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Atomic Carbon in the Atmosphere of Venus

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The densities of atomic carbon in the Venusian thermosphere are computed for a model which includes both chemistry and transport. The maximum density of C is $2.8 \times 10^7 \text{ cm}^{-3}$ near 150 km for an assumed O_2 mixing ratio of 1×10^{-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 Å, 1657 Å, and 1931 Å. 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 Å, 1657 Å, and 1931 Å. 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_2 , 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 [Oyama *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 3×10^{-3} or 1×10^{-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^+ ,

$\text{O}^+(^4S)$, $\text{O}^+(^2D)$, $\text{O}^+(^2P)$, CO^+ , C^+ , N^+ , O_2^+ , NO^+ , and O^{++}) and five neutral constituents (NO , $\text{N}(^4S)$, $\text{N}(^2D)$, $\text{N}(^2P)$, 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° .

The cross sections for photoionization, photoabsorption, and electron impact on CO_2 are the same as those employed by Fox and Dalgarno [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_2 and CO 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 Englander-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 $5 \times 10^{-17} \text{ cm}^2$ near 45 eV was assumed. Cross sections for photoionization of atomic carbon were taken from Cantu *et al.* [1981] and Daltabuit 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.

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Fig. 1. Altitude profiles of the sources of neutral atomic carbon.

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 4.5×10^{-5} compared to the value 8.5×10^{-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:

for an O₂ mixing ratio of 3×10^{-3} . If the mixing ratio is 1×10^{-4} , the following reactions ((R7), (R8), and (R10), respectively)

TABLE 1. Reactions Involving C and C⁺

	Reaction	Rate	Reference
(R1)	$\text{CO}^+ + e \rightarrow \text{C} + \text{O}$	$6.8 \times 10^{-7} (293/T_e)^{0.58}$	<i>Mentzoni and Donohoe</i> [1969]
(R2)	$\text{N}^+ + \text{CO} \rightarrow \text{NO}^+ + \text{C}$	5.4×10^{-11}	<i>Smith et al.</i> [1978]
(R3)	$\text{O}^{++} + \text{CO}_2 \rightarrow \text{C} + \text{O}^+ + \text{O}^+ + \text{O}$	5×10^{-10}	see text
(R4)	$\text{O}^{++} + \text{CO} \rightarrow \text{C} + \text{O}^+ + \text{O}^+$	8×10^{-10}	see text
(R5)	$\text{He}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{C} + \text{He}$	1.1×10^{-11}	<i>Adams and Smith</i> [1976]
(R6)	$\text{C}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{C}$	8.5×10^{-11}	<i>Anicich et al.</i> [1976]
(R7)	$\text{C} + \text{O}_2^+ \rightarrow \text{CO}^+ + \text{O}$	5×10^{-11}	<i>Prasad and Huntress</i> [1980]
(R8)	$\text{C} + \text{O}_2^+ \rightarrow \text{C}^+ + \text{O}_2$	5×10^{-11}	<i>Prasad and Huntress</i> [1980]
(R9)	$\text{C} + \text{O}_2 \rightarrow \text{CO} + \text{O}$	$3.3 \times 10^{-11} (T/300)^{1/2}$	<i>Braun et al.</i> [1969]
(R10)	$\text{C} + \text{NO} \rightarrow \text{CN} + \text{O}$	1.1×10^{-10}	<i>Braun et al.</i> [1969]
(R11)	$\text{C} + \text{CO}_2 \rightarrow \text{CO} + \text{CO}$	$4.4 \times 10^{-15} T^{1/2}$	estimate,
		$\exp(-3480/T)$	<i>McElroy and McConnell</i> [1971]
(R12)	$\text{He}^+ + \text{CO} \rightarrow \text{C}^+ + \text{O} + \text{He}$	1.4×10^{-9}	<i>Rakshit et al.</i> [1978]
(R13)	$\text{O}^{++} + \text{CO}_2 + \text{C}^+ + \text{O}^+ + \text{O} + \text{O}$	5×10^{-10}	see text
(R14)	$\text{O}^{++} + \text{CO} \rightarrow \text{C}^+ + \text{O}^+ + \text{O}$	8×10^{-10}	see text
(R15)	$\text{C}^+ + \text{O}_2 \rightarrow \text{O} + \text{CO}^+$	9×10^{-10}	<i>Rakshit et al.</i> [1968]
(R16)	$\text{C}^+ + \text{CO}_2 \rightarrow \text{CO}^+ + \text{CO}$	1.1×10^{-9}	<i>Fahey et al.</i> [1981]

are of comparable importance.

The resulting atomic carbon densities are shown in Figure 2. For $\text{O}_2/\text{CO}_2 = 10^{-4}$ the maximum C density is about $2.8 \times 10^7 \text{ cm}^{-3}$ at 145 km. For $\text{O}_2/\text{CO}_2 = 3 \times 10^{-3}$, the maximum is $4.9 \times 10^6 \text{ cm}^{-3}$ 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),

is more important and photoionization of atomic carbon dominates production of C^+ above 195 km. For $\text{O}_2/\text{CO}_2 = 3 \times 10^{-3}$ 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):

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 $\text{O}_2/\text{CO}_2 = 3 \times 10^{-3}$ the maximum density of C^+ is 3.8×10^3 ; for $\text{O}_2/\text{CO}_2 = 10^{-4}$ the maximum density is 7.5×10^3 . Agreement is good above 200 km for the low O_2 mixing ratio, and it appears that O_2/CO_2 mixing ratios of

Fig. 2. Computed densities of neutral atomic carbon as a function of altitude for O_2/CO_2 mixing ratios of 3×10^{-3} and 1×10^{-4} .

Fig. 3. Altitude profiles of the sources of C^+ ions for an assumed O_2/CO_2 mixing ratio of 1×10^{-4} .

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

	Electron Impact on CO_2	Photodissociation of CO_2	Photodissociation of CO	Total
1657Å	112	80	42	234
1561Å	66	45	27	138
1931Å		89	55	144

Fig. 4. Altitude profiles of the C^+ ion densities for O_2 mixing ratios of 3×10^{-3} and 1×10^{-4} . The solid lines are the computed densities. The dots are measurements from Taylor et al. [1980].

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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REFERENCES

- Adams, N. G., and D. Smith, Product ion distributions for some ion-molecule reactions, *J. Phys. B*, **9**, 1439, 1976.
- Ajello, J. M., Emission cross sections of CO_2 by electron impact in the interval 1260–4500 Å, II, *J. Chem. Phys.*, **55**, 3169, 1971.
- Anicich, V. G., W. T. Huntress, and J. H. Futrell, Ion cyclotron resonance studies of some reactions of C^+ ions, *Chem. Phys. Lett.*, **40**, 233, 1976.
- Braun, W., A. M. Bass, D. D. Davis, and J. J. Simmons, Flash photolysis of carbon suboxide: Absolute rate constants for reactions of $C(^3P)$ and $C(^1D)$ with H_2 , N_2 , CO , NO , O_2 and CH_4 , *Proc. R. Soc. London Ser. A*, **312**, 417, 1969.
- Broadfoot, A. L., S. Kumar, M. J. S. Belton, and M. B. McElroy, Ultraviolet observations of Venus from Mariner 10: Preliminary results, *Science*, **174**, 1315, 1974.
- Cantu, A. M., M. Mazzoni, M. Pettini, and G. D. Tozzi, Photoionization spectrum of the 3P ground state of neutral carbon, *Phys. Rev. A*, **23**, 1223, 1981.
- Cole, B. E., and R. N. Dexter, Photoabsorption and photoionization measurements on some atmospheric gases in the wavelength region 50–340 Å, *J. Phys. B*, **11**, 1011, 1978.
- Cook, G. R., P. H. Metzger, and M. Ogawa, Photoionization and absorption coefficients of CO in the 600 to 1000 Å region, *Can. J. Phys.*, **43**, 1706, 1965.
- Cravens, T. E., T. I. Gombosi, J. Kozyra, A. F. Nagy, L. H. Brace, and W. C. Knudsen, Model calculations of the dayside ionosphere of Venus: Energetics, *J. Geophys. Res.*, **85**, 7778, 1980.
- Daltabuit, E., and D. P. Cox, K-Shell photoionization cross sections, *Astrophys. J.*, **177**, 855, 1972.
- Fahey, D. W., F. C. Fehsenfeld, and E. E. Ferguson, Rate constant for the reaction $C^+ + CO_2$ at collision energies 0.04 to 2.5 eV, *Geophys. Res. Lett.*, **8**, 1115, 1981.
- Fox, J. L., The chemistry of metastable species in the Venusian ionosphere, *Icarus*, in press, 1982.
- Fox, J. L., and A. Dalgarno, Ionization, luminosity, and heating of the upper atmosphere of Mars, *J. Geophys. Res.*, **84**, 7315, 1979.
- Hoffman, J. H., R. R. Hodges, T. M. Donahue, and M. B. McElroy, Composition of the Venus lower atmosphere from the Pioneer Venus mass spectrometer, *J. Geophys. Res.*, **85**, 7882, 1980.
- Howorka, F., A. A. Viggiano, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, Laboratory studies of the O^{++} reactions of ionospheric importance, *J. Geophys. Res.*, **84**, 5941, 1979.
- Johnsen, R., and M. A. Biondi, Measurement of the reaction rates of O^{++} ions with N_2 and O_2 at thermal energy and their ionospheric implications, *Geophys. Res. Lett.*, **5**, 847, 1978.
- Knudsen, W. D., K. Spennner, R. C. Whitten, J. R. Spreiter, K. L. Miller, and V. Novak, Thermal structure and major ion composition of the Venus atmosphere: First RPA results from the Venus Orbiter, *Science*, **203**, 757, 1979.
- Masouka, T., and J. A. R. Samson, Dissociative and double photoionization of CO_2 from threshold to 90 Å, *J. Chim. Phys. Phys. Chim. Biol.*, **77**, 623, 1980.
- McElroy, M. B., and M. C. McConnell, Atomic carbon in the atmospheres of Mars and Venus, *J. Geophys. Res.*, **76**, 6674, 1971.
- McGuire, E. J., Photoionization cross sections of the elements helium to xenon, *Phys. Rev. A*, **175**, 20, 1968.
- Mentzoni, M. H., and J. Donohoe, Electron recombination and diffusion in CO at elevated temperature, *Can. J. Phys.*, **47**, 1789, 1969.
- Miller, K. L., W. C. Knudsen, K. Spennner, R. C. Whitten, and V. Novak, Solar zenith angle dependence of ionospheric ion and electron temperatures and density on Venus, *J. Geophys. Res.*, **85**, 7759, 1980.

- Mumma, M. J., E. J. Stone, W. L. Borst, and E. C. Zipf, Dissociative excitation of vacuum ultraviolet emission features by electron impact on molecular gases, III, CO₂, *J. Chem. Phys.*, **57**, 68, 1972.
- Nagy, A. F., T. E. Cravens, S. G. Smith, H. A. Taylor, and H. C. Brinton, Model calculations of the dayside ionosphere of Venus: Ionic composition, *J. Geophys. Res.*, **85**, 7795, 1980.
- Niemann, H. B., W. T. Kasprzak, A. E. Hedin, D. M. Hunten, and N. W. Spencer, Mass spectrometric measurements of the neutral gas composition of the thermosphere and exosphere of Venus, *J. Geophys. Res.*, **85**, 7817, 1980.
- Oyama, V. I., G. C. Carle, F. Woeller, J. B. Pollack, R. T. Reynolds, and R. A. Craig, Pioneer Venus gas chromatography of the lower atmosphere of Venus, *J. Geophys. Res.*, **85**, 7891, 1980.
- Prasad, S. S., and W. T. Huntress, A model for gas phase chemistry in interstellar clouds, I, The basic model, library of chemical reactions, and chemistry among C, N and O compounds, *Astrophys. J. Suppl.*, **43**, 1, 1980.
- Rakshit, A. B., H. M. P. Stock, D. P. Wareing, and N. D. Twiddy, Some ion-molecule reaction rate coefficient measurements at 300 K and 100 K in a temperature variable flowing afterflow apparatus, *J. Phys. B*, **11**, 4237, 1978.
- Rapp, D., and P. Englander-Golden, Total cross sections for ionization and attachment in gases by electron impact, I, Positive ionization, *J. Chem. Phys.*, **43**, 1464, 1965.
- Rapp, D., P. Englander-Golden, and D. D. Briglia, Cross sections for dissociative ionization of molecules by electron impact, *J. Chem. Phys.*, **42**, 4081, 1965.
- Samson, J. A. R., T. Masuoka, and W. T. Huntress, The production rate of C⁺ from the photoionization of CO and CO₂, *Geophys. Res. Lett.*, **8**, 405, 1981.
- Smith, D., N. G. Adams, and T. M. Miller, A laboratory study of the reaction of N⁺, N₂⁺, N₃⁺, N₄⁺, O⁺, O₂⁺ and NO⁺ ions with several molecules at 300 K, *J. Chem. Phys.*, **69**, 308, 1978.
- Taylor, H. A., H. C. Brinton, S. J. Bauer, R. E. Hartle, P. A. Cloutier, and R. E. Daniell, Global observations of the composition and dynamics of the ionosphere of Venus: Implications for the solar wind interaction, *J. Geophys. Res.*, **85**, 7765, 1980.
- Theis, R. F., L. H. Brace, and H. G. Mayr, Empirical models of the electron temperature and density in the Venus ionosphere, *J. Geophys. Res.*, **85**, 7787, 1980.
- von Zahn, U., D. Krankowsky, K. Mauersberger, A. O. Nier, and D. M. Hunten, Venus thermosphere: In situ composition measurements, the temperature profile and the homopause altitude, *Science*, **203**, 768, 1979.
- Wight, G. R., M. J. Van der Wiel, and C. B. Brion, Dipole excitation ionization and fragmentation of N₂ and CO in the 10–60 eV region, *J. Phys. B*, **9**, 675, 1976.
- Wu, C. Y. R., and D. L. Judge, Atomic carbon emission produced through photodissociative excitation of CO, *J. Chem. Phys.*, **75**, 2826, 1981.
- Wu, C. Y., E. Phillips, L. C. Lee, and D. L. Judge, Atomic carbon emission from photodissociation of CO₂, *J. Geophys. Res.*, **83**, 4869, 1978.

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