

Wright State University

CORE Scholar

Physics Faculty Publications

Physics

11-1-1999

Velocity Distributions of C Atoms in CO+ Dissociative Recombination: Implications for Photochemical Escape of C from Mars

Jane L. Fox

Wright State University - Main Campus, jane.fox@wright.edu

Aleksander Hać

Follow this and additional works at: <https://corescholar.libraries.wright.edu/physics>



Part of the [Physics Commons](#)

Repository Citation

Fox, J. L., & Hać, A. (1999). Velocity Distributions of C Atoms in CO+ Dissociative Recombination: Implications for Photochemical Escape of C from Mars. *Journal of Geophysical Research-Space Physics*, 104 (A11), 24729-24737.

<https://corescholar.libraries.wright.edu/physics/16>

This Article is brought to you for free and open access by the Physics at CORE Scholar. It has been accepted for inclusion in Physics Faculty Publications by an authorized administrator of CORE Scholar. For more information, please contact library-corescholar@wright.edu.

Velocity distributions of C atoms in CO⁺ dissociative recombination: Implications for photochemical escape of C from Mars

J. L. Fox¹

Institute for Terrestrial and Planetary Atmospheres, State University of New York at Stony Brook

Aleksander Hać

Delphi Chassis Systems, Engineering Technical Center, Dayton, Ohio

Abstract.

We have carried out Monte Carlo calculations to determine the velocity distributions of C atoms produced by dissociative recombination of CO⁺ using recent data for the branching ratios of various allowed channels and ion and electron temperatures appropriate to the Martian thermosphere. We find that the fractions of ¹²C atoms with velocities greater than the escape velocity are ~ 0.66 and ~ 0.62 , and those for ¹³C are ~ 0.47 and ~ 0.48 at the plasma temperatures characteristic of the exobases at low and high solar activities, respectively. The ratio of the escape fractions of ¹³C and ¹²C, which is a measure of the isotope effect inherent in the CO⁺ dissociative recombination mechanism, is thus in the range 0.72–0.77. Using model thermospheres and ionospheres for low solar activity from Viking, and for high solar activity from the Mars Thermospheric General Circulation Model, we have computed the global escape flux of C due to dissociative recombination of CO⁺ as $(3 - 5) \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$. This value is of the same order as current estimates for the escape flux of C in all forms due to sputtering by O⁺ pickup ions at the current epoch but may be much less than that due to sputtering at earlier times in the history of the planet.

1. Introduction

Loss of CO₂ from Mars is controlled by the escape rate of C, either as CO₂, CO, or atomic C. Since the escape energy of ¹²C from Mars is ~ 1.48 eV, only non-thermal processes can contribute significantly to the escape flux. The most important escape mechanisms are expected to be dissociative recombination of CO⁺ [McElroy, 1972] and sputtering of CO₂, CO, or C by O⁺ pickup ions. Sputtering rates for CO₂ at low solar activity were estimated by Luhmann *et al.* [1992] as $\sim 2 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ on a globally averaged basis. This value has been reduced to $1 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ by Jakosky *et al.* [1994] to account for a factor of 2 error in the sputtering efficiencies employed by Luhmann *et al.* Kass and Yung [1995] reported sputtering rates of

CO₂ of $\sim 1.7 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, but the cross sections used in that model were criticized as too large by Johnson and Liu [1996, 1998]. In response, Kass [1999] (see also Kass and Yung [1996]) revised his estimate of the current escape flux of CO₂ due to sputtering downward by a factor of ~ 3 to $5 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$.

Dissociative recombination of CO⁺



is a photochemical process that can produce atomic carbon atoms with enough energy to escape from the atmosphere. The energy released in this reaction depends on the electronic states of the product atoms; the branching ratios for the energetically allowed channels have recently been measured at 0 and 0.4 eV relative energy by Rosén *et al.* [1998]. The most exothermic channel is that which produces both C and O in their electronic ground states. Since 2.90 eV are released in this channel, most of the C atoms produced have enough energy to escape. Even those produced in less exothermic channels may travel to high altitudes forming a hot C corona similar to the hot O coronas observed for Earth and Venus and predicted for Mars

¹Also at Department of Physics, Wright State University, Dayton, Ohio.

[e.g., Yee *et al.*, 1980; Cotton *et al.*, 1993; Bisikalo *et al.*, 1995; Hickey *et al.*, 1995; Wallis, 1978; Nagy and Cravens, 1988; Ip, 1988, 1990; Nagy *et al.*, 1990; Kim *et al.*, 1998].

We have combined our models for the high and low solar activity Martian ionospheres with Monte Carlo calculations of the velocity distributions of C atoms produced by dissociative recombination of CO^+ at and near the Martian exobase for high and low solar activities. We report here the resulting altitude-dependent escape fractions and of ^{12}C and ^{13}C and their ratio, which is the isotope fractionation factor inherent in the dissociative recombination mechanism. We also estimate the solar activity averaged escape flux of C from dissociative recombination of CO^+ and compare it to estimates of the escape flux from sputtering.

2. The Model

The Martian thermospheric models for high and low solar activities that we have employed are similar to those we have used previously [e.g., Fox *et al.*, 1996; Fox, 1997; Kim *et al.*, 1998]. The high solar activity model is based on the Mars Thermospheric General Circulation Model (MTGCM) of Bougher *et al.* [1990] and the low solar activity model is that from Viking [Nier and McElroy, 1976; Fox and Dalgarno, 1979]. We have updated these models with new rate coefficients for dissociative recombination of CO^+ [Rosén *et al.*, 1998], CO_2^+ [Gougousi *et al.*, 1997], and NO^+ [Vejby-Christensen *et al.*, 1998]. We have computed density profiles both for “noneroded” and “eroded” ionospheres, that is, for models with zero-flux ion upper boundary conditions and maximum upward flux boundary conditions, respectively. Low solar activity models with zero flux (diffusive equilibrium) upper boundary conditions have been found to overestimate the topside ion densities compared to those measured by the Viking RPA [Hanson *et al.*, 1977], and some kind of physical or chemical loss process has usually been invoked in models to reduce the densities. For example, Chen *et al.* [1978] found that the O_2^+ profile could be reproduced if an upward velocity of $1 \times 10^5 \text{ cm s}^{-1}$, equivalent to an outward flux of $5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ were imposed at the top boundary of the model. Shinagawa and Cravens [1989; 1992] suggested that the loss process is the divergence of the horizontal fluxes of the ions, by analogy to Venus. On Venus, the ions flow from the dayside to the nightside, probably in response to the plasma pressure gradient force. When they reach the nightside the ions converge and flow downward, forming the nightside ionosphere [e.g., Knudsen, 1992]. Some of the ions also escape the gravitational field of the planet, although the magnitude of the escape rate is controversial [e.g., McComas *et al.*, 1986; Brace *et al.*, 1987]. Fox [1997] estimated the maximum escape fluxes of ions from Mars due to the limits on the production rates by determining numerically the maximum upward ion fluxes allowed by

the models, assuming all the ions had the same upward velocities. The models for the eroded ionospheres used here were computed in the same way as those described by Fox [1997] and differ only slightly from those models. The major ion density profiles at low and high solar activity are shown in Figures 1a and 1b, respectively.

The fraction of C atoms that escape depends on the exothermicity of the dissociative recombination reaction and on the ion, electron, and rotational temperatures at the altitude at which the dissociative recombination takes place. The model ion and electron temperatures are based on Viking measurements at low solar activity and are assumed to be only slightly larger at high solar activity. The values assumed are shown by Kim *et al.* [1998]. The energy released in the dissociative recombination reaction of CO^+ depends on the channel by which the reaction proceeds. The possible channels and the energies released are

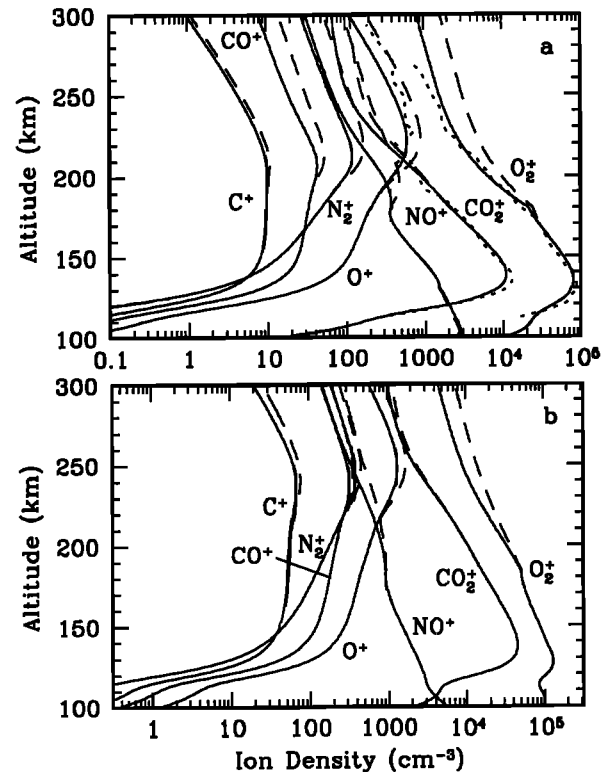
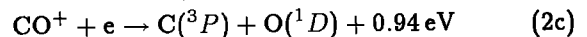
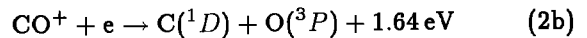
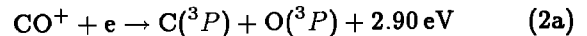
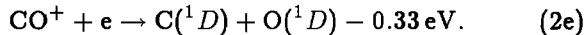
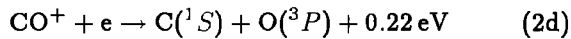


Figure 1. Altitude profiles of ion densities for (a) low solar activity and (b) high solar activity. The dashed curves are those for the “noneroded” ionosphere, that is, computed with zero-flux upper boundary conditions on the ions. The solid curves are those for the “eroded” ionosphere, that is, those computed with maximum upward ion velocity boundary conditions. The dotted curves in Figure 1a are the densities of O_2^+ and O^+ measured by the Viking retarding potential analyzer [Hanson *et al.*, 1977].



The branching ratios of channels 2a–2e have recently been measured by *Rosén et al.* [1998]. At 0 eV relative energy the branching ratios are found to be 0.761, 0.145, 0.094, and 0.0 for channels 2a, 2b, 2c and 2d, respectively. At 0.4 eV, the endothermic channel 2e is energetically possible, and branching ratios of 0.53, 0.34, 0.08, 0.0, and 0.05 were measured for channels 2a–2e, respectively. The electron temperatures assumed here, which were taken from the calculations of *Rohrbaugh et al.* [1979], do not exceed ~ 2500 K up to 250 km, so we have ignored channel 2e in our calculations. The electron temperatures computed by *Rohrbaugh et al.* [1979], and those of *Chen et al.* [1978] were found to be in acceptable agreement with the electron temperatures estimated from Viking 1 RPA data above 200 km by *Hanson and Mantas* [1988]. In computing the distributions of the channels at a given altitude, we have interpolated the branching ratios measured by *Rosén et al.* [1998] to the model electron temperature at that altitude. Although the branching ratios strictly apply to dissociative recombination of CO^+ in the ground vibrational level, we assumed the same branching ratios for all vibrational levels. This is not expected to introduce a significant error in our calculations, since the bulk of the CO^+ is expected to be in the vibrational ground state in the ionosphere. *Wallis* [1989] estimated the photochemical escape rates of C, but he assumed that the branching ratio for channel 2a was small and that CO^+ dissociative recombination did not lead to significant escape.

Although the rotational and vibrational temperatures may not be equilibrated to the ion temperatures at all altitudes, we assumed them to be equal in our calculations. Previous calculations of velocity distributions of atoms produced in dissociative recombination of N_2^+ and O_2^+ [*Fox and Hać*, 1997a, b] have shown that variations in the ion rotational temperature by factors of 2 or more have little effect on the atomic velocity distributions. Unlike homonuclear diatomics, such as N_2^+ and O_2^+ , where radiation from excited vibrational levels of the ground electronic state is dipole forbidden and the vibrational distributions may be significantly non-thermal, CO^+ has a dipole moment and thus radiative relaxation is expected to be efficient. At high altitudes, radiation will limit the actual fraction of vibrationally excited ions to less than that obtained with the assumption of local thermodynamic equilibrium. Since the vibrational spacing in CO^+ is 0.27 eV, however, and the ion temperatures are between 200 and 1000 K at the altitudes reported here, the ions are assumed to be overwhelmingly in the ground vibrational state.

To compute the vibrational and rotational energy levels, the ion was assumed to be a vibrating rotor, with relevant constants taken from *Herzberg* [1950]. For the isotopic species $^{13}\text{CO}^+$ and ^{13}CO , the vibrational and

rotational energy levels are slightly different from those of $^{12}\text{CO}^+$ and ^{12}CO . We have taken this into account, but the difference is small and does not have a significant effect on the results. For example, the exothermicities of channel 2a for $^{13}\text{CO}^+$ in low vibrational levels are ~ 0.003 eV smaller than those for $^{12}\text{CO}^+$. We have also taken into account the decrease in the cross section (σ) for dissociative recombination with the relative velocity (v_{rel}) of the ion and electron. The measurements of *Rosén et al.* [1998] showed that the cross section for CO^+ dissociative recombination is proportional to v_{rel}^{-2} . Since the probability of a dissociative recombination event occurring is proportional to $v\sigma(v)$, the relative probabilities were assumed to be proportional to v_{rel}^{-1} .

The Monte Carlo calculation of the velocity distribution of the atoms produced in dissociative recombination has been described in detail for N_2^+ and O_2^+ previously [*Fox and Hać*, 1997a, b] and will not be repeated here. Our calculations are also similar to those carried out by *Gérard et al.* [1995] for terrestrial hot oxygen. In each of the calculations we described here, we included a total of 2×10^5 events. The error introduced by the Monte Carlo calculation is expected to be of the order of 1% and is thus negligible compared to the other uncertainties inherent in the model.

3. Results

The exobases of the low and high solar activity models are at ~ 195 and 215 km, respectively. We have computed velocity distributions of the ^{12}C and ^{13}C atoms produced in dissociative recombination of CO^+ at the exobase, 15 km below and 15 and 30 km above the exobase. Since the CO^+ density peaks above the exobase, but the electron density decreases continuously with altitude, this is the region from which the bulk of the escaping C atoms is expected to arise. The predicted velocity distributions at four altitudes are presented in Figures 2 and 3 for the low and high solar activity models, respectively. The vertical line in each panel is the escape velocity at the labeled altitude for 30° latitude. The velocity distributions are functions only of the assumed temperatures and therefore do not differ for the eroded and noneroded models. At the lowest altitudes the velocity distributions are highly structured, and become less structured as the altitude and ion temperature increase for both models. At the low solar activity exobase (~ 195 km), where the escape velocity is found to be $\sim 4.88 \text{ km s}^{-1}$, the average velocity of a ^{13}C atom is $\sim 4.58 \text{ km s}^{-1}$ compared to 4.84 km s^{-1} for ^{12}C . The computed ^{12}C and ^{13}C escape fractions are shown in Table 1, along with their ratio.

Several factors affect the details of the velocity distributions and the escape fractions as altitude increases. First, the average velocity of the distributions increases as the ion and electron temperatures increase because of the greater exothermicity of the reaction. By itself this

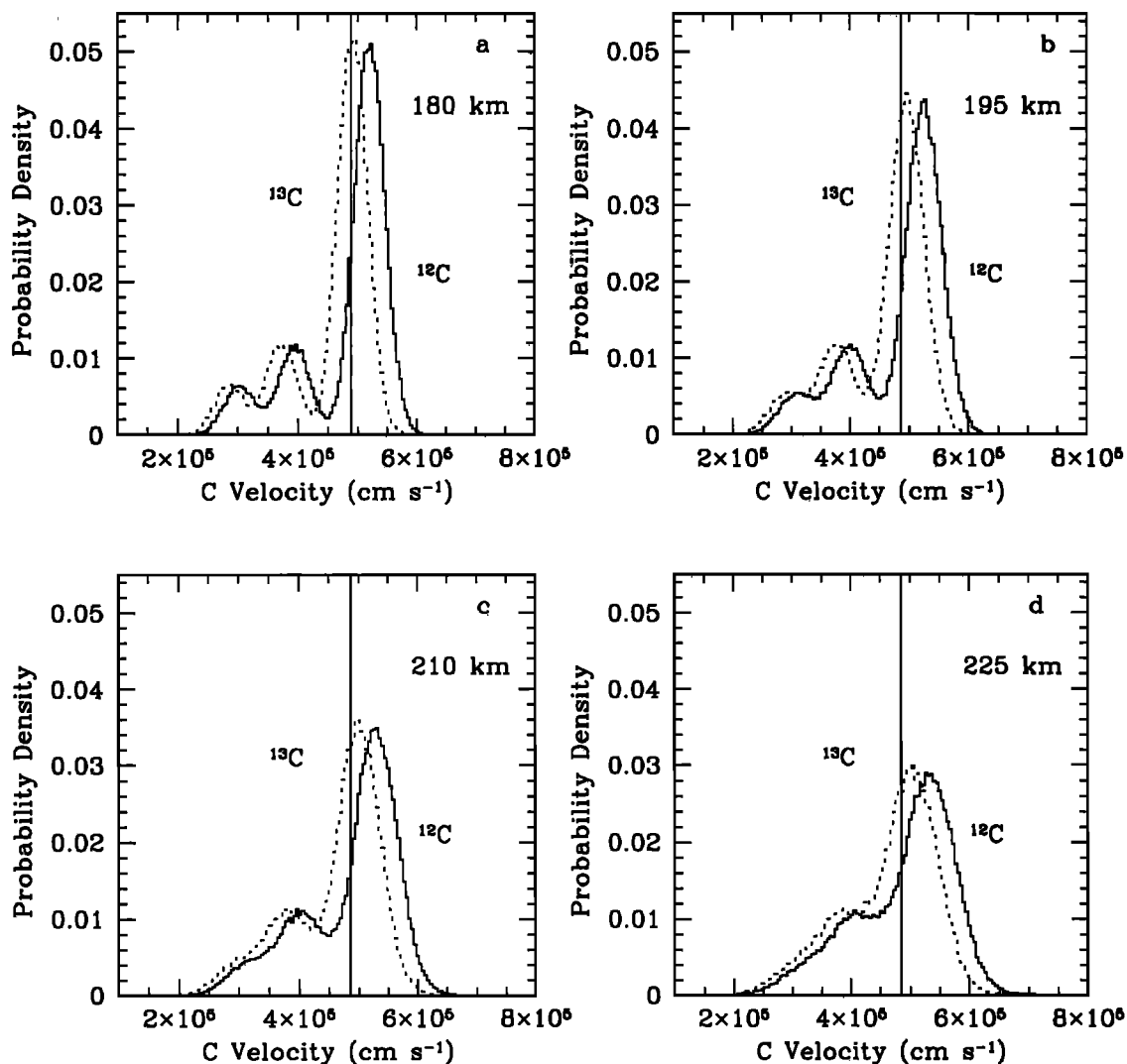


Figure 2. Velocity distributions of C atoms for the low solar activity model at four altitudes: (a) 180 km, (b) 195 km, (c) 210 km, (d) 225 km. The probability densities are in units of probability per velocity bin; each bin is $4.5 \times 10^3 \text{ cm s}^{-1}$ in width. The exobase is at $\sim 195 \text{ km}$. In each plot, the solid curve is the velocity distribution of ^{12}C and the dashed curve is that for ^{13}C . The solid vertical line is the escape velocity for the labeled altitude at 30° latitude.

would lead to larger escape fractions with increasing altitude. As the ion temperature increases, however, the velocity distribution also broadens. For velocity distributions whose peak is greater than the escape velocity (as is that for ^{12}C and channel 2a), this broadening increases the fraction of atoms with energies below the escape velocity. Conversely, if the peak of the distribution is below the escape velocity, the broadening of the distribution leads to an increase in the fraction of atoms with energies greater than the escape velocity. An additional factor is the increase in the probability of the smaller exothermicity channel 2b as the electron temperature increases. For ^{12}C , the net effect is a small decrease in the escape efficiency from 0.67 to 0.62 as the altitude increases from 180 to 225 km at low solar activity, and a nearly constant value of 0.62 ± 0.01 is predicted from 200 to 245 km at high solar activity.

For ^{13}C , a small increase in the escape efficiency is observed over the same altitude ranges at both low and high solar activities. The ^{13}C escape efficiencies range from 0.43 to 0.48 from 180 to 225 km at low solar activity and from 0.47 to 0.50 from 200 to 245 km at high solar activity.

The ratio of the escape fractions, which is the isotope fractionation factor that is inherent in the dissociative recombination mechanism, is thus ~ 0.72 at the low solar activity exobase and 0.77 at the high solar activity exobase. An additional fractionation factor arises from diffusive separation between the homopause and the exobase. Although the isotope fractionation effect of the escape rates is fairly large, the $^{13}\text{C}/^{12}\text{C}$ ratio measured by Viking was not measurably different from the terrestrial value; a value for $\delta^{13}\text{C}$ of $0 \pm 5\%$ was reported [Nier *et al.*, 1976]. The trapped gas in SNC mete-

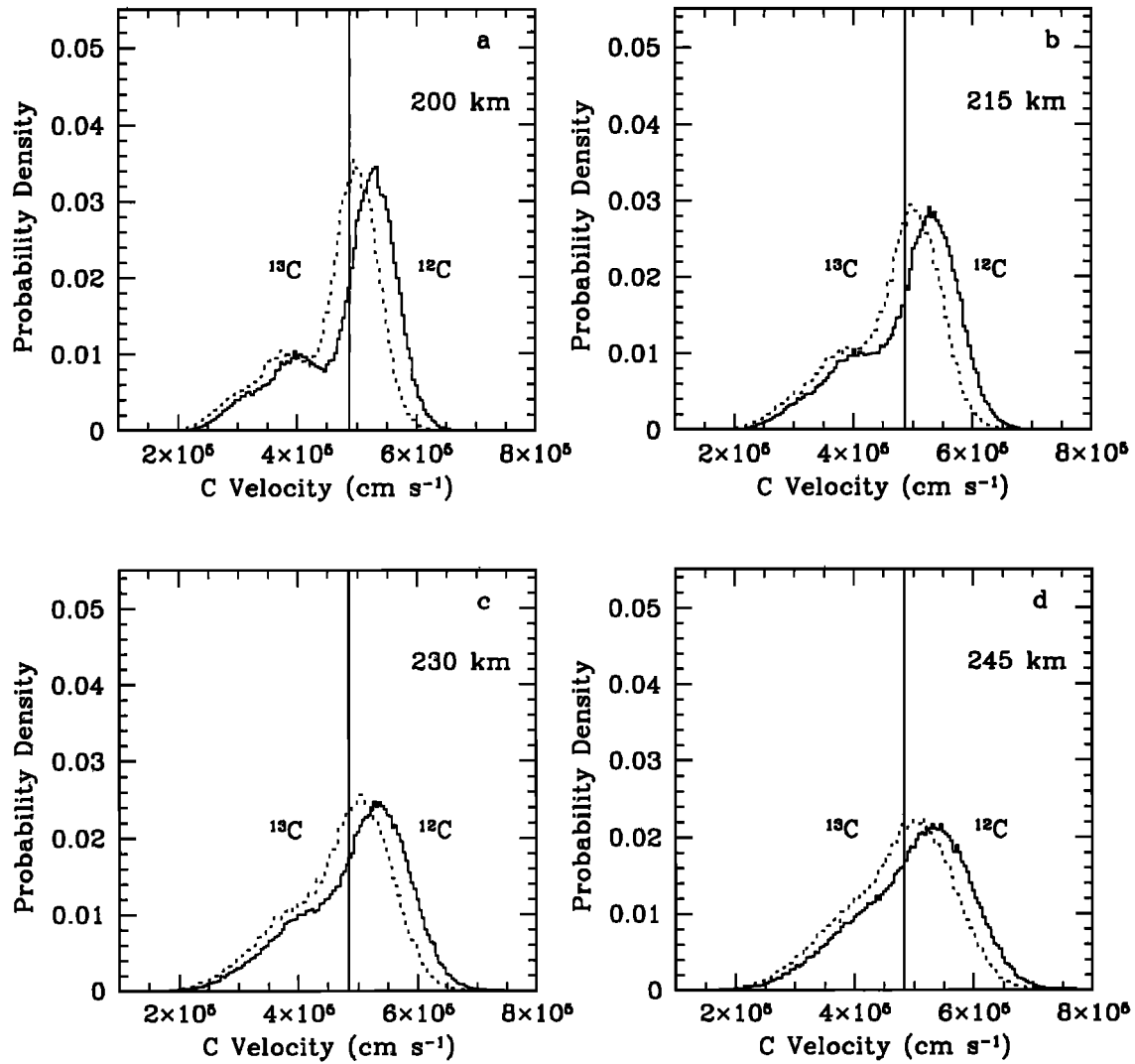


Figure 3. Velocity distributions of C atoms for the high solar activity model at four altitudes: (a) 200 km, (b) 215 km, (c) 230 km, (d) 245 km. The probability densities are in units of probability per velocity bin; each bin is $4.5 \times 10^3 \text{ cm s}^{-1}$ in width. The exobase is at $\sim 215 \text{ km}$. In each plot, the solid curve is the velocity distribution of ^{12}C and the dashed curve is that for ^{13}C . The solid vertical line is the escape velocity for the labeled altitude at 30° latitude.

Table 1. Escape Fractions and Ratios for ^{12}C and ^{13}C in CO^+ Dissociative Recombination at Several Altitudes for High and Low Solar Activities

Altitude, km	^{12}C Escape Fraction	^{13}C Escape Fraction	Ratio
<i>Low Solar Activity</i>			
180	0.673	0.434	0.64
195	0.659	0.475	0.72
210	0.632	0.477	0.75
225	0.617	0.482	0.78
<i>High Solar Activity</i>			
200	0.629	0.467	0.74
215	0.617	0.478	0.77
230	0.611	0.485	0.79
245	0.615	0.500	0.81

orites, which are widely believed to have originated from Mars, is characterized by a fractionation factor $\delta^{13}\text{C}$ of $3.6 \pm 1\%$ [Wright *et al.*, 1990]. This implies that there is a large reservoir of CO_2 , probably the polar caps, the regolith and carbonate deposits, that has exchanged with the atmosphere over time and has buffered the isotope ratio [e.g., Fanale *et al.*, 1982; Jakosky, 1991].

We can estimate the global average escape flux by integrating the dissociative recombination rate above the exobase, multiplying by the escape fraction, by 0.5 to account for the lack of escape from the nightside, and by another factor of 0.5 to account for the fraction of C atoms released in the downward direction. The results are shown in Table 2 for both high and low solar activity ionospheres (eroded and noneroded) where they are compared to the sputtering rates for the current epoch for low solar activity as estimated by Luhmann *et al.* [1992] and for moderate solar activity by Kass [1999] (see also Kass and Yung [1996]). Our computed escape rates for low solar activity range from $1.9 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$ for the eroded ionosphere to $4.1 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$ for the noneroded ionosphere. Viking observations suggest that the eroded ionosphere is the more appropriate model for low solar activity conditions. At high solar activity, the escape rates range from $5.8 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ for the eroded ionosphere to $9.1 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ for the noneroded ionosphere. It is possible that the solar wind interaction with the high solar activity ionosphere is different from that of the low solar activity ionosphere and that the high solar activity ionosphere may not exhibit the eroded appearance of the low solar activity ionosphere, but until there is in situ information about the ionosphere at high solar activity, it is impossible to be sure. In either case, our predicted global, solar cycle averaged escape flux of C from dissociative recombination is in the range $(3 - 5) \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$.

The calculated escape fluxes of C due to dissociative recombination of CO^+ are slightly smaller than, but of the same order as those due to sputtering by O^+ pickup ions at the current epoch as estimated by Luhmann *et al.* [1992] and Kass [1999]. The escape rates may have been exceeded at earlier times when the solar wind flux was larger [e.g., Newkirk, 1980]. Both the models of Luhmann *et al.* [1992] and Kass and Yung [1995, 1996] predict that the sputtering rate increases by more than three orders of magnitude from the current epoch to 3.5 Gyr before present, although there are large uncertainties involved in those predictions.

We expect the escape rates of C from dissociative recombination of CO^+ also to increase as the solar flux increases at earlier times for two reasons. First, since CO is a photolysis product of CO_2 and is also produced in ion chemistry, the fraction of CO in the thermosphere is expected to be enhanced as the solar fluxes in the FUV, EUV, and soft x-ray regions increase [e.g., Zahnle and Walker, 1982; Ayres, 1997]. Direct evidence for this increase can be seen by comparing the mixing ratio of CO at the Martian homopause, which is 4.2×10^{-3} at low

solar activity [Nier and McElroy, 1977] to that near the Venus homopause, which is much larger, $\sim 7 \times 10^{-2}$ at high solar activity [e.g., Hedin *et al.*, 1983]. At Venus, the solar fluxes are larger than those at Mars by a factor of ~ 4.4 due to the difference in distance from the Sun, in addition to the increase in the solar fluxes from low to high solar activity. Second, because of the increase in fluxes of ionizing radiation at earlier times, the CO^+ and electron densities will be larger also, thus increasing the rate of dissociative recombination. Therefore we expect the escape rate of C due to CO^+ dissociative recombination to be enhanced substantially over the approximate factor of 5 increase in solar fluxes over the period from the present to 3.5 Gy before present [Ayres, 1997]. There are other factors, however, such as the rise in the exobase altitude and changes in neutral densities, that come into play, and more detailed calculations are being carried out. Nonetheless, we expect the escape fluxes to increase between 1 and 2 orders of magnitude, with lower values more probable.

Thus, if the current estimates are correct, sputtering will play a much larger role in the early history of the planet, unless Mars possessed a significant paleomagnetic field that persisted beyond ~ 3.5 Gyr before present. Hutchins *et al.* [1997] showed that even a small intrinsic magnetic field diminishes the sputtering rates considerably. The escape rate due to dissociative recombination would not be directly affected by the presence of such a magnetic field, since the energetic particles are neutrals, but the structure of the ionosphere would almost certainly be different. In particular, if Mars possessed an intrinsic magnetic field the ionosphere would be more Earth-like than Venus-like; the ion density profiles would probably extend to higher altitudes and would not exhibit the eroded appearance characteristic of the Viking profiles. The rate of dissociative recombination and the concomitant escape flux would therefore be larger. The detection of small-scale crustal magnetic anomalies by the magnetometer on Mars Global Surveyor provides evidence for the existence of a paleomagnetic field, but the confinement of these sources to the ancient cratered terrain implies that the Martian dynamo may have operated for only a few hundred million years after planetary accretion [Acuña *et al.*, 1999]. Thus the early intrinsic magnetic field appears to have had little effect on the C escape rates from dissociative recombination computed here or those due to sputtering over at least the last 3.5 Gyr.

We should note here that evidence for directly escaping ions was obtained by measurements made by instruments on the Phobos orbiter. The automatic space plasma experiment with a rotating analyzer (ASPERA) and toroidal analyzer spectrometer (TAUS) instruments measured fluxes of heavy ions apparently of ionospheric origin in the optical shadow of Mars, although estimates of the global average ion escape flux derived from measurements by the two instruments dif-

Table 2. Global Average Escape Fluxes of C for Various Models

Model	Escape Rate, $\text{cm}^{-2} \text{s}^{-1}$
Low solar activity, eroded	1.9×10^4
Low solar activity, noneroded	4.1×10^4
High solar activity, eroded	5.8×10^5
High solar activity, noneroded	9.1×10^5
Sputtering ^a	1×10^5
Sputtering ^b	5×10^5

^aFrom *Luhmann et al.* [1992]; corrected by *Jakosky et al.* [1994]. This value applies to low solar activity.

^bFrom *Kass* [1999]. This value applies to moderate solar activity.

ferred substantially, from 3.5×10^6 to $2.1 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ [e.g., *Verigin et al.*, 1991; *Lundin et al.*, 1990]. While most of the escaping ions were identified as O^+ and O_2^+ , it is likely that some ions containing C, such as C^+ , CO^+ , and CO_2^+ were also present, but the mass resolution of the instruments was not sufficient to identify such ions. The escape of ions has been attributed to the direct interaction of the solar wind with the ionosphere, in which ions produced above the ionopause are picked up by the solar wind convection electric field [e.g., *Luhmann*, 1990]. The magnitude of the pickup ion escape flux has been estimated as the integrated ionization rate above the ionopause, which leads to values that are much smaller than the Phobos measurements suggest [*McElroy et al.*, 1977; *Luhmann*, 1990; *Zhang et al.*, 1993]. *Fox* [1997] pointed out, however, that if the ionopause is above the photochemical equilibrium region, as the ions are stripped off, the ions below will flow upward, greatly increasing the potential loss rate. Ultimately, most of the ions produced above the photochemical equilibrium region could, in principle, be removed. *Fox* [1997] computed upper limits to the global average escape fluxes of ions due to limits on the production rates, and the predicted values for C-containing ions were $(2.1 - 16) \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, where the range is from low to high solar activity. Thus direct escape of ions has the potential to be more important than either dissociative recombination or sputtering, but mechanisms that can produce such large escape fluxes have not been identified. Better measurements of fluxes of escaping ions with wider spatial coverage and sufficient mass resolution to identify the ions more precisely, as well as theoretical studies of solar-wind-induced ion escape processes are greatly needed.

4. Conclusions

We have modeled the velocity distributions of ^{12}C and ^{13}C produced in dissociative recombination of CO^+ near the exobase of Mars for high and low solar activities. We find that the velocity distributions broaden

and become less structured as the altitude (and ion temperature) increases. The escape fractions are in the range 0.61 to 0.67 for ^{12}C and 0.43 to 0.50 for ^{13}C from 15 km below to 30 km above the exobase. The isotope fractionation factor, that is, the isotope effect inherent in the dissociative recombination mechanism, is ~ 0.72 at the low solar activity exobase and 0.77 at the high solar activity exobase. This fractionation has not significantly affected the $^{13}\text{C}/^{12}\text{C}$ atmospheric isotope ratio because the CO_2 in the atmosphere is buffered by contact with a larger reservoir of CO_2 , probably in the regolith, polar caps and carbonate deposits [e.g., *Fanale et al.*, 1982; *Wright et al.*, 1990; *Jakosky*, 1991].

The computed global average escape flux of C averaged over low and high solar activities is in the range $(3 - 5) \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ and is of the same order as the escape flux due to sputtering as estimated by *Luhmann et al.* [1992] and *Kass* [1999] (see also *Kass and Yung* [1996]). If estimates of the solar wind flux at previous epochs are correct, however, photochemical escape will probably be greatly exceeded by sputtering 2–3 Gyr before present.

Acknowledgments. This work has been supported in part by NASA grant NAG5-6879 and by NSF grant AST-9802007 to the Research Foundation of the State University of New York at Stony Brook.

Janet G. Luhmann thanks Alexander Dalgarno and Andrew Nagy for their assistance in evaluating this paper.

References

- Acuña, M. H., et al., Global distribution of crustal magnetization discovered by the Mars Global Surveyor MAG/ER experiment, *Science*, **284**, 790–793, 1999.
- Ayres, T., Evolution of the solar ionizing flux, *J. Geophys. Res.*, **102**, 1641–1651, 1997.
- Bougher, S. W., R. G. Roble, E. C. Ridley, and R. E. Dickinson, The Mars thermosphere, 2, General circulation with coupled dynamics and composition, *J. Geophys. Res.*, **95**, 14811, 1990.
- Bisikalo, D. V., V. I. Shematovich, and J. C. Gérard, A kinetic model of the formation of the hot oxygen geocorona, 2, Influence of O^+ precipitation, *J. Geophys. Res.*, **100**, 3715–3720, 1995.
- Brace, L. H., W. T. Kasprzak, H. A. Taylor, R. F. Theis, C. T. Russell, A. Barnes, J. D. Mihalov, and D. M. Hunten, The ionotail of Venus: Its configuration and evidence for ion escape, *J. Geophys. Res.*, **92**, 15–26, 1987.
- Chen, R. H., T. E. Cravens, and A. F. Nagy, The Martian ionosphere in light of the Viking observations, *J. Geophys. Res.*, **83**, 3871–3876, 1978.
- Cotton, D. M., G. R. Gladstone, and S. Chakrabarti, Sounding rocket observation of a hot atomic oxygen geocorona, *J. Geophys. Res.*, **98**, 21,651–21,657, 1993.
- Fanale, F. P., J. R. Salvail, W. B. Banerdt, and R. S. Saunders, Mars: The regolith-atmosphere-cap system and climate change, *Icarus*, **50**, 381–407, 1982.
- Fox, J. L., On the escape of oxygen and hydrogen from Mars, *Geophys. Res. Lett.*, **20**, 1747–1750, 1993.
- Fox, J. L., Upper limits to the outflow of ions at Mars: Implications for atmospheric evolution, *Geophys. Res. Lett.*, **24**, 2901–2904, 1997.
- Fox, J. L., and S. W. Bougher, Structure, luminosity and dynamics of the Venus thermosphere, *Space Sci. Rev.*, **55**, 357–489, 1991.

- Fox, J. L., and A. Dalgarno, Ionization, luminosity and heating of the upper atmosphere of Mars. *J. Geophys. Res.* **84**, 7315-7333, 1979.
- Fox, J. L., and A. Hać, $^{15}\text{N}/^{14}\text{N}$ Isotope fractionation in N_2^+ dissociative recombination, *J. Geophys. Res.*, **102**, 9191-9204, 1997a.
- Fox, J. L., and A. Hać, The spectrum of hot O at the exobases of the terrestrial planets, *J. Geophys. Res.*, **102**, 24,005-24,011, 1997b.
- Fox, J. L., P. Zhou, and S. W. Bougher, The thermosphere/ionosphere of Mars at high and low solar activities, *Adv. Space Res.*, **17** (11), 203-218, 1996.
- Gérard, J.-C., P. G. Richards, V. I. Shematovich, and D. V. Bisikalo, The importance of new chemical sources for the hot oxygen geocorona, *Geophys. Res. Lett.*, **22**, 279-282, 1995.
- Gougousi, T., M. F. Golde, and R. Johnsen, Electron-ion recombination rate coefficient measurements in a flowing afterglow plasma, *Chem. Phys. Lett.*, **265**, 399-403, 1997.
- Hanson, W. B., and G. P. Mantas, Viking electron temperature measurements: Evidence for a magnetic field in the Martian atmosphere, *J. Geophys. Res.*, **93**, 7538-7544, 1988.
- Hanson, W. B., S. Sanatani, and D. R. Zuccaro, The Martian ionosphere as observed by the Viking retarding potential analyzers, *J. Geophys. Res.*, **82**, 4351, 1977.
- Hedin, A. E., H. B. Niemann, W. T. Kasprzak, and A. Seiff, Global empirical model of the Venus thermosphere, *J. Geophys. Res.*, **88**, 73, 1983.
- Herzberg, G., *Molecular Spectra and Molecular Structure*, Van Nostrand Reinhold, New York, 1950.
- Hickey, M. P., P. G. Richards, and D. G. Torr, New sources for the hot oxygen geocorona: Solar cycle, seasonal, latitudinal and diurnal variations, *J. Geophys. Res.*, **100**, 17,377-17,388, 1995.
- Hutchins, K. S., B. M. Jakosky, and J. G. Luhmann, Impact of a paleomagnetic field on sputtering loss of Martian atmospheric argon and neon, *J. Geophys. Res.*, **102**, 9183-9189, 1997.
- Ip, W.-H., On a hot oxygen corona of Mars, *Icarus*, **76**, 135-145, 1988.
- Ip, W.-H., The fast atomic oxygen corona extent of Mars, *Geophys. Res. Lett.*, **17**, 2289-2292, 1990.
- Jakosky, B. M., Mars volatile evolution: Evidence from stable isotopes, *Icarus*, **94**, 14-31, 1991.
- Jakosky, B. M., R. O. Pepin, R. E. Johnson, and J. L. Fox, Mars atmospheric loss and isotopic fractionation by solar-wind-induced sputtering and photochemical escape, *Icarus*, **111**, 271-288, 1994.
- Johnson, R. E., and M. Liu, The loss of atmosphere from Mars, *Science*, **274**, 1932, 1996.
- Johnson, R. E., and M. Liu, Sputtering of the atmosphere of Mars, 1, Collisional dissociation of CO_2 , *J. Geophys. Res.*, **103**, 3639-3647, 1998.
- Kass, D. M., Change in the Martian atmosphere, Ph.D. thesis, Calif. Inst. of Technol., Pasadena, 1999.
- Kass, D. M., and Y. L. Yung, Loss of atmosphere from Mars due to solar wind sputtering, *Science*, **268**, 697-699, 1995.
- Kass, D. M., and Y. L. Yung, Response: The loss of atmosphere from Mars, *Science*, **274**, 1932, 1996.
- Kim, J., A. F. Nagy, J. L. Fox, and T. E. Cravens, Solar cycle variation of hot oxygen atoms in the Martian upper atmosphere, *J. Geophys. Res.*, **103**, 29,339-29,342, 1998.
- Knudsen, W. C., The Venus ionosphere from in situ measurements, in *Venus and Mars: Atmospheres, Ionospheres and Solar Wind Interaction*, *Geophys. Monogr. Ser.*, vol. 66, edited by J. G. Luhmann, M. Tatrallyay, and R. Pepin, pp.237-263, AGU, Washington, D.C., 1992.
- Luhmann, J. G., The solar wind interaction with unmagnetized planets: A tutorial, in *Physics of Magnetic Flux Ropes*, *Geophys. Monogr. Ser.*, vol. 58, edited by C. T. Russell et al., pp. 401-411, AGU, Washington, D.C., 1990.
- Luhmann, J. G., R. E. Johnson, and M. H. G. Zhang, Evolutionary impact of sputtering of the Martian atmosphere by O^+ pickup ions, *Geophys. Res. Lett.*, **19**, 2151-2154, 1992.
- Lundin, R., A. Zakharov, R. Pellinen, S. W. Barabash, H. Borg, E. M. Dubinin, B. Hultqvist, H. Koskinen, I. Liede, and N. Pissarenko, ASPERA/Phobos measurements of the ion outflow from the Martian ionosphere, *Geophys. Res. Lett.*, **17**, 873, 1990.
- McComas, D. J., H. E. Spence, C. T. Russell, and M. A. Saunders, The average magnetic field draping and consistent plasma properties of the Venus magnetotail, *J. Geophys. Res.*, **91**, 7939-7953, 1986.
- McElroy, M. B., Mars: An evolving atmosphere, *Science*, **175**, 443, 1972.
- McElroy, M. B., and Y. L. Yung, Oxygen isotopes in the Martian atmosphere: Implications for the evolution of volatiles, *Planet. Space Sci.*, **24**, 1107, 1976.
- McElroy, M. B., T. Y. Kong, and Y. L. Yung, Photochemistry and evolution of Mars' atmosphere: A Viking perspective, *J. Geophys. Res.*, **82**, 4379-4388, 1977.
- Nagy, A. F., and T. E. Cravens, Hot oxygen atoms in the upper atmosphere of Venus and Mars, *Geophys. Res. Lett.* **15**, 433, 1988.
- Nagy, A. F., J. Kim, and T. E. Cravens, Hot hydrogen and oxygen atoms in the upper atmospheres of Venus and Mars, *Ann. Geophys.* **8**, 251, 1990.
- Nagy, A. F., T. E. Cravens, J.-H. Yee, and A. I. F. Stewart, Hot oxygen atoms in the upper atmosphere of Venus, *Geophys. Res. Lett.*, **8**, 629, 1981.
- Newkirk, G., Jr., Solar variability on time scales of 10^5 years to $10^{9.6}$ years, in *The Ancient Sun*, *Geochem. Cosmochem. Acta Suppl.*, edited by R. O. Pepin, J. A. Eddy, and R. B. Merrill, 293 pp., Pergamon, New York, 1980.
- Nier, A. O., and M. B. McElroy, Structure of the neutral upper atmosphere of Mars: Results from Viking 1 and Viking 2, *Science*, **194**, 1298-1300, 1976.
- Nier, A. O., and M. B. McElroy, Composition and structure of Mars' upper atmosphere: Results from the neutral mass spectrometers on Viking 1 and 2, *J. Geophys. Res.*, **82**, 4341-4349, 1977.
- Nier, A. O., M. B. McElroy, and Y. L. Yung, Isotopic composition of the Martian atmosphere, *Science*, **194**, 68, 1976.
- Paxton, L. J., Atomic carbon in the Venus thermosphere: Observations and theory, Ph.D. thesis, Univ. of Colo., Boulder, 1983.
- Richards, P. G., M. P. Hickey, and D. G. Torr, New sources for the hot O geocorona, *Geophys. Res. Lett.*, **21**, 657-660, 1994.
- Rohrbaugh, R. P., J. S. Nisbet, E. Bleuler, and J. R. Herman, The effect of energetically produced O_2^+ on the ion temperatures of the Martian thermosphere, *J. Geophys. Res.*, **84**, 3327, 1979.
- Rosén, S., R. Peverall, M. Larsson, A. Le Padellec, J. Semaniak, Å. Larson, C. Strömholm, W. J. van der Zande, H. Danared, and G. H. Dunn, Absolute cross sections and final state distributions for dissociative recombination and excitation of $\text{CO}^+(v=0)$ using an ion storage ring, *Phys. Rev. A*, **57**, 4462-4471, 1998.
- Shematovich, V. I., D. V. Bisikalo, and J. C. Gerard, A kinetic model of the formation of the hot oxygen geocorona, 1, Quiet geomagnetic conditions, *J. Geophys. Res.*, **99**, 23,217-23,228, 1994.
- Shinagawa, H., and T. E. Cravens, A one-dimensional mul-

- tispecies magnetohydrodynamic model of the dayside ionosphere of Mars, *J. Geophys. Res.*, *94*, 6506, 1989.
- Shinagawa, H., and T. E. Cravens, The ionospheric effects of a weak intrinsic magnetic field at Mars, *J. Geophys. Res.*, *97*, 1027, 1992.
- Vejby-Christensen, L., D. Kella, H. B. Pedersen, and L. H. Andersen, Dissociative recombination of NO^+ , *Phys. Rev. A*, *57*, 3627–3634, 1998.
- Verigin, M. I., et al., Ions of planetary origin in the Martian magnetosphere (PHOBOS 2/TAUS experiment), *Planet. Space Sci.*, *39*, 131–137, 1991.
- Wallis, M. K., Exospheric density and escape fluxes of atomic isotopes on Venus and Mars, *Planet. Space Sci.*, *26*, 949, 1978.
- Wallis, M. K., C, N, and O isotope fractionation on Mars: Implications for crustal H_2O and SNC meteorites, *Earth Planet. Science Letters*, *93*, 321–324, 1989.
- Wright, I. P., M. M. Grady, and C. T. Pillinger, The evolution of atmospheric CO_2 on Mars: The perspective from carbon isotope measurements, *J. Geophys. Res.*, *95*, 14,789–14,794, 1990.
- Yee, J.-H., J. W. Meriwether, and P. B. Hays, Detection of a corona of fast oxygen atoms during solar maximum, *J. Geophys. Res.*, *85*, 3396, 1980.
- Zahnle, K. J., and J. C. G. Walker, The evolution of solar ultraviolet luminosity, *Rev. Geophys.*, *20*, 280, 1982.
- Zhang, M. H. G., J. G. Luhmann, S. W. Bougher, and A. F. Nagy, The ancient oxygen exosphere of Mars: Implications for atmospheric evolution, *J. Geophys. Res.*, *98*, 10,915–10,923, 1993. Correction in Luhmann, J. G., Correction to “The ancient oxygen exosphere of Mars: Implications for atmospheric evolution,” *J. Geophys. Res.*, *102*, 1637, 1997.

J. L. Fox, Department of Physics, Wright State University, Dayton, OH 45435. (fox@platmo.phy.wright.edu)

A. Hać, Delphi Chassis Systems, Engineering Technical Center, Mail Code E-520, 1435 Cincinnati St., Dayton, OH 45408.

(Received May 21, 1999; revised July 19, 1999; accepted July 20, 1999.)