

The Photolysis of CO₂ at Wavelengths Exceeding 1740 Å

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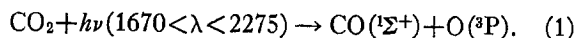
ABSTRACT

An experimental investigation is reported on the photolysis of CO₂ for $\lambda > 1740$ Å. It is shown that CO is indeed produced when CO₂ is exposed to radiation in the wavelength region 1740–2100 Å. Quantum yield measurements have been made for this process and a value of $\phi_{\text{CO}} = 1$ ($\pm 25\%$) has been obtained. It is deduced that this process should occur in the lower atmosphere of Mars, regardless of the details of the mechanism of photolysis. Accordingly, the results of this study tend to support the proposal made by McElroy and Hunten that absorption of solar radiation in the region 1670–2275 Å by CO₂ plays a dominant role in the photochemistry of CO₂ in the lower atmosphere of Mars.

1. Introduction

In developing a theory of the photochemistry of CO₂ in the Martian atmosphere, McElroy and Hunten (1970) proposed that photodissociation of CO₂ in the wavelength range 1670–2000 Å is of considerable importance in the lower atmosphere (i.e., below about 40 km). In fact, their calculations show that the photodissociation rate of CO₂ is greater by this process than that occurring at higher altitudes and for wavelengths < 1670 Å. The combination of the greater CO₂ density at the lower altitudes and the rapidly increasing solar flux for wavelengths > 1670 Å is responsible for this difference in photodissociation rates, despite the fact that the absorption cross section of CO₂ for $\lambda > 1670$ Å is significantly less than 0.1 of that at 1450 Å (Inn *et al.*, 1953; Thompson *et al.*, 1963).

The ground state of CO₂ is derived from CO(¹Σ⁺) + O(¹D), with the dissociation limit at 7.42 eV. The first excited state of CO₂ arises from CO(¹Σ⁺) + O(³P), the dissociation limit occurring at 5.45 eV. The wavelengths corresponding to the photon energies for these dissociation limits are 1670 and 2275 Å, respectively. Thus, McElroy and Hunten proposed the long-wavelength photodissociation of CO₂ to proceed as



This process would indeed be very important in the photochemistry of CO₂ in the lower atmosphere of Mars, particularly if it can be demonstrated that CO₂ does yield the products in (1) when exposed to radiation in the wavelength region indicated, and the quantum yield of this process is substantially unity. We are not aware

of any report of an experimental investigation of this process. Accordingly, we have undertaken such a study and reported the results here.

It should be noted that a gap existed in the data published on the absorption coefficient of CO₂ in the region between 1750 and 1850 Å (Inn *et al.* and Thompson *et al.*). This gap has been essentially filled by recent measurements (Heimerl, 1970) that have been very useful in the analysis of data obtained from this investigation.

2. The experiment

The arrangement for conducting the photolysis experiments is shown in Fig. 1. The photolysis cell consisted of a quartz cube, 3 cm on a side, with 1 mm thick windows 1 inch in diameter mounted as shown. The cell was connected to a conventional gas filling system, which was capable of evacuating the cell to pressures $\lesssim 3 \times 10^{-6}$ torr. A McLeod gage was used to measure pressures < 20 torr, but for pressures greater than this the gage was used as a manometer.

Fluorescence of the fourth positive bands of CO was used to detect and quantitatively measure any CO produced by photolysis. The CO probe lamp shown in Fig. 1 consisted of a 2450 MHz, electrodeless light source, in which a trace amount of CO in flowing argon was discharged to produce the required CO fourth positive bands for the fluorescence measurements. The fluorescent emission was detected by a combination of a 1 m vacuum spectrometer (McPherson Model 217) and an EMR 542G photomultiplier tube. Conventional pulse counting techniques at the output of the detector were used to measure the low-level fluorescence signals. In most of the measurements, fluorescence from the (1,4) band at 1728 Å was used to determine quantitatively

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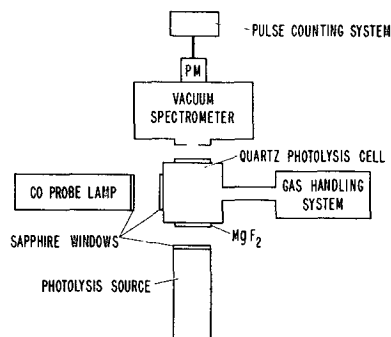


FIG. 1. Experimental arrangement for CO_2 photolysis.

the amount of CO. It was found that the fluorescence signals were linear with CO concentration only for CO pressures $\lesssim 1$ –2 millitorr. Thus, all experiments were adjusted to be in this linear range. The fluorescence signals were calibrated by adding measured amounts of CO in the cell. In an actual experiment the signal obtained from the CO produced by photolysis is compared with that when a known quantity of CO is added to the cell.

The photolysis light source displayed in Fig. 1 consisted of either a high-pressure Xe continuum source or an H_2 continuum source, each mounted with a sapphire window. These sources were excited in the same way as the CO probe lamp. Since both sources do emit below 1670 \AA , it was extremely important to filter all radiation effectively in the shorter wavelength region. It was found that a 2.3-cm air path filter between the photolysis source and cell was convenient and most effective in virtually attenuating completely all radiation $\lesssim 1740 \text{ \AA}$. The spectral distribution of the Xe continuum source is displayed in Fig. 2 with the attenuation due to the air filter indicated in the region 1730 – 1800 \AA . The attenuation in the latter region, which con-

sisted of the absorption in the discrete Schumann-Runge bands of O_2 , was actually measured for a 2.3-cm path length of air. This measurement was needed for the quantum yield determinations. Note also the inset in Fig. 1 showing the computed relative photon absorption rate by 1 torr of CO_2 in the photolysis cell (path length 3.0 cm). It displays very clearly the wavelength region in which the absorption by CO_2 is most important when the Xe continuum source is used in the experimental arrangement described above and shown in Fig. 1. Very similar spectral absorption would be obtained when the H_2 continuum source is used since the spectral distribution is quite similar to that of the Xe continuum in this wavelength region.

For the quantum yield measurements it was necessary to determine the absolute emission rate of the Xe source. The total ultraviolet energy (1400 – 2100 \AA) emitted by the source was measured with an Eppley thermopile, the latter calibrated against a National Bureau of Standards standard lamp. In order to relate this energy measurement to the spectral emission of the Xe source, it was necessary to correct the relative spectral distribution shown in Fig. 2 for the spectrometer-detector sensitivity and transmission of the MgF_2 window. The spectral distribution was determined with a 0.5 m Seya-Namioka type spectrometer (McPherson Model 235) and a sodium salicylate coated screen placed in front of an EMI 9514S photomultiplier tube. No further correction for the spectrometer-detector sensitivity was necessary since the spectral sensitivity was essentially constant in the region between 1500 and 2000 \AA as determined by the technique developed by Mumma and Zipf (1971). A small correction was applied for the MgF_2 window transmission. From these energy measurements we found that the vacuum ultraviolet flux emitted by the Xe continuum source was 3.6×10^{14} photons sec^{-1} through an area of 0.71 cm^2 .

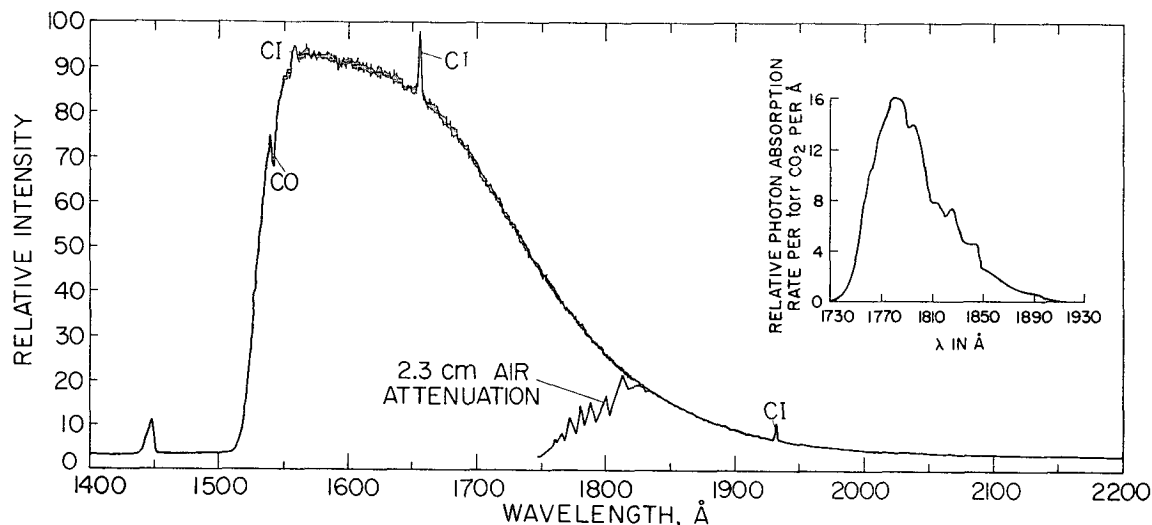


FIG. 2. Xe continuum spectral distribution. Note that the O light level is displaced, the displacement indicating the dark current of the photomultiplier detector. Scattered light amounted to much less than 0.5%.

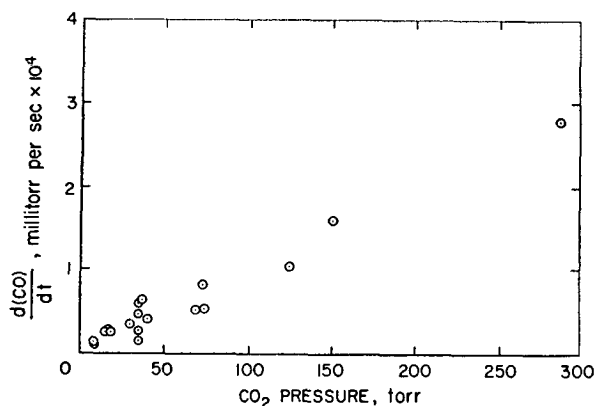


FIG. 3. CO production rate vs CO₂ pressure. The H₂ continuum source was used in these measurements.

In all the photolysis experiments Matheson's Coleman Grade CO₂ was used without further purification. After every photolysis the excess CO₂ was trapped with liquid N₂ and removed from the photolysis cell. This procedure was necessary since residual CO₂ would severely quench the fluorescence during the CO measurement. Furthermore, unwanted photolysis of the residual CO₂ by the CO probe lamp would occur, thereby introducing serious errors in the CO determination.

3. Results

The identity of the product of photolysis of CO₂ was established by its fluorescence spectrum. This spectrum, besides the (1,4) band, corresponded quite well with the other strong bands of the CO fourth positive system, namely, the (1,0), (1,1), (0,1) and (0,2) bands.

In all the results of CO₂ photolysis it was necessary to correct for outgassing from the walls (windows) of the cell when it was exposed to ultraviolet radiation. Similar observations of CO outgassing have been reported by Felder *et al.* (1970). Therefore, in all experiments a separate determination was made with an empty cell photolyzed under conditions identical to that when filled with CO₂. Since the outgassing was found to be linearly dependent on the exposure time, the magnitude of the outgassing time varied from negligible amounts for short exposure times (<400 sec) to rather large corrections for long exposure times (>1000 sec).

The results of CO₂ photolysis using the H₂ continuum source are displayed in Fig. 3. The rather large scatter in the data, especially at low CO₂ pressures, probably is due to the large outgassing corrections applied, as discussed above, and variations in the photolysis source intensity during long exposures and on separate days. Despite this scatter in the data, the plotted results do indicate a linear dependence of the CO production rate on the CO₂ pressure. For pressures <300 torr and wavelengths >1750 Å, CO₂ is optically thin. No attempt was made to conduct measurements below about 8.5 torr CO₂ (lowest pressure shown in Fig. 3) since extremely

long photolysis times (several thousand seconds) would be required to yield measurable amounts of CO. As discussed above, this would mean that very large outgassing corrections would have to be made.

For the quantum yield measurements the calibrated Xe continuum source was used (see Fig. 2), the photolyzing wavelength region extending between about 1750 to 1850 Å. The results are shown in Table 1 in which quantum yield measurements are included for photolysis at shorter wavelengths, effectively between 1500–1670 Å. Thus, for the latter measurements, the Xe source was the same as that used previously under identical experimental conditions, except there was no air filter between source and cell. Furthermore, measurements were conducted for each spectral region, one after the other on the same day. In calculating the quantum yield, the photon absorption rate, dn/dt , was calculated from

$$\frac{dn}{dt} = N_{\text{CO}_2} L \int I_{\lambda} T_{\lambda} \sigma_{\lambda} d\lambda, \quad (2)$$

where

$$\int I_{\lambda} d\lambda = P$$

is the total radiated power in the vacuum ultraviolet as measured by the thermopile, I_{λ} is the number of quanta per second per unit wavelength interval, T_{λ} the transmission of the 2.3-cm air filter, σ_{λ} the CO₂ absorption cross section, N_{CO_2} the CO₂ density, and L the path length in the cell (3.0 cm). Note that Eq. (2) is valid only for absorption under optically thin conditions, which was certainly true in these measurements. Thus, from the measured CO production rate we have the quantum yield

$$\phi_{\text{CO}} = \frac{d[\text{CO}]/dt}{dn/dt}. \quad (3)$$

It is interesting to note that in this technique for measuring quantum yields it can be readily shown that the ratio of the quantum yield for the short-wavelength region (1500–1670 Å) to the long-wavelength region (1750–1850 Å) is independent of the magnitude of the

TABLE 1. Quantum yield results.

Wavelength region (Å)	CO ₂ pressure (torr)	Photolysis time (sec)	CO pressure* (millitorr)	Quantum yield ϕ_{CO}
1750–1850	142	500	0.10	0.88
	82	500	0.078	1.20
	76	1000	0.14	1.11
	29	1500	0.069	0.95
Average				1.0
1500–1670	1.80	100	0.11	0.52
	3.70	100	0.22	0.54
	1.80	100	0.10	0.49
	0.18	500	0.055	0.54
Average				0.52

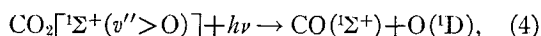
* Photolysis cell volume 50 cm³.

total intensity of the Xe source. That is, the ratio of the quantum yields is independent of the thermopile measurements. It is difficult to determine the absolute error in these results but we estimate that systematic errors could be as large as $\pm 25\%$. The error in the ratio of the quantum yields, of course, is much less than this.

4. Discussion

We have seen from Fig. 2 that in this experiment absorption by CO_2 takes place primarily at wavelengths $> 1750 \text{ \AA}$. In fact, it can be readily calculated that absorption at 1740 \AA contributes, for a band width of 10 \AA , about 10^{-2} of the total absorption. At 1670 \AA the contribution is about 10^{-7} of the total. Evidently, the strong Schumann-Runge continuum absorption of O_2 by the air filter effectively attenuates all radiation below 1740 \AA so that the observed photolysis arises from absorption by CO_2 for wavelengths $> 1740 \text{ \AA}$.

On the basis of the above considerations we deduce that, at thermal equilibrium at 295K , vibrationally excited CO_2 is unimportant for the absorption process according to



where the threshold wavelengths corresponding to ν_2 , ν_1 and ν_3 are at about 1690 , 1710 and 1739 \AA , respectively. Clearly, even for any nonthermally populated distributions of these vibrational levels the contribution from these can not be larger than 1% of the total absorption. We therefore believe that the observed photolysis is by process (1) although, at the present time, our investigations shed no light on the details of the actual process. The alternatives of the actual process are 1) direct photodissociation as depicted by Eq. (1), 2) predissociation, and 3) collision-induced predissociation.

Our results, displayed in Fig. 3, are inadequate to determine whether mechanism 3) is the appropriate one involved. Observations at much lower CO_2 pressures than reported here are needed to determine whether the CO production rate remains a linear function of the CO_2 pressure. However, if we assume that the photolysis of CO_2 observed in our experiment is typical of that expected to occur over the region $1670\text{--}2275 \text{ \AA}$, then we may infer that because of the very weak absorption displayed by CO_2 in this spectral region, the lifetime of the presumed bound upper state is estimated to be longer than 10^{-5} sec . This estimate is derived from a calculated lifetime of $\sim 10^{-7} \text{ sec}$ for the shorter wavelength absorption ($1500\text{--}1650 \text{ \AA}$) of CO_2 reported by Clark and Noxon (1970). Since the average absorption cross section of CO_2 in the long-wavelength region is less than 10^{-2} of that at shorter wavelengths, we arrive at the estimated bound upper state lifetime of about 10^{-5} sec . The density for which the time between collisions is 10^{-5} sec is about $3 \times 10^{14} \text{ cm}^{-3}$. The density corresponding to the lowest CO_2 pressure (8.5 torr) reported in our results is about $2.7 \times 10^{17} \text{ cm}^{-3}$. If mechanism 3) is the prevailing one, it seems reasonable from the preceding

argument to assume that departure from nonlinearity in the CO production rate would be observed only at pressures considerably lower than the above.

According to McElroy and Hunten (1970) the peak rate of process (1) on Mars occurs at an altitude of about 12 km where the CO_2 density is about $5 \times 10^{16} \text{ cm}^{-3}$; unit optical depth for the wavelength region $1900\text{--}2000 \text{ \AA}$ occurs at about this altitude. From the above discussion it would seem reasonable to state that the CO production rate is linear with CO_2 pressure over the range corresponding to that in the lower atmosphere of Mars below 40 km regardless of the detailed mechanism by which the photolysis occurs. Furthermore, this implies that the quantum yield for CO production is independent of the CO_2 pressure over this range. In view of this we feel that our results substantially support McElroy and Hunten's proposal that CO and O are produced in the lower atmosphere of Mars as a result of absorption of solar radiation between $1670\text{--}2000 \text{ \AA}$. Moreover, the production rates of CO and O they calculated are substantially correct for the model atmosphere they adopted in view of the quantum yield reported herein.

We will only briefly comment here on the quantum yield obtained from photolysis in the short-wavelength region. The values quoted in Table 1 are to be considered preliminary. The value $\phi_{\text{CO}} = 0.5$ appears to be low compared to recent measurements (Felder *et al.*, 1970; Stief *et al.*, 1969; Clark and Noxon, 1970; Slinger and Black²) that report $\phi_{\text{CO}} = 1$. We are continuing our effort in these measurements and it is expected that the results of this study will be published soon.

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