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Quarterly Report

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Abstract

This report summarizes project activity during the period 1 July 1970 to 30 September 1970. Instrument adjustments necessary to improve CO₂ spectra and the analysis of these spectra are discussed. Continued development of the ozone generating handling and measuring system are described. Additional progress in the analysis of the 9.6 μ m Ozone band is reviewed.

1. Introduction

This is the 4th Quarterly Progress Report on Contract No. NSR 23-005-376, covering the period 1 July 1970 to 30 September 1970.

The project effort during this time period was divided among the following tasks.

- A. High resolution measurements of the $15\mu\text{m}$ absorption band of CO_2 (L. W. Chaney).
- B. Theoretical analysis of high resolution $15\mu\text{m}$ CO_2 measurements (S. R. Drayson).
- C. Development of ozone generating, handling and measuring system (L. T. Loh and P. A. Titus).
- D. Theoretical analysis of $9.6\mu\text{m}$ ozone band (W. R. Kuhn).
- E. Survey of CO_2 in the Earth's Atmosphere (F. L. Bartman).

II. High Resolution Measurements of the $15\mu\text{m}$ Absorption Band of CO_2 (L. W. Chaney).

At the end of the last reporting period the new baffles were complete and a preliminary test spectrum had been run on the instrument.

It was noted that the new image height was approximately $1/2$ the detector height. The detector was masked to 2 mm and the pre-amplifier input resistance was optimized. As a result of using these techniques the signal to noise ratio was improved by a factor of 1.5.

Several tests were made to determine the best slit setting. With the new baffles which excluded all the first pass light it was possible to come very close to the theoretical resolution of less than 0.05 cm^{-1} . However, the signal to noise ratio under this condition was quite poor. Hence, we decided to open

the slits to the point that we had 0.06 cm^{-1} resolution. For the present study this represents a good compromise between resolution and adequate signal to noise ratio.

After selecting the slit size, the next task was to make a wavelength calibration. The calibration was made in terms of the stronger lines in the CO_2 spectrum. In the process of making these measurements it was discovered that extremely accurate temperature control of the room was required. This was accomplished by means of a strip heater, two air-conditioners, and two circulating fans. With care the entire room could be held within $\pm 0.5^\circ\text{C}$.

After completing the wavelength calibration a measurement program was started to repeat all the previous data. However, it was immediately noticed that the 100% line was not stable. Many tests were made of the source, the pre-amplifier, and the detector. A monitor was placed on the source to note any variations. The source varied considerably during the first few hours and the last few hours of its life (80 hr.). The intensity during the center 60 hrs seemed to be constant with an accuracy of better than 1%.

The greatest source of trouble seemed to be the detector. If the detector was cooled from room temperature, at least $1\frac{1}{2}$ hours was required after the helium fill to reach a stable sensitivity. Under the best of conditions the detector sensitivity might vary by $\pm 2\%$ over a period of 5 minutes.

All of the previous data taken with the 8.74 cm cell was repeated at pressures ranging from 2.5 mm to 680 mm. In all cases a background scan was taken before and after each data scan in order to obtain the best possible results. The data obtained was analyzed by Roland Drayson and a paper was presented to the Molecular Spectroscopy Symposium at Ohio State in September.

It is our conclusion that the instrument should be converted to double beam operation to improve its performance.

During the next period it is planned to take more data and investigate the possibility of converting the instrument to double beam. Particular emphasis will be placed on long path measurements.

III. Theoretical Analysis of High Resolution $15\mu\text{m CO}_2$ Spectra (S. R. Drayson).

The new baffle system installed in the Jarrell-Ash spectrometer considerably reduced the stray light in the instrument. However, another difficulty was encountered which impeded accurate quantitative measurements of absorption. Examination of the normalized spectra showed transmittances that sometimes exceeded 100%, caused by fluctuations in the 100% transmission background curve. An attempt was made to eliminate this problem by recording a background curve before and after taking each spectrum of carbon dioxide. The normalized spectra showed only a slight improvement, with errors typically of the order of a few percent, too large to be acceptable. Instrument modifications to make the spectrometer a double beam instrument are required.

Although quantitative measurements of absorption are not possible at the moment, excellent spectra showing many features can easily be obtained. Especially noteworthy is the low random noise level shown in the spectra. In view of the observation in the last quarterly report of some disagreement between the predicted and observed line wavenumbers, a number of spectra were run between 634 and 710 cm^{-1} . The lines of the ν_2 fundamental of $^{12}\text{C}^{16}\text{O}_2$ were used for calibration, since their positions have already been measured accurately. The wavenumbers of other absorption lines were determined by

assuming the wavelength to be a linear function of drum turn between these calibration lines. Typical spectra are shown in Figures 1 and 2.

Lines in the P and R branches can be used in the following way. The wavenumbers $P(J)$ and $R(J)$ are related to the band center ν_0 and the rotational constants of the upper and lower states B', D' and B'', D'' respectively by the following formula

$$P(J) + R(J) = 2 \Delta_0 + 2B'' + \beta(B' - B'') J(J+1) - 2D'' (3J^2 + 3J + 1) - 2(D' - D'') (J^4 + 2J^3 + 7J^2 + 6J + 2)$$

Assuming that the rotational constants B'', D'' for the lower state are known, a least squares fit to the measured values of $P(J)+R(J)$ will give ν_0 , B' and D' . If only low J values ($J \leq 30$) can be observed then it is better to force $D' - D'' \neq 0$ and solve for ν_0 and B' only. If a line of either the P or R branch could not be observed, its wavenumber was estimated from the formula

$$R(J-1) - P(J+1) = \Delta_2 F''(J) = (4B'' - 6D'')(J+1/2) - 8D''(J+1/2)^3$$

The corresponding value of $P(J)+R(J)$ was weighted by one half in the least squares analysis.

Lines of Q-branches may be analyzed from the formula

$$Q(J) = \nu_0 + (B' - B'') J(J+1) - (D' - D'') J^2 (J+1)^2$$

A least squares fit will give the rotational constants and the band center.

Tables I and II show the results of an analysis of the ν_2 fundamental of $^{13}\text{C}^{16}\text{O}_2$. The lower state constants are those given by Courta y (1959). Small errors in these constants produce a very small error in line position since the differences $(B' - B'')$, $(D' - D'')$, and ν_0 are the more important parameters. As can be seen in the tables, the RMS errors between the observed and calculated wavenumbers are very small, indicating that a considerable degree of confidence can be placed in the results. The wave number of the band center, 648.484 cm^{-1} differs significantly from that given by Courta y, 648.52 c .

Better spectra can be obtained by using a longer cell at lower pressure (the present spectra were taken with an 8.74 cm cell at pressures between 30 and 100 mm Hg). This will be the next measurement task in the program.

P and R BRANCHES 6 3 6 NU2 FUNDAMENTAL
 BAND CENTER = 648.484

BL= 0.390250 BU= 0.390602 BU-BL= .000352
 DL= 13.70D-08 DU= 13.70D-08 DU-DL= 0.0

J	P CALC	O-C	R CALC	O-C	P+R CALC	O-C
4	645.367	-0.003	652.397	-0.001	1297.764	-0.004
6	643.812	0.002	653.967	-0.002	1297.779	-0.000
8	642.260	0.005	655.540	0.001	1297.801	0.005
10	640.712	-0.001	657.116	0.000	1297.827	-0.000
12	639.166	-0.002	658.694	-0.002	1297.860	-0.004
14	637.623	0.005	660.275	-0.003	1297.898	0.002
16	636.083		661.858	0.000	1297.941	-0.002
18	634.546	0.005	663.444	0.000	1297.990	0.005
20	633.013		665.033	-0.004	1298.045	-0.003
22	631.482		666.624	0.000	1298.106	-0.003

RMS O-C = 0.0026 Wavenumbers

Table 1. Analysis of P and R branches of ν_2 fundamental $^{13}\text{C}^{16}\text{O}_2$ D'-D'' has been set equal to zero. All units are cm^{-1} .

Q BRANCH 6 3 6 NU2 FUNDAMENTAL

BAND CENTER= 648.484

BL= 0.390250

DL= 13.70D-08

BU=0.391256

DU= 13.66D-08

BU-BL= 0.001006

DU-DL= -43.66D-11

J	Q CALC	O-C
24	649.087	-0.000
30	649.420	0.000
32	649.646	-0.001
34	649.681	0.002
36	649.824	-0.000
40	650.134	-0.000

RMS O-C = 0.0010 Wavenumbers

Table 2. Analysis of Q-branch of ν_2 fundamental of $^{13}\text{C}^{16}\text{O}_2$. Band Center taken from Table 1.

All units are cm^{-1} .

IV. Development of Ozone Generating, Handling and Measuring System.

(L. T. Loh and P. A. Titus)

The construction and testing of component parts of ozone generating, handling and measuring system has continued.

Some confusion still exists in regard to the nature of output signals from the Jarrell Ash Monochromator. Communications by letter and phone have not yet completely answered all questions.

The shell of the 40 meter white cell was put back in place after shop work on its UV access holes. Connection of the plumbing, including the Heise pressure gage was completed and the entire system was leak-checked. Dow RTV 3145 was used to stop the major leaks. The UV optics including the Mercury lamp, lens system, monochromator, detector and electronics were installed and all six of the Mercury UV lines were checked.

A study of various air drying systems was made. Various ways and means will be used to keep the P. E. #221 spectrometer dry including a dehumidifier, an air dryer, bottled dry nitrogen or dry air, desiccants, and recirculation of dry air in a closed system. Following a flooding of the existing dryer system, a dehumidifier was bought and installed in the spectrometer room. The air dryer was used many times under close watch.

The P. E. #221 spectrometer was operated many times with the 40 meter white-cells in place. Problems uncovered included the following: the 0% transmission level shifted about 3% between runs, the 100% transmission level was low and fluctuated between 25% to 100% or more, and the switching of the stray light filter at $10\mu m$, caused spurious signals. The fluctuation of the 0% transmission level was fixed by putting black paint on the card used to stop the sample beam. The problem of the 100% transmission line was traced to the transfer optics of the white cell. Later, the screw holding mirror M-8 was established as the culprit and the problem was corrected. The spurious signal caused by the switching of the stray light filter at $10\mu m$ was avoided by not using this filter at all for the NaCl prism, since it provided very little improvement in the level of stray light.

The UV light source was found to be sensitive to power line voltage. Therefore it was connected to the regulated 110 V line. The regulated high voltage for operation of the photomultiplier tube (combination high voltage supply and electrometer amplifier) was found to be changing slowly. It was connected to the regulated 110V AC line, but this provided only a small improvement. A few ozone spectra in the ν_3 band were then run. After about one half hour of operation there was a flashover in the ozonizer and

a fuse was blown. Protective resistors were added to the ozonizer's power supply, to correct this problem.

The ozonizer and the spectrometer have now been operated on two different days for about 8 hours. The odor of ozone could be detected in the room. Also it was found that the temperature of the inner and outer electrodes of the ozonizer increased considerably. The O_3 in the room was determined to be around 0.05 ppm on one occasion (as compared to the 0.1 ppm threshold limit value). This measurement was made with the universal test kit distribute by Mine Safety Appliances Co., using an air sample of 1000 cc and operating the pump 10 times.

To prevent the heating of the ozonizer's electrodes circulating cold water was arranged for the outer electrode. The cooling of the inner electrode presents a problem, however, since the orifice is narrow and the voltage is high. It is planned to use a heavy copper electrode to increase heat conduction, or to arrange water circulation by a small battery operated pump, or to construct the copper electrode in the form of a "heat pipe".

Because of the noise of the air dryer system on the wall of the spectrometer room, the operation was stopped temporarily and a search for an alternative system was made. An air drying system manufactured by the McIntire Co. was selected and ordered.

It is desirable to be able to monitor the temperature of the inner electrode. Due to space limitations and high voltage, only two possibilities have been considered; the use of thermochron temperature crayons and the use of a thermistor after turning off the high voltage. Because the temperature crayon is a one shot device, a glass jacketed thermistor probe was prepared.

Because of the presence of O_3 , the possibilities of remote control and monitoring have been considered. The parameters which are to be monitored are the current of the ozonizer transformer primary winding, the temperature of the outer electrode of the ozonizer, and the Mercury absorption line-strength indication. Operations to be carried out are the operation of the "scan" button on the P. E. #221 spectrophotometer and the turning "on" and "off" of the chart recorder. A few of the operations still have to be done by personnel at the spectrometer. Part of the remote control apparatus has been installed.

Ozone is an extremely toxic gas; it has a distinctly pungent odor which is detectable in concentrations as low as 0.02 to 0.05 ppm. Hygienists are generally agreed that:

1. Sensitivity to ozone varies among individuals. Olfactory organs tend to become somewhat acclimated to it in a relatively short time.
2. A concentration of 1 ppm will cause considerable irritation to the eyes and respiratory tract in a short time.
3. A few parts per million will be safe for a few minutes provided latent or clinical respiratory infection is not present.
4. Exposure to 50 ppm will produce fatal results within minutes.
5. The recommended maximum concentration for an 8 hour working day is 0.1 ppm.

Our ozone generating system either does or could conceivably create each of the above hazardous environments. During a recent three-hour run,

ozone concentrations of 1 ppm and greater than 3 ppm were measured inside the high voltage transformer and ozonizer enclosures. These concentrations were reduced to 1ppm and 0.3 ppm respectively by mounting the transformer on top of the ozonizer box which reduced the length of the high voltage cable from 60 to 9 inches. Toward the end of the first run after this change the odor of ozone and a slight dryness of the eyes was detected but during the second run neither effect was noticed even though the transformer was not enclosed.

The ozonizer generates a mixture of 2% ozone in 98% oxygen and feeds it through glass, teflon and stainless steel tubing to the gas cell at a flow rate of 10 liters per hour. If a break in the tubing should occur, the space occupied by the ozone generating system and its immediate work area would rapidly become a hazardous environment. This same space would become a lethal environment if, however unlikely, the 2.3 cubic foot gas cell were to rupture and release an atmosphere of the mixture, and if the contaminated air was not vented immediately, the 6000 cubic foot spectrometer room could be filled with 7 ppm of ozone.

Therefore, plans for a safe working atmosphere around the ozone generating, handling and measuring system will include cutting a hole in the wall to the outdoors and installing a fan capable of changing the room air six to eight times an hour. A hood will be built above the high voltage transformer and connected to an existing stovepipe which runs from the gas cell exhaust pump to the ceiling vent, and a portable Mast Ozone Indicator plus strip chart recorder has been ordered. This instrument can operate continuously for thirty days on one container of sensing solution and will measure ozone in the range of 0-1 ppm. The indicator will be placed at the base of the ozonizer

and within one foot of the glass and teflon parts of the system tubing. It will be connected to a system which will sound an alarm and turn on the exhaust fan, when the O_3 level exceeds some predetermined amount, probably 0.1 ppm.

V. Theoretical Analysis of 9.6 μm Ozone Band (W. R. Kuhn)

Work on the ozone molecule has continued in two areas; developing of a computer code for line positions in the 9 μm region as well as initial work on the line intensities; methods for evaluating F factors (ratio between perturbed and rigid-rotor line strengths) have been investigated, and are presently being applied to the ν_1 (1103 cm^{-1}) and the ν_3 (1042 cm^{-1}) bands of ozone in order to determine the influence of centrifugal distortion on the line strengths. A method developed by Ben-Aryeh (1970) is being used, for which perturbations up to the second order are included. This technique requires parameters which can only be obtained from experimental data; as these data are not yet available, the coefficients will be determined from the theoretical study of Clough and Kneizys (1966), and results compared with their work.

A parameterization of transmission functions for single spectral lines has also been completed during this period. The motivation for this study was the need for accurate, yet rapidly attainable transmission functions for use in stratospheric equilibrium temperature calculations. Although present day computers can be used to determine transmissivities, equilibrium temperature calculations require a large number of transmission values and computer time becomes exorbitant. Even if one uses a band model, equilibrium temperatures in the stratosphere are difficult to obtain because of increased computer time due to the complexity of the absorption coefficient.

Accordingly, transmissivities have been calculated to five figure accuracy and tabulated as a function of the parameters Su/δ , a , and δ/α_0 , where the line strength, mass path, and interval over which the transmission is to be determined are S , u , δ respectively, a is the ratio of Lorentz to Doppler half-width, and α_D is the Doppler half-width. The ranges of parameters are $-6 \leq \log Su/\delta \leq 6$, $-7 \leq \log a \leq 3$, both in intervals of 0.1, and $2 \leq \log \delta/\alpha_0 \leq 6$ in an interval of 1.

The explicit form of the average transmission function τ over a spectral interval of width δ , is given by,

$$\tau = \int_0^1 \left[\exp \left\{ -\frac{Su}{\alpha_D} \frac{\ell_n^2}{\pi} K(a, f(x)) \right\} \right] dx$$

where $f(x) = \frac{\delta (\ln 2)^{\frac{1}{2}}}{2 \alpha_0} x$, and the Voigt function is given by;

$$K = \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{a^2 + [f(x) - y]^2}$$

There is no known analytical solution to this function and one must resort to numerical methods. One might expect that a quadrature technique could be used, but because of the large variation in the integrand over the interval from 0 to 1, for various values of the parameters, which vary over orders of magnitude, a quadrature technique over the entire interval is not possible. The evaluation technique used continually halves the interval, the areas being computed by parabolic quadrature. The area of the halved interval is then compared with the sum of the areas of this interval halved again, and if the difference is such that five significant figures are obtained, the

next interval is chosen. If the difference is greater than the preassigned accuracy, the final interval is halved and the procedure repeated again. We have found this program to be more efficient than preassigning x intervals and using a quadrature technique over these intervals. The Voigt function K was evaluated by the methods given by Armstrong (1967).

Although these values can be used in transmission calculations with an appropriate interpolation scheme, an effort is being made to represent the transmission as a polynomial expansion in terms of the parameters defined above. A complete discussion of the methodology, tabulated values, and, if successful, the polynomial expansions will appear as a separate report. An example of these calculations is shown in Figure 3.

VI Literature Survey of the Distribution of CO₂ in the Earth's Atmosphere

(F. L. Bartman)

Two significant studies of CO₂ in the earth's atmosphere published recently are those of Robinson and Robbins (1968, 1969) and Bolin and Bischoff (1970). Both studies contain good reviews of previous theoretical and experimental work, discussions of CO₂ emission, present CO₂ concentrations in the atmosphere, scavenging mechanisms for atmospheric CO₂ and possible effects of increasing atmospheric CO₂ on the radiation balance of the earth.

Measurements by Bolin and Bischoff during the years 1963-1968 indicate an increase of atmospheric CO₂ of 0.7 ± 0.1 ppm/year., about 1/3 of the annual industrial output of 1.9-2.3 ppm/year. Seasonal variations of 6.5 ppm at 2 Km and 3.5 ppm at the top of the troposphere were observed.

They observe that the annual increase and seasonal variations are now known very well for the purpose of indirect measurement of the atmospheric temperature structure using satellite measurements of infrared radiation (i. e. an accuracy of ± 2 ppm is given for the lower troposphere and ± 1.5 ppm for the upper troposphere and the lower stratosphere).

VII. Reports Published.

A paper on the high resolution measurements of CO₂ was presented to the Molecular Spectroscopy Symposium at Ohio State University in September. The paper presented by L. W. Chaney and S. R. Dryason was entitled, "High Resolution Measurements of Absorption Line Parameters for Carbon Dioxide in the 15 μ m. Region.

VIII. References.

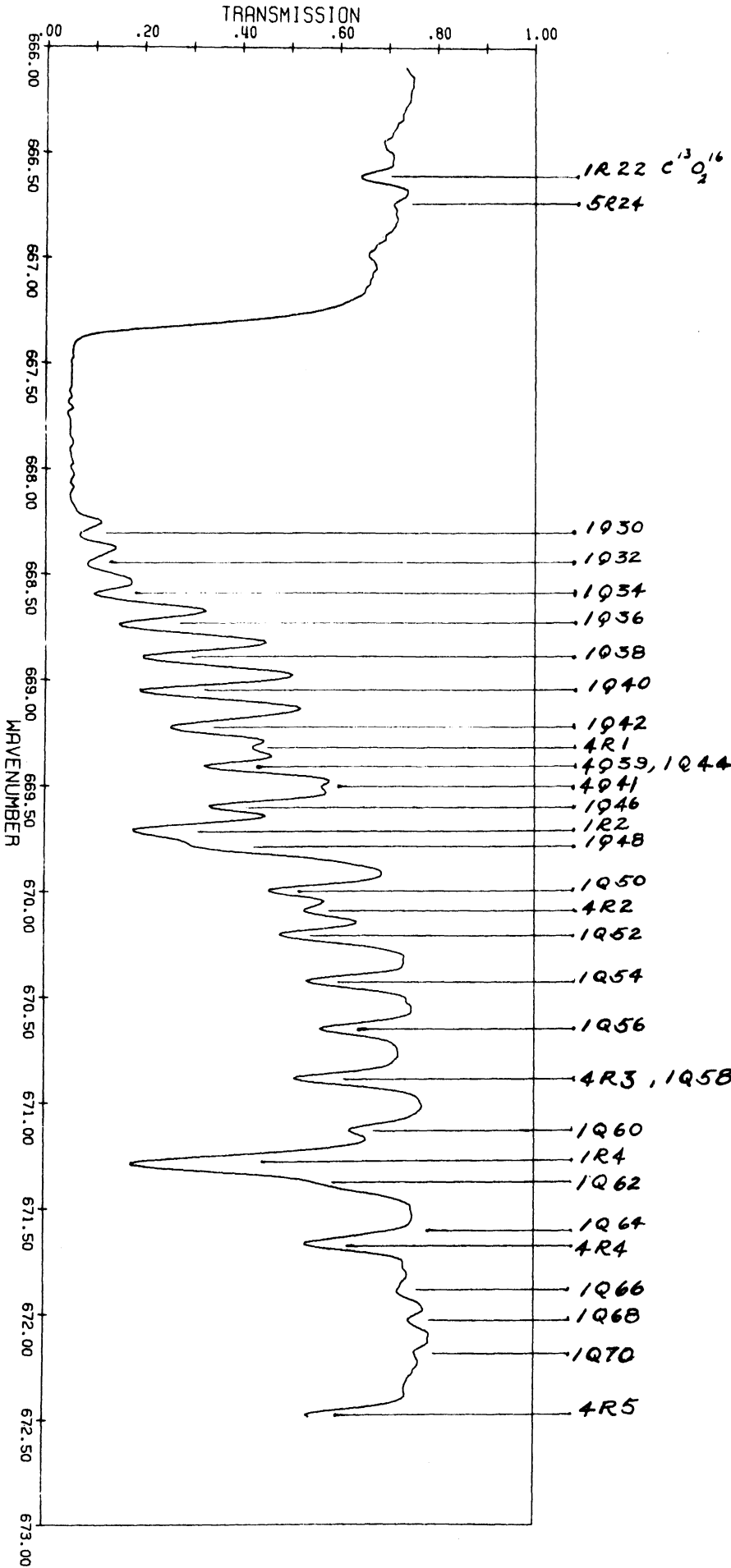
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BAND CODE - [BAND 1 00'0 - 01'0
 BAND 4 01'0 - 02'0
 BAND 5 02'0 - 03'0

Figure 1. CO_2 SPECTRUM, 8.74 CM CELL, 25°C, 50 MM Hg
 Portion of CO_2 spectrum near 670 cm^{-1}
 showing Q-branch of ν_2 fundamental

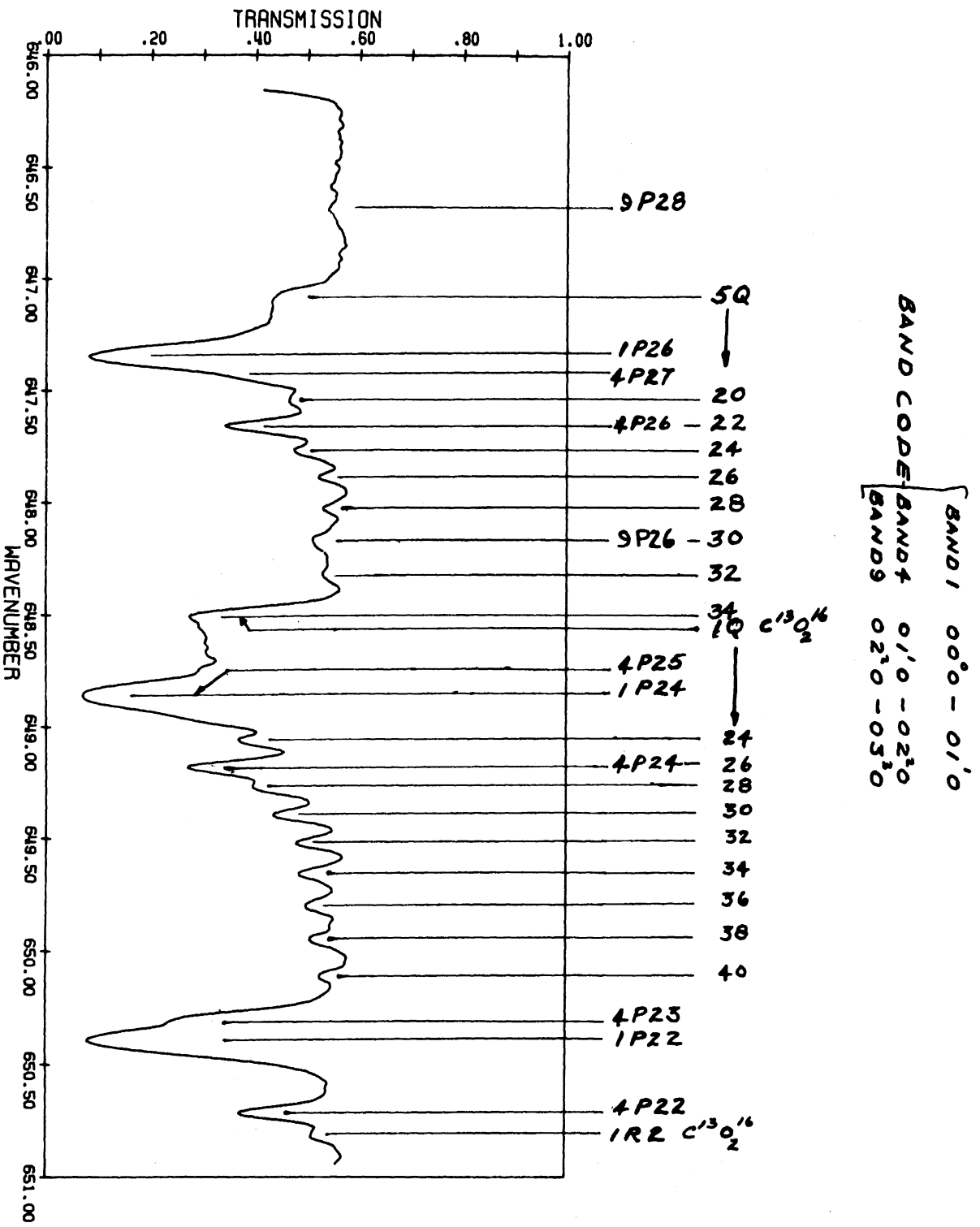


Figure 2. Portion of spectrum near 648 cm⁻¹ showing Q-branch of ν_2 fundamental of $^{13}\text{C}^{16}\text{O}_2$ and Q-branch of 02°-03° band of $^{12}\text{C}^{16}\text{O}_2$

CO₂ SPECTRUM, 8.74 cm CELL, 25°C, 50.00 mm Hg

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