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February 27, 1968

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NASA Headquarters, Code SL
Washington, D. C.

Dear Dr. Brunk:

This is the final report on NASA Contract No. NASr-65(19) (IITRI Project W6142). The contract was given a retroactive starting date of November 1, 1966 in order to encompass a preliminary observing run in late November. It ran to an extended termination date of January 31, 1968.

1. INTRODUCTION

The purpose of the research carried out under this contract was to redetermine the carbon dioxide and water vapor content of the atmosphere of Mars. Using observations made by other investigators, the carbon dioxide abundance can then be utilized to derive the atmospheric surface pressure, an important quantity from both a scientific and an engineering standpoint.

The derivation of the abundance of an absorbing gas depends on the following relation, provided the lines are weak:

$$\eta w = \frac{W}{S}$$

in which W is the equivalent width of the line in the planetary spectrum, S is the line strength, η the effective air mass, and w the abundance of gas in a vertical column under standard conditions. We are fortunate in having good laboratory values of S for all the lines that were observed. These values must simply be reduced to assumed conditions in the Martian atmosphere. The value of η is more subjective, but it can be demonstrated that a value near π is a very good approximation for weak lines observed across the full disk of the planet (Owen and Kuiper 1964). We may thus concentrate on measurements of W, and these are described in Section 3.

In order to make an advance over the results obtained in 1965, some improvements were required in the techniques used to record the Martian spectrum. Fortunately, as described in Section 2, instrumental developments at the McDonald and Kitt Peak Observatories during the intervening period permitted such improvements to be realized. It was thus possible to record more lines in more bands (and with considerably greater reliability) than in 1965.

Once the abundance of carbon dioxide is known, the atmospheric surface pressure may be determined from observations of strong, pressure broadened bands. Since the results of the 1965 opposition were published, there have been new observations of these strong absorption bands as well as new analyses of old observations. These matters are discussed in Section 4 which is followed by a discussion of some of the ways in which additional improvements in the data can be achieved.

2. OBSERVATIONS

Spectra of Mars were obtained during the five separate observing runs tabulated below:

1.	November 20-27, 1966	McDonald Observatory
2.	February 21-March 3, 1967	McDonald Observatory
3.	April 16-April 22, 1967	McDonald Observatory
4.	April 24-April 27, 1967	Kitt Peak National Observatory
5.	June 24-July 3, 1967	McDonald Observatory

The planet was at opposition on April 15 and thus the two April runs were ideal for studies of the CO_2 absorptions since the apparent diameter of the disk was at its maximum value. The February and June runs were designed to take advantage of the favorable Doppler shift to search for water vapor lines, while the run in November had only a preliminary role for the Mars work, viz., to evaluate the effect of new improvements on the McDonald coudé spectrograph.

As it turned out, neither of the attempts to observe the water vapor spectrum was successful owing to instrumental difficulties (in February) and bad weather (in June). Although several spectra of the 8200 and 9400 Å regions were obtained, they lacked the resolution required to give any additional information on the water vapor problem.

The situation was very different in the case of the observations near opposition. The successful installation of the Carnegie infrared image tube in the McDonald coudé spectrograph permitted the three carbon dioxide bands near 1.05μ to be recorded with ease. This represented an enormous improvement over conditions at the last opposition when only the strongest lines of the 1.05μ band could be detected. In addition, the acquisition of a 1200 line/mm grating for the Kitt Peak 84-inch coudé enabled the 8700 Å band to be recorded at a reciprocal dispersion of 2 Å/mm, a gain of a factor 2 over 1965. As a result of these two improvements, a number of high quality spectra of the weak CO_2 bands were obtained for the purpose of refining current estimates of the CO_2 abundance.

3. THE ABUNDANCE OF CARBON DIOXIDE

3.1 The 8700 Å Band ($5\nu_3$)

In the past, the greatest weight in the derivation of the Martian CO_2 abundance has been given to measurements of three lines in the R-branch of the 8700 Å band: J = 8, 10, and 12. During the 1965 opposition, it was possible to observe some lines in the P branch as well. The gain in resolution afforded by the new grating at Kitt Peak has made the measurement of the P branch lines very easy, in addition to improving the reliability of the analysis of the R branch. Figure 1 shows a reproduction of one of the best Kitt Peak spectrograms of Mars with the corresponding region of spectra of Venus and the sun for comparison. Whereas only P_J = 12, 14, 16, 20, and 22 were observed in 1965, the new spectra show J = 2-10, 18, and even 28. (J = 24 and 26 are present but are blended with solar lines.)

Similar improvements are visible in the R-branch. The Venus spectrogram shows the lines doubling back from the band head and clearly indicates that the correction used to account for these lines in previous work on the Martian CO_2 abundance is indeed necessary. Figure 2 contains a tracing of the solar spectrum taken from the Liège Atlas compiled by Delbouille and Roland (a) and two tracings of the $5\nu_3$ R branch in the spectrum of Mars (b and c). Tracing (b) is an average of spectrograms obtained in 1965, while (c) is a single tracing of one of the 1967 plates. The improvement in resolution and signal to noise is readily apparent.

The three best plates were reduced using the same procedure followed in the previous analysis (Owen 1966). Averaging J = 8/40, 10/38, and 12/36 together in the traditional fashion, one obtains a value of w = 68 m atm (the air mass $\eta \approx \pi$ and the value of S was the same one used in 1965). This is virtually identical with the final value of 67 m atm obtained by the writer during the previous opposition. However, much additional information is available with which the R-branch data must be combined to obtain a sounder value for the abundance.

3.2 The Bands Near 1.05μ

As mentioned in the discussion of the observations, one of the great improvements over results obtained in 1965 was the successful recording of the triad of bands near 1.05μ. In order of increasing strength, these are $4\nu_2 + 3\nu_3$ (1.06μ), $2\nu_1 + 3\nu_3$ (1.04μ), and $\nu_1 + 2\nu_2 + 3\nu_3$ (1.05μ). The appearance of the two strongest bands in spectra of Venus and Mars is shown in Figure 3. The 1.06μ band was only marginally detected, but enough lines were recorded to permit an average of two sets of two lines each (in the P branch) to be determined.

A total of seven spectrograms was used to obtain equivalent widths of the CO_2 lines. The reduction procedure was essentially the same as that followed in the case of the 0.87μ band. The values for the line strengths were computed from laboratory data kindly made available by Boese, Miller, and Inn; the effective temperature in the Martian atmosphere was again assumed to be 200°K. In order to indicate the relative strengths of the four bands that have been analyzed, a table of the values for P(16) in each band at T = 200°K is presented below. It is apparent that the range in values is sufficient to suggest the construction of a curve of growth for CO_2 absorption in the Martian atmosphere.

Table 1

RELATIVE STRENGTHS OF MARTIAN CO_2 BANDS

Band	S (P16)
1.05μ	0.281 cm^{-1}/km atm
1.04	0.102
1.06	0.047
0.87	0.023

3.3 A Curve of Growth for CO_2

The traditional curve of growth is constructed by plotting the log of some dimensionless function of equivalent width *vs*. a similar function of the product of line strength and the number of absorbing molecules. We have chosen to divide W by twice the Doppler half width (γ_D) to permit easy comparison with theoretical curves of growth. Since the number of absorbing molecules is to be determined, our abscissa is simply the log of the ratio of line strength (S) to $2\gamma_D$. If, as we expect, the CO_2 lines we have observed lie on the linear part of the curve of growth, then a line drawn through the plotted points should have unit slope. The separation of this line from a line of unit slope drawn through the origin will give the number of absorbing molecules, our unknown.

A curve of growth based on the observations of all four CO_2 bands is given in Figure 4. The line drawn through the individual points is a least squares fit to the observations, except for the stronger lines in the 1.05μ band. The latter were excluded since it is apparent that they do not lie on the same line as the others. In fact, they apparently correspond to the transition region of the curve of growth. On the other hand, the remaining points lie on a line with a slope of 0.97, essentially the line with unit slope which we had anticipated.

The mean separation of this line from the line through the origin is given by

$$\log N_J = -0.630$$

where the units of N_J are km atm. Solving for the abundance, we obtain $N_J = \eta w = 235$ m atm. Again assuming $\eta \approx \pi$, we find $w = 75$ m atm.

This result is in reasonably good agreement with the value of 68 m atm based on the three R branch lines from the 8700 Å band, but it has the great advantage of being derived from a total of 19 lines in three different bands. The mean error corresponding to this analysis is ± 20 percent. We may thus express the final result as

$$w = 75 \pm 15 \text{ m atm (NTP)}$$

3.4 Discussion of Results

Unlike the analysis carried out in 1965, no attempt has been made to correct the derived abundance for possible systematic errors in the evaluation of the equivalent widths. There are two reasons for this: First, the new spectra of Mars have a higher resolution than the laboratory spectra used as calibrations for the 1965 observations. There was a strong indication that the systematic error discovered at that time was resolution-dependent; the underestimate of the abundance was least at the highest resolution. Hence the higher value of the derived abundance obtained from the present results may be considered as a measure of the increase in the resolution of the Mars spectra. (Similar effects have been reported by D. H. Rank in the case of laboratory spectra of hydrogen.)

The second reason for not attempting to correct for systematic errors is the greater randomness of the present data. Using two different sets of absorption bands recorded with two different spectrographs employing two different techniques considerably reduces the chances for systematic instrumental effects. As an additional check, several of the spectra were analyzed independently by Mr. H. Mason, whose values for the equivalent widths showed no systematic difference from those obtained by the present writer.

One final comment seems to be required by recent interest in elevation differences on the surface of the planet. The observations reported here correspond roughly to a Martian longitude of 130°. At the sub-earth point, this meridian runs through a light area on Mars (Amazonis) which is known to be a relatively low region (Pettengill, private communication). However, the rotation of the planet during the course of the exposures in addition to guiding and seeing motions (and the apparent rotation of the image at Kitt Peak where no image rotator was available) prevented the establishment of an exact correspondence between the slit of the spectrograph and a planetary meridian. Thus it is not surprising that no systematic increase or decrease in absorption strength with position on the disk was found to occur, particularly in view of the still considerable uncertainty associated with the derived abundance.

4. THE SURFACE PRESSURE

With this revised figure for the CO_2 abundance in the Martian atmosphere, we are in a position to redetermine the surface pressure. This operation requires the observation of stronger bands that are pressure broadened. The bands near 1.6μ and 2.06μ have been used for this purpose in the past; the various interpretations of the strong band data have led to different values for the surface pressure, even for a given value of the abundance. In this discussion, we will confine ourselves to the graphical method of Owen and Kuiper (1964) based on an extensive series of laboratory observations of the 1.6μ bands, and the analytical method of Gray (1966), consisting of a band model fitted to observations of the 2.06μ band complex.

The only new observations of the strong bands that have been reported since 1965 are those of Binder and Cruikshank (1968) who have reobserved the 1.6μ bands at a dispersion comparable to Kuiper's (1964). Binder and Cruikshank have analyzed their results with special attention to the errors involved in determining the equivalent widths of these bands. They conclude that a realistic value for the mean of the two bands at 1.6μ is 17 ± 3Å. This effectively brackets the values obtained by Kuiper (16Å) and Moroz (19Å) and we shall adopt it for our discussion. Much more precise observations of individual lines in these strong bands should be forthcoming from the high resolution spectra of the Connes'.

4.1 The Method of Owen and Kuiper

In addition to its original use in the interpretation of 1963 observations of Mars, this method was employed by the present writer in 1965 (Owen 1966). Plots were made of log W vs. log p ηw for laboratory observations of the 1.6μ bands for two mixtures of CO_2 and N_2 in addition to the pure CO_2 itself. It is then possible to interpolate on these plots, knowing W and ηw for the observations of Mars, and solve for p. The surface pressure, $P_s = 2p$.

Following this procedure through in the present case, we find that the increase in w corresponding to the new observations of weak lines is compensated by the increase in W reported by Binder and Cruikshank (1968), so the derived pressure remains the same. However, we can reduce the uncertainty because of the increased precision in w. The result is thus

$$P_s = 8.5^{+6.5}_{-3.5} \text{ mb.}$$

4.2 The Method of Gray

Gray's method was adopted by Belton and Hunten (1966) in their analysis of their observations in addition to her own use of it which was given in a more general sense. Basically, the method involves the construction of a synthetic band profile based on an analytical model for the band which involves known parameters such as the band strength, line widths, line spacing, etc., and leads to a value for the product of the abundance and the pressure. Using two slightly different approaches, Gray obtained the result $wp_e = 550 \pm 200$ m atm mb, where p_e is an "effective" pressure which is determined by the dominant broadening gas. If we add to her quoted uncertainty the additional amount corresponding to Binder and Cruikshank's work, we obtain $wp_e = 550 \pm 215$ m atm mb. Solving for P_s with our new value of w, we find

$$P_s = 5.5 \begin{matrix} +4.5 \\ -1.5 \end{matrix} \text{ mb}$$

where we have rounded to the nearest 0.5 mb and the uncertainty includes the error in w. Note that for w = 75 m atm, this solution implies that the atmosphere is pure CO_2.

5. CONCLUSIONS

Since Gray's method involves less subjectivity and because her initial results have been essentially confirmed by a more refined analysis (Penner, Boni, and Gray 1967), we tend to favor the value of the pressure derived in this way. According it twice the weight of the Owen-Kuiper analysis, we find a final value of

$$P_s = 6.5 \begin{matrix} +4.5 \\ -2.5 \end{matrix} \text{ mb}$$

This is a considerable improvement over the precision obtained in 1965, and permits the discussion of the results obtained at that time to be critically reviewed.

A comparison of the composition of the atmosphere of Mars with the total amount of evolved volatiles on Earth indicated some rather convincing analogies (Owen 1966). It was pointed out that estimates of the $CO_2:N_2$ ratio for the terrestrial volatiles varied from 3:1 to 20:1. If the initial composition and the outgassing processes are the same on Mars as on Earth, we can predict Martian surface pressures on the basis of our knowledge of the abundance of CO_2. Using the new value for w obtained in this report, we would anticipate surface pressures on Mars in the range from 4.7-8.9 mb, allowing for the present uncertainty in w. The Mariner IV occultation experiment suggested a CO_2 content of at least 80%, which would lead to a surface pressure of 6.4 mb.

These numbers tend to suggest that our value for P_s is quite reasonable and tends to favor a common mode of origin for the atmospheres of Mars and Earth. This argument gains support from the recent spacecraft experiments that investigated the atmosphere of Venus. Here, too, it appears that the CO_2/N_2 ratio must be more than 5:1 and perhaps more than 14:1. An underlying unity in the composition of the atmospheres of the terrestrial planets is thus apparent. We are now in a position to investigate in more detail the reasons for the anomalous composition of the Earth's present atmosphere, particularly the large abundance of water.

6. SUGGESTIONS FOR FUTURE WORK

The success of these new observations of weak lines of CO_2 in reducing the uncertainty associated with the derived abundance and surface pressure gives a clear indication of the direction to be taken to insure additional progress. The most important need at this point is for greater dispersion in the 1.05μ region. The exposures with the Carnegie image tube are less than 60^m at maximum resolution with a dispersion of 3.5 Å/mm. The resolution is limited by the tube itself, so the only way to improve it is to increase the dispersion. This will be possible with the new coudè of the NASA 108-inch reflector, which will permit a dispersion of about 2 Å/mm to be achieved. It will then be possible to record the 1.06μ band and weak lines in the 1.04μ and 1.05μ bands with considerable precision, thereby reducing the mean error of the corresponding curve of growth.

Progress in recording the 8700 Å band is more difficult. Some gain can be achieved by narrowing the slit and making longer exposures (6-8 hours), but a large stride forward would require the use of a 1 Å/mm dispersion. This can also be achieved, with the aid of a cylindrical lens to compress the spectrum and thereby shorten the exposure times to reasonable values.

In both cases, it should be possible to obtain a decrease in the error in w to a value between 10 and 15%. At this point it should be possible to investigate the effects of elevation differences over the surface of the planet.

Finally, a large improvement in the state of our knowledge of the Martian water vapor abundance and its variation with season and position on the planet's disk is achievable with presently existing instrumentation. Observations under good conditions at 2 Å/mm should be far more reliable than previously published work.

7. **EXPENDITURES**

With the termination of the contract on January 31, 1968, the allotted funds have been exhausted.

Respectfully submitted,
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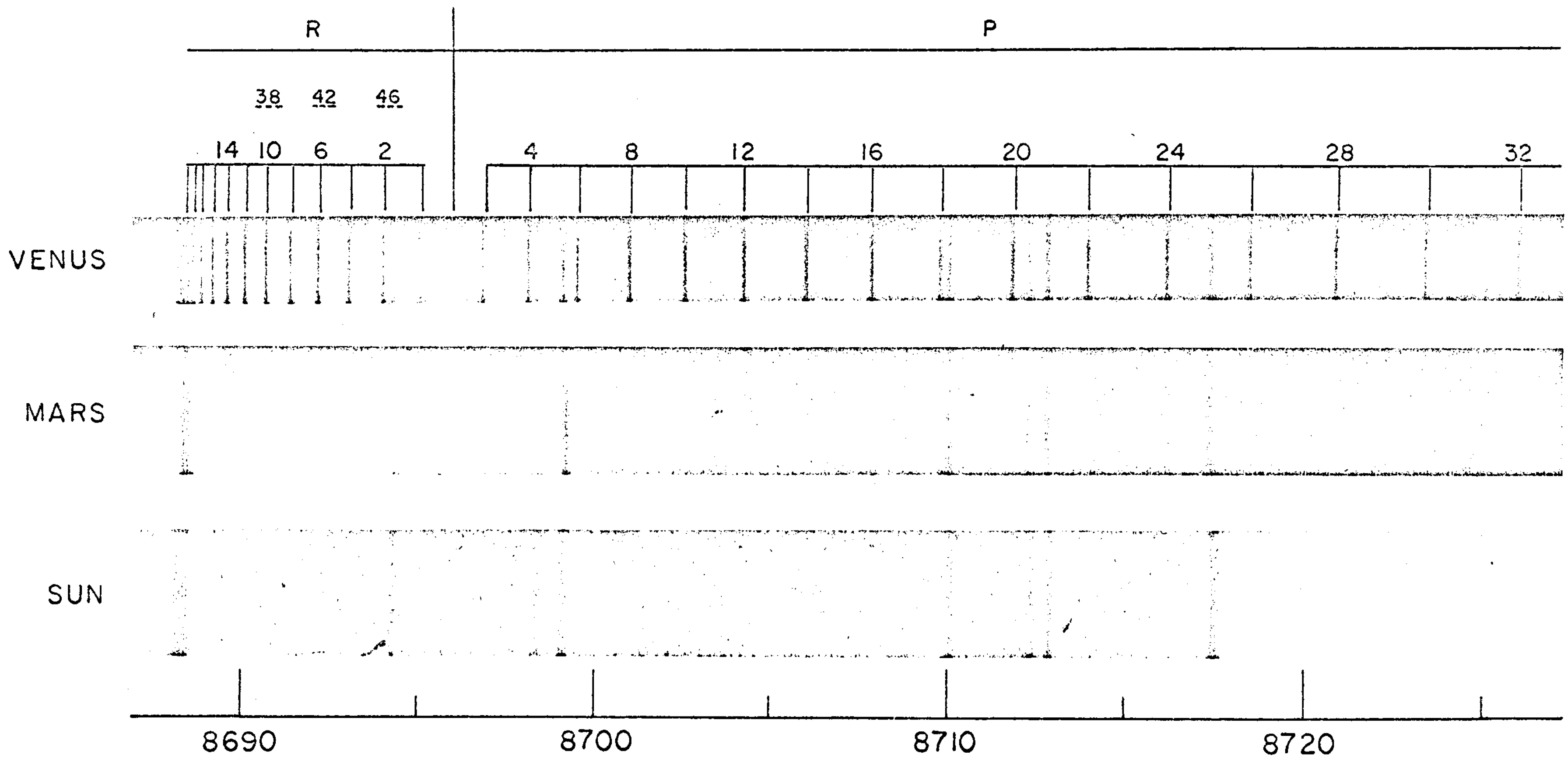
CAPTIONS FOR ILLUSTRATIONS

Figure 1. Spectra of Venus, Mars, and the Sun in the region of 8700 Å. The P and R branch lines of the $5\nu_3$ CO_2 band are indicated, including the high J components doubling back from the band head.

Figure 2. A tracing of the solar spectrum (a) from the Liège Atlas, compared with spectra of Mars obtained in 1965 (b) and 1967 (c) in the region of the $5\nu_3$ R branch. The CO_2 absorptions are indicated.

Figure 3. Spectra of Venus and Mars showing the CO_2 bands at 1.04μ $(2\nu_1 + 3\nu_3)$ and 1.05μ $(\nu_1 + 2\nu_2 + 3\nu_3)$.

Figure 4. A curve of growth for CO_2 in the Martian atmosphere. Each point refers to a single line except for the two points associated with the 1.06μ band which are averages of two points each.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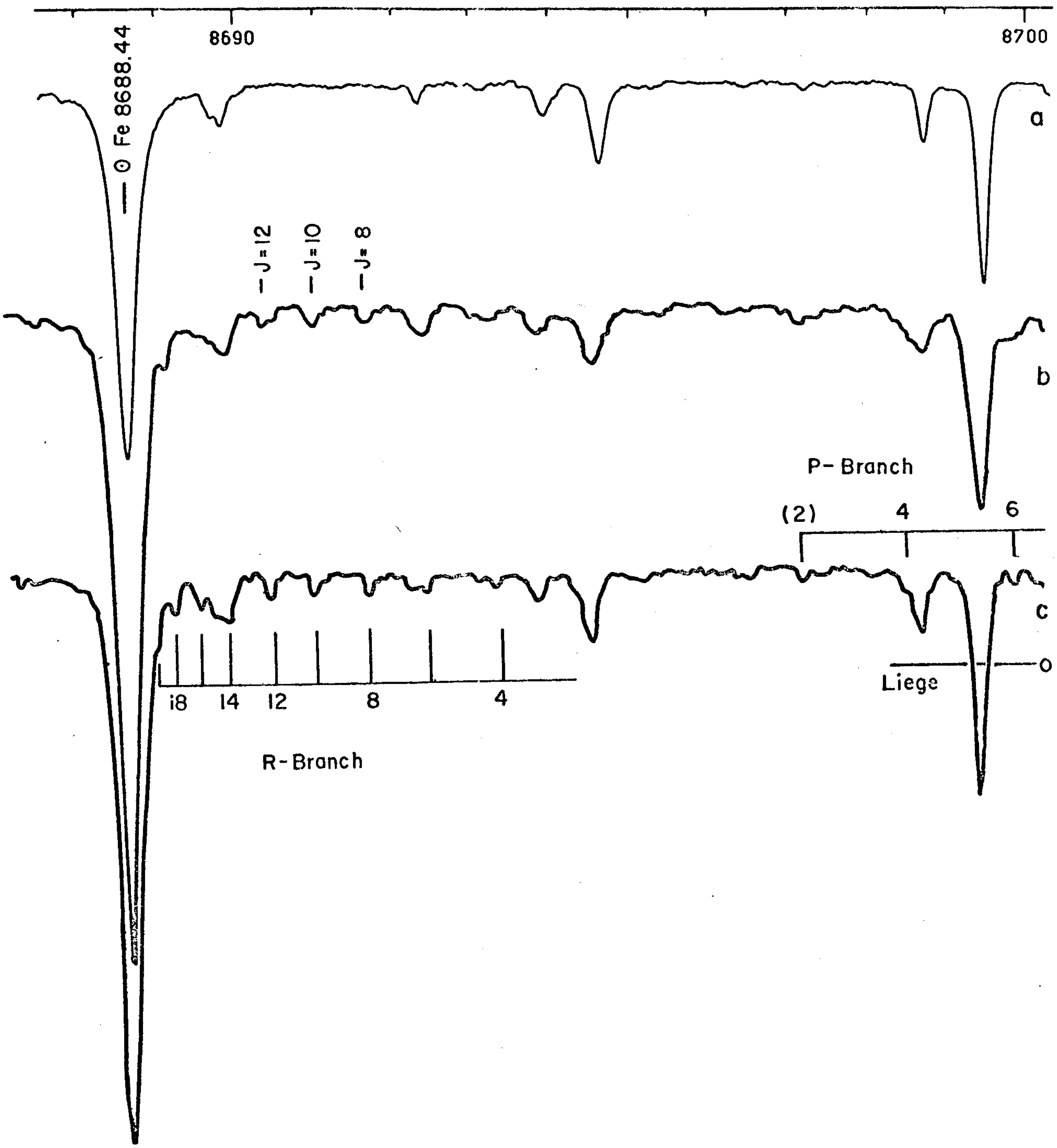

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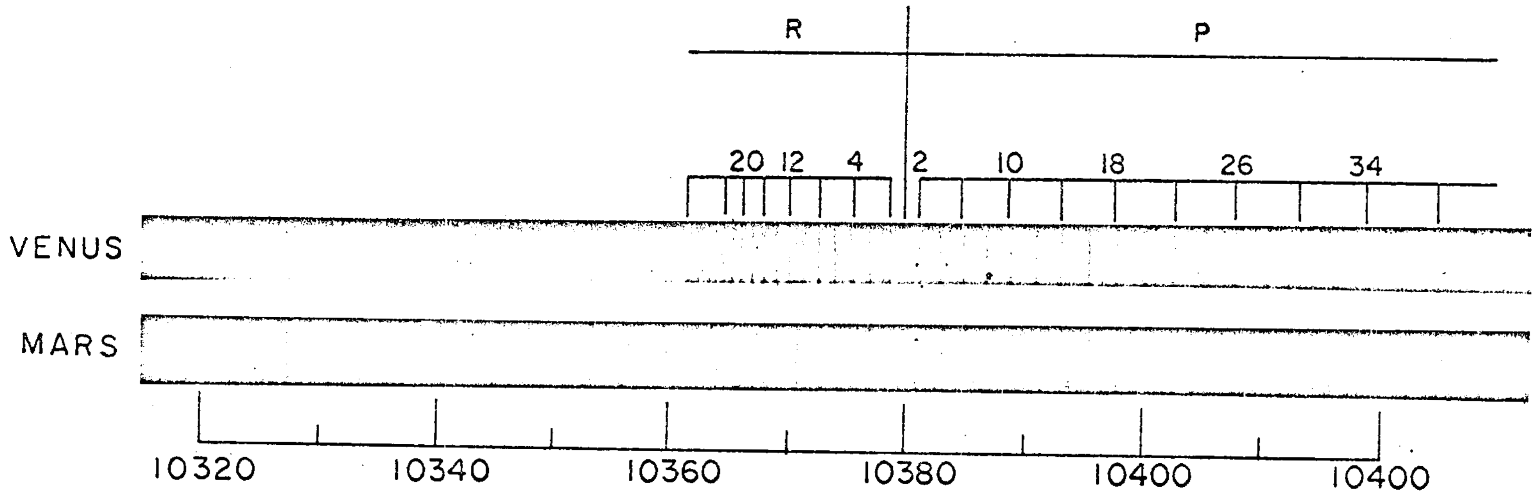
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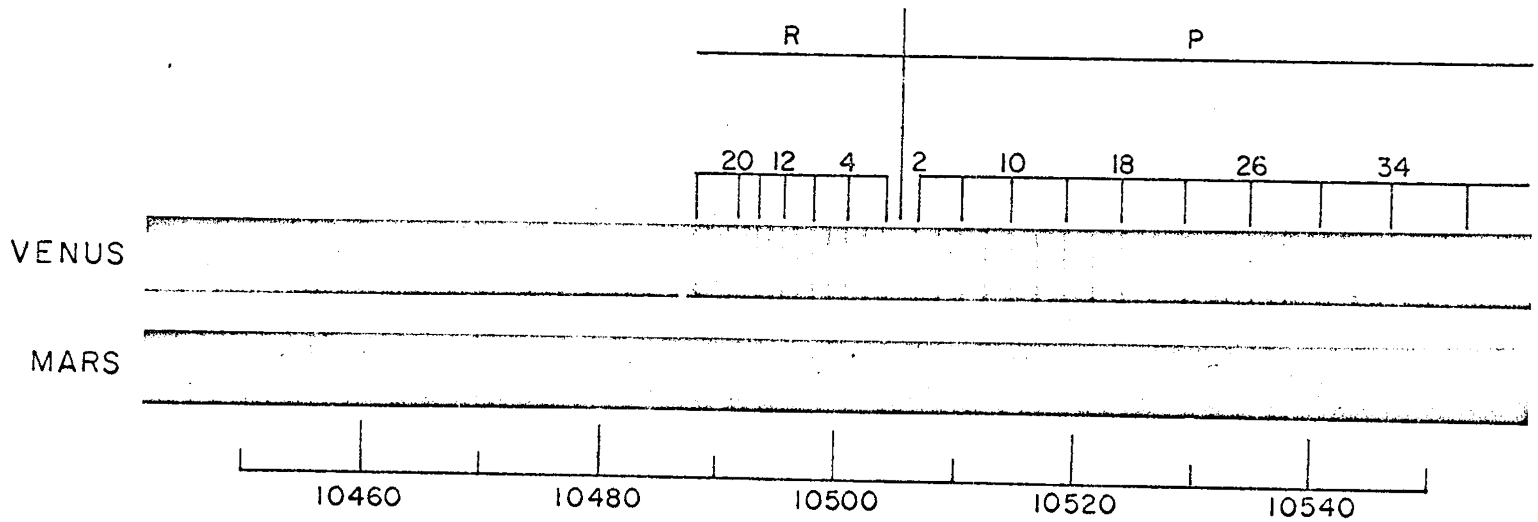
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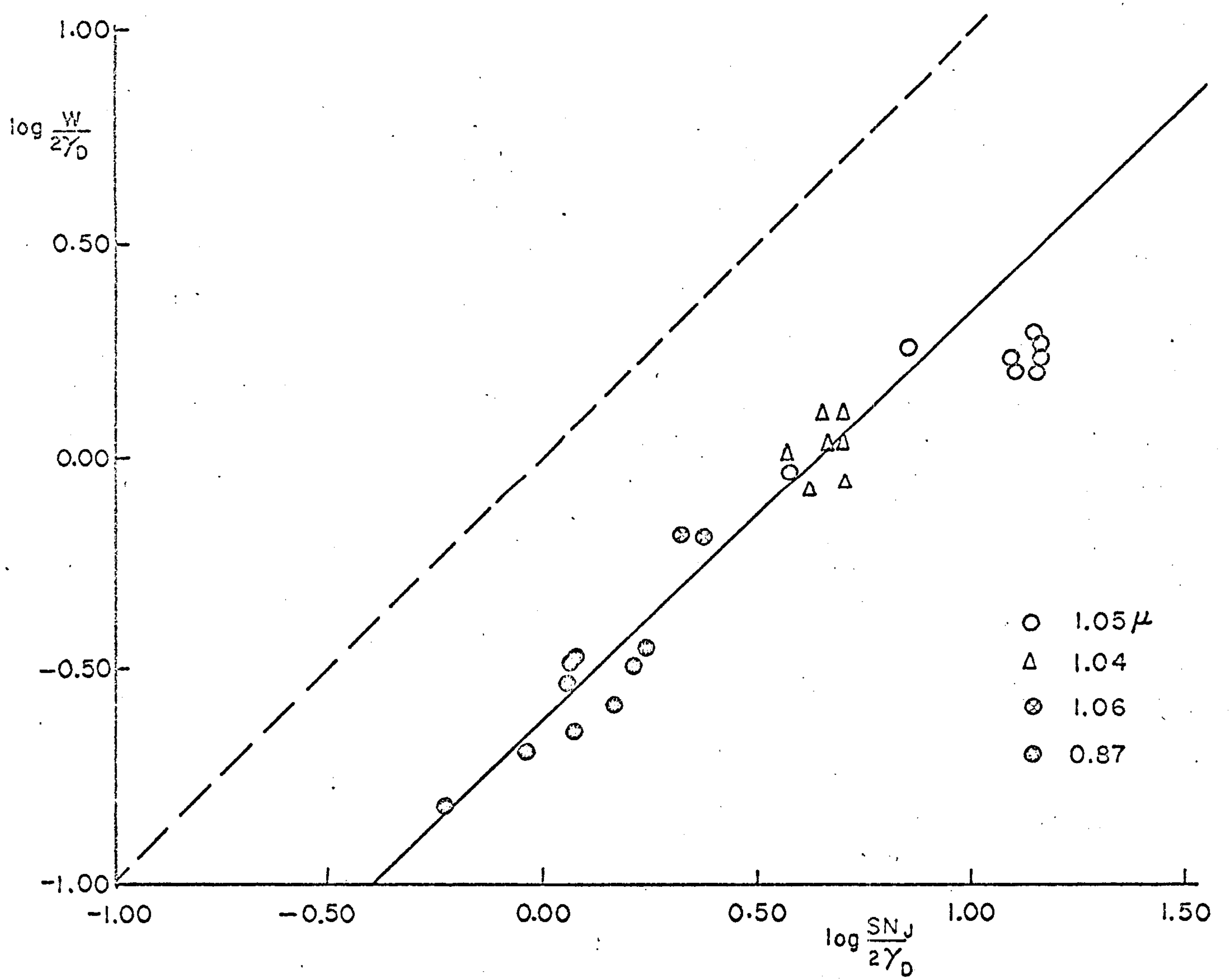
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