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

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Atomic Carbon in the Atmosphere of Venus

J. L. Fox

Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138

The densities of atomic carbon in the Venustian thermosphere are computed for a model which includes both chemistry and transport. The maximum density of C is $2.8 \times 10^7$ cm$^{-3}$ near 150 km for an assumed $O_2$ mixing ratio of $1 \times 10^{-4}$. Photoionization of atomic carbon is found to be the major source of $C^+$ above 200 km, and resonance scattering of sunlight by atomic carbon may be the major source of the $C$ I emissions at 1561 $\AA$, 1657 $\AA$, and 1931 $\AA$. The computed $C^+$ densities are found to be in substantial agreement with those measured by Pioneer Venus.

INTRODUCTION

The neutral mass spectrometer aboard Pioneer Venus has provided measurements of the altitude profiles of the constituents of the atmosphere of Venus [Niemann et al., 1980], and the ion mass spectrometer has provided measurements of the ionic abundances [Taylor et al., 1980]. A theoretical model of the ionospheric constituents by Nagy et al. [1980] fails by a factor of 3 to reproduce the measurements of the concentrations of $C^+$. We argue here that the abundance of neutral atomic carbon is such that photoionization of C, which was suggested as a possible source but was not included in the model of Nagy et al. [1980], is the major source of $C^+$ ions at altitudes above 200 km and that resonance scattering of sunlight by the carbon atoms is the major source of the $C$ I lines at 1561 $\AA$, 1657 $\AA$, and 1931 $\AA$. We also present estimates of the intensities of the emissions from photoionization of $CO_2$ and CO and electron impact dissociative excitation of $CO_2$.

THE MODEL ATMOSPHERE

We adopted the altitude profiles of CO, $N_2$, O, and CO and the neutral temperature given by a recent model of A. E. Hedin (private communication, 1981) which is based on data from the Pioneer Venus mass spectrometer [Niemann et al., 1980]. No measurements have been reported of the densities of $O_2$ in the upper atmosphere. The sounder probe gas chromatograph measured $O_2$ densities near 40 and 50 km of 16 and 44 ppm, respectively [Oyarna et al., 1980]. From measurements reported by the sounder probe mass spectrometer, Hoffman et al. [1980] placed an upper limit of 30 ppm on the $O_2$ abundance above the clouds. We expect, however, that differentiation may occur at high altitudes. We explore the effects of the alternative assumptions that the $O_2/CO_2$ density ratio at 135 km is $3 \times 10^{-3}$ or $1 \times 10^{-4}$. The ion temperatures and electron temperatures were taken from the data gathered by the Pioneer Venus retarding potential analyzer [Knudsen et al., 1979; Miller et al., 1980] and the Langmuir probe [Theis et al., 1980; cf. Cravens et al., 1980].

CALCULATIONS

We have solved the coupled continuity and momentum equations for twelve ionic constituents ($CO_2^+$, $Ar^+$, $N_2^+$, $O^+$, $Ni^+$, $O_2^+$, $NO^+$, $N^+$, $O^+$, $O_2^+$, $O^+$), and five neutral constituents ($NO$, $N(S^2)$, $N(2D)$, $N(2P)$, and $C$). We included the effects of thermal and ambipolar diffusion for ions and eddy and molecular diffusion for neutrals [cf. Fox, 1982]. The eddy diffusion coefficients were taken from von Zahn et al. [1979]. We assumed that at the lower boundary, taken at 115 km, the $C^+$ ions are in photochemical equilibrium, and we imposed a boundary condition of zero flux for neutral carbon at that altitude. We located the upper boundary at 400 km, and we assumed that diffusive equilibrium prevails there for all constituents.

The solar fluxes were taken from the revised 79050N fluxes of H. Hinteregger (private communication, 1981) for which $F_{10.7}$ was 238 and which are appropriate to the period of high solar activity in which the first Pioneer Venus measurements were made. The solar zenith angle was 18$^\circ$.

The cross sections for photoionization, photoabsorption, and electron impact on CO are the same as those employed by Fox and Dalgarino [1979]. The measurements of production of carbon [Ajello, 1971; Mumma et al., 1972; Wu et al., 1978] refer to C in excited states. The cross section for photodissociative ionization of CO and C were taken from Masuoka and Samson [1980] and Samson et al. [1981]. The CO photoabsorption and photoionization cross sections were taken from Cook et al. [1965], McGuire [1968], Wight et al. [1976], and Cole and Dexter [1978]. Branching ratios for the production of excited states of atomic carbon are given by Wu and Judge [1981]. The rate of electron impact ionization of CO was computed from data provided by Rapp and Engleander-Golden [1965] and Rapp et al. [1965]. Cross sections for the production of ground state atomic carbon by electron impact on CO are not available. In order to test the sensitivity of the model to this source, a cross section with a maximum of $5 \times 10^{-17}$ cm$^2$ near 45 eV was assumed. Cross sections for photoionization of atomic carbon were taken from Cantu et al. [1981] and Dultzubui and Cox [1972].

The chemical reaction scheme is that given by Fox [1982]. The chemical sources and sinks of C and $C^+$ are summarized in Table 1. The rate coefficient for reaction of $O^+$ with CO$_2$ has been measured by R. Johnsen and M. A. Biondi (private communication, 1981). We assume that reaction with CO proceeds at the same rate as that with the isoelectronic molecule $N_2$ [Howorka et al., 1979; Johnsen and Biondi, 1978]. The products of these reactions are unknown. We assume arbitrarily that C and $C^+$ are each produced with a probability of 0.25 in the reaction of O$^+$ with CO$_2$ and with a probability of 0.5 in the reaction with CO.
RESULTS

The altitude profiles of the sources of C are shown in Figures 1a and 1b. Below 190 km the major source is photodissociation of CO. Dissociative recombination of CO dominates above 190 km. McElroy and McConnell [1971] found dissociative recombination to be unimportant, but their assumed CO/CO₂ mixing ratio is \(4.5 \times 10^{-5}\) compared to the value \(8.5 \times 10^{-2}\) at 135 km of the Hedin model. If the adopted cross section is correct, electron impact dissociation of CO is important only below 135 km. Electron impacts on CO₂ are dominant at least below 125 km. The total cross section for production of C may be substantially larger, and electron impact dissociation may be a major source over a more extended altitude range. Other chemical sources of C are not important.

The major chemical sink for atomic carbon is reaction (R9) of Table 1:

\[ C + O₂ → CO + O \]

for an O₂ mixing ratio of \(3 \times 10^{-3}\). If the mixing ratio is \(1 \times 10^{-4}\), the following reactions ((R7), (R8), and (R10), respectively)
TABLE 1. Reactions Involving C and C+

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1) CO(^+) + e \rightarrow C + O</td>
<td>(6.8 \times 10^{-7}) ((293/T_e))^{0.58}</td>
<td>Mentzoni and Donohoe [1969]</td>
</tr>
<tr>
<td>(R2) N(^+) + CO \rightarrow NO(^+) + C</td>
<td>(5.4 \times 10^{-11})</td>
<td>Smith et al. [1978]</td>
</tr>
<tr>
<td>(R3) O(^{++}) + CO(_2) \rightarrow C + O(^+) + O(^+) + O</td>
<td>(5 \times 10^{-10})</td>
<td>see text</td>
</tr>
<tr>
<td>(R4) O(^{++}) + CO \rightarrow C + O(^+) + O(^+)</td>
<td>(8 \times 10^{-10})</td>
<td>see text</td>
</tr>
<tr>
<td>(R5) He(^+) + CO(_2) \rightarrow O(_2)^{+} + C + He</td>
<td>(1.1 \times 10^{-11})</td>
<td>Adams and Smith [1976]</td>
</tr>
<tr>
<td>(R6) C(^+) + NO \rightarrow NO(^+) + C</td>
<td>(8.5 \times 10^{-11})</td>
<td>Anicich et al. [1976]</td>
</tr>
<tr>
<td>(R7) C + O(_2)^{+} \rightarrow CO(^+) + O</td>
<td>(5 \times 10^{-11})</td>
<td>Prasad and Huntress [1980]</td>
</tr>
<tr>
<td>(R8) C + O(_2)^{+} \rightarrow C(^+) + O(_2)</td>
<td>(5 \times 10^{-11})</td>
<td>Prasad and Huntress [1980]</td>
</tr>
<tr>
<td>(R9) C + O(_2) \rightarrow CO + O</td>
<td>(3.3 \times 10^{-11}(T/300)^{1/2})</td>
<td>Braun et al. [1969]</td>
</tr>
<tr>
<td>(R10) C + NO \rightarrow CN + O</td>
<td>(1.1 \times 10^{-10})</td>
<td>Braun et al. [1969]</td>
</tr>
<tr>
<td>(R11) C + CO(_2) \rightarrow CO + CO</td>
<td>(4.4 \times 10^{-15}T^{3/2})</td>
<td>estimate.</td>
</tr>
<tr>
<td>(R12) He(^+) + CO \rightarrow C(^+) + O + He</td>
<td>(1.4 \times 10^{-9})</td>
<td>McElroy and McConnell [1971]</td>
</tr>
<tr>
<td>(R13) O(^{++}) + CO(_2) + C(^+) + O(^+)</td>
<td>(5 \times 10^{-10})</td>
<td>see text</td>
</tr>
<tr>
<td>(R14) O(^{++}) + CO \rightarrow C(^+) + O(^+) + O</td>
<td>(8 \times 10^{-10})</td>
<td>see text</td>
</tr>
<tr>
<td>(R15) C(^+) + O(_2) \rightarrow O + CO(^+)</td>
<td>(9 \times 10^{-10})</td>
<td>Rakshit et al. [1968]</td>
</tr>
<tr>
<td>(R16) C(^+) + CO(_2) \rightarrow CO(^+) + CO</td>
<td>(1.1 \times 10^{-9})</td>
<td>Fahey et al. [1981]</td>
</tr>
</tbody>
</table>

C + O\(_2\)^{+} \rightarrow C\(^+\) + O

C + O\(_2\)^{+} \rightarrow C\(^+\) + O\(_2\)

are of comparable importance.

The resulting atomic carbon densities are shown in Figure 2. For O\(_2\)/CO\(_2\) = 10\(^{-4}\) the maximum C density is about \(2.8 \times 10^7\) cm\(^{-3}\) at 145 km. For O\(_2\)/CO\(_2\) = 3 \times 10\(^{-3}\), the maximum is \(4.9 \times 10^6\) cm\(^{-3}\) at 155 km. These densities are an order of magnitude or more larger than those reported by McElroy and McConnell [1971], mostly due to the higher densities of CO and CO\(^+\) in our model.

Altitude profiles of the sources of C\(^+\) are presented in Figures 3a and 3b.

The largest source of C\(^+\) below 155 km is photodissociative ionization of CO\(_2\). Between 155 km and 195 km, reaction (R8), C + O\(_2\)^{+} \rightarrow C\(^+\) + O\(_2\)

is more important and photoionization of atomic carbon dominates production of C\(^+\) above 195 km. For O\(_2\)/CO\(_2\) = 3 \times 10\(^{-3}\) the processes involving atomic carbon are less rapid, and between 175 km and 200 km photodissociative ionization of CO is comparable to reaction (R8).

C\(^+\) is lost mainly by reaction (R16):

C\(^+\) + CO\(_2\) \rightarrow CO\(^+\) + CO

and reaction with O\(_2\) has a minor effect for the mixing ratios of O\(_2\) considered here.

The resulting C\(^+\) densities are shown in Figure 4, where they are compared to the measured densities of Taylor et al. [1980]. For O\(_2\)/CO\(_2\) = 3 \times 10\(^{-3}\) the maximum density of C\(^+\) is \(3.8 \times 10^4\); for O\(_2\)/CO\(_2\) = 10\(^{-4}\) the maximum density is \(7.5 \times 10^3\). Agreement is good above 200 km for the low O\(_2\) mixing ratio, and it appears that O\(_2\)/CO\(_2\) mixing ratios of...
$10^{-4}$ or less may prevail in the Venusian ionosphere. For smaller values of O$_2$/CO$_2$ the C$^+$ densities would not be appreciably enhanced, since reaction with O$_2$ is no longer the major loss mechanism for C. Below 200 km the calculated densities are low by about a factor of 2. The sources of C$^+$ in this region, dissociative ionization of CO$_2$ and CO, may be underestimated.

The total integrated intensities of the 1657-Å, 1561-Å, and 1931-Å lines of atomic carbon from photodissociation of CO and CO$_2$ and electron impact on CO$_2$ are given in Table 2.

**TABLE 2. Overhead Intensities of Atomic Carbon Lines in Rayleighs**

<table>
<thead>
<tr>
<th></th>
<th>Electron Impact on CO$_2$</th>
<th>Photodissociation of CO$_2$</th>
<th>Photodissociation of CO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1657Å</td>
<td>112</td>
<td>80</td>
<td>42</td>
<td>234</td>
</tr>
<tr>
<td>1561Å</td>
<td>66</td>
<td>45</td>
<td>27</td>
<td>138</td>
</tr>
<tr>
<td>1931Å</td>
<td>89</td>
<td>55</td>
<td>55</td>
<td>144</td>
</tr>
</tbody>
</table>
The integrated vertical column intensity of the 1657-Å line is 234 R compared with a limb intensity of 30 kR measured by Mariner 10 [Broadfoot et al., 1974].

If we assume that the lines are optically thin, we can use the $g$ value reported by McElroy and McConnell to compute upper limits to the overhead intensity due to resonance scattering of the 1657-Å line of 0.56 kR for $O_2/CO_2 = 3 \times 10^{-3}$ and 1.4 kR for $O_2/CO_2 = 1 \times 10^{-4}$. In practice the phenomenon is complex and more detailed calculations which include radiative transfer are necessary to compute the resonance scattering contribution. It is probably comparable to or exceeds the contribution from dissociative excitation. Thus the larger atomic carbon densities predicted by this model explain both the $C^+$ densities measured by Pioneer Venus and the large atomic carbon dayglow intensities measured by Mariner 10.

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