Photodissociation of Carbon Dioxide in the Mars Upper Atmosphere

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Dedicated to Professor W. Groth on his 70th Birthday

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Photodissociation of carbon dioxide produces O(^{1}S) atoms and CO(a$^3\Pi$) molecules in the Mars upper atmosphere. Calculations of the emission rate of the atomic oxygen 2972 Å line and the carbon monoxide Cameron bands produced by the photodissociation mechanism are factors of 3 and 10, respectively, smaller than the emission rates observed by Mariner ultraviolet spectrometers. Laboratory measurements are needed to understand the discrepancies.

In the upper atmosphere of Mars, carbon dioxide, the major constituent, is directly illuminated by solar ultraviolet radiation. Solar photons of sufficiently short wavelength are not only energetically capable of dissociating carbon dioxide, but of producing dissociation products in excited states. Emissions produced during the dissociative excitation of carbon dioxide are part of the airglow of Mars. It is the purpose of this study to calculate the intensity of two of these emissions using laboratory measurements and to compare the results with spacecraft observations.

Laboratory Measurements

In early laboratory work, Groth [1] recognized that the photodissociation products of carbon dioxide by 1470 Å radiation were carbon monoxide and atomic oxygen. While ultraviolet photons of wavelength shortward of 1671 Å are energetically capable of producing O(^{1}D) atoms, collisional deactivation of this excited state by carbon dioxide is very rapid [2] and dominates the radiative process throughout the Mars atmosphere [3]. In contrast, solar ultraviolet photons of wavelength shortward of 1286 Å have sufficient energy to produce O(^{1}S) atoms and the atomic oxygen 2972 Å line has been observed in the ultraviolet airglow of Mars from Mariner 6, 7, and 9 [4–6]. Similarly, photons of wavelength shortward of 1082 Å are energetically capable of producing CO(a$^3\Pi$) molecules and carbon monoxide Cameron band emissions have been observed by the Mariner ultraviolet spectrometers [4–6]. Following the Mariner observations of the atomic oxygen 2972 Å line and the carbon dioxide Cameron bands in the Mars airglow, Lawrence [7] measured the quantum yield for the production of O(^{1}S) atoms and CO(a$^3\Pi$) molecules in the laboratory. Other mechanisms suggested as sources of these excited atoms and molecules in the Mars atmosphere are electron impact dissociative excitation of carbon dioxide and dissociative recombination of ionized carbon dioxide [8, 9].

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Calculations

To calculate the rate of production of O(^{1}S) atoms and CO(a$^3\Pi$) molecules in the Mars atmosphere, it is necessary to know the intensity of the ultraviolet solar flux, the absorption cross section of carbon dioxide, and the quantum yield for the production of the excited states, as well as the density distribution of carbon dioxide in the Mars atmosphere [3]. The product of the first three quantities, summed over wavelength, is the production frequency. Satellite measurements of the sun show that the solar spectrum between 1286 Å (the threshold for O(^{1}S) production) and 900 Å (the photoionization threshold of carbon dioxide) consists of strong emission lines with underlying continua. In the upper part of Fig. 1, a solar ultraviolet spectrum from OSO-3 [10] indicates that the strongest line in this wavelength interval is the atomic hydrogen Lyman alpha line at 1216 Å. Other members of the Lyman series are present in the solar spectrum as well as strong emission lines of O VI, N II, C III, and S VI. In addition, the Lyman continuum shortward of 911 Å makes a substantial contribution to the solar ultraviolet intensity in this wavelength region[10]. Table 1 gives the values of the intensities of the emission lines and continua which were calculated by extrapolating the OSO-3 measurements to the orbit of Mars. Absorption cross sections of carbon dioxide at the wavelengths of the solar emission lines were obtained by Hudson[11] (personal communication) from the laboratory measurements of Nakata et al.[12]. These cross sections, multiplied by the quantum yield measurements of Lawrence[7], produce cross sections for photodissociative excitation of $O(^1S)$ atoms and $CO(a^3\Pi)$ molecules which are also listed in Table 1. The production frequencies of $O(^1S)$ atoms and $CO(a^3\Pi)$ molecules for each of the solar emissions are included in Table 1 and plotted in the lower two-thirds of Figure 1.

Figure 1 shows that the principal solar emissions contributing to the production of $O(^1S)$ atoms are the O VI lines at 1038 and 1032 Å, the Lyman beta line at 1026 Å, the C III line at 977 Å, and the Lyman continuum shortward of 911 Å. For the production of $CO(a^3\Pi)$ molecules from the photodissociation of carbon dioxide, Fig. 1 shows that the principal solar emissions that contribute are the Lyman continuum between 900 and 911 Å and the 977 Å C III line.

Comparision with Observations

In order to compare the calculated photoproduction rates of $O(^1S)$ atoms and $CO(a^3\Pi)$ molecules with the Mariner observations of emissions from these excited species in the Mars airglow, the product of the production frequency and the density of carbon dioxide in the Mars atmosphere as a function of altitude is required. A model atmosphere derived from Mariner observations[6] was used for this calculation. In addition, the emission rate of excited atoms and molecules must be calculated along a column with the atmosphere viewed tangentially in the manner of the Mariner observations[5]. The calculated results are compared with the measurements of the OI 2972 Å line and the CO Cameron bands made by the ultraviolet spectrometers on Mariner 6 and 7[5] in Figs. 2 and 3. Oxygen atoms in the ^1S state radiate both the 5577 Å and 2972 Å lines in the ratio of 20:1 while carbon monoxide molecules in the $a^3\Pi$ state radiate only the Cameron bands.

Discussion

In Fig. 2, the calculated tangential column emission rate of the 2972 Å line is smaller than the

Table 1.

Wavelength (Å)	Solar Flux (photons cm^{-2} sec^{-1})	Cross Section (cm^2)		Production Frequency (sec^{-1})	
		$O(^1S)$	$CO(a^3\Pi)$	$O(^1S)$	$CO(a^3\Pi)$
1265	2.0 (08)*	4.2 (−21)		8.5 (−13)	
1261	1.0 (08)	5.1 (−21)		5.0 (−13)	
1243	1.3 (08)	8.7 (−21)		1.1 (−12)	
1239	1.9 (08)	1.0 (−20)		1.9 (−12)	
1216	1.3 (11)	1.1 (−20)		1.4 (−09)	
1207	1.6 (09)	1.1 (−20)		1.7 (−11)	
1175	9.5 (08)	3.4 (−19)		3.2 (−10)	
1027/1265	1.6 (09)	3.9 (−18)		6.3 (−09)	
1128	1.2 (08)	3.0 (−18)		3.5 (−10)	
1123	9.5 (07)	3.0 (−18)		2.8 (−10)	
1085	2.6 (08)	8.2 (−18)	5.8 (−20)	2.1 (−09)	1.5 (−11)
1037	7.4 (08)	5.4 (−17)	7.8 (−18)	4.0 (−08)	5.7 (−09)
1032	1.0 (09)	1.5 (−17)	2.4 (−18)	1.4 (−08)	2.4 (−09)
1026	1.5 (09)	1.7 (−17)	3.2 (−18)	2.5 (−08)	4.8 (−09)
990	2.6 (08)	2.3 (−17)	8.8 (−18)	5.9 (−09)	2.3 (−09)
977	1.9 (09)	1.6 (−17)	7.8 (−18)	3.0 (−08)	1.5 (−08)
973	3.5 (08)	1.6 (−17)	8.5 (−18)	5.6 (−09)	2.9 (−09)
911/1027	5.2 (08)	2.0 (−17)	1.1 (−17)	1.1 (−08)	6.0 (−09)
950	1.7 (08)	3.2 (−17)	2.6 (−17)	5.4 (−09)	4.4 (−09)
945	4.3 (07)	2.2 (−17)	2.1 (−17)	9.6 (−10)	8.9 (−10)
938	9.5 (07)	1.9 (−17)	2.1 (−17)	1.9 (−09)	2.0 (−09)
933	5.6 (07)	2.1 (−17)	2.4 (−17)	1.2 (−09)	1.4 (−09)
931	5.6 (07)	2.0 (−17)	2.5 (−17)	1.1 (−09)	1.4 (−09)
926	5.6 (07)	1.9 (−17)	2.6 (−17)	1.1 (−09)	1.5 (−09)
904	5.6 (07)	2.4 (−17)	4.1 (−17)	1.4 (−09)	2.3 (−09)
900/911	7.6 (08)	2.5 (−17)	4.3 (−17)	1.9 (−08)	3.3 (−08)

* (08) denotes 10^8

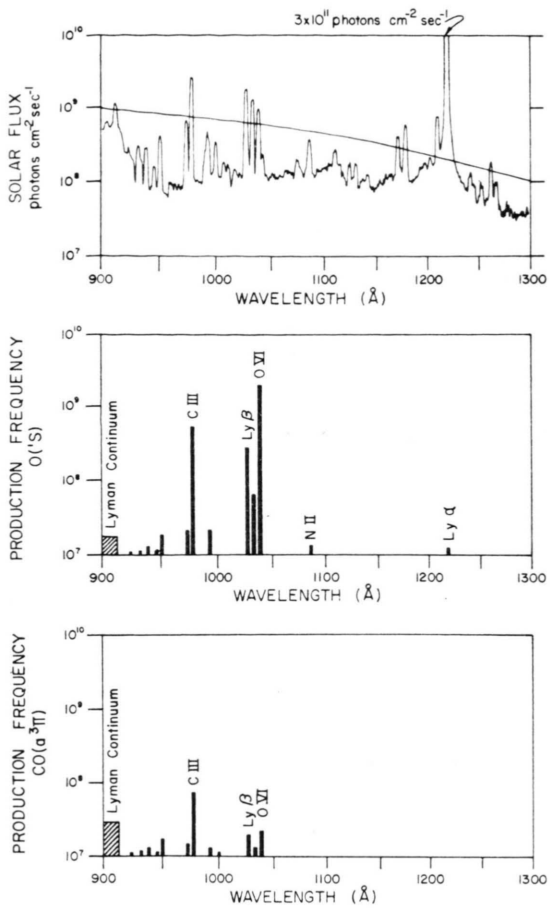

Fig. 1. Upper. Solar flux measurements from OSO-3 in the wavelength interval 900—1300 Å showing the prominent emission lines and underlying continua. The solid line indicates how the instrument sensitivity varies as a function of wavelength. — Center. Production frequency of O (^1S) from the principal solar emission lines and the Lyman continuum, calculated for the orbit of Mars. — Lower. Production frequency of CO ($a^3\Pi$) from the principal solar emission lines and the Lyman continuum, calculated for the orbit of Mars.

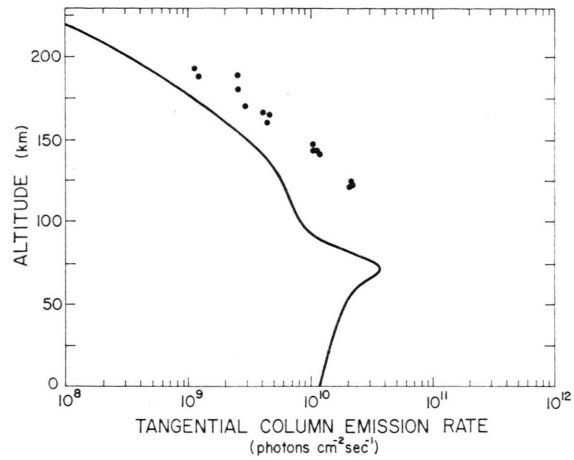

Fig. 2. The calculated tangential column emission rate of 2972 Å OI (solid line) together with observed Mars airglow (dots), showing the altitude distribution.

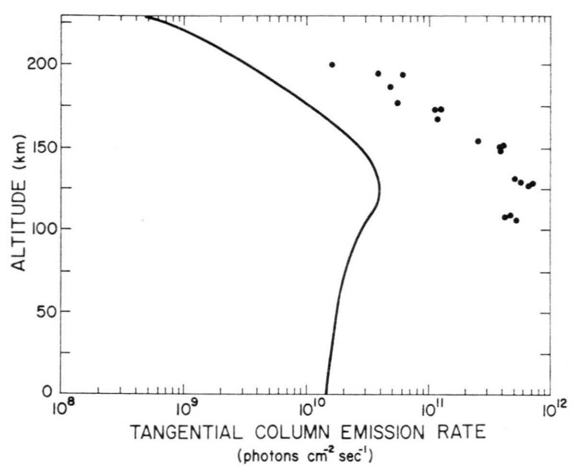

Fig. 3. The calculated tangential column emission rate of the CO Cameron bands (solid line) together with the observed Mars airglow (dots), showing the altitude distribution.

observed airglow by about a factor of about three. This discrepancy may indicate that, in addition to potential errors in the Mariner observations, there may be other excitation mechanisms as well as photodissociative excitation of carbon dioxide or that some of the parameters used in the photoproduction rate calculation may be in error. If the intensity of the solar flux is actually greater than the values reported by the OSO-3 experiment, the discrepancy may be accounted for. Laboratory measurements of carbon dioxide cross sections may not have sufficient wavelength accuracy to provide sufficiently precise values at the wavelengths of the effective solar emission lines; namely, O IV 1032 and 1038 Å, Lyman beta 1026 Å, and C III 977 Å. In this wavelength region, the absorption spectrum is highly structured. Laboratory measurements carried out with light sources containing the solar emission lines would remove this possible error. Dissociative recombination of CO_2^+ and O_2^+ in the Mars ionosphere is a potential additional source of excitation of O (^1S) atoms [9] as well as the dissociative excitation of carbon dioxide by photoelectrons [8].

In Fig. 3, the calculated tangential column emission rate of the carbon monoxide Cameron bands is smaller than the observed airglow by about a factor of ten. The same remarks can be made about potential errors in laboratory cross section measurements or in satellite solar flux observations as were made about the OI 2972 Å emission; however, because of the larger discrepancy between observation and the calculation of the photodissociative excitation rate, it is more likely that there is another strong excitation mechanism and the best candidate is the electron impact dissociative excitation of carbon dioxide to produce $CO(a^3\Pi)$ molecules [8]. Laboratory measurements need to be made of the electron impact cross section for dissociative excitation of carbon dioxide to produce $CO(a^3\Pi)$ molecules, particularly for electron energies near the threshold energy of 11.5 eV where the photoelectron flux is the most intense.

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