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PHOTODISSOCIATION OF CO IN THE THERMOSPHERE OF VENUS

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Abstract. Recent investigations of CO photoabsorption demonstrate that photodissociation longward of the ionization threshold at 88.5 nm occurs primarily through line absorptions rather than continuous processes. We have constructed high resolution photoabsorption cross sections for CO at rotational temperatures near 250 K from the improved data on dissociating transitions. We examine the effects of the new cross sections on the rate of solar photodissociation of CO in the thermosphere of Venus and compare the results to values obtained with the lower resolution cross sections available previously. We find that the photodissociation profile peaks slightly higher in the atmosphere and the peak value and integrated total rate both decrease by about a factor of two.

Introduction

Recent studies of photodissociation of CO, both theoretical and experimental, have shown that at wavelengths between about 88.5 nm and the dissociation threshold at 111.8 nm, dissociation occurs by line absorption into predissociating states, rather than through continuous absorption. Previous measurements of the absorption spectrum of CO, such as those of Cook *et al.* [1965], whose cross sections have been used in planetary models [e.g. Fox, 1982], failed to resolve the band structure. The spectrum of Cook *et al.* [1965] showed peaks that were attributed to band structure, but the measurements were interpreted as showing also the presence of a dissociation continuum in the 60 to 100 nm region. Hudson [1971] noted that there was no reason to expect an absorption continuum longward of the ionization threshold (88.5 nm); indeed, *ab initio* calculations of the electronic structure of CO show no repulsive states of appropriate symmetry below 14 eV [Cooper and Kirby, 1987]. The development of synchrotron sources for UV radiation has allowed the measurement of the CO absorption cross sections at very high resolution. Letzelter *et al.* [1987] measured the absorption cross sections and fluorescence yields with a resolution of 0.015 nm, which is still coarse in relation to the rotational line spacings (≤ 0.001 nm) within some of the bands. They set an upper limit on the continuum cross section at 90 nm of 1.2×10^{-18} cm²; longward of 100 nm, the limit was smaller, about 6×10^{-20} cm². Absorption measurements of even higher resolution have been performed by G. Stark, P. L. Smith, K. Yoshino, and W. H. Parkinson [private communication, 1987] and Yoshino *et al.* [1988] in which the rotational structure of the bands has been nearly completely re-

solved. Yoshino *et al.* [1988] presented photoabsorption coefficients between 97.1 and 100.4 nm with a resolution of 7×10^{-4} nm. The cross sections derived from their measurements are larger than those of Letzelter *et al.* [1987].

Van Dishoeck and Black [1988] and Viala *et al.* [1988] have incorporated the new spectroscopic data on CO photodissociation into detailed models of interstellar clouds. Mamon *et al.* [1988] have explored the corresponding application to the description of cool circumstellar envelopes. The new data lead to a larger unshielded photodissociation rate of CO in typical interstellar radiation fields than was adopted in earlier work. The depth dependences of the CO photodissociation and of isotope-selective effects are also found to be sensitive to details of line positions and line broadening. In contrast to interstellar radiation fields which are taken to vary smoothly between 91.2 and 111.8 nm, solar radiation has no cut-off at 91.2 nm and is dominated by discrete emission lines. Solar photodissociation of CO is of interest for investigations of planetary atmospheres and comets. The measurement of CO [Eberhardt *et al.* 1987, Woods *et al.* 1986] and of its neutral fragments [Stewart, 1987] in comet Halley make a re-examination of its lifetime against photodissociation timely. The photochemistry of cometary CO will be discussed elsewhere. We investigate here the implications of the new cross sections for solar photodissociation of CO in the thermosphere of Venus. Photodissociation of CO is the major source of atomic carbon in the Venus atmosphere, and photoionization of atomic carbon is the major source of C⁺ at high altitudes in the ionosphere [e.g. Fox, 1982; Krasnopolsky, 1982].

A list of the CO bands and their assignments was provided by G. Stark, P. L. Smith, K. Yoshino, and W. H. Parkinson [private communication, 1987] to van Dishoeck and Black [1988] and presented in their Table 1. Also given in that table are the oscillator strengths and rotational constants adopted by van Dishoeck and Black [1988] and the predissociation widths that they estimated for each band from unpublished spectra of Stark *et al.* We have computed the positions and oscillator strengths of lines arising from rotational levels up to $J = 30$ of the ground state for the bands listed in Table 1 of van Dishoeck and Black and for six additional bands, which lie shortward of the ionization threshold of atomic hydrogen at 91.2 nm. The additional bands are listed here in Table 1. Using this spectroscopic information, we have computed absorption cross sections of CO from 88.9 to 111.8 nm, at 10^{-4} nm intervals. The individual line profiles are assumed to be either Lorentzian or Gaussian, depending on whether the natural or Doppler width is larger. At temperatures less than 300 K, and for most of the lines, the natural width is larger. Because the solar fluxes vary slowly over the widths of the CO lines, the results are insensitive to the assumed shape of the lines. Figure 1 shows our computed cross sections as a function of wavelength from 88.9 to 110 nm for a CO rotational temperature of 250 K.

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TABLE 1. Additional Spectroscopic Data for CO^a

Band No.	Band No.	λ (nm)	f	ν_0 (cm ⁻¹)
34	1	88.997	5.4(-2)	112363.3
35	2	89.672	3.3(-2)	111517.5
36	3	90.059	1.7(-2)	111038.3
37	4	90.509	1.6(-2)	110486.3
38	5	90.640	1.1(-2)	110326.6
39	6	90.958	2.7(-2)	109940.9

^aThe band index numbers of column 1 follow those in Table 1 of van Dishoeck and Black [1988]. Column 2 refers to the numbering of Letzelter *et al.* [1987], which is the source of the band positions λ and ν_0 and of the oscillator strengths f . Following van Dishoeck and Black [1988], we assume that the upper states are all ¹ Σ^+ states with rotational constants $B' = 1.9225$ cm⁻¹ and $D' = 6.121 \times 10^{-6}$ cm⁻¹ and that the total inverse lifetimes and predissociation probabilities are $A = 3 \times 10^{11}$ s⁻¹ and $\eta = 1.0$, respectively.

The Model

The densities of the species CO₂, N₂, CO, O, and N in the thermosphere of Venus were adopted from a model of Hedin *et al.* [1983 and private communication] for high solar activity ($F_{10.7} = 200$) and 45° solar zenith angle. This model is based on measurements from the Pioneer Venus Orbiter Mass Spectrometer [e.g. Niemann *et al.*, 1980]. Atomic carbon was also included, with densities from Fox [1982]. The photoabsorption, photoionization and photodissociation cross sections are from Fox [1982] and from an updated compilation of cross sections for use in aeronomy [Kim and Fox, unpublished data].

We have adopted the F79050N solar spectrum of Hinteregger [private communication; see also Torr *et al.*, 1979] to represent the solar fluxes for high solar activity and the SC#21REFW spectrum of Hinteregger for low solar activity. The continuum photon fluxes are given approximately every 0.1 nm from 1.4 to 200 nm and the integrated fluxes are given for the strong solar lines. In the wavelength range from 88.9 to 111.8 nm, we have interpolated the continuum fluxes and divided the spectrum into 10⁻⁴ nm intervals. The shapes of the strong solar lines are potentially important for line absorptions such as these, but, except for Lyman α and Lyman β [e.g., Lemaire *et al.*, 1978] not much information is available about the profiles of EUV lines, most of which originate in the chromosphere and the transition region to the corona, where the temperatures range from 8×10^3 to 4×10^6 K [Timothy, 1977]. For the strong solar lines other than the Lyman lines we have assumed Doppler profiles with a characteristic temperature of 1×10^6 K. Although the lines may originate at lower temperatures, the effects of optical thickness cause the lines to appear broader than the Doppler width determined by the temperature in their region of origin [R. Kurucz, private communication]. For Lyman β and γ , we have assumed a profile consisting of two Gaussians each of half width 0.018 nm, offset by 0.04 nm, to approximate the shape for Lyman β reported by Lemaire *et al.* [1978]. For lines other than the Lyman lines, we have not attempted to reproduce structure such as absorption or emission cores in the lines. For a CO rotational temperature of 250 K, that appropriate to the region of maximum absorption in the Venus thermosphere, the results are insensitive to the assumed shape of the solar lines.

Results

Figure 2 shows the computed CO photodissociation profile in our model atmosphere, compared to that obtained with the low resolution measurements of Cook *et al.* [1965]. The components due to continuous absorption shortward of 88.9 nm and to predissociation through line absorption at longer wavelengths are shown separately. The cross sections and dissociation yields in the continuum region shortward of 74.5 nm were adopted from Samson and Gardner [1976]. The integrated photodissociation rates due to continuous absorption shortward of 88.9 nm are reduced by a factor of less than a third (or about 10% of the total) from those obtained with the Cook *et al.* [1965] data. The optically thin photodissociation frequency at Venus is 2.31×10^{-6} s⁻¹ (corresponding to 1.21×10^{-6} s⁻¹ at 1 AU), which is 24% less than the value 3.04×10^{-6} s⁻¹ computed using the absorption coefficients of Cook *et al.* [1965]. The altitude of the absorption peak is at about 148 km, slightly higher than the previous value, and the magnitude of the peak is about a factor of two smaller. The total integrated photodissociation rate, 4.90×10^9 cm⁻²s⁻¹, is also smaller by a factor of two than that obtained using the low resolution data.

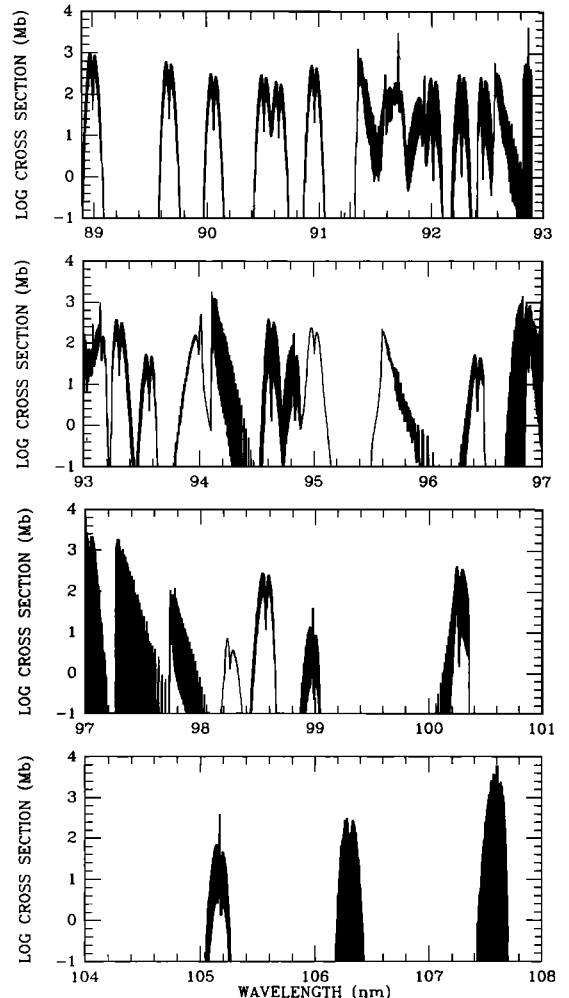


Fig. 1. CO photodissociation cross sections constructed from the molecular data for a rotational temperature of 250 K. The cross sections were computed and the absorption calculation was done at intervals of 10⁻⁴ nm over the range from 88.9 to 111.8 nm.

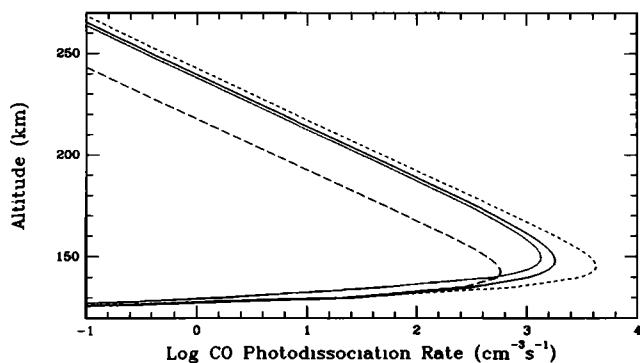


Fig. 2. Altitude profiles of CO photodissociation rates computed with the new high resolution data compared to those computed with the low resolution data. The solid line is the total dissociation rate. The contributions from line absorption longward of 88.9 nm (dotted line) and continuous absorption shortward of 88.9 nm (long dashed line) are shown separately. The short-dashed line is the photodissociation rate computed using the low resolution data of Cook et al. [1965].

We have divided the spectrum from 88.9 to 111.8 nm into eight wavelength regions and have displayed altitude profiles of the CO photodissociation rates for each region in Figure 3. The integrated column dissociation rates are presented in Table 2. The most important region for line dissociation is the Lyman continuum at wavelengths less than 91.3 nm.

The integrated photodissociation rates are insensitive to the assumed Doppler widths of the solar lines. A 50% increase in the characteristic temperature to 1.5×10^6 K reduces the integrated rate by only about 1%; a 50% decrease in the temperature to 5×10^5 K increases the integrated rate by about 2%. Varying the CO rotational temperature from the assumed value of 250 K to 200 K and 300 K changes the integrated rates by -2.6% and $+1.8\%$, respectively.

Discussion

From about 110 to 89 nm, the line structure in the CO photoabsorption causes the values of the cross sections to vary over more than 5 orders of magnitude from the peaks of strong lines to the valleys between bands. If CO were the major absorber, such a variation could produce a very broad altitude profile of absorption rates composed

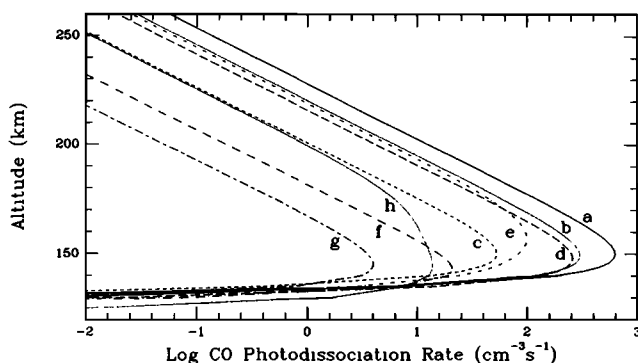


Fig. 3. Altitude profiles of the contributions to the CO photodissociation rate from the eight wavelength regions. The curves are labeled by the designations in Table 2.

TABLE 2. The integrated photodissociation rates of CO in the Venus atmosphere contributed by the continuum shortward of 88.9 nm and by line absorption in 8 different wavelength regions longward of 88.9 nm. The labels refer to the photodissociation profiles in Figure 3.

Label	Wavelength range (nm)	Photodissociation rate ($10^8 \text{ cm}^{-2} \text{ s}^{-1}$)
	< 88.9	13.4
a	88.9 – 91.3	15.7
b	91.3 – 93.2	7.74
c	93.2 – 94.5	1.31
d	94.5 – 95.5	6.44
e	95.5 – 98.0	3.25
f	98.0 – 99.5	0.466
g	99.5 – 104.0	0.0973
h	104.0 – 110.0	0.553
	TOTAL	49.0

of a superposition of profiles with maxima occurring at quite different altitudes. Figure 3 shows, however, that the absorption profiles of seven of the eight wavelength regions look similar to profiles for monochromatic absorption, with maxima spread over a 10 km region from 145 to 155 km. The peak optical depths in most of the CO bands approach unity only at altitudes of the order of 150 km, where continuous absorption by other species is becoming significant; therefore, self-shielding in the CO lines does not have a dramatic effect on the altitude profiles of the dissociation rate. CO_2 , C and O, and to a lesser extent, N_2 and N have significant cross sections in this region of the spectrum.

Although CO can be an efficient absorber in narrow wavelength intervals around strong lines, it does not dominate the opacity at 89 to 110 nm in an average sense. CO_2 is the major absorber in all eight wavelength channels below 165–170 km. Atomic oxygen dominates above 150 km. Its ionization threshold is at 91.2 nm, so absorption by O is important for the two shortest wavelength regions in Table 2, which together account for over half the integrated dissociation rate. The ionization threshold of atomic carbon is at 110.1 nm, and its absorption is important above 190–200 km. The N_2 densities have the same altitude dependence as CO, and absorption by N_2 is a factor of 2 to 6 less than that of CO in most of the wavelength regions, but is comparable to CO in the 95.5 to 98.0 nm region. Photodissociation of N_2 , which occurs by excitation to predissociating states of the singlet manifold, may need to be treated similarly to that of CO. Only in the wavelength region longward of 104 nm is CO the major absorber over a significant altitude range, from 165 to 200 km. Furthermore, this region contains the narrowest CO lines, which suffer the most severe effects of self-shielding. Figure 3 shows that the dissociation profile in that altitude range is anomalously broad.

The altitude profile of the total CO photodissociation rate, shown in Figure 2, is similar to that based on the Cook et al. [1965] data, although the integrated rate is a factor of 2 smaller for the new data than that obtained with the low resolution data. The effect is considerably larger in the interstellar medium [van Dishoeck and Black, 1988; Gredel et al. 1987], where fewer rotational levels are populated and CO itself is the dominant absorber at the wavelengths of most of its dissociating transitions. The rotational temperatures in the Venus thermosphere are comparable to that in the measurements of Cook et al. [1965], which were performed near room temperature. At these high temperatures, the

bands overlap and fill much of the 90 – 100 nm region of the spectrum.

We averaged our cross sections over 0.1 nm intervals for comparison with those reported by Cook et al. [1965]. The peak values of the cross sections measured by Cook et al. [1965] are in good agreement with our averaged values, except in the wavelength range from 98.5 to 100 nm, where the few tabulated points of Cook et al. suggest significant absorption, but only one strong band appears in the high resolution measurements. The optically thin photodissociation frequency computed with our averaged cross sections is about 3% less than for the higher resolution cross sections, although the peak of the altitude profile and the integrated rate are larger by about 23% and 13%, respectively. Tabulated values of the smoothed cross sections are available from the authors.

Photodissociation of CO is sensitive to variations in the solar fluxes as pointed out by Torr et al. [1979] and Oppenheimer and Downey [1980]. We find photodissociation frequencies at 1 AU of $1.21 \times 10^{-6} \text{ s}^{-1}$ for high solar activity and $4.4 \times 10^{-7} \text{ s}^{-1}$ for low solar activity. Oppenheimer and Downey [1980] tabulate frequencies of total absorption and ionization of CO for high activity (spectrum 79011) and low activity ("July 1976") based on the cross sections of Cook et al. [1965] as weighted by Torr et al. [1979]. Their corresponding photodissociation frequencies are 1.4×10^{-6} and $5.6 \times 10^{-7} \text{ s}^{-1}$, respectively, and these differ from our values as expected for the different fluxes and cross sections. Huebner and Carpenter [1979] list a photodissociation frequency of CO at 1 AU of $3.2 \times 10^{-7} \text{ s}^{-1}$, which reflects the lower solar fluxes they assumed.

Conclusions

Recent studies have shown that CO photoabsorption in the 88.9 – 110 nm region of the spectrum occurs by line absorption into predissociating states rather than by continuous absorption. We have constructed cross sections appropriate to the rotational temperatures in the region of maximum absorption in the Venus atmosphere and modeled the effect on the CO dissociation rates. The shape of the altitude profile remains largely unchanged, but the peak value and the total integrated dissociation rate are reduced by a factor of two from previous models [e.g., Fox, 1982]. A factor of two difference in the photodissociation rate does, however, have important implications for the production and chemistry of atomic carbon in the thermosphere of Venus, where photodissociation of CO is the major source of atomic carbon. Further studies of the implications of this effect are in progress.

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