On the Interpretation of Strong CO₂ Absorption Bands in the Spectrum of Mars

G. Münch and G. Neugebauer
California Institute of Technology, Pasadena, California

The determination of the atmospheric pressure at the surface of Mars by spectroscopic means is based on the comparison of broad-band measurements of strong CO₂ bands in the instrumental infrared with the intensity of weak lines of the same molecule at lower wavelengths (Kaplan, Münch and Spinrad, 1964). The absorption in a strong band, formed by non-overlapping pressure-broadened lines, is asymptotically proportional to the product (wp) between the amount of absorber w and the pressure p of the broadening gas. The weak line absorption, in contrast, depends only on the net amount of absorber. At present, it appears that much of the uncertainty affecting estimates of the pressure in Mars’ atmosphere arises from the difficulties associated with the measurement of the equivalent widths of the very weak lines (Chamberlain and Hunten, 1965). In addition, the interpretation of the absorption by strong bands is affected by uncertainties arising from estimating the level of a “continuum” from which the absorption is measured and the procedures followed to allow for the CO₂ absorption in the earth’s atmosphere.

As a part of the general problem of determining the pressure in the Martian atmosphere, we have studied the problem of interpreting strong bands using observables independent of estimates of the “continuum”. The considerable amount of structure shown by very strong bands, saturated to an extent that the total absorption they produce varies only slightly with the amount of absorber, suggests that detailed considerations of such a structure may be a sensitive measure of the amount of absorber. In the case of bands as regular in line structure as those of the CO₂ molecule it would appear obvious to attempt to use the ratio between the maxima and minima in the rotational structure as a criterion for the amount (wp) of absorber. Naturally, this requires resolving powers sufficiently high to resolve the rotational structure of the bands. In practice, this requirement amounts to slit widths equal to at most one half the wavelength separation δ of the rotational lines. Let wavelengths x be measured from an arbitrary origin in units of δ and suppose that the response of the spectrometer-detecting system to a monochromatic source is T(x). We propose, as a measure of the absorption, to use the ratio between the power detected at the maximum between two rotational lines

\[ H = \frac{T(x) \, e^{-\tau(x)}}{\text{peak}} \]  

and the power detected at the minimum in the center of one line

\[ L = \frac{T(x) \, e^{-\tau(x)}}{\text{min}} \]  

where \( \tau(x) \) is the net optical depth arising from the superposition of all the lines in the band or from the extreme wings of lines in other bands.

An analytical evaluation of the ratio H/L is instructive for the case of an Elsasser band model and an idealized apparatus function T(x). For the Elsasser model we have (Goody, 1964)

\[ \tau(x) = 2\pi y \frac{\sinh 2\pi y}{\cosh 2\pi y - \cos 2\pi x} \]  

where \( y = a_L / \delta \) measures the collision width \( a_L \) of the lines in units of the separation, and \( u = S \, a / 2\pi \, a_L \) depends on the line strength \( S \) and the amount of absorber \( a \). If the apparatus function is assumed to be of the form

\[ T(x) = \cos^2 \pi x \]  

it can be shown that in the case \( y \neq 1 \), we have

\[ \frac{H}{L} = \frac{(\delta - \rho) \, \text{Erfc} \left( \sqrt{\rho} + \sqrt{\rho / \pi} \right)}{(\delta + \rho) \, \text{Erfc} \left( \sqrt{\rho} - \sqrt{\rho / \pi} \right)} \, e^{-\rho} \]  

where \( \rho = 2\pi^2 u^2 \). In the limit \( \rho \to \infty \) it may be further shown that the dominant term in the asymptotic expansion of Eq. (5) is

\[ \frac{H}{L} \to 2(\rho + 2) \quad \text{as} \quad \rho \to \infty \]  

The asymptotically linear dependence of H/L on \( \rho \) is obviously a consequence of the assumption \( T(x) = \cos^2 \pi x \). A slit function of the form \( \cos^{2m} \pi x \), in fact, can be shown to imply ratios H/L depending asymptotically on \( \rho^m \). In practice, a slit as wide as suggested above, namely \( \Delta x = 1/2 \), will not differ much from \( \cos^2 \pi x \), except in the extended wings. It would be expected, then, that for a true apparatus function...
the ratio \( H/L \) will vary nearly linearly for large amounts of absorber.

In order to apply these general principles to the interpretation of the (0, 4, 1) \( \text{CO}_2 \) band at 2.06\( \mu \)m, we have observed the spectrum of Mars at the 114'' camera of the Coudé spectrograph of the Mt. Wilson 100-inch reflector. A 300 groove/mm Bausch and Lomb replica grating provided a dispersion of 11.3 \( \lambda/mm \) in the first order. In order to increase the signal-to-noise ratio a single exit slit was replaced by a multislit of 3 units, with a separation such that their centers agree with the position of the lines \( J = 12, 14 \) and 16 of the R-branch of the (0, 4, 1) band, and their width corresponds to half the 6 \( \AA \) separation of the lines. The effective resolving power is thus about 7000. The exit multislit, together with an 8 mm focal length Si lens, a long pass (1.9\( \mu \)) filter, an image deslicer, and a 0.5 x 0.5 mm\(^2\) PbS detector are mounted within the vacuum chamber of a dewar cooled with liquid nitrogen. The spectrum is scanned by rotating the grating with a micrometer drive. A scan of the \( \lambda 2.0583\mu \) line of He obtained using an entrance slit just matching that of the exit slits, is shown in Fig. 1, and is the basis for determining the spectrometer instrumental profile.

A typical tracing of the Moon spectrum obtained with a 40 mm long entrance slit and with a time constant of 0.6 sec is shown in Fig. 2. A spectrum of the equatorial strip of Mars, obtained with a time constant of 25 sec is shown in Fig. 3. From tracings such as these, obtained on Feb. 18-24, 1965, the ratios \( H/L \) between the maxima and minima, corresponding to \( J = 14 \), have been read off, with the results shown in Fig. 4.

In a preliminary analysis of the data, we have attempted to find out how well the ratio \( H/L \) observed in the Moon, as well as its dependence on the Earth’s air mass, can be accounted for by using the Elsasser model to give the net optical depth in the.

Figure 1. Instrumental profile obtained by scanning the He line \( \lambda 2.0583 \) \( \AA \).

Figure 2. Scan of the Moon spectrum in the R-branch of the (0, 4, 1) band of \( \text{CO}_2 \). Time constant 0.6 sec.

Figure 3. Scan of Mars in the R-branch of the (0, 4, 1) band of \( \text{CO}_2 \). Time constant 25 sec.

Figure 4. Dependence of the ratio between the maxima and minima corresponding to the line \( J = 14 \) (ordinates) on air mass. The empty circles refer to the Moon and the dots to Mars. The curves represent calculations in the Elsasser model for a value \( y = 0.05 \) and for the values of S indicated in cm\(^{-1}\) per atm. cm.
line. The results of numerical integration of Eqs. (1) and (2) with $y = 0.05$ and a range of $S$ is included in Fig. 4; in all cases the experimentally determined instrumental slit profile was used. Extended calculations like this show that for the earth’s atmosphere with $y$ as large as 0.05, the ratio $R$ is not solely a function of (wp); thus the difficulties in deriving the correct (wp) for the Martian atmosphere from the combined absorption in the Martian and Earth’s atmosphere are compounded.

The attempts to fit the Martian data have so far not been as successful as those shown for the Moon. In particular, the apparent steeper slope of $H/L$ vs sec $z$ has not been predicted, which means that any interpretation of the (wp) of the Martian atmosphere is premature. Very roughly, however, we can say that at sec $z = 1$ the ratios obtained with Mars’ plus the Earth’s atmosphere are roughly the same as for a passage through 3 earth air masses. Detailed interpretation of these results must wait until better band model calculations are made.

References