + e \rightarrow \text{O} + \text{O} \]

with rate coefficient \( 1.9 \times 10^{-7} (300/T_e)^{0.55} \text{ cm}^3 \text{ s}^{-1} \) (Refs 78, 79) charge exchange and ion-atom interchange as follows

\[(R10) : \quad \text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2 \]
\[(R11) : \quad \text{O}_2^+ + \text{N}(^2\text{D}) \rightarrow \text{NO}^+ + \text{O} \]

where \( T_e \) is the electron temperature. The rate coefficients for reactions (R10) and (R11) are taken as \( 6.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) and \( 1.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \), respectively.\(^{76,80}\) The process of dissociative recombination with O\(_2^+\) is important at all altitudes. The maximum loss rate due to this process is \( 4.0 \times 10^{3} \) cm\(^{-3} \) s\(^{-1} \) at about 130 km. The other two loss processes due to reactions (R10) and (R11) are not so important as compared to this process. The ion O\(_2^+\) is produced by seven processes. Among them, reaction (R4a) is a primary source. The second major source of O\(_2^+\) is given by

\[(R12) : \quad \text{O}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{CO} \]

with rate coefficients \( 9.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) (Ref. 81). The production rates of O\(_2^+\) due to reactions (R4a) and (R12) are approximately same and have peak value about \( 2.0 \times 10^{3} \) cm\(^{-3} \) s\(^{-1} \). The amount of O\(_2^+\) produced due to charge exchange reactions

\[(R13) : \quad \text{N}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2 \]
\[(R14) : \quad \text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O} \]

are very low and can be neglected. The rate coefficients for reactions (R13) and (R14) are taken as \( 5.0 \times 10^{-11} \) and \( 2.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \) (Refs 82, 83). The neutral temperature, \( T_n \), is adopted from Fox and Dalgarno\(^{74}\). The ionization of O\(_2\) due to photon and photoelectron impact are also negligible. The reaction (R7) is found to be an important source of O\(_2^+\) at low altitude after source reactions (R4a) and (R12). The density of O\(_2^+\) is approximately given by

\[
\left[ \text{O}_2^+ \right] = \frac{K_{4a}[\text{CO}_2^+][O]}{K_9[n_e]} \quad \ldots (18)
\]

where \( K_{4a} \) and \( K_9 \) are the rate constants for the reactions (R4a) and (R9), respectively. Viking-1 and 2 have measured densities of O\(_2^+\), CO\(_2^+\) and \( n_e \) which can be used in Eq. (18) to derive atomic oxygen density.
the second major source of NO\(^+\) below ~160 km, where CO\(_2\)\(^+\) is a dominant ionospheric gas after O\(_3\)\(^+\). Above this altitude atomic oxygen is a dominant gas which plays a major role for large production of O\(_2\)\(^+\) in the Martian ionosphere. Therefore, reaction (R11) and

\[
\text{(R15): } \quad \text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}
\]

with rate coefficient 1.4\(\times 10^{-10}\) cm\(^3\) s\(^{-1}\) are the major production mechanisms for NO\(^+\) above 160 km (Refs 84, 85). Below this altitude, reactions (R11), (R15) and (R6a) are minor sources of this ion. The photoionization of NO is greater than photoelectron-impact ionization by five orders of magnitude due to large differences in their ionization frequencies 1.28 \(\times 10^{-6}\) and 5.9 \(\times 10^{-11}\) s\(^{-1}\), respectively\(^42\). The densities of H\(^+\) and NO are very small in the Martian ionosphere. Therefore, the production of NO\(^+\) due to their exchange reaction is negligible. The remaining four reactions, given as follows, are also minor sources of this ion.

\[
\begin{align*}
\text{(R16): } & \quad \text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N} \\
\text{(R17): } & \quad \text{O}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O} \\
\text{(R18): } & \quad \text{CO}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{CO} \\
\text{(R19): } & \quad \text{N}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}_2
\end{align*}
\]

The rate coefficients for reactions (R16) - (R19) are taken from Ferguson\(^6\), McFarland \textit{et al.}\(^8\), Fehsenfeld and Ferguson\(^7\) and Fehsenfeld \textit{et al.}\(^7\), respectively.

The ion NO\(^+\) whose parent neutral has the lowest ionization potential among the major atmospheric gases is destroyed entirely by dissociative recombination reaction

\[
\text{(R20): } \quad \text{NO}^+ + \text{e} \rightarrow \text{N} + \text{O}
\]

in the Martian ionosphere. The rate coefficient\(^7\) for this reaction is taken as 2.3\(\times 10^{-7}\) (300/T\(_e\))\(^{0.5}\) cm\(^3\) s\(^{-1}\). Below ~160 km, the density of NO\(^+\) is approximately given by

\[
\left[\text{NO}^+\right] = \frac{K_{10} \left[\text{O}_2^+\right] \left[\text{NO}\right]}{K_{24} \left[\text{n}_e\right]} \quad \ldots (19)
\]

where, \(K_{10}\) and \(K_{24}\) are rate constants for reactions (R10) and (R24) (appearing later), respectively. Since O\(_2\)\(^+\) is the major ion in the dayside ionosphere of Mars, we find [O\(_2\)] = [n\(_e\)] near the peak altitude. Equation (19) reduces to

\[
\left[\text{NO}^+\right] = \frac{K_{10} \left[\text{NO}\right]}{K_{24}} \quad \ldots (20)
\]

Under these conditions the density of [NO\(^+\)] is directly proportional to the density of NO.

### 3.2 Chemistry of minor ions

Figures 8 and 9 show the production and loss rates of N\(_2\)\(^+\) and C\(^+\), respectively. The N\(_2\)\(^+\) ion is produced by the photoionization and photoelectron-impact ionization processes which are destroyed mainly by charge exchange reaction (R1). The loss of N\(_2\)\(^+\) by reactions (R13) and (R19) are smaller as compared to (R15). These loss processes do not contribute much in the chemistry of N\(_2\)\(^+\). The other minor loss process of this ion are

\[
\begin{align*}
\text{(R21): } & \quad \text{N}_2^+ + \text{CO} \rightarrow \text{CO}^+ + \text{N}_2 \\
\text{(R22): } & \quad \text{N}_2^+ + \text{e} \rightarrow \text{N} + \text{N}
\end{align*}
\]

The rate coefficients for these reactions\(^7\),\(^8\) are taken to be 7.4\(\times 10^{-11}\) and 3.5\(\times 10^{-7}\) (300/T\(_e\))\(^{0.5}\) cm\(^3\) s\(^{-1}\), respectively. Thus, the density of N\(_2\)\(^+\) is directly (photoionization rate + photoelectron-impact ionization rate) and indirectly related to the density of CO\(_2\). The ion C\(^+\) is produced by dissociation of
CO₂ due to photon and photoelectron-impact ionizations which are destroyed by the following reaction

\[(R23) : \quad \text{C}^+ + \text{CO}_2 \rightarrow \text{CO}^+ + \text{CO}\]

The photodissociative and photoelectron-impact dissociative ionizations of CO are the minor sources of C⁺. The dissociation of CO₂ due to photon-impact ionization is approximately equal to the density of C⁺. The rate coefficient for this calculation is taken from Huebner and Carpenter. The dissociative ionization frequency of C⁺ produced by photoelectron impact on CO₂ is calculated from Eq. (8).

The source and sink processes for N⁺ and H⁺ are shown in Figs. 10 and 11, respectively. There are six source processes of N⁺. Among them, the photon and photoelectron dissociative ionizations of N₂ are important sources which are mainly destroyed by reaction (R3). The photoionization and photoelectron-impact ionization rates of atomic nitrogen are very small and can be neglected in the chemistry of N⁺. The dissociative ionizations of NO by photon and photoelectron-impact processes

![Production and loss rates for N₂⁺ (Fig. 8)](image)

![Production and loss rates for N⁺ (Fig. 10)](image)

![Production and loss rates for C⁺ (Fig. 9)](image)

![Production and loss rates for H⁺ (Fig. 11)](image)
are also negligible sources of \( N'\). The ionization frequencies for these calculations are taken from different sources\(^{42,88,89}\). The major source and loss processes of \( H'\) are obtained from the following chemical reactions

\[
\begin{align*}
(R24): & \quad h\nu + H \rightarrow H' + e_p \\
(R25): & \quad H' + CO_2 \rightarrow CHO^+ + O
\end{align*}
\]

In the chemistry of \( H'\), maximum energy of solar EUV radiation is absorbed by photoionization. The photoelectrons emitted by this process produce very small amount of \( H'\) as compared to photoionization rate. The other productions and losses of this ion due to charge exchange reactions are not important. The rate coefficients for these calculations are taken from Hollenbach and McKee\(^{89}\), Huebner and Carpenter\(^{88}\) and Fehsenfeld and Ferguson\(^{90}\).

Figures 12 and 13 show the production and loss rates of \( O'\) and \( CO'\), respectively. The ions \( O'\), \( CO'\), \( CO_2^+\) and \( H'\) are coupled to each other. Therefore, many reactions are involved in the chemistry of \( O'\). There are three major sources of \( O'\) in the vicinity of peak altitude, namely (i) charge exchange reaction \((R4b)\), (ii) dissociative ionizations of \( CO_2\) by photon and (iii) photoelectron-impact processes. Above 170 km, the first process is dominant over the last two, because there the density of carbondioxide is less than that of atomic oxygen. The \( O'\) ion produced by this process quickly recombines with carbondioxide and produces \( O_2^+\) as a dominant ion in the dayside Martian ionosphere. The other reactions \((R14), (R16)\) and \((R17)\) are minor sink processes of \( O'\). The loss due to charge exchange reaction between \( H'\) and \( O\) is also negligible source of \( O'\). The rate coefficient for this reaction is taken from Fehsenfeld and Ferguson\(^{87}\). The photodissociative ionization rates of \( O'\) are obtained from different gases like \( O_2\), \( CO\) and \( NO\) using frequencies given by Huebner and Carpenter\(^{88}\) and Schmidt et al.\(^{42}\). The dissociative ionization rates of \( O'\) due to photoelectron impact on these gases are calculated from Eq. (8). These are minor sources of \( O'\). The large amount of \( CO'\) is obtained by reaction \((R23)\) and photon / photoelectron dissociative ionizations of \( CO_2\). The great loss of this ion occurs due to reaction \((R2)\). The charge exchange \((R18)\) and dissociative recombination reactions are minor loss processes of \( CO'\). The photoionization and photoelectron-impact ionization rates of this ion are not much different, but are found to be larger than those of reactions \((R6b)\) and \((R21)\).

4 Summary

The chemistry of nine ions \( CO_2^+, N_2^+, O_2^+, O', CO^+, NO^+, N'^+, H'\) and \( C'\) is studied in the dayside Martian ionosphere using analytical yield spectrum approach and coupled continuity equation for steady state condition. The horizontal momentum
between CO₂⁺ and O⁺, dissociative ionizations of CO₂ by photon and photoelectron impact processes. The dominant O₂⁺ ion is produced in the atmosphere of Mars. The density of H⁺ is directly related to the ion temperature. Thus, the presence of extra heat source at the top of the Martian ionosphere possibly due to solar wind-Mars interaction as suggested by Hanson and Mantas, Chen et al., and Rohrbaugh et al. seems to be incorrect. Solar EUV radiation is found to be only source for the dayside ionosphere of Mars. In the chemistry of the dayside ionosphere, O₂⁺, NO⁺ and CO₂⁺ are major ions, while others are minor. The NO⁺ ion is mainly produced by reactions of O₂⁺ with NO, which is entirely destroyed by dissociative recombination. The density of NO⁺ is directly proportional to its parent density. The large amount of CO₂⁺ are produced by photoionization and photoelectron-impact ionization processes. The ion CO₂⁺ is lost by atomic oxygen and dissociative recombination reaction. The dominant O₂⁺ ion is produced in the dayside ionosphere of Mars mainly due to reactions of CO₂⁺ with O. The dissociative recombination is an important loss process at all altitudes for O₂⁺. Among the minor ions, N₂⁺ is produced by photoionization and photon-electron-impact ionization processes which are destroyed mainly by charge exchange reaction (R1). The ion C⁺ is produced by dissociative ionizations of CO₂⁺ due to photon and photoelectron-impact processes. These processes are destroyed by ion-molecule interchange reaction (R23). The photon and photoelectron impact on N₂ are major source processes of N⁺. The great loss of this ion is obtained due to reaction between C⁺ and CO₂⁺. The production and loss rates of H⁺ are very small in comparison to other ions of the dayside ionosphere of Mars. The density of H⁺ is directly related to photoionization rate which is lost by proton impact on CO₂⁺. There are three major sources of O⁺ in the vicinity of peak altitude, namely, charge exchange between CO₂⁺ and O⁺, dissociative ionizations of CO₂⁺ by photon and photoelectron impact processes. The ion O⁺ produced by these processes quickly combine with CO₂⁺ and produces O₂⁺ as a dominant ion in the dayside Martian ionosphere. The large amount of CO₂⁺ is obtained by reaction (R23) and photon/photoelectron dissociative ionizations of CO₂⁺. The great loss of this ion occurs due to charge exchange reaction between CO₂⁺ and CO₂⁺.

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### References