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Effects of dissociative recombination on the composition of planetary atmospheres

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Abstract. Because dissociative recombination (DR) reactions of molecular ions are often highly exothermic, in the thermospheres of the Earth and planets DR may be a source of translationally and internally excited fragments. DR is important, therefore, for thermospheric neutral heating; if the excited fragments radiate to space, however, DR may be also a source of thermospheric cooling. DR may produce metastable fragments, which may live long enough to participate in reactions that are not available to ground state species. It is rare, however, for DR to be a significant source of minor species in their ground states. An exception appears to be the DR of CO_2^+ , which has recently been found to produce $\text{C} + \text{O}_2$ about 9% of the time by Seiersen *et al.* [1]. Because of the significant rearrangement of bonds that must take place, the branching ratio for the latter channel has been assumed to be negligible, and DR of CO_2^+ has been assumed to produce mainly $\text{CO} + \text{O}$. In order to test the effect of including the branching ratio of CO_2^+ DR that produces $\text{C} + \text{O}_2$ on the ambient densities of thermal and escaping C in planetary thermospheres, we have constructed revised models of the thermospheres/ionospheres of Mars and Venus. Because of space limitations, we discuss here only the high solar activity models. For Mars, we find that DR of CO_2^+ is the most important source of thermal C, but that the production rate of escaping C is not increased. There are important differences between the thermospheres of Venus and Mars, and we find that the inclusion of the $\text{C} + \text{O}_2$ channel in the Venus models increases the production rate of atomic carbon in the Venus thermosphere by only 10–16%. At high altitudes on Venus, C^+ is mostly produced by photoionization and electron-impact ionization of C, with some contribution from the charge transfer reaction, $\text{O}^+ + \text{C} \rightarrow \text{C}^+ + \text{O}$. We compare our computed C density altitude profiles to those inferred by Paxton [2] from Pioneer Venus Orbiter Ultraviolet Spectrometer limb scans of the atomic carbon emission features at 1561 and 1657 Å. Since the most important loss process for C is reaction with O_2 , this allows us to constrain the abundance of O_2 in the Venus thermosphere. We then compute density profiles of C^+ and compare them to those measured by the Pioneer Venus Orbiter Ion Mass Spectrometer (OIMS) (e.g., Taylor *et al.* [3]) to determine the rate coefficient for the charge transfer reaction of O^+ to C.

1. Introduction

Dissociative recombination reactions are, in general, highly exothermic and are important sources of translationally and internally excited neutral fragments. Translationally excited fragments contribute significantly to local heating (e.g., Fox [4]; Roble *et al.* [5]). Electronically excited states may radiate to lower energy levels producing airglow emissions. Examples of such emissions include the CO Fourth positive bands ($A^1\Pi \rightarrow X^1\Sigma$), and Cameron bands ($a^3\Pi \rightarrow X^1\Sigma$) on Mars and Venus, which are produced in part by DR of CO_2^+ (cf. Fox [6]). The branching ratios for production of excited states of CO are not well known, but it is clear that a significant fraction of the CO fragments are formed in excited states (e.g., Wauchop and Broida [7]; Gutchek and Zipf [8]; Tsuji *et al.* [9]; Skrzypkowski *et al.* [10]). The fraction of the total CO dayglow emissions produced by DR of CO_2^+ is uncertain, partly because the

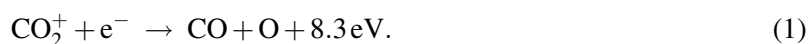
branching ratios to these excited states are not well known, and partly because the cross sections for production of excited states of CO by other processes, such as electron impact excitation of CO and dissociative excitation of CO₂ are uncertain.

Dissociative recombination can produce fragments in metastable excited states that either radiate or survive to participate in chemical reactions that are not available to ground state species. For example, DR of O₂⁺ can produce O(¹D) and O(¹S), which can radiate, producing the visible O(¹D → ³P) 6300 Å red line, the O(¹S → ¹D) 5577 Å green line, and the ultraviolet O(¹S → ³P) 2972 Å emission. Branching ratios for the production of the channels of DR that produce the ground and excited states have been measured by Kella *et al.* [11], and by Peverall *et al.* [12]. Recently, the branching fractions and the cross sections for DR of O₂⁺ in vibrational levels 0–2 have been reported by Petrigani *et al.* [13]. The radiative lifetime of O(¹D) is of the order of 130 s, but that of O(¹S) is less than 1 s. Therefore O(¹D) atoms can survive to participate in chemical reactions before they radiate over large regions of the atmospheres of the terrestrial planets. An important reaction of O⁺(¹D) in the mesospheres of the terrestrial planets is that with H₂O to create 2 OH radicals.

Dissociative recombination of N₂⁺ can produce N atoms in the ground N(⁴S) and excited N(²D) and N(²P) states, which have lifetimes against radiation of 7.8 × 10⁴ s and 12 s, respectively. Branching ratios for the energetically allowed channels in which various combinations of ground and excited N atoms are produced have been reported by Kella *et al.* [14]. The particularly long-lived metastable species N(²D) participates in reactions with major species in the thermospheres of all three terrestrial planets. It is difficult to break the strong N₂ bond, and there are few known mechanisms for producing molecules with an odd number of N atoms, known collectively as “odd nitrogen”, at altitudes below the thermosphere. Among the possibilities are ionization of N₂ and subsequent ion-molecule reactions and DR, followed by downward transport from the thermosphere to the mesosphere. Although DR of N₂⁺ is a source of odd-nitrogen in the thermosphere, the magnitude of that source is limited in the lower thermosphere because N₂⁺ reacts efficiently with neutral species at low altitudes where the neutral densities are larger. DR of N₂⁺ becomes important as a loss process for N₂⁺ only at high altitudes. Owing to the small ionization potential of NO, however, DR is the major loss mechanism for NO⁺ over most of the ionosphere. This reaction is an important source of N(²D) (Vejby-Christensen *et al.* [15]), but not of odd-nitrogen, since NO⁺ itself is an odd-nitrogen species. Because NO can be ionized by solar Lyman alpha photons, which penetrate in a window in the O₂ photoabsorption cross sections, NO can be ionized in the terrestrial upper mesosphere. The production of NO⁺ followed by DR to produce N(²D) is a source of NO over a larger range of the mesosphere because the long lived N(²D) radical can be transported away from the source region.

DR of molecular ions can be a source of high velocity atoms, which may escape from planets or satellites that have a small gravity well, such as Mars or Titan (cf. Fox [16]; [17–19]). Even on larger bodies, such as the Earth and Venus, however, the product atoms oriented in the upward hemisphere may travel to great heights before falling again under the influence of gravity, forming “hot atom” coronas (e.g., Yee and Hays [20], Cotton *et al.* [21]; Nagy and Cravens [22], Hodges 2000 [23], Nagy *et al.* [24]). See Fox [25] for a more complete discussion of the ways in which DR is important for planetary ionospheres.

Although DR is important for many different atmospheric phenomena, some of which were described above, it is rarely important as a source of thermal ground state species. Recently, however, Seiersen *et al.* [1] have measured the branching ratio for energetically allowed channels in the DR of CO₂⁺ using the Aarhus ion storage ring in Denmark. Usually this reaction is assumed to proceed via the channel



Because of the significant rearrangement of bonds that must take place, the branching ratio for the channel that produces C



has been assumed to be negligible. Seiersen *et al.* [1] reported branching ratios for reactions (1) and (2) of 0.87 ± 0.04 and 0.09 ± 0.03 , respectively. This is the first reported detection of C atoms in DR of CO_2^+ . They also reported a branching ratio of 0.04 ± 0.03 for the channel



The latter channel is not allowed at the low pressures of planetary thermospheres unless a photon is emitted during the recombination process. Such radiative recombinations are usually characterized by very small rate coefficients. Reaction (3) could proceed by three-body recombination only at higher pressures. Therefore, we have adopted slightly different branching ratios for reactions (1) and (2) of 0.907, and 0.093, respectively, in our models.

2. Models

We have constructed model atmospheres for Mars and Venus at low and high solar activities for different solar flux models. Because of space limitations we discuss here only the high solar activity models. The solar fluxes that we use here are the Solar2000 v1.24 models of Tobiska [26], which are normalized to the Student Nitric Oxide Explorer soft X-ray measurements (e.g., Barth *et al.* [27]; Bailey *et al.* [28]). Our background model thermosphere consists of 12 major neutral species (CO_2 , Ar, N_2 , O, CO, O_2 , He, H, H_2 , C, N and NO), and we compute the density profiles of 14 ions (CO_2^+ , N_2^+ , Ar^+ , $\text{O}^+(^4S)$, $\text{O}^+(^2D)$, $\text{O}^+(^2P)$, CO^+ , C^+ , N^+ , O_2^+ , NO^+ , O^{++} , He^+ and H^+), and 9 minor neutral species (NO, $\text{N}(^4S)$, $\text{N}(^2D)$, $\text{N}(^2P)$, C, $\text{O}(^1S)$, $\text{O}(^1D)$, H and H_2). We have adopted the cross sections for the interaction of photons and photoelectrons with background species, and chemical reactions as given by Fox and Sung [29], with slight modifications as discussed by Fox [30–32].

The density profiles for neutrals and ions in the high solar activity model of the Martian thermosphere / ionosphere are shown in figures 1 and 2, respectively. Computed altitude profiles for the production

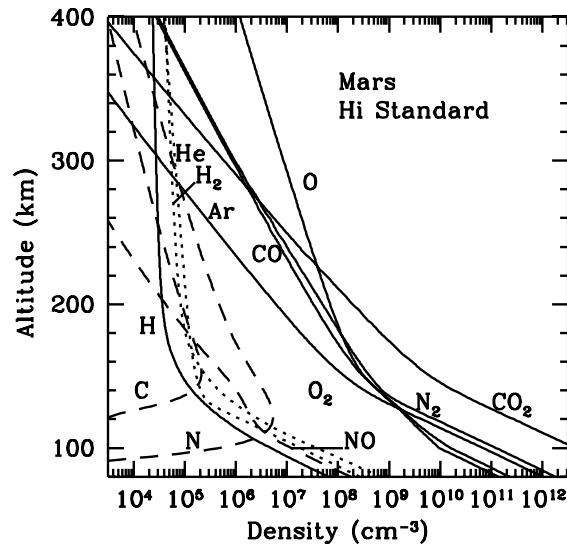


Figure 1. Standard high solar activity background model for the thermosphere of Mars. The solid curves represent densities of the major background species and H, the dotted curves represent those of He and H_2 , and the dashed curves are for the species (C, NO and N), that are computed self-consistently in the model.

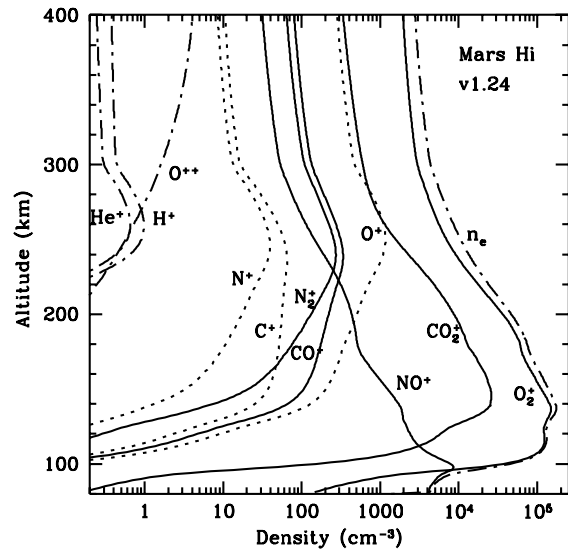


Figure 2. Ion density profiles for the standard high solar activity model of the Martian ionosphere. The solid curves are molecular ion density profiles, the dotted and dot-dashed curves are density profiles for the atomic ions. The total electron density profile is shown as a dot-dashed curve.

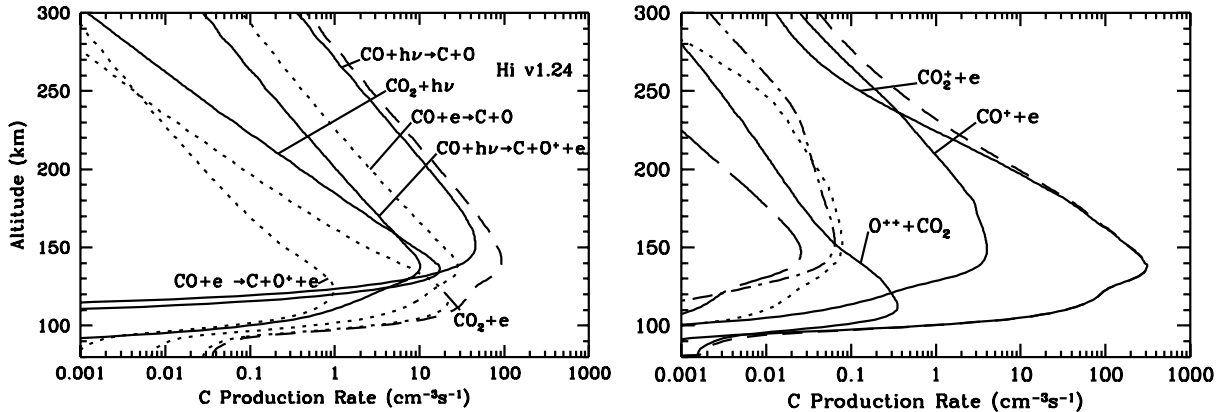


Figure 3. Altitude profiles of the rates of production of C for the high solar activity model on Mars. “Hi V1.24” denotes the solar flux model adopted: the 79050 S2K v1.24 solar flux model of Tobiska [26]. The left panel shows the sources due to interactions of solar photons (solid curves) or photoelectrons (dotted curves) with atmospheric species. The right panel shows the sources due to chemical reactions. The solid curves are labeled. The dotted curve is the source due to reaction of $N^+ + CO$, the dot-dashed curve is the source due to reaction of CO^+ with N, and the long-dashed curve is the source due to the reaction of $C^+ + NO$. The short-dashed curve represents the total production rate.

rates of atomic carbon are shown in figure 3. It is clear that the largest source of atomic carbon in this model is the dissociative recombination of CO_2^+ , with an integrated column production rate of $1.07 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$, compared to that from photodissociation of CO of $2.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$, and a total column production rate of $1.64 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$. Thus dissociative recombination of CO_2^+ provides more than half the total source of ambient C in the Mars thermosphere. The resulting C density profile is shown in figure 1; it is computed self-consistently with the other species in the model.

The exothermicity of reaction (2), 2.3 eV, is large enough that there would be enough energy for the product C atoms to escape from Mars, if the O_2 were produced with no internal energy. The product O_2 is, however, expected to be produced vibrationally and rotationally excited, especially since a new bond is formed in the reaction. We have carried out a statistical calculation of the energy deposition, and find that less than 4% of the C atoms produced have enough energy to escape. Although this calculation does not include the initial velocities of the ion and electron, the proportion of C atoms that escape is expected to be small. Further details may be found in Fox [32].

The model neutral and ion density profiles for the Venus high solar activity thermosphere/ionosphere are shown in figures 4 and 5, respectively. For CO_2 , N_2 , O, N, and O_2 we have adopted the VTS3 model, which is based on the Pioneer Venus Orbiter Neutral Mass Spectrometer measurements, and normalized to the Orbiter Ion Drag measurements. The model shown is that for $F_{10.7} = 200$, near equatorial and 16:00 local time. (e.g., Hedin *et al.* [33]). A full explanation of the method of determination of the density profiles for the other species is given by Fox and Sung [29].

The thermosphere of Venus is different from that of Mars in several ways, but most important for the C profile are the abundances of O and CO, which are much larger in the Venus thermosphere. Because O reacts with CO_2^+ to produce O_2^+ , on Venus, a larger fraction of the CO_2^+ ions produced are transformed into O_2^+ . This reduces the importance of DR of CO_2^+ in the production of C. In addition, owing to the larger mixing ratio of CO, production mechanisms for C such as photodissociation, photoelectron impact dissociation, photodissociative ionization and photoelectron impact dissociative ionization of CO are more important on Venus than on Mars. Altitude profiles for the production of atomic carbon are shown in figure 6.

The predicted column production rate of atomic carbon for this model is $1.03 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$, of which nearly half, $4.5 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ arise from photodissociation of CO. The integrated source of C

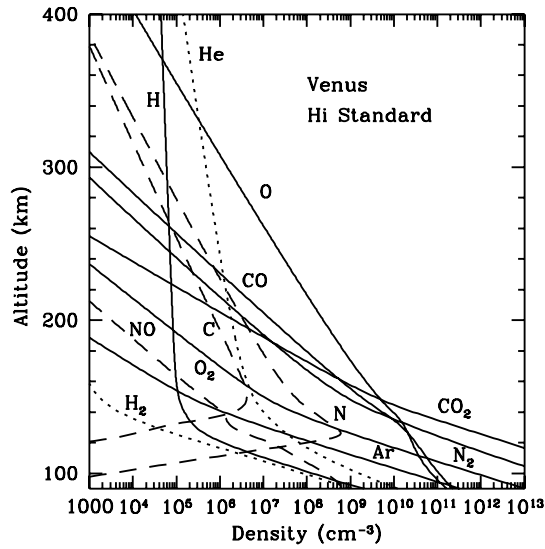


Figure 4. Standard high solar activity background model for the thermosphere of Venus. The density profiles for CO_2 , N_2 , CO , O , and Ar are represented as solid curves, those of He and H_2 as dotted curves, and N , NO and C as dashed curves.

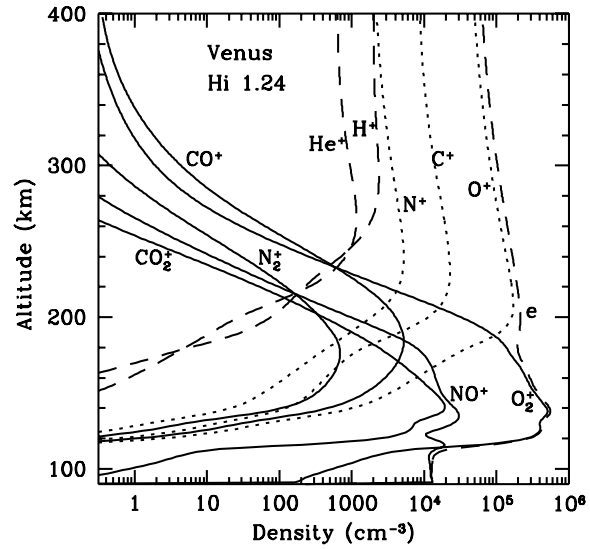


Figure 5. Ionospheric density profiles for the standard high solar activity Venus model. The molecular ion densities are represented as solid curves, the atomic ions are represented as dotted and dashed curves, and the total electron density is shown as a dashed curve.

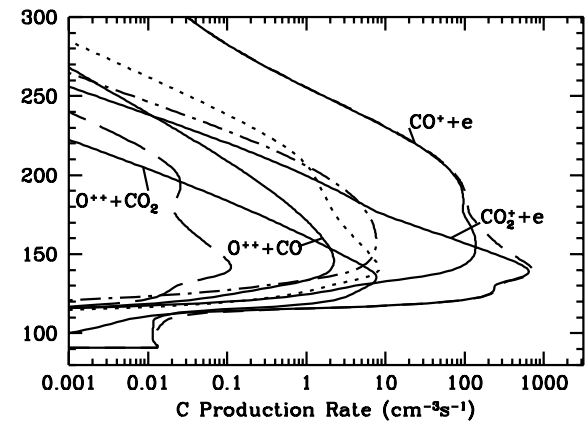
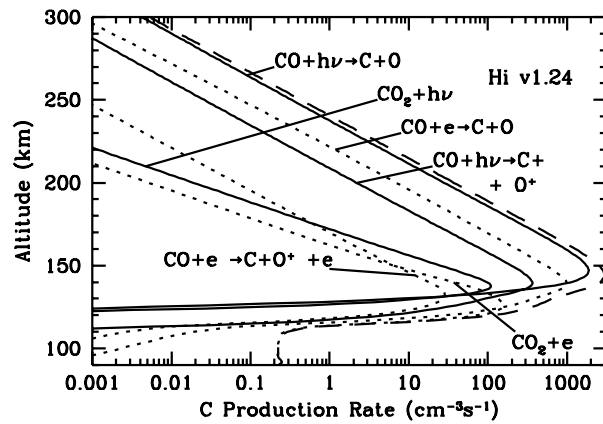


Figure 6. Altitude profiles of the rates of production mechanisms for C in the Venus thermosphere. The left panel shows the sources due to interactions of solar photons or photoelectrons with atmospheric species. The right panel shows the sources due to chemical reactions. The various processes are represented as in figure 3.

from DR of CO_2^+ is only $1.30 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$, or 13% of the total production.

C^+ is produced at high altitudes in the Venus atmosphere mainly in photoionization and electron impact ionization of C , and in the reaction



The rate coefficient for reaction (4) is unknown. In our standard models we have adopted a value of $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. In order to constrain the value of k_4 , we have also constructed a moderately high solar activity model of the Venus thermosphere/ionosphere that more closely represents the solar activity during the first year of Pioneer Venus in situ data, in late 1978–1979 (c.f., Fox and Paxton [34]). The

solar flux model that we have adopted for this model is the S2K v2.22 99178 model of Tobiska [26]. We have predicted the O₂ abundance by identifying the C density profile that best fits that suggested by the model of the 1561 and 1657 Å resonance features of C (Paxton [2]). After fitting the O₂ abundance, we also determined by best fit rate coefficient for reaction (4) by comparing the computed C⁺ density profiles to that measured by the Pioneer Venus Orbiter Ion Mass Spectrometer (Taylor *et al.* [3]; Fox and Kliore [35]). We find the most likely O₂ abundance is slightly larger than 3×10^{-4} and the rate coefficient for reaction (4) is predicted to be in the range $(0.9-1.3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [34].

Acknowledgments

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