No. 33 A DETERMINATION OF THE MARTIAN CO_2 ABUNDANCE

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ABSTRACT

Two independent determinations are presented of the CO_2 content of the Martian atmosphere derived from the Mt. Wilson plate obtained by Kaplan, Münch, and Spinrad.

1. *Introduction*

The two preceding papers (*Comm. LPL* 31 and 32) present new spectra of the planet Mars in the 1.0–2.5 μ region and their laboratory calibration with a long absorption tube. This calibration leads to a relationship between total atmospheric pressure and CO_2 abundance. Before the atmospheric pressure (and, by inference, an approximate composition) can be found, independent data on the Martian CO_2 abundance are required. The best source of this information at present is the Martian λ 8689Å CO_2 band observed by Kaplan, Münch, and Spinrad (1964) (referred to hereafter as KMS). These authors themselves calibrated this CO_2 band from laboratory observations supplied by Rank, but because of the peculiar role played in this band by the effects of blending by solar Fraunhofer lines it appeared important to recalibrate the spectrum in such a manner that the effects of solar blending would be accurately allowed for. The interest in the λ 8689Å band stems from the fact that the lines in this band are very weak so there is almost no saturation. Thus they are on the linear part of the curve of growth and their intensities are directly proportional to the abundance.

After calculating the effective air mass corresponding to the Martian observation and making slight corrections for collisional broadening and saturation effects due to the narrowness of the lines, KMS derived a value of 55 ± 20 m atm for the CO_2 abundance. This value corresponds to an assumed temperature of 230°K in the Martian atmosphere. For 200°K, the corresponding value was 50 ± 20 m atm. The reason cited for the large probable error associated with these values was the difficulty in determining the equivalent widths of the weak CO_2 lines.

The new calibration of the Mt. Wilson spectrogram was done in two steps. A preliminary calibration was made prior to the completion of our high-dispersion laboratory spectrograph by means of observations of the 8689Å band of CO_2 in the

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solar spectrum at sunrise. When the spectrograph was finished, laboratory spectra of CO_2 were obtained from which a more precise value for the Martian abundance could be derived. For the sake of completeness and because of the intrinsic interest in the solar observation, both of these techniques are described below.

2. *Observations and Experimental Procedure*

The observations of the Sun were made with the McMath Solar Telescope of the Kitt Peak National Observatory. The 30-foot spectrograph employed with this instrument gives a dispersion of 1Å/mm when the grating is used in the first order (blaze at 8000Å). The solar spectrum was obtained by setting up the image of the eastern horizon on the spectrograph with the slit oriented parallel to the horizon and just above it, slightly southwest of the sunrise point. The Sun was allowed to drift past the slit during the course of the exposure, which was made at a fixed zenith angle. The heliostat was then moved to position the slit ahead of the Sun and the procedure was repeated. In this way a series of exposures corresponding to decreasing values of zenith angle could be obtained within a few minutes while conditions were optimum.

The laboratory work was carried out with the help of a 72-foot multiple path absorption tube. The aim of the program was the acquisition of a series of spectra of different amounts of CO_2 that could be compared directly with the Mt. Wilson spectrogram of Mars. To achieve this end, spectra were obtained at a range of pressures between 10 and 20 cm Hg and a corresponding range of pathlengths using the Sun as a light source. The laboratory spectrograph is of the Czerny-Turner type and has a 10-foot focal length. A 600 line/mm grating blazed at 1.6 μ was used in the second order to produce a dispersion of 2.5Å/mm. This configuration matched the resolution of the Mt. Wilson spectrogram rather well when the slit was opened to 100 μ. As a final precaution, hypersensitized IV-N, the type of emulsion that recorded the spectrum of Mars, was employed for the laboratory work.

3. *The Martian CO_2 Abundance*

(a) *The Solar Observations*

The most suitable solar spectra for the present purpose were obtained on November 12, 1963. A reproduction of the spectrum corresponding to the largest zenith angle is given in Figure 1 together with a comparison spectrum taken with the Sun two hours past the meridian. These spectra indicate one of the problems encountered in the calibration of the intensities of the Martian CO_2 lines by revealing the large number of faint solar lines which occur in this spectral region. Nevertheless, the interval between the two lines at 8689.79Å and 8692.34Å is clear, and on the spectrum obtained with the Sun at the horizon, the $J = 8$, 10, and 12 lines of the R branch of the $5\nu_3$ band of CO_2 are faintly visible. The presence of R(4) is revealed by the enhancement of the solar line at 8693.15Å. The many weak solar absorptions in this region essentially exclude the P branch lines of the CO_2 band from consideration in the abundance determination.

A comparison of these spectra with the spectrum of Mars, reproduced in Figure 2, reveals that the resolution of the former is considerably higher (the group of lines at 8680Å is a good indicator). It is evident that the telluric CO_2 lines are considerably weaker than those in the spectrum of Mars, even at this large zenith angle. This difference is easily seen by comparing the intensity of R(10) with the solar lines at 8682.99Å and 8728.60Å on each spectrum. From such a comparison it is possible to estimate that the telluric lines are weaker by a factor of about 4. This indicates that at normal air paths the Martian CO_2 lines will be roughly 100 times stronger than the telluric equivalents. Thus there should be no problem due to blending with the telluric features.

To proceed from these observations to a rough estimate of the Martian CO_2 abundance, it is necessary to know the air mass through which the observations were made. For such large zenith angles it is no longer possible to use the customary approximations employed in calculating air masses for use in photometric extinction determinations. Instead, a graphical interpolation method was employed, based on data tabulated by Allen (1963). The zenith angles were computed from readings of the setting circles and verified by calculation of the position of the center of the Sun's disc from the recorded times (correcting for refraction). The air mass was then read from a plot of zenith angle vs air mass constructed from Allen's data and corrected for the local temperature and pressure. This led to a value of 30 $\pm$ 3 air masses which corresponds to roughly 66 m atm of CO_2. Thus the Martian CO_2 lines would require about 264 m atm or roughly 73 m atm of CO_2 in the atmosphere of Mars when account is

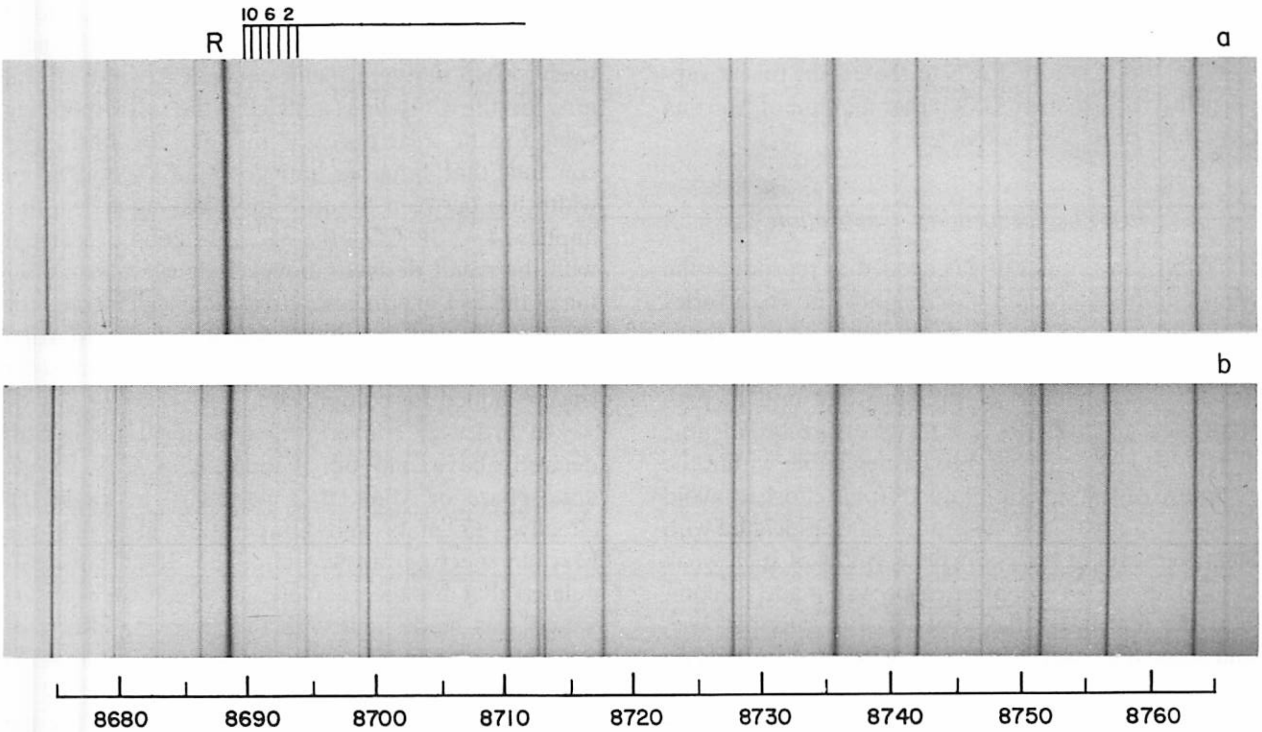

Fig. 1. Spectra of the Sun with McMath Solar Telescope at two zenith angles to show the presence of telluric absorption of $5\nu_3$ (λ8696) of CO_2 with a large air mass: (*a*) Z = 89°57′; (*b*) Z = 32°30′.

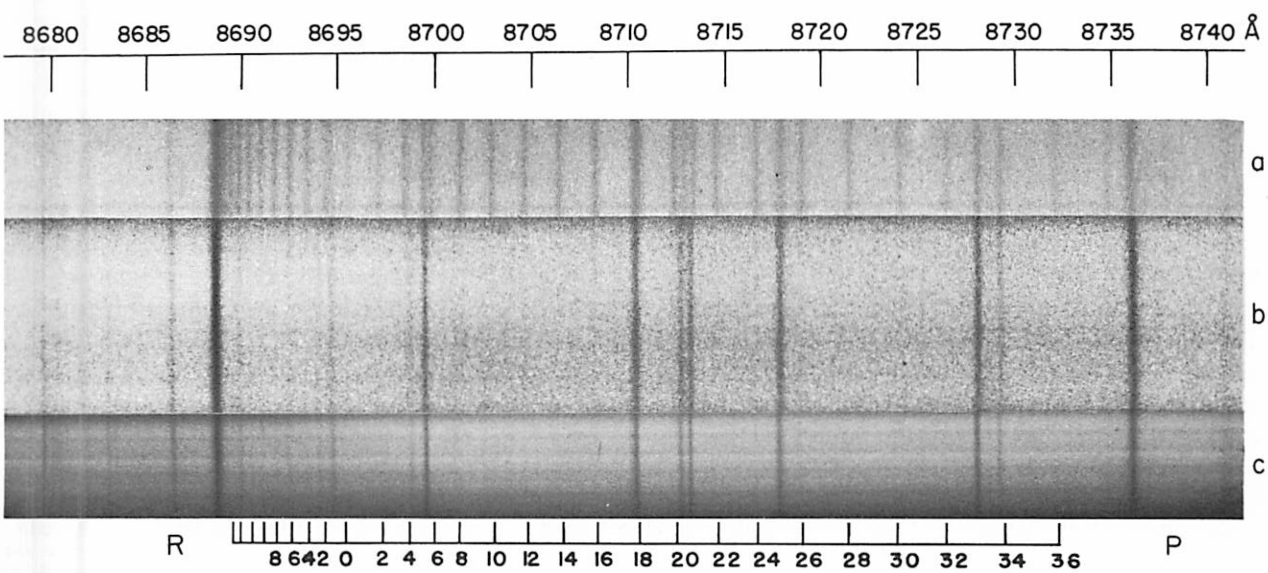

Fig. 2. Spectra of: (*a*) Venus; (*b*) Mars, and (*c*) a laboratory pathlength of 223 m atm (NTP) of CO_2 with the Sun as light source. The *J* numbers of R and P branch lines of the $5\nu_3$ band are shown at the bottom.

taken of the geometry of the Mars observation (see below). This admittedly crude determination served to verify the result of KMS to the extent that it supports the requirement for a larger amount of Martian CO_2 than previously expected.

(b) The Laboratory Calibration

After the amount of gas needed to reproduce the Martian line intensities was roughly known, a series of laboratory spectra was obtained with a range in equivalent pathlength from 85 to 350 m atm. Several combinations of pressure and optical path were used in order to test for pressure-broadening effects, which were found to be negligible within the accuracy of the determination. In an effort to avoid the uncertainty that KMS found to be associated with measurements of the equivalent widths of such weak lines as these, an initial attempt was made to compare the line intensities visually. For this purpose, four solar lines were chosen to serve as standards on each plate: λ8667.37 (Si, –1); λ8668.46 (⊙, –2d?); λ8680.41 (S, 0); and λ8728.60 (Si, –2) (identifications and intensities from Babcock and Moore [1947]). On reproductions of the Mars spectrogram kindly made available by Dr. Spinrad, it is evident that the Martian CO_2 lines exhibit intensities intermediate between that of λ8667.37 and λ8668.46 or λ8728.60. Of the latter two lines, the last one is barely indicated on the reproductions, the other line is not visible. This difference in intensity is also apparent on the laboratory plates. On this basis, it was found necessary for the laboratory pathlengths to lie within the range 241 ± 44 m atm in order to give intensities comparable with the Martian CO_2 lines. The laboratory plate giving the closest match is reproduced with a copy of the Martian spectrogram in Figure 2. As a further check, densitometer tracings were made of the plates corresponding to the indicated range in pathlength and the relative intensities of the solar and CO_2 lines were measured. The difficulties experienced in making these measurements corroborated the remarks of KMS, but the results served to confirm the visual estimate. The ratio of the mean intensity of the three CO_2 lines to that of the solar line at 8667.37Å was .4, .6, and .9 for pathlengths of 197, 241, and 289 m atm, respectively. KMS derive a mean equivalent width of 3.8 mÅ for the CO_2 lines and give the corresponding value for the solar line as 7 mÅ. On this basis they conclude that an upper limit for the CO_2 equivalent width lies between 5 and 6 mÅ. Taking ratios, this implies $.4 \leq W\ CO_2/W_\odot \leq .8$, in good agreement with the result derived above. A densitometer tracing of the 241 m atm laboratory plate is presented for comparison with a similar tracing of the Martian spectrogram in Figure 3. A high-resolution solar trace is added for comparison.

In order to convert the equivalent pathlength derived above into an abundance of CO_2 in the atmosphere of Mars, it is necessary to know the effective air mass and temperature at which the Martian spectrogram was obtained. KMS have calculated that for the geometry at which their observation was made, and with the smearing effects of seeing and guiding errors, the effective air mass is 3.6*. Use of this air mass leads to a value of 67 ± 15 m atm. It remains to correct this figure for the difference in temperature between the laboratory and the Martian atmosphere. From a rough analysis of the relative intensities of the Martian CO_2 lines, KMS conclude that "the apparent positions of the band maxima are consistent with an atmospheric temperature of about 230°K." They note that the blending with solar lines and the uncertainty of their measures makes this an unreliable value. In view of the fact that the mean Martian surface temperature at aphelion is roughly 240°K (Pettit, 1961), an atmospheric temperature of 230°K seems rather high. Perhaps with this in mind, KMS also use a value of 200°K, which would appear to be more reasonable. It would be highly desirable to obtain observations of an unblended CO_2 band (e.g., $\nu_1 + 2\nu_2 + 3\nu_3$ at 1.05 μ), the rotational structure of which could be analyzed less ambiguously. For the present we will use the same two values for the temperature as KMS (cf. Appendix).

For a linear molecule such as CO_2 the intensity of a rotational line in absorption is given by the expression (R branch lines)

*In computing this air mass, KMS restricted themselves to the southern third of the planet. The present comparison was made using both the upper and lower thirds of the reproduced spectrum, although the densitometer tracings were compared to the tracing of the southern third prepared by KMS. As shown in *Comm.* 32, the air mass corresponding to a slit placed pole to pole on the planet is 3.14 for weak lines. For a "polar" third of the disk this would be increased to 4.18. The reduction to the cited value of 3.6 presumably comes about as a result of the seeing and guiding errors the authors estimate to be present. These two effects will cause an apparent motion of the slit with respect to the disk of the planet and will diminish the correspondence between a given position on the planet and a given part of the spectrum. We assume a probable error of ± 0.4 in this value.

$$I_{abs} = \frac{S_{abs}}{Q_r} 2(J+1) \exp\left[\frac{-BJ(J+1)hc}{kT}\right]. \quad (1)$$

The intensity ratio of a line at temperatures T_1 and T_2 is then

$$\frac{I_1}{I_2} = \frac{T_2}{T_1} \exp\left[-BJ(J+1)\frac{hc}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right], \quad (2)$$

in which the rotational state sum Q_r has been approximated by an integral:

$$Q_r \approx \int_0^\infty (2J+1) \exp\left[\frac{-hcBJ(J+1)}{kT}\right] dJ = \frac{kT}{hcB} \quad (3)$$

The latter should be a close approximation owing to the small value of B for CO_2 (Herzberg, 1950). For $J = 10, B = 0.3866, T_1 = 297°K$, and $T_2 = 230°K$, 200°K we obtain

$$\frac{I_1}{I_2} = .82\ (T_2 = 230°K), .74\ (T_2 = 200°K).$$

Reducing the laboratory abundance to NTP, we obtain 62 ± 11 m atm. If this figure is now multiplied by the factors derived above, the Martian CO_2 abundance is found to be 51 ± 15 m atm (T = 230°K) or 46 ± 15 m atm (T = 200°K). These figures represent the amount of gas at NTP which would give the intensities observed in the Martian spectrum if the gas were cooled to the assumed mean atmospheric temperature of Mars.

It is evident that the agreement with the results of KMS is quite good. Although the abundances reported here are somewhat lower than theirs, each set of figures falls well within the range of error corresponding to the other set. The agreement may even be better than it appears, since it is not clear what temperature has been used by KMS to standardize their meter atmosphere. It has not been possible to reduce the probable error as much as had been hoped, but the accordance of the two sets of values strengthens the validity of each. It appears that additional observations of Mars are needed to increase the accuracy of the determination.

Acknowledgments. The author is grateful to Dr. Hyron Spinrad for providing copies of the Mt.

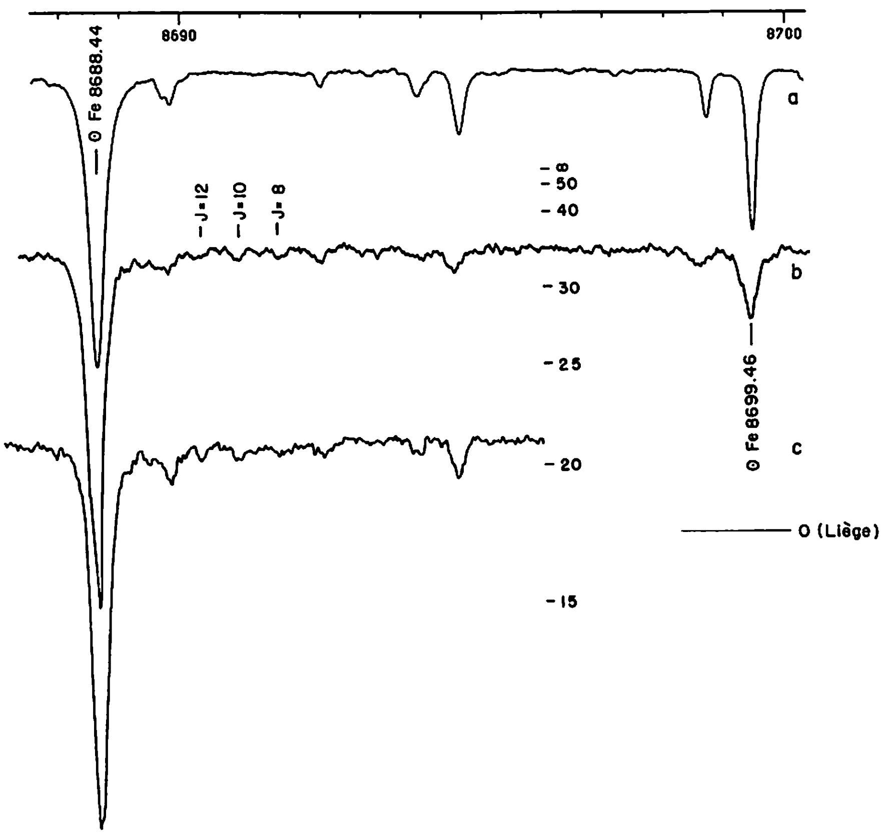

Fig. 3. Solar spectrum (Liège, 1963), Mt. Wilson Mars spectrum, and laboratory comparison (Sun + CO_2). Last two show three rotational lines of CO_2.

Wilson spectrogram and for helpful discussions. The Kitt Peak Solar Telescope was made available for the solar observations through the courtesy of Dr. Keith Pierce, who also provided a batch of photographic plates for the laboratory work at a crucial moment. Advice and encouragement were given throughout the course of this study by Dr. Gerard Kuiper. The laboratory program was supported by the Office of Naval Research under contract NR046-791.

APPENDIX

Atmospheric Temperature and the 1.05μ CO_2 Bands

As a first approximation, we can assume that the atmosphere is adiabatic to the height above the surface corresponding to the mean level at which the CO_2 absorption occurs. At this level, the pressure is equal to one-half that at the surface (*Comm.* 32). If we adopt the atmospheric mixture derived in the previous paper, the adiabatic lapse rate for the Martian atmosphere is 3.7°C/km. (It is noted that a considerable range in proportions of CO_2 and N_2 results in roughly the same lapse rate.) The adiabatic assumption then leads to the relation $T_M = 0.833 T_S$ where T_M is the temperature at the mean absorbing level and T_S is the surface temperature. Using Pettit's value for $T_S = 240°K$, one finds $T_M = 200°K$. It should be pointed out that since the abundance determination is essentially restricted to the polar thirds of the planet, an even lower mean surface temperature than that assumed here is probably appropriate, so 200°K may be an upper limit.

Ideally, of course, one would like to determine the atmospheric temperature from the same bands used for the abundance analysis. This is not possible in the case of the 8689Å band, since only three rotational lines are unblended and these are very weak. One is thus led to an investigation of the stronger bands near 1.05 μ. These bands are described in Table 1, which is based on a similar table prepared by Herzberg and Herzberg (1953). On the intensity scale in this table, the $5\nu_3$ band at 8689Å has the value unity. Figure 4 shows the appearance of the bands at 1.036 μ and 1.049 μ at three pathlengths which bracket the equivalent optical path for absorption in the Martian atmosphere, as deduced in this paper. All three spectra were obtained at atmospheric pressure (~ 700 mb). The Sun is again used as a light source, so these spectra are very similar to what one would actually observe when obtaining spectra of Mars. It is apparent that even at the smallest observed pathlengths, the 1.048 μ band is much stronger than $5\nu_3$ and both P and R branch lines are easily visible. The strongest of these lines may be slightly saturated at the low pressure of the Martian atmosphere, but the presence of the weaker band at 1.036 μ allows an empirical evaluation of this possibility. There is a still weaker band at 1.063 μ (not shown), which is barely visible at the intermediate pathlength and relatively easy to discern at the maximum pathlength. Thus the three bands taken together should provide a valuable independent check on both the CO_2 abundance and the mean atmospheric temperature.

Such a study would not be free of observational difficulties, however. This region of the spectrum requires the use of the I-Z emulsion which is notoriously slow and grainy. It is doubtful that the resolution illustrated in Figure 4 could be achieved on Martian spectrograms, but a considerable sacrifice can be afforded. As an illustration, we can consider the lines in the P branch of the 1.049 μ band. The original dispersion of the laboratory plate was 5Å/mm and the spacing of these lines is roughly 2.4Å. Thus a dispersion of 15Å/mm would leave the lines separated by .16 mm. This is slightly greater than the separation of the last resolvable lines of the R branch on the present plates and would therefore be acceptable if the projected slit width remains the same. This is not a prohibitive assignment for a suitably designed spectrograph.

The remaining difficulty is the problem of blending with solar features. Inspection of Figure 4 indicates that several such blends occur, but there are a

TABLE 1
CO_2 BANDS NEAR 1.05 μ

λ_h (air)	ν_h (vac)	INTENSITY	ν_0 (vac)	ASSIGNMENT	λ_0 (air)
10626.7	9407.7	4	9389.0	$4\nu_2 + 3\nu_3$	10647.8
10487.6	9532.3	20	9517.0	$\nu_1 + 2\nu_2 + 3\nu_3$	10504.6
10361.8	9648.2	8	9631.4	$2\nu_1 + 3\nu_3$	10381.0

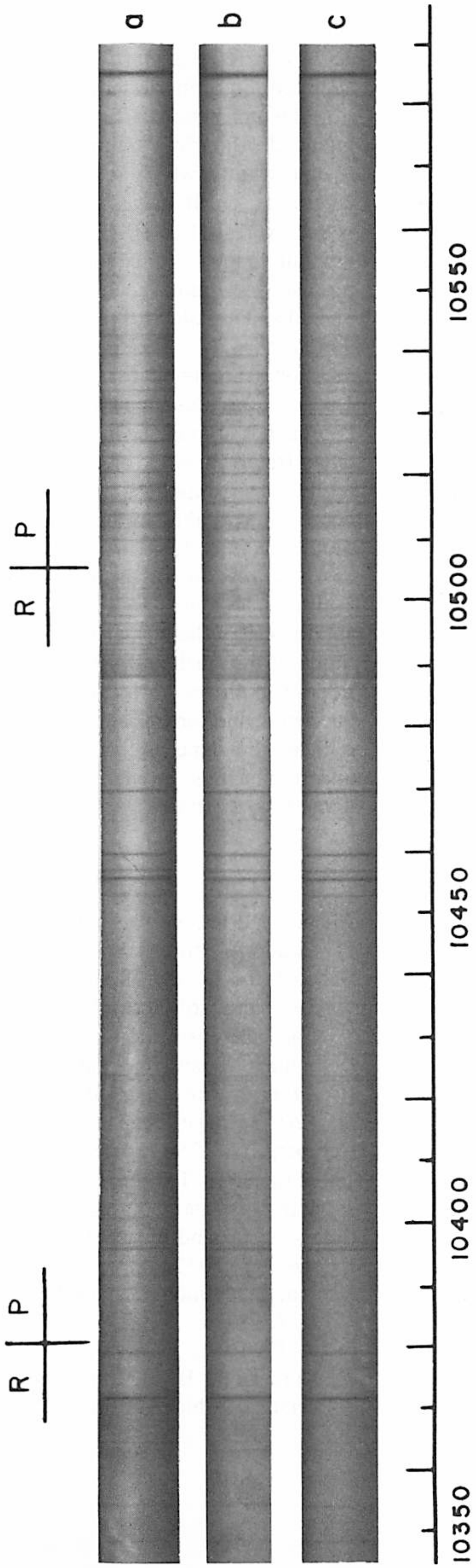

Fig. 4. Laboratory spectra of $2\nu_1 + 2\nu_3$ and $\nu_1 + 2\nu_2 + 3\nu_3$ of CO_2 at three pathlengths (NTP). The Sun was again used as light source. (*a*) 333 m atm; (*b*) 250 m atm; (*c*) 166 m atm.

sufficient number of unblended lines to give reliable results, particularly if all three bands are used.

Note added in proof. After the above was written, Dr. J. Chamberlain suggested to the writer that one might expect overlapping in the R branch of the 8689Å band of CO_2 due to doubling back of the rotational lines after formation of the band head. This will complicate the analysis because the temperature dependence of the lines with high J numbers will be different from that of the rotational lines considered here (mean $J = 10$).The writer was unable to find accurate observed wavelengths of the higher rotational lines reported in the literature and could not resolve them on the plates discussed above. Therefore the rotational constants given by Herzberg and Herzberg (1953) were used to predict the positions of these lines according to the approximate relation

$$\nu_J = \nu_0 + 2B' + (3B' - B'')\,J + (B' - B'')\,J^2. \quad (4)$$

The line $J = 40$ was subsequently chosen as having a position close to that of $J = 10$ and thus being representative of the problem. Using equation (1), we find the relative intensities of $J = 40$ and $J = 10$ are as follows:

$$T = 297°\text{K}, \frac{I_{10}}{I_{40}} = 4.85$$

$$T = 200°\text{K}, \frac{I_{10}}{I_{40}} = 20.$$

If we now express the observed intensity as a simple sum of the intensities of $J = 10$ and $J = 40$ we have

$$\frac{I_{\text{lab}}}{I_{\text{Mars}}} = \frac{I_{10}\left(1 + \frac{1}{4.85}\right)}{I_{10}'\left(1 + \frac{1}{20}\right)} = 0.85$$

where

$$\frac{I_{10}}{I_{10}'} = \frac{I_1}{I_2} = 0.74 \text{ for } T_1 = 297°\text{K}, T_2 = 200°\text{K}.$$

In other words, the fact that we are dealing with a blend of two lines whose intensities change in opposite ways with a decrease in temperature implies that the amount of gas required in the Martian atmosphere to reproduce the observed intensities is somewhat greater than it would be otherwise. Using the NTP laboratory value derived above, we find 53 ± 15 m atm for the Martian CO_2 abundance with an assumed atmospheric temperature of 200°K.

This correction is obviously very rough and is intended primarily as an indication of another kind of uncertainty which is present in the abundance determination. It suggests that the latter is probably better expressed as 50 ± 20 m atm to incorporate the full range of uncertainty, and thus brings the present work into exact agreement with the result of KMS. The added difficulty in correcting for the doubling back of the rotational lines represents an additional argument for attempting to observe the 1.05 μ bands, described in the Appendix, where the P branches (which have no overlapping) are relatively free from solar blends.

Brooks (unpublished) has shown that the air mass corresponding to the KMS observation of Mars should be $\eta = 3.9$. His corrections include a more exact expression for the variation of air mass with zenith angle, a greater smearing effect due to seeing and the use of the proper value for the angular separation of the earth and sun as seen from Mars. Considering both the correction for doubling back and the new value for the air mass, the CO_2 abundance remains the same as that given previously, but the uncertainty must be increased. The revised value is then 46 ± 20 m atm.

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