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## HOT CO ON MARS

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The Mariner 6 and 7 spacecraft, which flew by the planet Mars on July 31 and August 5, 1969, featured onboard ultraviolet scanning spectrometers. These spectrometers produced the first spectra of the dayglow of the Mars upper atmosphere over the wavelength region 100 to 400 nm. The spectra showed emissions that were characteristic of the carbon dioxide ion and neutral molecule, the carbon monoxide ion and neutral molecule, and the atomic species of hydrogen, oxygen, and carbon. The spectra between 200 and 400 nm showed emission features from each of these molecules. Between 100 and 200 nm the only observed molecular feature was the fourth positive group of CO, as shown in Figure 1 (Ref. 1). Starting at the low-wavelength end of the spectrum, we see a very prominent Lyman-alpha atomic hydrogen line, then the resonance line of atomic oxygen at 130.4 nm, the metastable oxygen line at 135.6 nm, a variety of atomic carbon lines, and then prominent features that represent the resonance band system of the CO molecule, the fourth positive group. These spectra were taken at 1-nm resolution, which is not sufficient to resolve the shape of the individual band in the fourth positive group.



Figure 1-Ultraviolet spectrum of the upper atmosphere of Mars, 110 to 180 nm, 1-nm resolution. Spectrum was obtained by observing the atmosphere tangentially at an altitude between 140 and 160 km. This spectrum was obtained from the sum of four individual observations (from Ref. 1).

In anticipation of the Mariner 6 and 7 flybys, Mumma, Stone, Borst, and Zipf (Refs. 2 and 3) at the University of Pittsburgh and Ajello (Refs. 4 and 5) at the University of Colorado performed experimental studies of production of this band system by electron impact on CO and on  $CO_2$ . In light of these laboratory data, Barth and coworkers (Ref. 1) concluded that the fourth positive emission intensities measured by the Mariner spectrometers could be explained by photoelectron impact on  $CO_2$  in the Mars upper atmosphere.

This presented an intriguing problem: namely, could one assign an effective rotational temperature to the excited CO fragment produced in the dissociative excitation of  $CO_2$ ? If the excited CO could be characterized by an effective temperature and if the thermal distribution of the ambient CO in the Mars atmosphere were known, then the variation of emission intensity with altitude would yield the column density of CO of Mars.

The Mariner spectra were taken at too low a resolution to shown the rotational profiles. We decided to measure the rotational profiles of the fourth positive bands in the laboratory. The results of that experiment are shown in Figure 2. Here we plot the relative intensity against the wavelength for bands originating from the  $\nu' = 1$  vibrational level of the CO  $(A^1 \pi)$  state. The spectra were taken at 0.09-nm resolution and individual rotational lines are not resolved. The envelope of the lines, however, is sufficient to show that the bands are much broader in wavelength for electron impact on CO<sub>2</sub> than for electron impact on CO. This means that the excited CO molecule is rotating much faster when produced from CO<sub>2</sub> than it is when produced by electron impact on CO.

Our results show that when electrons impact on thermal CO<sub>2</sub> at 300 K, the rotational temperature of the CO  $(A^1 \pi)$  fragment exceeds 1500 K. Furthermore, the rotational temperature is not independent of the incident electron energy but depends sensitively upon it just in the energy range at which we would expect the Mars photoelectron flux to be large, i.e., <6.4 aJ (<40 eV). In view of these results we conclude that an attempt to unfold the CO column density from the fourth positive emission intensities is presently not feasible.

We conclude that rotationally hot CO is produced on Mars by photoelectron impact on CO<sub>2</sub> and that the effective rotational temperature of CO  $(A^1 \pi)$  is much higher than the equilibrium rotational temperature of ambient CO in the Mars upper atmosphere.



Figure 2-Emission profiles of bands of the fourth positive group. x denotes the (1, 4) band, e + CO; + denotes the (1, 0) band,  $e + CO_2$ .

We conclude further that the high effective rotational temperatures will result in reduced self-absorption of the CO fourth positive bands on Mars.

A wavelength resolution of 0.01 nm is needed for rotational band profiles to enable an unfolding of the CO column density on Mars. The present Mariner has a wavelength resolution of 0.75 nm and is therefore incapable of the required observations.

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