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HIGH ALTITUDE RADIATION MEASUREMENTS

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Abstract

This report summarizes project activity during
the period 1 October 1970 to 31 December 1970. Plans
for continued experimental measurements of CO_2 spectra
and the analysis of this data are described. Sample spectra
are shown. Progress in experimental measurements of O_3
spectra are described. Sample O_3 spectra are shown.
Progress in the analysis of the O_3 data is reviewed.

1. Introduction

This is the 5th Quarterly Progress Report on Contract No. NSR 23-005-376, covering the period 1 October 1970 to 31 December 1970.

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

A. High Resolution measurements of the 15 μ m absorption band of CO_2 (L. W. Chaney).

B. Theoretical analysis of high resolution 15 μ m CO_2 spectra (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 μ 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 μ m Absorption Band of CO_2 (L. W. Chaney).

The experimental effect herein reported was carried out during November and the first week of December. The month of October was spent in completing another project. As a result of an accident on December 8, no further work was done during the balance of December.

During the previous reporting period data was obtained using the 8.74 cm cell. An examination of the data indicated that it would be useful to accurately measure the frequencies of many of the weaker lines. A long path was required in order to have a large CO_2 path without pressure broadening. The path through the complete spectrometer is about 20 meters (Fig. 1), which is ideally suited to our purpose.

The spectrometer main body was connected with suitable valves to the gas handling manifold used to mix and measure the gas placed in the sample cells.

Long path spectra were first obtained in a few selected regions. It was then decided that it would be useful to obtain high resolution spectra throughout the entire band, (540 to 830 cm^{-1}).

After starting the project it was determined that the maximum information could be obtained if the pressure was adjusted to almost saturate the strongest lines. The project was in process at the end of the reporting period.

The accurate determination of the frequencies of some of the lines due to CO_2 isotopes was difficult because of the low intensities. In order to improve the accuracy, isotope enriched samples of $C_{13}O_{16}O_{16}$, $C_{12}O_{18}O_{16}$, and $C_{12}O_{17}O_{16}$ are being purchased.

A more careful study of the modification of the spectrometer to double beam was made. The essential features of the design (Fig. 2) have been determined. It is estimated that 2 to 3 months would be required to imple-ment the design.

The infra-red Laboratory which has jurisdiction over the spectro-meter will have a need for the instrument for other measurements for a period of as much as 6 months. Hence, the double beam design has been temporarily set aside in order to concentrate on collecting data from the instrument in its present form.

Plans for next period:

1. Finish the high resolution survey of the entire 15μm band.

2. Complete the high resolution survey of isotopes $C_{13}O_{11}O_{16}$, $C_{12}O_{18}O_{16}$ and $C_{12}O_{17}O_{16}$.

3. Place a new Cu:Ge detector in service and make line width and strength measurements in selected wavelength areas:

III. Theoretical Analysis of High Resolution 15 μ m CO_2 Spectra (S. R. Drayson).

Work was continued to obtain more accurate vibrational and rotational constants for the CO_2 bands in the region between about 12 and 18 μ m. Earlier spectra had been obtained with a short cell (8.74 cm). To enhance the weaker spectral lines a much longer path at low pressure is required, easily accomplished by filling the entire spectrometer with small amounts of CO_2. Spectra taken in this manner showed many more lines which were previously lost in the general noise level of the instrument (see figure 3 a and 3 b). Some regions showed sequences of weak lines that have not yet been identified.

Tests of repeatability of the wavenumber measurements showed that, except for very weak lines where random noise was a considerable factor, differences between determinations from two data sets were seldom more than .004 cm^{-1}. Larger differences between measured wavenumbers and those predicted from the least squares fitting procedures could nearly always be attributed to a blending with weaker lines nearby. The data taken with the short cell is much better in this respect and is always used if the line can be clearly identified on one of these spectra.

The analysis of the spectra is not yet complete, and some data

remains to be taken.   In particular samples of gas enriched in ^{13}C, ^{17}O and ^{18}O have been ordered and will be used to fill the short cell.   Spectra of these samples will provide much better constants for molecules of CO_2 containing these isotopes, which are of considerable importance in the atmospheres of Mars and Venus.

IV. Development of ozone generating, handling and measuring system (L. T. Loh and P. A. Titus).

A solution to the problem of overheating of the inner electrode of the ozonizer has apparently been arrived at.   The cooling jacket on the ozonizer was connected to the tap water line.   The copper wire originally used inside the copper sulfate solution of the inner electrode was replaced by one made of a piece of thin walled copper tubing.   Near the top end of this tubing, a few small holes were drilled.   The copper tubing was placed in the solution so that the warm solution could move up outside the copper tubing, while the cold solution could move down inside the copper tubing. The ozonizer, with cooling, has now been operated over extended periods of time without overheating.

For safety purposes a survey of concentrations of ozone around the ozonizer during its operation was made using a borrowed Mast ozone meter, model H-100-LC, Welsbach Corp.   Since this meter did not have a calibration resistor for recording its output, one was improvised after measuring the voltage drop across the ozone meter while it was inside a plastic bag filled with ozonized air.   The initial survey showed ozone concentrations near the immediate vicinity of the ozonizer to be high (1 ppm), particularly near the high voltage cable.   As a result, the high voltage transformer

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was moved to the top of the ozonizer box inside a plastic cover. Since then the working area was found to be safe from ozone. Later, an ozone meter plus recorder and accessories were purchased.

The Jarrell-Ash power supply/amplifier was again checked according to the suggestions of Mr. Stockellburg of the Company. None of his suggestions helped.

Due to the detrimental effect of ozone and aging of materials, leaks did develop in the ozone system and the White cell. Thus far, we have found 1 O-ring in a relief valve badly cracked by ozone and the teflon packing of a Whitey valve coldflowed. There might be a leak in the window end of the sample White cell.

A complete dry air system was purchased from the McIntire Co. of N. J. It will be used as a portable system whenever and wherever dry air is needed.

The ozone system and the Perkin-Elmer #221 worked quite well in spite of minor troubles here and there. Several sets of ozone spectra covering the wavelength region 2-15 μ m have been recorded. Figure 4 is an example. Quantitative measurements of ozone were made by ultra-violet spectroscopy.

It is desirable to keep the ozone concentration constant during a run. For ozone this is difficult. The best approach is to make the run as fast as instrumentally possible. With enough ozone in the White cell and with the ozonizer off, the concentration of O_3 will decrease rather slowly. The Perkin-Elmer #221 has a few controls to speed up the run. It will be necessary to experiment with various controls to find the best combination for the fastest run.

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

In order to gain the expertise to treat the 9μm infrared vibrational

line intensities of the ozone molecule, the symmetric and asymmetric

rotor problems are being studied without the effect of perturbations, such

as centrifugal distortion. The intensity of a vibrational rotational line

can be written,

$$S = \frac{8\pi^3 \omega N g_n'' \, (1-e^{hc\omega/kt}) \, \exp(-E_n''/kT)}{3 \, hc \sum_n g_n'' \, \exp(-E_n/kT)} \, \left| \langle n'' | M | n' \rangle \right|^2$$

where ω is the wavenumber of the transition, N is number density (STP),

g the nuclear spin degeneracy, h is Planck's constant, k Boltzmann's

constant, T temperature, c the speed of light, E'' and E the energies

of the lower and upper states respectively, and the last term contains

the matrix elements of the electric moment M, which are found by ex-

panding the electric moment relative to a molecule fixed set of axes, and re-

taining only the first two terms in the expansion. If one is concerned with

relative intensities, then this term is proportional to

$$\left| \langle R' | \Phi_{Fg} | R'' \rangle \right|^2$$

which are the matrix elements of the direction cosines, Φ_{Fg} (F refers to

space fixed and g molecule fixed axes)

The theory for the symmetric rotor line strengths has been reviewed

and sample calculations have been completed as a check on the understanding

of the theory. The theory for the asymmetric rotor line strengths is

presently being studied. The direction cosine matrices for the symmetric

rotor are transformed to a form appropriate for the internal rotation V

group. This is done by applying the Wang functions X,

$$\Phi_{Fg}^{\,s} = X' \, \Phi_{Fg} X$$

where Φ_{Fg} are tabulated (see, e.g., Allen and Cross, 1963)[1] and the Wang function is,

$$X = \frac{1}{2} \begin{bmatrix} -1 & & 1 \\ & \frac{1}{\sqrt{2}} & \\ 1 & & 1 \end{bmatrix}$$

The asymmetric rotor direction cosine matrix elements are then linear combinations of the Wang functions,

$$\Phi_{Fg}^{\,A} = T' \, \Phi_{Fg}^{\,s} \, T$$

where it is assumed both states have approximately the same asymmetry. The evaluation for the transformation matrix T is given in, e.g., Allen and Cross. Comparisons will be made with the work of Clough and Kneizys, 1965.[2]

VI. <u>Literature Survey of the Distribution of CO_2 in the Earth's Atmosphere</u>
(F. L. Bartman).

The problem of CO_2 in the upper stratosphere is discussed in the recent paper by P. B. Hays and J. J. Olivero[3]. This work can be summarized by quoting the abstract. "The dependence of atmospheric distributions of CO_2 and CO upon the combined effects of photochemical production and loss, and transport is examined. It is found that, for CO_2, deviations

from complete mixing are possible in the mesosphere and upper strato-
sphere. Further, sufficient quantities of CO may be maintained, as a
product of CO_2 photodissociation, to be aeronomically significant."

Another related paper, dealing only with CO in stratosphere by
Pressman and Warneck[4] concludes that "the stratospheric sink contributes
significantly, but only partially, to the overall removal of CO from the
atmosphere."

VII. References

1. Allen, Harry C. and Cross, Paul C., 1963, "Molecular Vib-Rotors,"
John Wiley, Pub., 24 pages.

2. Clough, S. A., and Kneizy's, F. Y., 1965, "Ozone Absorption in the
9 Micron Region", Report, AFCRL 65-862.

3. Hays, P. B. and Olivero, J. J., 1970, "Carbon Dioxide and Monoxide
above the Troposphere," Planet. Space Sci., Vol. 18, pp 1729-1733.

4. Pressman, J. and Warneck, P., 1970, "The Stratosphere as a
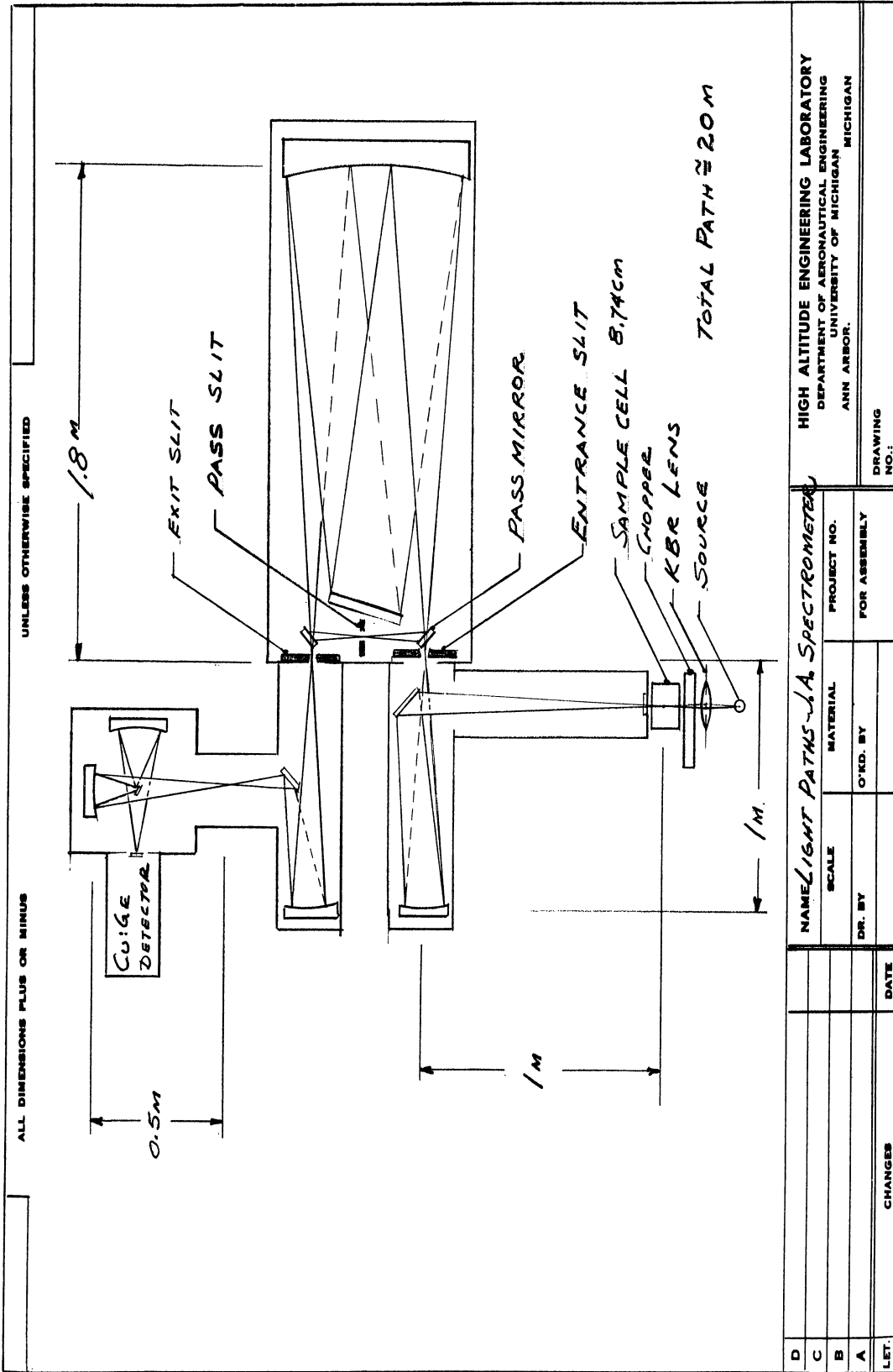Chemical Sink for Carbon Monoxide", J. Atmos. Sci. 27, no. 1,
155-163.

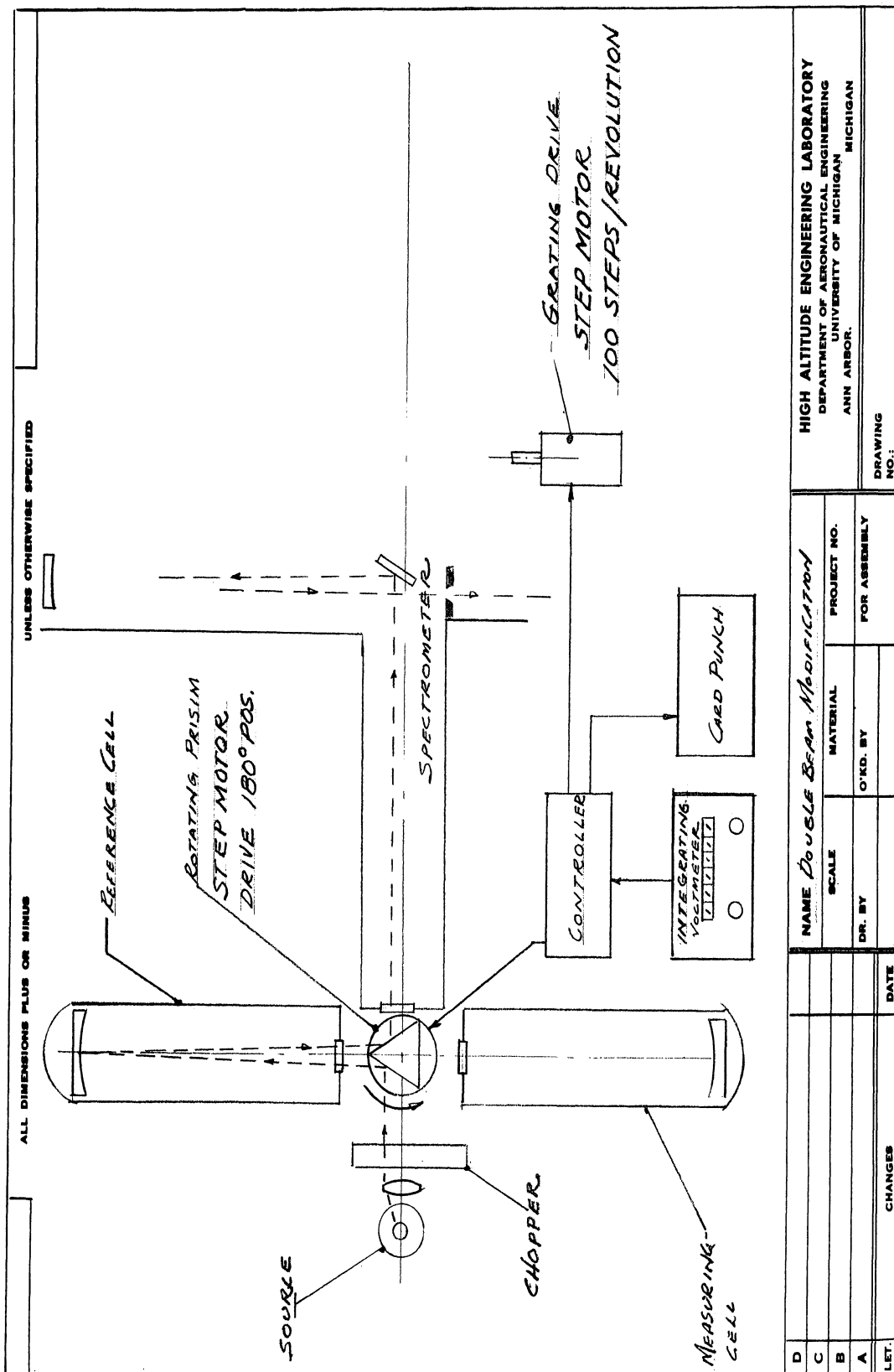Figure 1. Light paths in the Jarrell Ash spectrometer

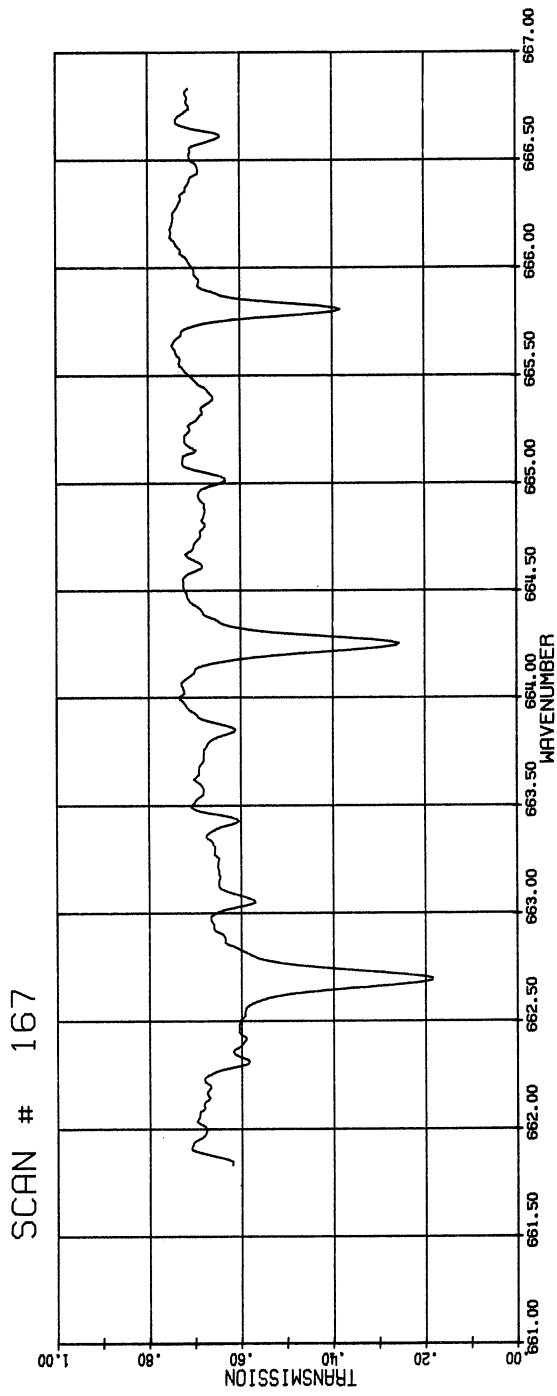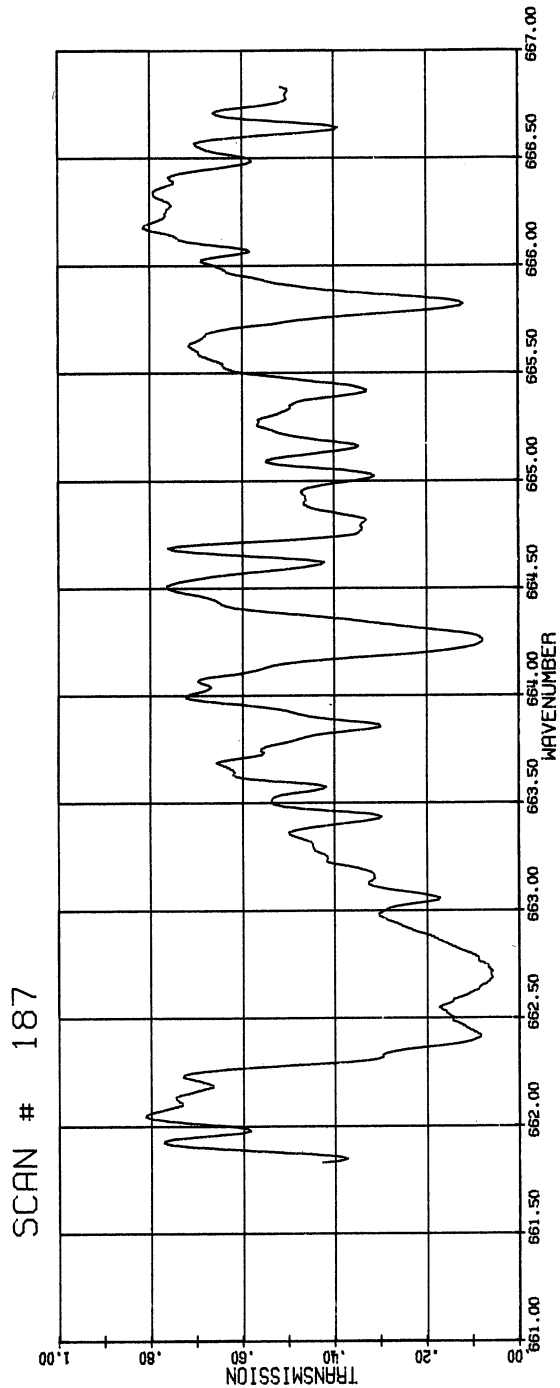Figure 2.   Double beam modification for the Jarrell Ash spectrometer.

Figure 3a. CO_2 spectrum between 661.8 and 666.8 cm^{-1}, taken with the short cell (8.74 cm) at a pressure of 30.0 torr. The dominant features are lines of the P-branch of the ν_2 fundamental of $^{12}C^{16}O_2$

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Figure 3b. CO_2 spectrum in the same region with CO_2 filling the main tank of the spectrometer to a pressure of 6.3 torr. In addition to the P-branch of the ν_2 fundamental of $^{12}C^{16}O_2$, the Q-branches of the ν_2 fundamentals of $^{12}C^{16}O^{17}O$ (band center 664.8 cm^{-1}) produce considerable absorption, as well as numerous lines of overtone bands and other isotopic species of CO_2. All lines have been identified.