INFORMATION TO USERS

This dissertation was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from “photographs" if essential to the understanding of the dissertation. Silver prints of “photographs” may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106
A Xerox Education Company
TRUSTY, Gary Lee, 1941-
ABSORPTION MEASUREMENTS OF THE 10.4 MICRON REGION USING A CO$_2$ LASER AND A SPECTROPHONE.
The Ohio State University, Ph.D., 1972
Engineering, electrical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED.
ABSORPTION MEASUREMENTS OF THE 10.4 MICRON REGION USING A CO$_2$ LASER AND A SPECTROPHONE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Gary Lee Trusty, B.S., M.Sc.

The Ohio State University
1972

Approved by

[Signature]
Adviser
Department of Electrical Engineering
PLEASE NOTE:

Some pages may have indistinct print.

Filmed as received.

University Microfilms, A Xerox Education Company
ACKNOWLEDGMENT

Three men have been instrumental in the development of this dissertation. My advisor, Said H. Koozekanani, has contributed much to my understanding of the fundamental problems involved. As my supervisor, Ronald K. Long has been a continuing source of encouragement and assistance. Many discussions with Edward K. Damon have provided me with many valuable ideas and solutions. I wish to express my sincere appreciation to them all.

I also wish to thank Frank S. Mills for his computer programming and Josann W. Trusty for her helpful discussions and patience.

The research reported in this dissertation was sponsored in part by Air Force Systems Command, Wright-Patterson Air Force Base, Ohio under Contract F33615-69-C-1807, and by The Ohio State University Research Foundation.
VITA

May 24, 1941.............. Born - Dayton, Ohio

1964........................ B.S. in Electrical Engineering,
University of Cincinnati, Cincinnati, Ohio

1964-1965................. Staff Scientist, Systems Research
Laboratory, Dayton, Ohio

1966........................ M.Sc. in Electrical Engineering,
The Ohio State University,
Columbus, Ohio

1966--1972.............. Research Associate, The ElectroScience
Laboratory, The Ohio State University,
Columbus, Ohio
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Error introduced by intensity distribution modification</td>
<td>32</td>
</tr>
<tr>
<td>2.</td>
<td>Self-broadening coefficient of the P(20) line of the 10.4(\mu) band of CO(_2)</td>
<td>59</td>
</tr>
<tr>
<td>3.</td>
<td>Line strengths of the 10.4(\mu) band of CO(_2) at 300(^\circ)K</td>
<td>60</td>
</tr>
<tr>
<td>4.</td>
<td>A comparison of the values (S_0/\alpha_0) obtained in this study with those given by McCubbin and Mooney</td>
<td>62</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Solar spectrum showing the contribution of the various atmospheric constituents (After Shaw)</td>
<td>2</td>
</tr>
<tr>
<td>2.</td>
<td>Energy levels of carbon dioxide involved in the carbon dioxide laser</td>
<td>3</td>
</tr>
<tr>
<td>3.</td>
<td>Theoretical absorption of the carbon dioxide 10.4μm absorption band. 10 km path at 330 PPM at 1 atm.</td>
<td>4</td>
</tr>
<tr>
<td>4.</td>
<td>Error multiplication factor plotted versus transmittance for error in absorption coefficient</td>
<td>7</td>
</tr>
<tr>
<td>5.</td>
<td>Percentage error in absorption coefficient plotted versus percentage error in transmittances</td>
<td>8</td>
</tr>
<tr>
<td>6.</td>
<td>Comparison of the Lorentz and Doppler profiles with equal half widths</td>
<td>15</td>
</tr>
<tr>
<td>7.</td>
<td>Transmittance of the carbon dioxide P(20) line of the 10.4 μm band at line center plotted versus pressure showing the linearity at low pressures (After McCoy).</td>
<td>16</td>
</tr>
<tr>
<td>8.</td>
<td>Transmittance of the carbon dioxide P(20) line of the 10.4 μm band at line center plotted versus pressure showing the constant transmittance at high pressures (After McCubbin and Mooney).</td>
<td>16</td>
</tr>
<tr>
<td>9.</td>
<td>Normalized Maxwell distribution of speeds (After Present)</td>
<td>25</td>
</tr>
<tr>
<td>10.</td>
<td>Pressure dependence of the life time of the CO₂ 00°1 level (After Weber and Deutsch)</td>
<td>27</td>
</tr>
<tr>
<td>11.</td>
<td>Intensity distributions for three beam shapes with equal power and radius</td>
<td>36</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>12.</td>
<td>Beam irradiation factor plotted versus beam radius for three beam shapes</td>
<td>37</td>
</tr>
<tr>
<td>13.</td>
<td>Diagram for explaining alignment procedure for the carbon dioxide laser</td>
<td>39</td>
</tr>
<tr>
<td>14.</td>
<td>Beam reducing telescope</td>
<td>40</td>
</tr>
<tr>
<td>15.</td>
<td>Spot size plotted versus distance from grating. Second lens at position 1</td>
<td>41</td>
</tr>
<tr>
<td>16.</td>
<td>Spot size plotted versus distance from grating. Second lens at position 2</td>
<td>42</td>
</tr>
<tr>
<td>17.</td>
<td>Spot size plotted versus distance from grating. Second lens at position 3</td>
<td>43</td>
</tr>
<tr>
<td>18.</td>
<td>Schematic of spectrophone cell</td>
<td>46</td>
</tr>
<tr>
<td>19.</td>
<td>Diagram of original spectrophone electronics</td>
<td>47</td>
</tr>
<tr>
<td>20.</td>
<td>Diagram of major equipment in the experiment</td>
<td>49</td>
</tr>
<tr>
<td>21.</td>
<td>Computer plotter output for averaging only</td>
<td>53</td>
</tr>
<tr>
<td>22.</td>
<td>Computer plotter output for averaging plus 9-point smoothing</td>
<td>54</td>
</tr>
<tr>
<td>23.</td>
<td>Tracing of computer plotter output showing result of leak valve too far open</td>
<td>55</td>
</tr>
<tr>
<td>24.</td>
<td>Tracing of computer plotter output showing pulse shape for 3/8 inch spectrophone cell</td>
<td>56</td>
</tr>
<tr>
<td>25.</td>
<td>Collisional halfwidth of the P-branch lines of the 10.4 μm band of CO2 for self broadening as a function of rotational quantum number</td>
<td>64</td>
</tr>
<tr>
<td>26.</td>
<td>Parameter study of the spectrophone system output as a function of pressure in the cell</td>
<td>64</td>
</tr>
<tr>
<td>27.</td>
<td>Linearity study of the spectrophone system with respect to absorber amount</td>
<td>65</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS (Contd.)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.</td>
<td>Self-broadened and foreign-broadened half-widths of the lines in the P-branch of the 10.4μ CO2 band as a function of rotational quantum number</td>
<td>67</td>
</tr>
<tr>
<td>29.</td>
<td>The absorption coefficients of water vapor-nitrogen mixtures as a function of the partial pressure of water vapor</td>
<td>68</td>
</tr>
<tr>
<td>30.</td>
<td>Manifold used for original H2O-N2 mixing procedure</td>
<td>68</td>
</tr>
<tr>
<td>31.</td>
<td>Diagram of spectrophone with dew point hygrometer added</td>
<td>69</td>
</tr>
<tr>
<td>32.</td>
<td>Water vapor-nitrogen absorption for 8 of the P-branch CO2 laser lines</td>
<td>70</td>
</tr>
<tr>
<td>33.</td>
<td>Temperature dependence of water vapor-nitrogen absorption at 2 of the P-branch CO2 laser lines</td>
<td>73</td>
</tr>
</tbody>
</table>
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>ii</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>ILLUSTRATIONS</td>
<td>v</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I  INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II MOLECULAR ABSORPTION OF RADIATION</td>
<td>11</td>
</tr>
<tr>
<td>A. Lambert's Law</td>
<td>11</td>
</tr>
<tr>
<td>B. Absorption Line Parameters</td>
<td>12</td>
</tr>
<tr>
<td>III GASES</td>
<td>18</td>
</tr>
<tr>
<td>A. Introduction</td>
<td>18</td>
</tr>
<tr>
<td>B. Microscopic Quantities of Interest</td>
<td>18</td>
</tr>
<tr>
<td>C. Macroscopic Properties</td>
<td>20</td>
</tr>
<tr>
<td>D. Energy and Particle Transfer</td>
<td>22</td>
</tr>
<tr>
<td>E. Molecular Energy Transfer</td>
<td>23</td>
</tr>
<tr>
<td>F. Relaxation Rates</td>
<td>25</td>
</tr>
<tr>
<td>IV HEAT TRANSFER PROBLEM</td>
<td>29</td>
</tr>
<tr>
<td>A. Introduction</td>
<td>29</td>
</tr>
<tr>
<td>B. Heat Flow Equation</td>
<td>29</td>
</tr>
<tr>
<td>C. Steady State Solution</td>
<td>30</td>
</tr>
<tr>
<td>D. Effect of Beam Shape on Solution</td>
<td>35</td>
</tr>
</tbody>
</table>

viii
<table>
<thead>
<tr>
<th>VII</th>
<th>CONTENTS (Contd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>EXPERIMENTAL APPARATUS</td>
</tr>
</tbody>
</table>
|     | A. The Laser                                                                     | 36   
|     | B. Telescope                                                                      | 36   
|     | C. Spectrophone Cell                                                             | 37   
|     | D. Pressure Sensor                                                               | 45   
|     | E. Peripheral Equipment                                                          | 46   
| VI  | DISCUSSION OF MEASUREMENTS                                                       | 48   
|     | A. Measurements Made                                                             | 50   
|     | B. Experimental Procedure                                                        | 50   
|     | 1. Filling the cell                                                              | 50   
|     | 2. Tuning the laser                                                              | 51   
|     | C. Data Taking Program                                                           | 52   
|     | D. Results                                                                        | 54   
|     | 1. CO₂ linewidth measurements                                                    | 54   
|     |   a. Background and other results                                                | 55   
|     |   b. Results from this investigation                                             | 60   
|     | 2. Water vapor continuum measurements                                            | 66   
| VII | SUMMARY                                                                         | 74   
| REFERENCES |                                                                                     | 75   

ix
CHAPTER I
INTRODUCTION

The study of the transmission of radiation through the atmosphere is one having several aspects. Radiation transmission in general is adversely affected by turbulence, Rayleigh scattering by molecules, scattering by aerosols of many forms and molecular absorption. This study will not only be restricted to the latter, but will involve only a very small portion of that expansive field. Although a great deal of work has been done in this area and an enormous amount of molecular absorption spectral data is available, the development of lasers along with their many applications involving transmission has shown that a more detailed look at the problem is necessary.

This need is, in part, due to the fact that many of the lasers of interest have extremely narrow output line widths. The other half of the problem is that molecular absorption in the atmosphere is a rapidly varying function of frequency. An example of this variation is shown in Fig. 1. This figure shows a low resolution solar spectrum[1] covering the infrared region from 1 to 15μ. Also shown are the absorption spectra of the important atmospheric constituents which cause the absorption. As can be seen there are certain spectral windows where there is relatively little absorption. These are the regions where laser use is most attractive since they present the least energy loss to the laser system due to this absorption.

A CO₂ laser (which has output lines near 9.4 and 10.4μ) was used as the radiation source in this study. Therefore the spectral region of interest is the window between 8 and 12μ. The three absorbers in this region are seen to be ozone (O₃), carbon dioxide (CO₂) and water vapor (H₂O). Of the three, carbon dioxide is of particular interest because the unique situation exists where the vibrational-rotational transitions which produce the absorption are exactly those which produce the laser emission spectra. These transitions and the energy levels involved are depicted in Fig. 2. The absorption spectrum for the 10.4μ band of CO₂ is shown in Fig. 3. This figure is a theoretical absorption plot. Further discussion of the data used for the plot is given in Chapter VI.

This absorption band is a difference or "hot" band and is very weak compared to fundamental bands such as those at 4.3 and 15. Also the carbon dioxide concentration in the atmosphere is low, about 330 ppm. Thus the absorption by this band in the atmosphere is quite low - as was noted in Fig. 1.
Fig. 1.—Solar spectrum showing the contribution of the various atmospheric constituents (After Shaw).
Fig. 2.—Energy levels of carbon dioxide involved in the carbon dioxide laser.
Fig. 3.—Theoretical absorption of the carbon dioxide 10.4 μm micron absorption band. 10 km path at 330 PPM at 1 atmosphere.
Although low absorption is obviously desirable from an engineering viewpoint it also causes some problems. For long paths absorption may still be considerable and if this absorption is to be accurately predicted it is necessary to know the absorption coefficient accurately. If the usual method of obtaining the absorption coefficient is used then achieving this accuracy can present some difficulty.

The usual method of measuring the absorption coefficient is through the use of Lambert's law

\[ I_{\text{out}} = I_{\text{in}} e^{-Ku} \]

where \( I_{\text{in}} \) and \( I_{\text{out}} \) are the powers into and out of the medium of interest, \( u \) is the amount of medium traversed and \( K \) is the desired absorption coefficient in units reciprocal to those of \( u \). The definition of transmittance

\[ T = \frac{I_{\text{out}}}{I_{\text{in}}} \]

gives, then

\[ T = e^{-Ku} \]

Solving for the absorption coefficient gives

\[ K = \frac{1}{u} \ln \frac{1}{T} = -\frac{1}{u} \ln T. \]

In an experiment one can measure both \( I_{\text{in}} \) and \( I_{\text{out}} \), then find \( K \) using Eqs. (2) and (4). A look into the error in \( K \) due to a given error in \( T \) for this approach is of interest. An increment of \( K \) is

\[ \Delta K = -\frac{1}{u} \frac{\Delta T}{T}. \]

The relative change in \( K \) is found by dividing Eq. (5) by Eq. (4), giving

\[ \frac{\Delta K}{K} = -\frac{\Delta T}{T} \frac{T}{\ln T} = \frac{\Delta T/T}{\ln T}. \]
for small $\Delta T/T$. Fig. 4 shows a plot of $-1/\ln T$ vs $T$, i.e., a plot of the ratio of $\Delta K/K$ to $\Delta T/T$ as a function of $T$. This plot shows that for transmissions greater than about 91% the relative change in $K$ is more than 10 times the relative change in $T$. Thus expected errors in $T$ are magnified similarly when related to the expected error in $K$.

Figure 5 shows the same information in a slightly different form. The percentage change in $K$ is plotted versus the percentage change in $T$ for various values of $T$ using Eq. (6). It was stated above that Eq. (6) held for small changes. For a general change we write

$$
\Delta K = -\frac{1}{\ln T} [\ln (T + \Delta T) - \ln T]
$$

$$
\Delta K = -\frac{1}{\ln T} \ln (1 + \frac{\Delta T}{T})
$$

$$
= -\frac{1}{\ln T} \frac{\Delta T}{T} - \frac{1}{2} (\frac{\Delta T}{T})^2 + \frac{1}{3} (\frac{\Delta T}{T})^3 \ldots
$$
giving

$$
\frac{\Delta K}{K} = \frac{\Delta T}{T} \left[1 - \frac{1}{2} (\frac{\Delta T}{T}) + \frac{1}{3} (\frac{\Delta T}{T})^2 \ldots\right].
$$

Figure 5 shows a maximum value for $\Delta T/T * 100$ as 10%. Using Eq. (8) instead of Eq. (6) would give a value for $\Delta K/K$ only 5% smaller than that shown. This is only slightly perceivable on the log plot.

Thus to achieve accuracies in the absorption coefficient comparable to those of the transmission measurement a substantial absorption is required. If pressures and concentrations of the absorbers are to be kept at levels found in the atmosphere a very long path length may be necessary to achieve the required absorption at certain wavelengths. Path lengths of 1 Km (3281 ft) are readily achieved in a 50 ft White cell[20] but even this length may not be satisfactory. (Outdoors, much longer path lengths are achievable but the lack of control of the environmental conditions is very undesirable for absorption studies. Not only are the concentrations of the absorbers uncertain, but aerosol and turbulence effects also interfere with the measurements.) The object here is to investigate an alternative approach to absorption studies which does not have this inherent accuracy problem due to high transmission.

The approach to be studied is one involving a phenomenon observed originally by Alexander Graham Bell[3] in 1880. He noted that an audible sound could be produced by irradiating various substances with intermittent light. Shortly thereafter, experiments were done by
FOR $T = \exp(-KL)$

$-\Delta K / K = (\Delta T / T) / \ln(1/T)$

Fig. 4.--Error multiplication factor plotted versus transmittance for error in absorption coefficient.
FOR T = \exp(-KxL)
-\frac{\Delta K}{K} = \left(\frac{\Delta T}{T}\right) / \ln\left(\frac{1}{T}\right)

Fig. 5.—Percentage error in absorption coefficient plotted versus percentage error in transmittances.
Bell[4], Tyndal[5] and Roentgen[6] using enclosed gases as the irradiated substances. The basic concept is simply that a constant-volume gas cell experiences a temperature and pressure increase when the gas absorbs radiation. The intermittent light source produces a modulated pressure signal which, for appropriate conditions, is audible. It was clear to Bell that this device could be used for the investigation of the absorption spectra of gases. He thus gave the name "spectrophone" to the device when used for that purpose.

Since then, modified versions of this device have found many uses. Delany[7] gives an excellent account of the history of the investigations and applications of this optic-acoustic effect up until 1959, the date of that report. One of the applications is gas analysis. There are currently several commercial CO\textsubscript{2} level monitors which employ this effect. Another application is the study of the vibrational lifetimes of molecular gases. This particular use will be discussed further in Chapter III. Finally, in 1946 it was successfully used for studying the infrared spectrum of a gas, as Bell had suggested. This was done by irradiating the cell with "monochromatic" radiation and measuring amplitude of the pressure signal as a function of the frequency of the illuminating radiation.

In the last sentence the word "monochromatic" is placed between quotation marks because the use of the term in 1946 did not imply the small frequency range which is now implied since the advent of lasers. With the very narrow linewidth attainable with many lasers the spectrophone has become more powerful as a spectroscopic tool.

The first use of a laser irradiated spectrophone cell was reported by Kerr and Atwood in 1968[8]. For their measurements they used two basic types of lasers. One was a pulsed ruby laser. The other, of special interest here, was a cw CO\textsubscript{2} laser operating multiline. For a cw laser as a source it will be shown in Chapter IV that the absorption coefficient, $\alpha$, of a gas in a cylindrical spectrophone cell is given by the relationship

$$\alpha = \frac{4\pi kTA}{B WP}$$

where $k$ is the thermal conductivity of the gas, $T$ is the ambient temperature of the gas, $A$ is the pressure rise from ambient when irradiated with a laser of power $W$, $P$ is the ambient pressure and $B$ is a dimensionless geometrical term relating illuminated gas volume to total gas volume. Using a 10 watt cw CO\textsubscript{2} laser Kerr and Atwood reported measurements of absorption of the order of $2 \times 10^{-7}$ cm$^{-1}$ or 0.02 km$^{-1}$. If a measurement at this level were attempted in a 1 km White cell, the transmission would be found to be about 98%. Figures 4 and 5 show this to be a highly inaccurate measurement using the transmission method due to the very low absorption. Specifically, the error magnification factor $(\Delta K/K)/\Delta T/T$ is approximately $1/K\cdot L=50$
for this example, i.e., it would be necessary to achieve 0.2 percent accuracy in the transmission measurement in order to obtain 10 percent accuracy in the value of $K$. Thus the spectrophone offers a method of measuring low absorptions without the inherent accuracy problem.

The lower limit of measurable absorption with the spectrophone is a function of several factors. One very obvious one is seen in Eq. (9). The pressure rise signal $A$ for a given absorption is proportional to the laser power $W$. Therefore one major limitation is a combination of the sensitivity of the pressure transducer and the available laser power. This limitation as well as others will be discussed further in Chapter VI.

McCoy[9,10,11] made transmission measurements of the CO$_2$ P(20) laser line near 10.59$\mu$m in a 1 km White cell using 344 ppm CO$_2$ broadened with N$_2$. The transmission for this line was found to be about 92 percent. The spectrophone lends itself to spectroscopic study in this region. One area of interest in the region is the variation of half widths of absorption lines within an absorption band. A portion of Chapter II includes a discussion of the background of this problem and Chapter VI discusses the results found in this study. Also presented in Chapter II is other spectroscopic background pertinent to this work.

The theory of the operation of the spectrophone does not, of course, involve only the field of spectroscopy. Also included is the field of molecular energy transfer in gases. In Chapter III is presented some of the molecular theory of gases.

Chapter IV gives the solution to the heat transfer problem involved in the calibration of the device. Chapter V describes the apparatus used in the experiments. Chapter VI gives the results of those experiments.
A. Lambert's Law

Basic to the study of radiation transmission is Lambert's law. For the simplest situation it is assumed that the gas is homogeneous and that the light beam is parallel. Then, the fraction of radiation intensity lost due to absorption in each length \( x \) of medium is the same. For an infinitesimal length \( dx \) of medium the intensity \( I_v \) at frequency \( v \) changes by \( dI_v \). If the fractional absorption per unit length of absorber is \( \alpha_v \) then

\[
\frac{dI_v}{dx} = -\alpha_v I_v.
\]

Integrating Eq. (10) gives

\[
I_v = I_v^0 e^{-\alpha_v x}
\]

where \( I_v \) is the intensity at \( x \) and \( I_v^0 \) is the intensity at \( x=0 \). The coefficient \( \alpha_v \) called the absorption coefficient. Here \( \alpha_v \) is given in units of reciprocal length since \( x \) is a length. Other circumstances have made it convenient to express \( \alpha_v \) and \( x \) in different units. This is done by writing, in general,

\[
K_v W = \alpha_v x,
\]

where \( K_v \) is also called either the extinction or absorption coefficient and \( W \) is the "amount" of absorber in the light path.

An important quantity involved is the number of molecules available to the radiation beam for absorption. Knowledge of this quantity is necessary if the amount of radiation absorbed is to be related to the quantum mechanical transition probabilities for the molecules. Thus, instead of \( x \), a simple distance through the absorbing medium, the term \( W \) is used which contains some information about the number of absorbing molecules in the path. The term \( K_v \) is then given in units reciprocal to those of \( W \).
Various forms have been and are used for $W$. McCoy[9] gives a good discussion and summary of these forms. Quantities put into $W$ to indicate the number of molecules involved include pressure, mass, and the number itself. In this work the units of $W$ to be used will be atm-cm when discussing $CO_2$ absorption. Note that for these units in order to completely specify the number of molecules, it is also necessary to give some reference temperature. Many of the contributors in the field have agreed to use $300^\circ K$ as the reference temperature. That will be done here also.

B. Absorption Line Parameters

In the previous section the absorption coefficient $K_\nu$ at a single frequency $\nu$ was discussed as being related to the number of molecules. It should be clearly pointed out that $K_\nu$ is not generally proportional to the number of molecules in the path when the absorber is a gas, i.e., Beer's law, which states that this proportionality does hold, is not applicable to gases but, rather, states that $K_\nu$ is proportional to concentrations in solutions. The reason for this is that in a gas the shape of an absorption line changes with pressure, i.e., concentration.

If, however, it is assumed that gas pressures are not so high as to change the way an absorption transition occurs, then there is a quantity which is constant with concentration. This is the integrated absorption over the frequency of the line, viz. the line strength $S$, defined as

$$S = \int_{-\infty}^{\infty} K_\nu \, d\nu.$$  \hspace{1cm} (13)

The quantity $Sp$, where $p$ is the pressure, is then also proportional to pressure if the gas is considered to follow the perfect gas law, i.e., that density is proportional to pressure. These two assumptions will readily hold for atmospheric conditions of interest here.

The line strength is, then, one of the primary quantities used for the description of an absorption line. The other important parameter is the line width. Generally, this quantity is given as the half-width which is half the width of the $K_\nu$ versus $\nu$ curve at the half maximum point.

The width of an absorption line is finite because of several factors. These broadening factors also determine the shape of the line as well as the width. Four types of line shapes which occur in molecular absorption are caused by natural broadening, Doppler broadening, pressure broadening and a combination of the last two which gives a line shape called the Voigt[12,13] profile. The first type of broadening is called natural broadening because it is a
result of the uncertainty relationship due to the finite lifetime of the transition. The natural width of molecular lines is negligibly small (of the order of $10^{-8}$ cm$^{-1}$) compared to widths produced by the other mechanisms and will not be considered further here.

The Doppler profile is caused, as can be inferred by the name, by the fact that molecules are moving at high velocities while emitting or absorbing. The Doppler line shape is given by the expression

$$K_{\nu D} = \left(\frac{2n}{\pi}\right)^{1/2} \left(\frac{S}{\alpha_D}\right) \exp\left\{\left(-\frac{2n}{\pi}\right) \left[\left(\nu - \nu_0\right)/\alpha_D\right]^2\right\}$$

where $S$ is the line strength, $\nu_0$ is the line center frequency and $\alpha_D$ is the Doppler half width which is given by, for a molecule of mass $m$,

$$\alpha_D = \frac{[d \ln 2/(mc^2/kT)]^{1/2}}{\nu_0}$$

For convenience of calculation this can be reduced to

$$\alpha_D = 3.58 \times 10^{-7} \left(\frac{T}{M}\right)^{1/2} \nu_0,$$

where $T$ is the temperature in °K, $M$ is the molecular weight and $\nu_0$ is the frequency of the line.

The Doppler line shape is predominant at low pressures. McCoy[9] found that it was good for pressures up to about 0.07 torr for the P(20) line in the 10.4μ band of CO$_2$. At that point the effect of collision broadening began to appear. Above 70 torr the effect of Doppler broadening became negligible. Then the line shape is determined completely by pressure or collision broadening. The line shape in this region is called a Lorentz[12] profile and is given by

$$K_{\nu L} = \frac{S}{\pi} \frac{\alpha_L}{(\nu - \nu_0)^2 + \alpha_L^2}$$

where $\alpha_L$ is the Lorentz halfwidth which is both temperature and pressure dependent in the following manner.

$$\alpha_L = \alpha_L^0 \left(\frac{T_0}{T}\right)^{1/2} \left(\frac{p}{p_0}\right)$$
where \( T_0 \) and \( P_0 \) are some reference temperature and pressure at which \( \alpha^0 \) occurs. The exponent on the temperature ratio has been empirically determined to vary somewhat from the theoretical value\[14\]. The reference pressure \( P_0 \) is usually taken to be one atmosphere and dropped from the equation, giving \( \alpha_L \) in units of \( \text{cm}^{-1} \text{ atm}^{-1} \). True line shapes vary from this ideal profile in that there is less absorption in the wings than is predicted by the equation. Benedict et al\[14\] have experimentally investigated this phenomenon and have suggested that beyond a certain distance from line center the equation be damped with an exponential multiplier.

One point of interest here is that \( \alpha^0 \) (for a given absorption line) is a function of the gases which are involved in the pressure broadening. That is, a CO\(_2\) absorption line at 1 atmosphere may be narrower if the primary broadening gas is nitrogen, e.g., than it would be if it were pure carbon dioxide. In other words, N\(_2\)-CO\(_2\) collisions have a different broadening effect than CO\(_2\)-CO\(_2\) collisions. Coefficients have been defined which relate these broadening differences and the general effects are referred to as foreign broadening and self broadening. Further discussion of this phenomenon will be given in the discussion of the measurements in Chapter VI.

In Fig. 6 two plots are presented which show a comparison between the Doppler and Lorentz line shapes. The line strengths and halfwidths have been chosen to be the same for both curves to demonstrate shape differences.

Figures 7 and 8 are taken from McCoy\[9\] and McCubbin and Mooney\[15\] respectively. They represent the absorption at line center of the P(20) line of the CO\(_2\) 10.4\(\mu\) band as a function of pressure. The curve in Fig. 7 shows where the line begins to become nonlinear at about 0.07 torr as the pressure is increased. From Eqs. (14) and (16) it is seen that \( K_{v_0,D} \) is not a function of pressure and therefore \( K_{v_0,D} \cdot W \) should increase linearly as a function of pressure. Thus the Doppler profile fails to satisfactorily describe the line shape beyond the 0.07 torr pressure level.

At the other end of the pressure range of interest here, viz. where the Lorentz profile holds, Eqs. (17) and (18) show that at line center

\[
(19) \quad K_{v_0,L} = \frac{S}{\pi \alpha_L}.
\]

But since \( \alpha_L \) is proportional to \( P \), then

\[
(20) \quad K_{v_0,L} \cdot W = \text{const}
\]
Fig. 6.—Comparison of the Lorentz and Doppler profiles with equal half widths.
Fig. 7.—Transmittance of the carbon dioxide P(20) line of the 10.4 micron band at line center plotted versus pressure showing the linearity at low pressures (After McCoy).

Fig. 8.—Transmittance of the carbon dioxide (P20) line of the 10.4 micron band at line center plotted versus pressure showing the constant transmittance at high pressures (After McCubbin and Mooney).
as \( P \) changes. The curve in Fig. 8 shows this to be true as \( P \) is decreased to somewhere between 70 and 50 torr. Then the Lorentz profile begins to fail.

In the pressure region between these two limits a third line shape called the Voigt profile is used. This profile reduces to the Doppler and Lorentz profiles at the respective ends of the pressure range. The equation for the absorption coefficient for this line shape is [16,17]

\[
(21) \quad K_{v,v} = \frac{S a_L}{\pi^{3/2}} \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{\alpha_L^2 + \left[ v - v_0 - \frac{\alpha_D t}{\ln 2} \right]^{1/2}} \, dt
\]

where \( S \) is the line strength, \( \alpha_D \) is the Doppler halfwidth as in Eq. 6 and \( \alpha_L \) is the Lorentz halfwidth as in Eq. (18). A Fortran computer program for the evaluation of Eq. (21) has been made available by the author of Reference [16].

For this study the Lorentz profile is of most interest since the measurements are made at pressures near 1 atmosphere.
CHAPTER III
GASES

A. Introduction

Chapter II discussed the absorption of radiation by molecules. However, absorption is not the only fundamental process involved in the operation of the spectrophone. The quantity measured in the spectrophone is a pressure rise in a gas. Thus, some energy transfer and conversion takes place between the absorption process and the detection process. This chapter presents some of the background necessary for the study of this energy transfer process which occurs in gases.

One area involved is the kinetic theory of gases. This theory has as a basis several fundamental hypotheses. One of these is the molecular hypothesis which states that there exists some smallest element for all substances which still retains the chemical properties of that substance. (Liquids and solids are also included in this hypothesis but will not be considered here.) The kinetic theory of gases then presents descriptions of the properties of these microscopic particles in such a manner as to allow a satisfactory extension to the descriptions of measurable macroscopic properties.

First, one definitive property of a gas is that the molecules are widely spaced, i.e., with respect to the size of the molecules themselves, and moving at high speeds. The wide spacing is manifested in the compressibility of the gas. The speeds will be discussed further below.

B. Microscopic Quantities of Interest

Some of the quantities of interest which relate directly to the microscopic particles, i.e., the molecules, are the model for the molecule, the density of the gas, the velocities of the molecules, the mean free path of the molecules and the collision frequency of the molecules.

The model used is generally only slightly more sophisticated than the simple one which depicts solid billiard balls which rebound from walls and each other in a totally elastic manner. The sophistication added is that rather than being solid the molecule has some repulsive force field of some given intensity distribution. Like the billiard ball this field is usually taken to be symmetric, however, because the problem of the description of collisions soon
becomes intractable for a more complicated form. The elasticity of the collisions also is kept since on the whole, this must be true. If it were not, then when a container was filled with a gas, valved off and left undisturbed the molecules would eventually all settle to the bottom due to energy lost in inelastic collisions - which does not happen.

The density of a gas is characteristically low and is found from Avagadro's hypothesis. This hypothesis states that the number density of all gases is the same when the gases are at the same temperature and pressure. The mass density is then found by using the molecular weight of the gas involved.

The speeds of the molecules of a gas are directly related, by definition, to the temperature of the gas. The average translational kinetic energy of a molecule in a gas is given by

\[ \frac{1}{2} m v^2, \]

where \( m \) is the mass of the molecule and \( v^2 \) is the rms value of the speeds of all the molecules in the gas. The kinetic energy used here is termed "translational" so as to exclude any internal kinetic energy which might be found in the oscillatory motion of some internal structure of the molecule. This translational kinetic energy is related to the absolute or Kelvin temperature \( T \) by the equation

\[ \frac{\text{mv}^2}{2} = \frac{3}{2} kT \]

where \( k \) is Boltzmann's constant. The numerical value for Boltzmann's constant is \( k = 1.3804 \times 10^{-16} \text{ erg/°C} \). As an example of typical molecular speeds, Eq. (22) gives a rms speed of \( 3.94 \times 10^4 \text{ cm/sec} \) for a \( \text{CO}_2 \) molecule at 0°C.

The above three microscopic quantities, i.e., the model, the density and the velocities are independent of one another. The next two concepts to be discussed are both functions of the first three. The first of these concepts is the mean free path. As the name implies, it is concerned with the average distance which a molecule travels in a gas without striking another molecule. The mean free path is defined by the following statement. The probability that a molecule will travel a distance \( x \) without hitting another molecule is defined[18] to be \( e^{-x/\lambda} \) where \( \lambda \) is the mean free path. The general relationships between this concept and the molecular model and the density are rather apparent. If the number density is increased the mean free path would be decreased since there would be more molecules available for collision. For the model, the obvious characteristic affecting the mean free path is the effective diameter. If the number density is fixed and the diameters are increased the mean free path would decrease because the collision cross sections would be greater.
The last microscopic concept to be discussed is the collision frequency $\theta$. The quantity $\theta$ is defined as the average number of collisions made by a molecule in unit time. This definition leads to a very simple relationship between the mean velocity $\bar{v}$ and the mean free path $\lambda$. In a long time $t$ a molecule makes $\theta t$ collisions which are, on the average, $\lambda$ apart, i.e., the molecule travels a distance of $\lambda \theta t$. In this same time $t$ the molecule has traveled at a mean velocity $\bar{v}$ and hence has traveled a distance of $\bar{v}t$. Since the distance is the same, then $\lambda \theta t = \bar{v}t$ or

\[ \bar{v} = \lambda \theta. \]

Thus the collision frequency is also related to the molecular diameter and number density as was the mean free path but in an inverse manner. Use of the spherical model along with the number density $n$ and the velocity $\bar{v}$ gives the relation $\theta = \pi d^2 \bar{v}n$, where $d$ is the molecular diameter, if it is assumed that one molecule is moving at velocity $\bar{v}$ and all the others are at rest. By adding relative motions and including all the velocities included in a Maxwellian distribution of velocities the collision frequency $\theta$ becomes

\[ \theta = \sqrt{2} \pi d^2 \bar{v}n. \]

Now the mean free path can be related directly to the molecular size and density by combining Eq. (23) and Eq. (24) to get

\[ \lambda = \frac{1}{\sqrt{2} \pi d^2 n}. \]

C. Macroscopic Properties

In order to relate the microscopic properties discussed above to the observable, macroscopic properties of a gas it is necessary to add another hypothesis to those mentioned earlier. This is the statistical hypothesis. Due to the tremendous number of particles involved in a gas (the standard number density at 1 atmosphere and 0 °C is $2.6871 \times 10^{19} \text{ cm}^{-3}$) any attempt to describe the behavior of even a small portion of gas using Newtonian mechanics involving the individual particles would be totally fruitless.

It is, however, possible to deal with large numbers of objects and systems using statistical methods. These methods, in general, tend to be more reliable the larger the sample. Hence kinetic theory is ideally suited to the statistical approach.
In the discussions of the previous section use was made of root mean square velocities, mean velocities and mean free paths, i.e., statistical concepts. That these can have meaning is due to the enormous number of molecules involved. To say that they have meaning simply implies that these quantities fluctuate imperceptibly under normal equilibrium conditions. The pressure on a wall of a vessel containing a gas, for example, is due to the force imparted by bombardment of the molecules. A pressure measurement reflects the mean velocity of the molecules which strike this wall and does not vary with time nor location on the wall under normal conditions even though, in fact, molecules of many different velocities are involved. A similar discussion would hold for temperature and other observable phenomena.

Both of these observables, i.e., pressure and temperature are related through the natural gas law which will be used in a later chapter in this study. Two common forms of this law are

\[ pV = \nu RT \quad (26) \]

where \( V \) is the volume, \( \nu \) is the number of moles, and \( R \) is the universal gas constant, and

\[ p = nkT, \quad (27) \]

where \( k \) is Boltzmann's constant.

Another observable quantity of interest is the specific heat of gas. The specific heat at constant volume is defined as the change in thermal energy per degree, i.e.,

\[ C_V = \frac{du}{dT}, \quad (28) \]

where \( u \) is the thermal energy per mole. If the gas is monatomic, i.e., if the model is such that there is no internal energy which could be altered by collisions, then the thermal energy is totally translational. This energy per mole is given then by

\[ u = \frac{\nu m v^2}{2} \quad (29) \]

where \( L \) is Avagadro's number. Using Eq. (22) gives

\[ u = L \frac{3}{2} kT. \quad (30) \]
Molecules which satisfy the model requirement of no collision alterable internal energy, viz. the noble gases, give experimental results which closely agree with this prediction. However if a molecule is made up of two or more atoms then collisions may involve vibrational and rotational energies of the molecules as well as translational energies. Experimental measurements show that the specific heats for polyatomic gases are greater than \( \frac{3R}{2} \). Thus the simple model with no internal energy must be modified when dealing with polyatomic molecules.

D. Energy and Particle Transfer

Energy and particle transfer in a gas are referred to as transport phenomena. The quantities involved in this area are viscosity, diffusion and heat conduction. Approximate expressions can be found for the three coefficients using the microscopic concepts described earlier in this chapter, i.e., the billiard ball model, mean velocity and mean free path.

Viscosity involves fluids in motion and, hence, is not of direct interest here. Briefly it concerns the transfer of momentum between two layers of a fluid moving at different speeds. If a gas is confined between two horizontal plates, one moving laterally and one fixed, then there would be some vertical velocity profile of the gas molecules in this system. The speeds range from the speed of the moving plate to zero at the fixed plate. The shearing stress between any two adjacent layers of gas is given by

\[
P_{zy} = \eta \frac{du}{dz},
\]

where \( P_{zy} \) denotes the stress in the y direction (the direction of motion of the moving plate) on the shearing plane perpendicular to the z direction, \( \eta \) is the coefficient of viscosity and \( du/dz \) is the velocity gradient at the shear plane. Elementary mean free path methods give the viscosity coefficient as

\[
\eta = \frac{1}{3} \frac{m \bar{v}}{\pi}.
\]

Diffusion is concerned with particle transfer from one position in a gas to another. For the case where two gases which are diffusing through one another having similar mean free paths and mean velocities, the equation describing diffusion of gas one into gas two is

\[
G_1 = -D_{11} \frac{du_1}{dz}
\]
where $G_1$ is the particle transfer of gas one in the $z$ direction in molecules per unit area per unit time, $D_{11}$ is the diffusion coefficient and $n_1$ is the density of gas one molecules. In terms of mean free paths,

$$D_{11} = \frac{v}{3}.$$  

The third transport phenomenon describes the transfer of thermal energy through a gas. This concept, heat conduction, is the most important of the three to this study. The derivation of the spectrophone pressure rise versus absorption equation has the heat conduction equation as its basis. The one dimensional heat flow through a plane in a gas is proportional to the temperature gradient at the plane. The direction of heat flow is in that of decreasing temperature. The proportionality constant is called the heat conduction coefficient or, more generally, the thermal conductivity. The equation is, then

$$g = -K \frac{dT}{dz}.$$  

where $g$ is the heat flow per unit time per unit area through a plane normal to the flow and $K$ is the thermal conductivity.

The principle behind this phenomenon is straightforward. If one wall of a container of gas is hot and the side opposite is cooler then molecules which strike the hot wall gain energy. This energy then migrates through the gas through collisions with other molecules until the cooler wall is reached. Thus there is net energy transport through the gas.

The thermal conductivity for a polyatomic gas using the mean free path terms is

$$K = \frac{1}{3} m n \lambda C_v.$$  

where $m$ is the mass of one molecule and $C_v$ is the constant volume specific heat referred to one unit mass. It is important to note that since $\lambda$ is inversely proportional to $n$ (from Eq. (25)), then $K$ is independent of density and hence pressure.

E. Molecular Energy Transfer

Energy transfer in the billiard ball model of a gas is straightforward. For energy and momentum conservative collisions two molecules depart from a collision in translational states easily
found from the states they occupied prior to the collision. However the addition of internal structure to a molecule makes the problem more complicated. Besides translational energies, molecules can possess both vibrational and rotational energies which can be altered during collisions. (Molecules also possess electronic energies but the amount of energy required to increase this electronic energy from one quantum level to another is ordinarily much larger than that which would be transferred in a molecule-molecule collision at ordinary temperatures. Thus this internal energy will not be considered here.)

As in the case of the billiard ball model, translational energies are easily altered during a collision due to the fact that the energy is a continuum. Thus after a disruption in the equilibrium of a gas the equilibrium state with the normal distribution of velocities can be reached quite rapidly due to the enormous number of collisions which occur per unit time.

The rotational energies of a molecule are quantized; however the energy difference between levels is small enough that relatively low energy collisions can easily change the levels such that they have a classical distribution. Thus, equilibration of the rotational levels is also a rapid process.

For vibrational energy states, equilibration is not as fast. Differences in energy between vibrational levels are typically several \( kT \) at room temperature. Since (from Eq. (22)) the energy associated with a molecule with the root mean square velocity is only \( \frac{3}{2} kT \), only molecules with higher velocities would have enough translational energy to change the vibrational energy levels during a collision. The numbers of molecules traveling at various speeds is given by the classical Maxwell speed distribution. A plot (after Present[18]) of this speed distribution is given in Fig. 9. In this figure the fraction of molecules traveling at speeds between \( v \) and \( v+dv \) is plotted versus the speed relative to the mean speed. From the plot it is seen that less than 3 per cent of the molecules travel at speeds greater than twice the mean speed. Hence equilibration takes a longer time for the vibrational states since there are fewer molecules traveling at the higher velocities.

If the equilibrium of the vibrational states is upset by, e.g., some of the molecules reaching higher energy states by absorption of radiation then a new equilibrium is reached at a higher temperature (i.e., a higher mean speed is attained by the molecules). This occurs when the excited molecules strike others and the vibrational energy is transferred to translational energy.

This description is greatly simplified of course. Other types of energy transfer processes are also available to the excited molecule. Re-radiation of the energy, by either spontaneous or
stimulated emission may occur. Transfer of vibrational energy between molecules during a collision is also a possibility. (A good example of this last process is the pumping mechanism of a CO$_2$-N$_2$ laser in which vibrational energy in the N$_2$ molecule is transferred to vibrational energy in the CO$_2$ molecule.) Also, for many molecules, combinations of these processes certainly exist.

These processes are, then, the ones which occur which allow a measurement of absorption to be made with a device such as the spectrophone. Note also that the important energy transfer process which must be present is the vibrational to translational transfer since, if all the absorbed energy was reemitted such that it left the gas as radiation again then the gas temperature would not rise and the spectrophone would detect nothing. It is important, then, to investigate the probabilities of occurrence of these various processes. This is done in the following section.

F. Relaxation Rates

Consider, as above, a gas which is irradiated by an infrared source. Further simplify the situation by assuming that the molecules are all the same and that they have only two vibrational levels, i.e.,
the ground state and an excited state denoted by 0 and 1 respectively. Kaiser[19] and, more recently, Kreuzer[20] have described this system in terms of the rate equation for the upper state

\[
\frac{dn_1}{dt} = -n_1 (\rho B + A + f_{10}) + n_0 (\rho B + f_{01})
\]

where \(n_1\) and \(n_0\) are the population densities of levels 1 and 0 respectively, \(\rho\) is the photon density, \(A\) is the Einstein coefficient for spontaneous radiation, \(B\) is the Einstein coefficient for induced or stimulated transition, \(f_{01}\) and \(f_{10}\) are the collisional transition probability coefficients for transitions from 0 to 1 and 1 to 0 respectively and \(t\) is time.

It was stated earlier that at room temperature the transition probability for the 0 to 1 transition due to collisions is extremely small. (The relation between \(f_{01}\) and \(f_{10}\) is \(f_{01} = f_{10} e^{-E/\kappa T}\) where \(E\) is the energy separation between levels and \(T\) is the translational temperature.) Therefore \(f_{01}\) is considered negligible. If the constant total number density \(N = n_1 + n_0\) is introduced then the equation can be written

\[
\frac{dn_1}{dt} = -n_1 (2\rho B + A + f_{10}) + N_0 B,
\]

or, in terms of time constants,

\[
\frac{dn_1}{dt} = -n_1 (2\rho B + \frac{1}{\tau_r} + \frac{1}{\tau_c}) + N_0 B
\]

where \(\tau_r\) is the radiative relaxation time constant and \(\tau_c\) is the collisional relaxation time constant.

If the parenthetical term in Eq. (39) is replaced by \(1/\tau\) and if \(\rho\) is taken to be constant, as it is in the experimental portion of this study, then the solution of Eq. (39) is

\[
n_1 = C e^{-t/\tau} + N_0 B \tau.
\]

The steady state solution is

\[
\frac{n_1}{N} = \frac{\rho B}{2\rho B + \frac{1}{\tau_r} + \frac{1}{\tau_c}}.
\]
The interest in the term $1/\tau$ is two-fold. First, the idea is to measure the temperature rise due to absorption. It would be highly desirable if this temperature rise were proportional to the absorbed energy. Since the temperature rise is due to the relaxation of the $n_1$ states by collisions which convert the energy to the translational form, then the requirement that the temperature rise be proportional to absorbed energy imposes the restriction that the $1/\tau_c$ term in the denominator be totally dominant.

Unless $p$ is very large, i.e., unless the irradiating source is sufficiently intense to saturate the upper level $n_1/N$ will be proportional to $p$ and the $2\beta B$ term will be small compared to the other two terms in $1/\tau$. In CO$_2$ for the levels involved in this study, Gerry and Leonard[21] measured $\tau_r$ for the 00°1 to 10°0 transition and found it to be of the order of 1 second. Weber and Deutsch[22] measured the lifetime of the 00°1 level as a function of pressure using a pulsed CO$_2$ laser. The results of that measurement are shown in Fig. 10. They used this plot to extrapolate down to zero pressure to find the radiation lifetime $\tau_r$, obtaining a value of about 3 msec.

![Fig. 10.-Pressure dependence of the life time of the CO$_2$ 00°1 level (After Weber and Deutsch).](image)
For $\tau_c$ many measurements have been made for CO$_2$ using many methods. Cottrell and McCoubrey[23] give the results of a large number of these measurements. A nominal average value for 1 atmosphere and room temperature is about 5 $\mu$sec. These measurements included many of the vibrational states of CO$_2$. Returning to Fig. 10, another extrapolation (in the high pressure direction) of the results of Weber and Deutsch gives a value of 2.5 $\mu$sec for the $00^01$ level. Thus, the $1/\tau_c$ term is dominant by a factor of about $10^3$, at least, satisfying the criteria necessary for the temperature rise to be proportional to the absorbed radiation.

The second interest in the $1/\tau$ term is the part it plays in the transient portion of the solution in Eq. (30). In the next chapter the heat flow equation is solved and the temperature rise in the cell is converted to an average pressure rise. For measurement purposes the radiation source is slowly chopped to remove the possibility of dc drift in the electronics. The upper limit on the chopping frequency is determined by either the $\tau$ term above or the time constant associated with the solution of the heat flow equation. The latter proves to be the limiting factor by about 2 orders of magnitude.
CHAPTER IV
HEAT TRANSFER PROBLEM

A. Introduction

The method of measurement in this study is to observe the pressure rise in a confined gas when it is irradiated with a laser. The gas is confined in a long cylindrical cell and the laser beam passes through the cell concentrically along the axis with a beam diameter smaller than the internal cell diameter. Hence the energy absorbed is described by a function which has the radius of the cylinder as a variable. Therefore, the temperature rise and hence the pressure rise in the cell is also a function of radius. However, the pressure is measured at the end of a tube which is connected to one side of the cylinder, and thus measures the average pressure rise in the cylinder. The object of this chapter is to set up and solve the equations which will relate the average pressure rise to the energy absorbed. This is done by first finding the temperature rise distribution using the heat flow equation. The resulting function is then converted to a pressure rise distribution by use of the perfect gas law. Finally the pressure rise distribution is integrated over the radius of the cell to get the average pressure rise.

B. Heat Flow Equation

The general heat conduction equation for an isotropic material is given by Reference [24]

\[ \nabla^2 \theta + \frac{Q}{\kappa} = \frac{1}{\gamma} \frac{d\theta}{dt}, \]  

(42)

where \( \theta \) is the temperature above ambient, \( Q \) is the source heat per unit volume, \( \gamma \) is the heat conductivity and \( \kappa \) is the thermal diffusivity. The problem of interest has cylindrical geometry hence the \( \nabla^2 \theta \) is replaced by

\[ \nabla^2 \theta = \frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \theta}{\partial \phi^2} + \frac{\partial^2 \theta}{\partial z^2}. \]  

(43)

Two simplifications can reduce the complexity of the problem. First, the angular symmetry removes the \( \frac{\partial^2 \theta}{\partial \phi^2} \) term. The second
simplification requires two assumptions. First it is assumed that the energy absorbed by the gas is small enough that the laser power is approximately constant for the full length of the cell. The second assumption is that the cell is long enough that the end effects will be negligible over all. With these two assumptions the dependence of $\theta$ on $z$ is removed. Thus, Eq. (42) becomes, under these conditions,

\[
\frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} + \frac{Q}{\kappa} \frac{\partial \theta}{\partial t} = 0.
\]

Of special interest in this study is the steady state solution to the problem. If $\theta(r,t)$ is written as the combination of the transient solution and the steady state solution as

\[
\theta(r,t) = u(r,t) + v(r),
\]

then the steady state equation can be written as

\[
\frac{d^2 v}{dr^2} + \frac{1}{r} \frac{dv}{dr} + \frac{Q}{\kappa} = 0.
\]

The solution of this equation requires a set of boundary conditions and a function which describes the heat source $Q$. The boundary conditions are that $v(0) = 0$ and that $v$ at the wall of the cell equal zero. The first requirement is obvious for physical reasons. The second condition can be assumed due to the large difference in heat capacities of the gas in the cell and the aluminum cell wall. The specific heats are of the same order of magnitude[25] for air and aluminum but the density ratio is about $2 \times 10^3$, thus, the assumption is justified since the same energy input into two equal volumes of air and aluminum would raise the temperature of the aluminum $10^3$ times less than it would raise the temperature of the air. A description of the heat source function $Q$ plus a solution to the steady state equation is given in the following section.

C. Steady State Solution

For a laser source the radial intensity distribution of the beam is usually taken to be Gaussian, i.e., it is given by the equation

\[
I_L(r) = \frac{W}{\pi b^2} e^{-r^2/b^2},
\]

where $b$ is the halfwidth at the 1/e point and $W$ is the total beam power, i.e.,
For simplicity, assume a cell radius of unity. Then $b$ becomes not only the halfwidth, but also the fraction of the cell radius where the halfwidth is located. One problem with the Gaussian beam shape is that the intensity is not zero at the walls. For small $b$ the intensity distribution function is not changed much and intensity at the walls is zero if it is modified as shown in Eq. (49).

\begin{equation}
I(r) = \frac{W}{\pi b^2} \left[ e^{-r^2/b^2} - e^{-1/b^2} \right].
\end{equation}

The error introduced into the intensity distribution function by this modification is, as noted by Kerr and Atwood\cite{8}, obviously quite small for small $b$. It is important, however, to also examine the error introduced into the expression for the total power through the cell, since the final result is dependent upon it. Let $W_L$ be the power through the cell using the intensity function given in Eq. (47) and $W_M$ be the power through the cell using the modified intensity function given in Eq. (49). Integrating over the cell dimensions gives

\begin{equation}
W_L = 2\pi \int_0^1 I(r) r \, dr
= W (1 - e^{-1/b^2}),
\end{equation}

and similarly

\begin{equation}
W_M = W \left[ (1 - e^{-1/b^2}) - \frac{e^{-1/b^2}}{b^2} \right].
\end{equation}

Thus, the error introduced into the power expression is $e^{-1/b^2}/b^2$ larger than that introduced into the intensity expression. Table I lists these errors for 3 values of $b$. 
Table 1
ERROR INTRODUCED BY INTENSITY DISTRIBUTION MODIFICATION

<table>
<thead>
<tr>
<th>b</th>
<th>Intensity</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.83</td>
<td>7.32</td>
</tr>
<tr>
<td>0.4</td>
<td>0.193</td>
<td>1.21</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0015</td>
<td>0.017</td>
</tr>
</tbody>
</table>

For values of b near 0.3, then, the error introduced due to the modification is quite obviously below experimental error, however, for b near 0.5 this may not be the case.

Using Eq. (49) as the intensity distribution and assuming a unit volume to be the cell radius squared times a unit length and taking the absorptivity per unit length as \( \alpha \) then the power absorbed per unit length is \( W \) and the heat generated per unit length is

\[
Q(r) = \frac{\alpha W}{\pi b^2} \left[ e^{-r^2/b^2} - e^{-1/b^2} \right].
\]

The differential equation for the steady state temperature distribution to be solved is, combining Eq. (46) and Eq. (52),

\[
\frac{d^2 v}{dr^2} + \frac{1}{r} \frac{dv}{dr} = -\frac{\alpha W}{\kappa \pi b^2} \left[ e^{-r^2/b^2} - e^{-1/b^2} \right].
\]

This equation can be rearranged and written as

\[
\frac{d}{dr} \left( r^2 \frac{dv}{dr} \right) = -\frac{\alpha W r}{\kappa \pi b^2} \left[ e^{-r^2/b^2} - e^{-1/b^2} \right].
\]

The first integration followed by a division by \( r \) gives

\[
\frac{dv}{dr} = \frac{\alpha W}{\kappa \pi} \left[ \frac{e^{-r^2/b^2}}{2r} - \frac{e^{-1/b^2}}{2b^2} \frac{r}{r} + \frac{C}{r} \right].
\]
The first term in brackets can be written as

\[(56) \quad \frac{e^{-r^2/b^2}}{2\pi} = \frac{1}{2\pi} \sum_{n=0}^{\infty} (-1)^n \frac{(r/b)^{2n}}{n!} = \frac{1}{2\pi} + \frac{1}{2} \sum_{n=1}^{\infty} (-1)^n \frac{r^{2n-1}}{b^{2n} n!} .\]

Putting Eq. (56) into Eq. (55) and integrating term by term gives

\[v = \frac{\alpha W}{K\pi} \left[ \frac{1}{2} \ln r + \frac{1}{4} \sum_{n=1}^{\infty} (-1)^n \frac{(r/b)^{2n}}{n!} \right.\]
\[\left. + \frac{r^2}{4b^2} e^{-1/b^2} \right] + C_1 \ln r + C_2.\]

To satisfy the boundary condition that \(v(0) \neq \infty\), choose \(C_1 = -\frac{\alpha W}{K\pi}\) to remove the \(\ln r\) terms. To satisfy the condition that \(v\) equal zero at the walls let

\[C_2 = -\frac{1}{4} \sum_{n=1}^{\infty} (-1)^n \frac{(r/b)^{2n}}{n!} - \frac{1}{4b^2} e^{-1/b^2},\]

giving the desired steady state temperature distribution as

\[(57) \quad v = \frac{\alpha W}{4K\pi} \left[ \sum_{n=1}^{\infty} (-1)^n \frac{(r/b)^{2n}}{n!} + \frac{(r/b)^{2n}}{b^{2n}} e^{-1/b^2} \right].\]

The next step is to convert this temperature distribution function to a pressure distribution function which is then integrated over the volume of the cell to find the average pressure rise. The perfect gas law,

\[(58) \quad P = nR \frac{T}{V},\]

is differentiated to get \(dP = nR \frac{dT}{V}\) which is then divided by Eq. (58) to get \(\frac{dP}{P} = \frac{dT}{T}\) where \(P\) and \(T\) are the nominal pressure and the ambient absolute temperature respectively. Using \(p = dP\) and \(v = dT\) the average pressure rise is given by

\[(59) \quad p = \frac{P}{TV} \int_0^{2\pi} \int_0^1 v rdrd\theta .\]
Since this equation is for unit length $V = \pi \cdot l^2$, therefore

$$(60) \quad p = \frac{2p}{T} \int_0^1 v r \, dr.$$  

Substituting Eq. (57) into Eq. (60) and integrating gives

$$p = \frac{\alpha WP}{4\kappa T} \left[ \sum_{n=0}^{\infty} (-1)^n \left( \frac{r^{2n+2}}{2n+2} - \frac{r^2}{2} \right) \right] \frac{1}{b^{2n+1} \cdot n!} + \left[ \frac{r^4}{4b^2} - \frac{r^2}{2b^2} \right] e^{-1/b^2} \bigg|_0^1.$$  

Therefore

$$(61) \quad p = \frac{\alpha WP}{4\kappa T} \left[ \sum_{n=0}^{\infty} (-1)^{n+1} \frac{1}{b^{2n+1} \cdot (n+1)!} - \frac{1}{2b^2} e^{-1/b^2} \right].$$

The object here was to find an expression for the absorptivity per unit length $\alpha$. The desired equation is

$$(62) \quad \alpha = \frac{4\pi T p}{WP B(b)}$$

where $B(b) = 1 - b^2 + (b^2 - 1/2b^2) e^{-1/b^2}$ which relates the effect of the partial irradiation of the gas in the cell. The next section gives some values of $B(b)$ of interest along with some results using beam shapes other than Gaussian.

An examination of Eq. (62) can give information concerning the low absorptivity limit of the spectrophone system. (Some results from Chapter VI will be used for this purpose.) If $\kappa$ is given in watts cm$^{-1}$ K$^{-1}$, $T$ in K, the pressures $p$ and $p$ in torr and the power $W$ in watts, then the units of $\alpha$ are cm$^{-1}$. For the system used in this study the lowest measurable absorptivity was limited by a false signal, proportional to the laser power, from heating of the windows. This value was approximately $5 \times 10^{-8}$ cm$^{-1}$ using 1 watt of laser radiation. This signal was also near the noise limit of
the pressure sensor (some of which was due to extraneous mechanical vibrations). Thus, assuming that the false signal could be subtracted from a true signal of twice its size, the lower limit of the absorptivity measuring capabilities of the system was of the order of $10^{-7}$ cm$^{-1}$ watts for laser powers of 1 watt or below. This level might be lowered considerably in a system using windows other than NaCl.

D. Effect of Beam Shape on Solution

The Gaussian beam shape for a laser is rather an idealized configuration which is quite often altered by such things as laser windows, mirrors or gratings which are dirty or imperfect for some reason. To get a grasp of how a change in the beam shape might affect the final solution as in Eq. (62) two other simple beam shapes were chosen and analyzed as in the last section. They were normalized such that they both had a total power $W$ and filled the cell to a fraction $b$ of its radius.

Figure 11 shows a schematic of all three of the beam shapes which were analyzed. For the figure a value of 0.3 was chosen for $b$. The solutions were put in a form identical to Eq. (62) so that the illumination factor $B(b)$ could be compared for the three intensity distributions. Figure 12 is a plot of $B(b)$ versus $b$ for the 3 cases.

Even though the two sample beam shapes chosen are quite exaggerated in comparison to probable deviations from a Gaussian shape the results are quite similar. The conclusion is, then, that slight changes in the beam intensity distribution are not likely to have much effect on measurements made with this method. Observations of the beam shape during the experiment were made using thermal imaging plates. The spots did not appear to deviate far from the Gaussian shape.
Fig. 11. — Intensity distributions for three beam shapes with equal power and radius.

\[ I(r) = \frac{3W}{\pi b^2} \left( 1 - \frac{r}{b} \right) \]

\[ I(r) = \frac{2W}{\pi b^2} \left( 1 - \frac{r}{b} \right) \]

\[ I(r) = \frac{W}{\pi b^2} \left( e^{-\frac{r^2}{b^2}} - e^{-\frac{1}{b^2}} \right) \]
Fig. 12.—Beam irradiation factor plotted versus beam radius for three beam shapes.
CHAP T E R V
EXPERIMENTAL APPARATUS

A. The Laser

A flowing gas carbon dioxide laser was used as the energy source for this experiment. The gas used as the lasing medium was a commercially available premixed gas consisting of 10% carbon dioxide, 10% nitrogen and 80% helium. The laser tube had Brewster windows and was excited with a DC power supply at electrodes placed such that the total active medium length was about 90 cm. The optical cavity length was 1.5 meter. The cavity configuration was flat-spherical with the flat mirror replaced by a grating to allow single line operation. The grating was aluminum, had 1800 grooves/in and was blazed at 10 microns. The germanium output mirror had a 10 meter radius with an 80% reflective coating on the inside and an antireflective coating on the outside. This mirror was mounted in a piezoelectric mount to allow cavity length adjustment for proper tuning.

The 1 inch grating was mounted in a Lansing element rotator mounted in a Lansing mount. The element rotator and one of the micrometer drives on the Lansing mount were used to properly orient the grating during the initial alignment of the grating. The second micrometer drive was used to sweep the grating through the angle required to allow lasing at the various wavelengths of the laser. The angular change necessary to change the laser oscillation from one rotational transition to a neighboring one is quite small (approximately $7 \times 10^{-4}$ rad which means about a 0.0011 inch movement of the micrometer screw). Rather than using a differential micrometer head a 36:1 gear reduction box was simply attached to the regular micrometer screw. The ability to obtain lasing on a single given line was quite good with this arrangement. The regular micrometer screw also allowed for a large and rapid angular change which is not possible with the differential type. This greatly facilitated the alignment of the laser as will now be described.

With external cavity optics, the alignment of this laser proved to be relatively simple even though the output mirror was opaque to the visible. This was due to the optical properties of the grating. Figure 13 shows a schematic diagram of the laser with the associated optics. Also shown is a helium-neon alignment laser. The lines marked A, B and C are white cards with small holes punched in them. The several arrows pointing away from the grating depict the various orders of the red laser which reflect from the grating. First the
Fig. 13.—Diagram for explaining alignment procedure for the carbon dioxide laser.

alignment laser is maintained such that the beam always strikes the axis of rotation of the grating (the axis out of the page). Then by observing the various reflected red spots on cards A and C while moving the grating over a large angle about this axis the other axis of the grating, the height of the red laser, and the rotation of the grating in its plane can be readily adjusted such that the output mirror and the red laser are in the plane swept out by a line normal to the grating angular rotation axis and that the grooves of the grating are perpendicular to that plane. Then Card B is inserted and the grating is adjusted such that one of the red beams goes through the hole in the card and to the center of the output mirror. The output mirror is then adjusted such that the beam then returns through the hole in card B. This completes the alignment. A rotation of the grating to the proper angle will cause lasing.

The measurement method required that the laser output be chopped. A simple mechanical 50 percent duty cycle chopper was used external to the cavity.

B. Telescope

The transient solution of the heat flow equation shows that the rise time of the pressure signal of the spectrophone increases with increasing cell radius. For a cell of a diameter large enough to pass the laser beam at the size as it comes directly out of the laser the required chopping period is several seconds. Since it is desirable to have a faster-chopping frequency in order to reduce
problems due to DC drift a telescope was constructed to allow the beam to be focussed to a smaller diameter, i.e., so a smaller diameter spectrophone cell could be used.

The optical elements used in the telescope were two germanium f/1 lenses. The focal lengths were 1.5 in and 1.0 in. Both were antireflection coated for 10 microns. Using an Oriel lens translator a focussing mount was constructed to allow attainment of the desired effective focal length from the two lenses. The telescope is shown in Fig. 14.

Fig. 14.—Beam reducing telescope.

The choice of lenses for the telescope was made through the use of an optical resonator chart[26]. The chart itself was not actually used but the equations which describe the chart were incorporated into a computer program which gave as output a graphical display of the laser spot size as a function of the distance from the laser grating. Figures 15, 16 and 17 show examples of the output of
Fig. 15.—Spot size plotted versus distance from grating. Second lens at position 1.
Fig. 16.—Spot size plotted versus distance from grating. Second lens at position 2.
Fig. 17.—Spot size plotted versus distance from grating. Second lens at position 3.
that program with the telescope oriented such that the laser went through the 1.5 inch focal length lens first, then the 1.0 inch focal length lens.

Looking at Fig. 15 as an example the spot size on the grating is seen to be about 3.5 mm. (The spot size is defined to be the half width of the beam at 1/e of the maximum field.) It slowly increases to about 3.75 mm at the 10 meter output mirror located at 1.5 meters. Then the divergence increases suddenly. This is due to the fact that the output mirror acts as a diverging lens because it has one concave spherical surface and one flat surface. The lens makers formula,

\[ \frac{1}{f} = (n-1) \left( \frac{1}{r_1} - \frac{1}{r_2} \right), \]

reduces to an even simpler form since the flat side of the mirror implies that \( r_2 = \infty \). Thus, the focal length is given by

\[ f = \frac{r}{n-1}. \]

(This number is negative because \( r_1 \) was negative by convention in Eq. (63).) For the mirror used in this study, the index \( n \) was 4.0 and the radius \( r \) was 10 meters. Therefore it formed a diverging lens with a focal length of -3.33 meters.

Continuing to follow the curve on Fig. 15 past the output mirror a break in the curve occurs. This denotes the location of the 1.5 inch focal length lens in the telescope. Here the spot size is about 4.25 mm. Up to this point all the plots are the same since the laser cavity is not changed nor is the location of the input lens of the telescope. The second lens in the telescope is movable since this is the method of focussing the telescope and the curve begins again at the location of this second lens. The three figures (15, 16 and 17) show the resultant spot size plots for three locations of the second lens. The effective focal length of the telescope can be calculated using the Gaussian formula

\[ \frac{1}{f} = \frac{1}{f_1} + \frac{1}{f_2} - \frac{d}{f_1 f_2} \]

where \( f_1 \) and \( f_2 \) are the focal lengths of the first and second lens respectively and \( d \) is the separation between them. However, it was not done since the focussing was done in the experiment by observing the location of the smallest spot (on thermal imaging plates) and
similarly in the computer program by changing the location of the second lens. It is interesting to note, however, that the distance change from Fig. 15 to Fig. 17 is only 1 mm.

The spectrophone was 50 cm long with its center located at the 2.5 meter point on the three plots. Since it was desirable to have the spot size remain constant through the length of the tube a focus adjustment was chosen such that it gave results which were somewhere between those in Fig. 16 and Fig. 17. The spot size for this region under these conditions was taken to be 2.5 mm. It should be pointed out that this spot size is not the same as the term b used in Chapter IV. Here the spot size is, as stated above, the halfwidth at 1/e maximum field. In Chapter IV b was the halfwidth at 1/e maximum intensity. Since the intensity is proportional to the electric field squared, the spot size in terms of the intensity is the halfwidth at the (1/e)² point. That is, since the field (as well as the intensity) is Gaussian,

\[
\frac{I_x}{I_0} = e^{-2}
\]

\[
= \exp(-x_0^2/x_0^2)
\]

where \(x_0\) is the spot size as used in this chapter. However

\[
\frac{I_{x_0}/\sqrt{2}}{I_0} = e^{-1}
\]

Therefore the 1/e point for the intensity occurs at \(x_0/\sqrt{2}\). This value was used in the calculations of the beam size factor B(b).

C. Spectrophone Cell

The cell portion of the spectrophone is of relatively simple design. Two models were used, both of the same design except for the bore diameter. The cell is schematically shown in Fig. 18 along with the associated valving and the pressure sensor. As noted in the figure the cell was constructed by boring a hole lengthwise through a 50 cm long piece of 1-1/2 inch aluminum round bar stock. Aluminum was chosen as the material because of its high heat conductivity. (Copper has a higher conductivity but is more expensive and more difficult to machine.) Two side ports were drilled into the cell. One, near the center, was for attaching the differential pressure sensor. The other, near one end was for attaching a leak valve which allowed an equilibrium pressure to be obtained. In operation the
leak valve was set at a very small leak rate such that the time constant of the pressure signal would be many times longer to the back of the sensor than to the front.

To remove reflections both ends of the cell were cut at Brewster's angle. The windows were NaCl flats and were vacuum sealed with O-rings. As stated above two models were used, identical except for bore diameter. The first model had a 1/4 inch hole. Measurements made with it gave results in agreement with those of the second model which had a 3/8 inch hole but difficulty of alignment prompted the increased size since wall reflections lead to erratic measurements.

D. Pressure Sensor

Two different pressure sensors were used. The first one was a B and K Instruments 4146 microphone. It was a capacitor type microphone with a capacitance of about 50 picofarads. The microphone was mounted such that the only gas flow path from the front to the back of the diaphragm was through the leak valve discussed above. The general method of measuring a front to back pressure differential, i.e., a movement of the microphone diaphragm is depicted in Fig. 19. First with zero pressure differential the rf bridge is balanced such that a null is found while observing the output of the rf receiver. Then a change in the pressure differential across the diaphragm moves it which changes the capacitance. This unbalance of the bridge causes a signal at the output of the rf receiver. By calibrating the pressure change versus the receiver output a pressure sensor is obtained.
Fig. 19.—Diagram of original spectrophone electronics.

The equipment used for this set up was as follows. The rf generator was a Hewlett Packard 606A. The frequency chosen was 1 MHz because the receiver, a Drake SPR-4 and the bridge, a General Radio Type 1606-A, both had good sensitivity at this frequency. The procedure for calibrating the system as described above was attempted several times, using a known volume change and the perfect gas law. The calibrations, however, were not satisfactory, neither in repeatability nor linearity.

One particular problem was the bridge. It was very difficult to null it to the level necessary for the measurement. This was not a deficiency of the bridge. It simply was not designed to be so accurately nulled. Also the unbalance from this null was not linear beyond a certain point. The balance also depends on the frequency and the rf generator drifted enough that balancing had to be repeated to compensate for this drift.

The system was sufficiently sensitive and a few measurements were made using it but the constant attention it required made it unsatisfactory as a useful tool for measurements. An added disadvantage was that should a high differential pressure occur across the microphone diaphragm due to a cracked window, a power failure of a
vacuum pump, a mistakenly opened valve, or something similar the diaphragm would certainly be damaged.

Thus, a new pressure sensing device was introduced into the spectrophone system. The device is a commercial pressure sensor called a Barocel, manufactured by CGS Datametrics, Model 523-15. Its operation, in principle, is quite similar to the first system described above. It too, like the microphone, has a diaphragm which forms a capacitor which changes capacitance under a pressure change which in turn unbalances a bridge. However, the construction is such that the diaphragm is located between two reference plates thus forming two capacitors in series which make up two of the legs of the bridge. Hence, the amount of unbalance for a given movement is greater for a device of this type since the capacitance in one leg of the bridge increases while it decreases in the other leg. Even so, its lower limit of pressure change detection is still not equal to that of the microphone. However, while making measurements it was discovered that the lower limit of absorption detection was not the lower limit of either device but rather due to a false pressure signal which arose from absorption at the windows or walls or both. Therefore, changing to this new device did not decrease the sensitivity of the spectrophone.

Its advantages were many. One was that it was already accurately calibrated in pressure (±0.25 per cent fractional accuracy) with a meter readout from 1 torr full scale to $10^{-4}$ torr full scale. For the measurement an analog output from the device was used which gave a 0 to 1 volt signal for pressures down to $10^{-3}$ torr full scale. Another definite advantage was the fact that the sensor head itself had a construction which allowed a large pressure differential without damage to the diaphragm. All of the data presented in the next chapter were taken with this pressure sensor and the cell with the 3/8 inch bore.

E. Peripheral Equipment

Figure 20 is a block diagram of the experiment which shows the other various equipment used for the measurement. The oscilloscope shown was used only as a monitor for checking signal levels, drift, signal strength, etc. The CRL power meter was not used during a measurement because of its slow response time but was used to calibrate the unchopped reference detector (a Reeder thermocouple) before each measurement was taken.

The vacuum system was a relatively simple one, containing a roughing pump and a Varion 8 liter/sec pump with appropriate valving. An NRC Type 530 Alphatron was used as the main pressure gauge. The maximum vacuum obtained was $2 \times 10^{-6}$ torr. All lines were made of metal to assure that the system would remain free of water.
After the cell was filled with the desired gas mixture and the laser was set at the desired frequency the data taking was controlled from the teletype. The data were taken by the digital computer and analyzed. The resultant answers were obtained on the plotter and the teletype. A description of the process of data taking along with the results are given in the next chapter.
CHAPTER VI
DISCUSSION OF MEASUREMENTS

A. Measurements Made

Measurements were made of the absorptions of each of the P Branch lines available from the 10.6 micron CO\textsubscript{2} laser. There were 14 lines which were measured, from P(6) through P(32). The absorbing gas used for most of the measurements was carbon dioxide. One of the primary interests which prompted this investigation was that of the study of laser propagation through the atmosphere. Therefore, the concentrations of carbon dioxide used were kept near that found in the atmosphere (in the region of 330 PPM). As broadening gases, nitrogen, argon and oxygen were used. Nitrogen is of special interest since it is the primary broadener in the atmosphere.

Some measurements of room air were made. A measurement was first made with the air dried by passing it through a dry ice and alcohol bath cold trap. Then the same measurement was made without the trap. This was done to measure the resultant absorption from the water vapor continuum in the region. The results of these and other water vapor measurements will be given in the final section of this chapter.

B. Experimental Procedure

1. Filling the cell

Prior to each measurement the cell was evacuated. Since the absorptions to be measured were quite small, the cell was initially pumped down to 2 x 10\textsuperscript{-6} torr with a Vacion pump while baking at about 100°C in order to remove any residual gases which might give measurable absorption. This lower limit pressure was reached only after two days of continuous pumping and baking. A dry ice and alcohol cold trap was also in the system during this time. After this initial outgassing procedure only the roughing pump was used to evacuate the cell between measurements. (An exception was after the water vapor measurements were made.) The vacuum reached with the roughing pump was about 5 x 10\textsuperscript{-3} torr. A molecular sieve was located between the roughing pump and the rest of the system to keep pump oil hydrocarbon vapors from reaching the cell.

All mixtures of CO\textsubscript{2} and broadening gases were made in an external tank. To obtain a mixture of 330 PPM, i.e., 0.033\% carbon dioxide and the balance nitrogen, first CO\textsubscript{2} was added until a pressure of 3.3 x 10\textsuperscript{-4} atmosphere or 0.251 torr was reached in the tank.
total pressure left in the tank by the roughing pump was about 2% of this value but only a small percentage of that was CO$_2$ since the tank was flushed with pure N$_2$ previous to filling. The Alphatron was inaccurate for this range for CO$_2$, therefore, the Barocel pressure sensor was used for this initial filling. This was done as follows. After evacuating and closing the roughing pump valve the BACK VALVE shown in Fig. 18 was closed and CO$_2$ was added through a leak valve (not the one in the figure, which was fully open for this step) until the Barocel read 0.251 torr. The mixing tank valve was shut and the rest of the system was again evacuated. The vacuum valve was closed and the system was filled to above 1 atmosphere with pure N$_2$. The mixing tank valve was opened and allowed to fill with N$_2$, while adding more N$_2$ to the system until a total of 1 atmosphere was read on a u-tube manometer. Mass spectrometer analysis showed this filling procedure to be accurate to within less than ±3%. The purity of the N$_2$ as previously noted was 99.999%. The purity of the CO$_2$ was 99.995%.

2. Tuning the laser

After initially aligning the laser such that the beam passed through the center of the spectrophone cell, the laser could then be tuned to each line for a measurement without further adjustment of the output beam. However each line had to be tuned properly both by angular adjustment of the grating and by length adjustment of the cavity. To accomplish this a thermal imaging plate was placed between the output mirror and the telescope shown in Fig. 20. The form of the spot could be observed and adjusted to a "clean" round spot.

At first an attempt to make sure that the laser was lasing on line center was made by tweaking the cavity length until maximum power was attained. This was done because the absorber was CO$_2$ and it seemed desirable to stay at line center for the measurements. However, due to the combined facts that the low pressure in the CO$_2$ laser causes the gain profile to be only about 75 MHz wide and the CO$_2$ absorber is broadened at 1 atmosphere to about 0.07 cm (2100 MHz) for a halfwidth, this final "fine" adjustment was not really necessary. That is, for a gain profile of about 75 MHz the laser could operate, say, 40 MHz on either side of the line center. This is about $1.33 \times 10^{-3}$ cm$^{-1}$. If the Lorentz profile is taken to be

$$k(v-v_0) = \frac{S}{\pi \alpha_L} \frac{1}{(\frac{v-v_0}{\alpha_L})^2 + 1},$$

then $k(0) = \frac{S}{\pi \alpha_L}$.
\[ k(40 \text{ MHz}) = \frac{S}{\pi \alpha L} \left( \frac{1}{1.33 \times 10^{-3}} \right) + 1 \]

\[ = \frac{S}{\pi \alpha L} \frac{1}{1 + 0.00035} \]

which means that \( k(0) \) and \( k(40 \text{ MHz}) \) are not experimentally discernable. Thus, the final tweaking beyond finding the round spot was discontinued for the CO\(_2\) measurements.

After the line was properly tuned the chopper was stopped temporarily and an output power to reference power reading ratio was taken by reading meters connected to each detector. This ratio was then used as one of the input parameters into the data taking program described below. It was found that it was important to obtain this ratio for each laser output line, since the value varied as much as 25% from line to line. This variation was attributed to the fact that the reference detector was small and the plane parallel beam splitter probably set up interference patterns which varied with wavelength and changed the total energy striking the surface of the detector.

C. Data Taking Program

The output signal from the Barocel was a damped square wave, synchronous with the square wave power input by the chopped laser. The object of the data taking program was to detect and record this signal and to measure its amplitude in a repeatable manner.

The procedure for taking data was an interactive process between the experimenter and the computer. After inputting requested initial data into the teletype, (data input will be discussed later), the computer did the following upon receiving a command from the teletype. It began repeatedly checking the A/D converter connected to a synch device at the chopper (Refer to Fig. 20) until it read a level which signified that the laser power was about to be inputted into the cell. It then took a reading from the A/D channel connected to the output of the Barocel. This value was stored and a reading was then immediately taken from the A/D channel connected to the reference detector. This value was stored, then a delay occurred and the process of reading the last two channels was repeated. The delay was chosen such that 100 pairs of readings (for one of the programs) were taken in somewhat less than one cycle. Enough time was left before the next cycle started so that an average value of the reference detector signal could be taken and stored. Then the computer waited for another synch pulse and the process was repeated. After 10 cycles the 1000 values of the signal were normalized by dividing each 100 by the average reference signal over its particular cycle.
At this point an average cycle was found by point by point averaging of the 10 signals. As an option this average cycle could be plotted on the Calcomp plotter. One of these plots is shown in Fig. 21 for a relatively low signal level. To find the amplitude of this pulse, the computer ran through the 100 points of the average cycle and found an average value for each successive 5 points. The minimum result of this operation was subtracted from the maximum result to get the desired amplitude.

For low level signals the ripple as seen at the top of the pulse in Fig. 21 gave results that were not as repeatable as desired. Therefore further data manipulation was done on this average cycle before finding the amplitude. The approach was that reported by Savitzky and Golay[27]. The process is to fit a least squares curve to each successive 9 points (other numbers can be used, of course, in fact, both 5 and 17 were tried for comparison), take the value of the fit at the central point of the 9, move over one point and repeat the least squares fit, again saving the fit at the central point, etc. This is not as time consuming as it appears due to the simplifying tables for finding the central point which are provided in the above report.

A resulting curve from this 9-point smoothing process is shown in Fig. 22. This measurement was taken immediately after that shown in Fig. 21 at the same signal level. When the amplitude-finding...
procedure was used after this smoothing process the results were found to be very repeatable, usually within 1 or 2 percent at the noise level as shown in Fig. 21. Thus, the 9-point smoothing process was used in all the following measurements.

The amplitude of the plots shown in Figs. 21 and 22 were normalized to a certain size for plotting purposes. However the value of the amplitude was outputted on the teletype as a number corresponding to that obtained from Eq. 9, i.e., \( \alpha = \frac{4\pi KT_A}{B_{NP}} \). The inputs into the data taking program by the experimenter at the teletype were the thermal conductivity \( K \), the temperature \( T \) (although \( T \) is in °K in the equation, the input was given in °C for convenience, then converted internal to the program), the beam irradiation factor \( B \) and the total pressure \( P \). Also there were three multiplying constants which were inputs used for scaling. Any of these values could be changed at any time before a measurement by using a certain delimiter. In this way one of the multiply constants was used for inputting the output power to reference power ratio which was found for each line as described in a previous section of this chapter. Another constant multiplier was used to designate the range on the Barocel manometer. The values for \( A \), the Barocel pressure signal and \( W \), the laser power are those read in by the computer and processed as described. The smoothed amplitude is, in fact, actually a constant times the value \( A/W \).
The computer plots were only used to observe pulse shape and proper operation in general at the beginning of each run. For example Fig. 23 shows the pulse rising and then decreasing before the end of the power input cycle. This implied that the leak valve in the spectrophone cell was too far open, although only by a slight amount. A more exaggerated form of this problem could easily be seen on the monitoring oscilloscope. After this initial wave form check the plots were discontinued by throwing a sense switch on the computer and the only output was the value for $\alpha$ on the teletype.

Before going on to the results of the measurements Fig. 24 is given to compare the plots obtained for the two cell diameters. Figure 24 is for the larger (3/8") cell diameter and the time constant is seen to be larger as predicted. In fact the signal is probably a couple of percent short of reaching maximum amplitude.

D. Results

1. CO$_2$ line width measurements

   a. Background and other results

   At line center the Lorentz profile gives an absorption coefficient of
Fig. 24.--Tracing of computer plotter output showing pulse shape for 3/8 inch spectrophone cell.

(70) \[ k(0) = \frac{S_j}{\pi \alpha_{L,J}} \]

where \( S_j \) is the line strength of the \( J \)th rotational line and \( \alpha_{L,J} \) is the Lorentz halfwidth of that line. Thus, if the line strength is known then the halfwidth can be found directly from Eq. (69), as noted by McCubbin, et al [28], by measuring the absorption at line center. One special problem that the approach lends itself to is the study of the \( J \) dependence of the halfwidth. In particular, how does this variation change with different broadening gases? Atmospheric gases are of special interest for the study of the transmission in the 10\( \mu \) window. For pure CO\(_2\), obtaining \( \alpha_{L,J} \) through the use of Eq. (70) is relatively easily done. For pressures above 50 torr (as pointed out in Chapter II) the absorption coefficient becomes constant with pressure and is large enough such that a 50 percent or lower transmission can be obtained over a fairly short path length. As discussed in Chapter I this low transmittance is necessary to give good accuracy to the measurement of the absorption coefficient. As an example, for the experiment depicted in Fig. 8 the path length was 5.22 meters which gave less than 50 percent transmission. Path lengths of this size are readily achieved with a small White cell or a long tube. Several investigators have used this method for finding the \( J \) dependence of the self broadened half width[15,30,31,32,33].
However the halfwidth $\alpha_{LJ}$ is proportional to the collision frequency of the absorbing molecules and since the collision frequency depends on, as shown in Eq. (24), the mean speed, the cross section and the density of the molecules then $\alpha_{LJ}$ is not expected to be the same when the CO$_2$ molecules have an appreciable percentage of collisions with molecules other than those like themselves. Thus it is of interest to look into the broadening effects of other molecules.

To find the foreign broadened half width using Eq. (70) directly, it is necessary that the ratio of foreign molecules (or atoms) to CO$_2$ molecules be quite large such that most of the collisions will be with the foreign molecules. This requires mixing only a small amount of CO$_2$ with the broadener, which reduces the absorption so that long path lengths or a device such as the spectrophone is required.

Other investigators have devised methods for studying this foreign broadening effect which do not use this direct approach and thus do not require the high absorption. McCubbin and Mooney[15] did the following. They first filled their 20 meter cell with pure CO$_2$ at 1 torr and measured the transmittance (of the P(20) line). Then they introduced a broadening gas, taking transmittance measurements at various pressures until the total pressure was about 30 torr. In this pressure range the Voigt profile holds which, although rather complicated (Eq. (21)), reduces to a relatively simple form at the line center

\[
K_{vo} = \frac{S_J}{\alpha_D} \left( \frac{\pi}{2} \right)^{1/2} [1 - \text{erf}(a)] \exp(a^2)
\]

where

\[
a = \frac{\alpha_L}{\alpha_D} \ln 2
\]

with $\alpha_D$ and $\alpha_L$ being the Doppler and Lorentz halfwidths respectively. Both tables and algorithms for the evaluation of the error function are readily available, making the computation of this expression straightforward. By plotting this function for various values of $\alpha_L$, the desired collision broadened halfwidth, their experimental data could be compared with this family of curves to obtain a value for $\alpha_L$. The value they obtained for N$_2$ broadening using this method was 0.07 cm$^{-1}$ atm$^{-1}$ for the P(20) line. This method could be used to find the J dependence of $\alpha_L$ by repeating the experiment for the various laser lines.
Patty, et al[34] used another approach to find foreign broadening effects: This requires first some discussion of the terms effective pressure and self-broadening coefficient. Eq. (18) stated that the halfwidth is proportional to the pressure \( P \). This presents no problems if the gas is pure since an increase in pressure is simply an increase in density and hence in collision frequency. But if, along with the absorbing gas, a broadening gas is present, then \( \alpha \) is still proportional to the pressure but to one referred to as the effective pressure \( P_e \), where[35]

\[
(72) \quad P_e = p_b + B p_a
\]

where \( p_b \) and \( p_a \) are the partial pressures of the broadening and absorbing gases respectively and \( B \) is referred to as the self-broadening coefficient. It has been common in the literature[35] to refer all the self-broadening coefficients to nitrogen, i.e., \( p_b \) above would always be the partial pressure of nitrogen. Patty, et al chose to simply relate the self-broadening ability of CO\(_2\) to any other broadening gas by defining the self-broadening coefficient as

\[
P_e = p_b + B_{a,b} p_a
\]

where the subscript \( a \) is for CO\(_2\) for this case.

The method for the measurement of \( B \) used by Patty, et al is as follows. First a short cell is filled with pure absorbing gas to a pressure which is above the Voigt profile region, e.g. 100 torr, and the transmittance is measured. Then path length is doubled and the pressure is reduced by a factor of two. This particular change in path length and pressure is not necessary but it is convenient if the two cells give the same absorber optical thickness. For CO\(_2\) at the line center the transmittance will be less for the long cell since the transmittance at constant path length is not a function of pressure above 50 torr, as mentioned previously. Then the broadening gas is added and the transmittance is measured as a function of total pressure. When the transmittances become equal then the absorption coefficients

\[
k_{\nu_0} = \frac{S}{\pi \alpha_L}
\]

must also be equal since the absorber thicknesses are the same; from

\[
T = e^{-k_{\nu_0} W}
\]

where \( W \) is the absorber thickness as discussed in Chapter II. This implies also that the halfwidths and hence, the effective pressures must be the same, i.e.,

\[
(p_b + B p_a)_{\text{short}} = (p_b + B p_a)_{\text{long}}
\]
But $p_b$ for the short cell is zero, therefore

$$B = \frac{p_b \text{ long}}{p_{a\text{ short}} - p_{a\text{ long}}}$$

Patty, et al used this method to obtain $B$ for several broadening gases for the P(20) line.

Young et al [32] used this approach to find the $J$ dependence of $a_1$ for the P-branch of CO$_2$ broadened by nitrogen. In Eq. (72), for large $p_b$ the halfwidth is proportional to $p_b$; for large $p_a$ the halfwidth is proportional to $B p_a$. Therefore $B$ is the ratio of self-broadened halfwidth to the foreign-broadened halfwidth. Thus by first finding the CO$_2$-CO$_2$ collision halfwidths as a function of $J$ using the straightforward method connected with Eq. (70), then finding the self-broadening coefficient $B(J)$ with respect to N$_2$ as a function of $J$, they obtained the foreign-broadened halfwidths as a function of $J$ by simply dividing the self-broadened halfwidths by the appropriate $B(J)$. Their results show that $B$ is not a constant with respect to $J$.

Table 2 shows a comparison of the values of $B(20)$ for nitrogen broadened CO$_2$ from the three investigations just described. The value given there for Young, et al is less accurate due to the fact that this author obtained it by dividing two numbers read from a graph.

<table>
<thead>
<tr>
<th>Investigators</th>
<th>$B(20)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>McCubbin and Mooney[15]</td>
<td>1.37</td>
</tr>
<tr>
<td>Patty et al [34]</td>
<td>1.33</td>
</tr>
<tr>
<td>Young et al [32]</td>
<td>1.40</td>
</tr>
</tbody>
</table>

McCoy[10], using a 980 meter path in a White cell obtained a value for the air-broadened halfwidth of CO$_2$ using Eq. (70). He obtained a value of 0.069 cm$^{-1}$ atm$^{-1}$ as compared to the value of 0.080 cm$^{-1}$ atm$^{-1}$ obtained by McCubbin and Mooney[15] using their method.
b. Results from this investigation

The spectrophone is ideally suited to this study of the J dependency of $q_L$ with different broadening gases. Its sensitivity allows the measurement to be made using Eq. (70) directly without the use of a very long path length. The absorption coefficient is measured directly as described earlier in this chapter. Thus, if $S_J$ in Eq. (70) is known then the J dependence of $q_L$ is readily obtained. Several workers [2,15,28,32] have obtained values for $S_{20}$ which agree quite closely (within 2.5%). The value chosen for this work is a weighted average of these data, a value of $S_{20} = 5.5 \times 10^{-4}$ (atm-cm$^{300K}$)$^{-1}$ cm$^{-1}$. Knowing the line strength of one line in the band it is possible to calculate the rest of the line strengths in that same band by the relationship [30]

$$\frac{S_{m1}}{S_{m2}} = \frac{v_{m1}}{v_{m2}} \frac{m_1}{m_2} \exp\left[-\frac{E_{1J} - E_{2J}}{kT}\right]$$

where $v_m$ is the frequency of the mth rotational line, with $m=-J$ for the P branch and $m=J+1$ for the R branch. Using Eq. (70) and the chosen value for $S_{20}$ along with the rotational constants of the vibrational levels of CO$_2$ given in Yamamoto, et al [36] values of $S_J$ were calculated for all $S_J$ between P(40) and R(40). The equations used for calculating the upper and lower levels were, respectively

$$E_{000J} = 2349.16 + 0.38714J(J+1) - 18.10^{-8}J^2(J+1)^2$$

and

$$E_{100J} = 1388.187 + 0.39020J(J+1) - 12.810^{-8}J^2(J+1)^2.$$  

McCubbin and Mooney [15] have also measured $S_J$ for the P(16), P(18), P(22) and P(24) lines. Table 3 gives a comparison of the values calculated using Eqs. (74), (75) and (76) and their measured values. The agreement is considered acceptable.

<table>
<thead>
<tr>
<th>Line, Sj(atm-cm)$^{-1}$cm$^{-1}$</th>
<th>Calculated</th>
<th>McCubbin and Mooney</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(16)</td>
<td>0.583 $\times 10^{-3}$</td>
<td>0.584 $\times 10^{-3}$</td>
</tr>
<tr>
<td>P(18)</td>
<td>0.574</td>
<td>0.565</td>
</tr>
<tr>
<td>P(20)</td>
<td>0.550</td>
<td>0.549</td>
</tr>
<tr>
<td>P(22)</td>
<td>0.514</td>
<td>0.516</td>
</tr>
<tr>
<td>P(24)</td>
<td>0.469</td>
<td>0.475</td>
</tr>
</tbody>
</table>
In this study the calculated values of $S_j$ were used to find $\alpha_{L,j}$ for the P-branch lines of the band. Also since the measurements were not made at 300°K the results had to be corrected for the temperature difference. Equations (77) and (78) were used for the temperature correction of the line strength and widths respectively[37], i.e.,

\begin{equation}
S = S_0 \left(\frac{T_0}{T}\right)^2 \exp \left[\frac{E_L}{0.6951} \frac{1}{T_0^2} \left(\frac{T}{T_0}\right)\right]
\end{equation}

and

\begin{equation}
\alpha = \alpha_0 \left(\frac{T_0}{T}\right)^{0.5} \frac{p}{p_0},
\end{equation}

where the subscript zero stands for the value at 300°K and $E_L$ is the lower energy level of the transition.

The optical thickness change due to temperature also had to be accounted for when correcting the data to 300°K. McCubbin and Mooney[15] make the statement that at line center for the Lorentz line

\begin{equation}
k(v_o) = \frac{S}{\pi \alpha} = \frac{S_0}{\pi \alpha_0}
\end{equation}

where $S$ is the line strength, $\alpha$ is the halfwidth, $S_0$ and $\alpha_0$ are the line strength and halfwidth at a pressure of one atmosphere. In this form the pressure has been included in the line strength, i.e., the optical thickness is

\begin{equation}
-k(v_o) = \frac{S^1 p \chi}{\pi \alpha}
\end{equation}

where $S^1$ is the line strength in cm$^{-2}$ atm$^{-1}$ which makes the strength referenced to a given number of molecules, such that for their notation $S = S^1 p$, since they state that $S$ is proportional to pressure. This would mean that for Eq. (79) to be true, all measurements would necessarily be made at the reference temperature, since the temperature correction for the absorber amount is not taken into account because the pressure $p$ has been cancelled with that in the denominator. A further correction consisting of a multiplier $\frac{T_0}{T}$ is needed to correct for the proper absorber concentration. They may have done this but it is not apparent in their report.

For an absorption coefficient given in reciprocal length, which is measured with the spectrophone,
\[ k_{\nu_0} = \frac{S_P}{\pi \alpha} \]

where the \( \varepsilon \) cancels. To change to a reference temperature and density at \( T_0 \) using Eqs. (77), (78) and (80),

\[
S_0 \left( \frac{T_0}{T} \right)^2 \exp \left[ -\frac{E_L}{0.6951} \left( \frac{T_0 - T}{T_0} \right) \right] \left( \frac{T_0}{T} \right) \]

\[ k_{\nu_0} = \frac{\pi \alpha_0 \left( \frac{T_0}{T} \right)^{0.5} \frac{p}{P_0}}{P} \]

where \( P \) is the total pressure and \( p \) is the partial pressure of the absorber. The reference pressure \( P_0 \) is usually 1 atmosphere and thus we have

\[
k_{\nu_0} = \frac{S_0}{\alpha_0 \pi} \left( \frac{T_0}{T} \right)^{2.5} \exp \left[ -\frac{E_L}{0.6951} \left( \frac{T_0 - T}{T_0} \right) \right] \frac{p}{P} \]

For pure CO\(_2\), \( p = P \). McCubbin and Mooney[15] give values of \( S_0/\alpha_0 \) which have good accuracy due to the low transmittance they achieved in the 5.22 m path. Table 4 gives a comparison of their results for this term compared to the results obtained in this investigation using the spectrophone.

Table 4

<table>
<thead>
<tr>
<th>Line</th>
<th>( S_0/\alpha_0 (\text{cm}^{-1}) )</th>
<th>( S_0/\alpha_0 (\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>McCubbin and Mooney[15]</td>
<td>This investigation</td>
</tr>
<tr>
<td>P16</td>
<td>5.52 x 10^{-3}</td>
<td>5.94 x 10^{-3}</td>
</tr>
<tr>
<td>P18</td>
<td>5.37 x 10^{-3}</td>
<td>6.04 x 10^{-3}</td>
</tr>
<tr>
<td>P20</td>
<td>5.69 x 10^{-3}</td>
<td>6.11 x 10^{-3}</td>
</tr>
<tr>
<td>P22</td>
<td>5.18 x 10^{-3}</td>
<td>5.52 x 10^{-3}</td>
</tr>
<tr>
<td>P24</td>
<td>5.07 x 10^{-3}</td>
<td>5.15 x 10^{-3}</td>
</tr>
</tbody>
</table>

All of the values obtained here are larger than those of McCubbin and Mooney but the agreement is within 10% in most cases. Thus the theoretical calibration of the spectrophone for this level of absorption is acceptable.
Figure 25 shows a plot of the self broadened halfwidths obtained by solving Eq. (82) for $\alpha_0$, using the line strengths obtained from Eq. (74) and the values of the absorption coefficients measured with the spectrophone. Included in the plot are data presented by Young, et al., McCubbin and Mooney, and Devir and Oppenheim.

The basic equation describing the spectrophone cell operation is Eq. (9), i.e., $\alpha = 4\pi k T A / B W P$. Two parameter studies of this equation involving the use of CO$_2$ as an absorber were also done. Due to the special properties of the absorption of a pressure broadened line at line center it is possible to check, over a certain range of pressures, to see if the relation $A/P$ of Eq. (9) is, in fact, constant if the other parameters are held fixed. That is, is the Barocel signal $A$ proportional to the total pressure $P$?

As discussed in Chapter II, for pressures above 50 torr the absorption at line center of pure CO$_2$ in a cell does not change with increased pressure, i.e., the absorption coefficient $\alpha$ is constant with respect to pressure above 50 torr. Thus the laser was set at the P(20) line and the pressure was varied over as large a range as possible. This range was from 50 torr to 203 torr. The upper limit was due to the maximum pressure signal which could be read by the Barocel. Figure 26 is a plot of the results of that measurement. The main contribution to the data scatter is thought to be the error in reading the total pressure.

The second parameter study using CO$_2$ was a check to see if the Barocel pressure signal was linear with respect to absorption for the low absorption region. For a fixed total pressure the absorption should be proportional to the absorber concentration as long as that concentration remains small enough to allow self-broadening effects to be ignored. Measurements were made of the absorption of the P(20) line center with concentrations of CO$_2$ varying from 400 PPM to 1100 PPM in one atmosphere of nitrogen. The results are given in Fig. 27.

Although Fig. 27 shows the absorption to be linear in this region the values obtained were found to be low when a comparison was made with other measurements. Thus it appears that the simple relationship given by Eq. 9 does not hold for the entire range of absorption which is a factor of about 10$^4$.

However, since the system does give linear results over smaller regions a method of calibrating it was devised for the region of interest, the low absorption region. This method involves the use of reliable results of other measurements. On page 59 it was noted that the self-broadening coefficient $B$ is a ratio of the self-broadened halfwidth to the foreign-broadened halfwidth. The measurements made by Patty et al.[32] of the self-broadening
Fig. 25--Collisional halfwidth of the P-branch lines of the 10.4\textmu m band of CO$_2$ for self broadening as a function of rotational quantum number.

Fig. 26--Parameter study of the spectrophone system output as a function of pressure in the cell.
coefficient $B$ of the $P(20)$ line of $CO_2$ near 10.6\textmu and the various measurements of the self-broadened halfwidth of that line were all made using the usual (IN-OUT)/IN method of measuring absorption, but in a region of sufficiently high absorption to give accurate results. Thus using these two parameters to find the foreign-broadened halfwidth a calibration of reasonable accuracy could be obtained through the use of Eq. (82) and a measurement of the absorption of a nitrogen broadened line.

A value of 1.33 was taken for the self-broadening coefficient $B_{CO_2,N_2}$ at the $P(20)$ line from Table 2. An average self-broadened halfwidth was taken to be 0.095 cm$^{-1}$ atm$^{-1}$ from Fig. 25. This gave a value of 0.071 cm$^{-1}$ atm$^{-1}$ for the nitrogen broadened halfwidth. Using mixtures of $CO_2$ and $N_2$ of the order of 1000 PPM $CO_2$ a calibration constant was obtained. This constant was put into the computer program by the use of the volume irradiation factor. It should be noted here that the measurement or calculation of the beam size which is used to compute the original volume irradiation factor is definitely a source of error in the theoretical calibration. This calibration against a known absorption removes this source of error.
Results of some measurements which used this calibration constant are given in Fig. 28. Shown there is the halfwidth dependence on J for various broadening gases. This calibration constant was also used for the measurement of the water vapor absorption discussed in the following section.

2. Water Vapor Continuum Measurements

Of considerable interest is the absorption due to water vapor in the 10μ atmospheric window. Generally this absorption is attributed to the water vapor continuum as first proposed by Elsasser[38]. For air-water vapor mixtures McCoy[11] made measurements of the absorption of the CO₂ laser P(20) line. His results indicated that the absorption coefficient has a strong partial pressure dependence. Bignell et al[39] found similar results in the 17 to 21μ region. They suggested that this supported Elsasser's theory that the continuum absorption was due to the extreme wings of the H₂O absorption lines in the bands at 6.3μ and 50μ. Using this hypothesis, McCoy[11] used his data to calculate a self-broadening coefficient for the water vapor at 10.6μ, obtaining for an absorption coefficient,

\[(83) \quad k(10.6) = 4.32 \times 10^{-6} \text{ p}(P + 193 \text{ p}) \text{ km}^{-1},\]

where the self-broadening coefficient, B = 193. This indicated that if the wing theory was correct then the H₂O-H₂O collisions were dominant to a greater degree than had been encountered previously.

In this study the absorption coefficients of water-vapor nitrogen mixtures were measured in this spectral region near 10μ. The results of the measurements of the absorption coefficient at the P(20) line is plotted versus the partial pressure of water vapor in Fig. 29. The total pressure was 760 torr with nitrogen as the broadener. Also included in that figure is a plot of Eq. (83) from McCoy's[11] results. One possible reason for the difference in the two results is that the broadening gas was different. McCoy used air which contained 20% oxygen.

Another more likely reason is due to the difficulty encountered in accurately measuring the amount of water vapor in a given mixture. With the spectrophone an attempt was first made to mix the water vapor and nitrogen in an external tank, then to introduce it into the spectrophone cell.

The procedure for obtaining the mixtures was as follows, with reference to Fig. 30. A manifold was used which contained valves for H₂O and N₂ inputs, a valve to the mixing cell which was a large high pressure nitrogen tank, a valve to the pressure gauges, and one to the vacuum pump. The H₂O supply was a glass bottle containing a quantity of distilled water which was evacuated
Fig. 28—Self-broadened and foreign-broadened halfwidths of the lines in the P-branch of the 10.4 μ CO₂ band as a function of rotational quantum number.
Fig. 29--The absorption coefficients of water vapor nitrogen mixtures as a function of the partial pressure of water vapor.

\[ k(P_{20}) = 4.32 \times 10^{-6} \times \rho (P+193\rho) \text{ km}^{-1} \]

(McCOY'S FIT)

Fig. 30--Manifold used for original H$_2$O-N$_2$ mixing procedure.
to obtain pure water vapor in the bottle. The manifold and mixing tank were evacuated to about 100\mu, then the pump valve was closed and the water valve was opened allowing the mixing tank to begin filling with water vapor. The gauge used for measuring the pressure of the water vapor was a Gilmont model 906 mercury micrometric manometer which could easily be read to 0.1 torr. The system was filled to 1.1 percent of the desired value of H₂O, the H₂O valve was shut and the system was filled to 1.1 atmosphere total with nitrogen, reading the total pressure on a u-tube manometer. The over-fill above 1 atmosphere was to allow the spectrophone cell to be filled to 1 atmosphere. The mixing tank valve was closed and allowed to mix for several hours, usually overnight.

When the spectrophone cell, which had been evacuated to below 10\mu, was initially filled with this mixture it was found that the amount of absorption measured decreased with time. This indicated that adsorption of water vapor to the walls was occurring, thus reducing the actual partial pressure of the water vapor in the gaseous mixture to a lower and unknown level.

To alleviate this problem the cell was modified as shown in Fig. 31. An extra hole was drilled in the side of the cell and some valves were added to allow a water vapor-nitrogen mixture to be flowed through the cell in series with a Cambridge Systems Model 880 Dew Point Hygrometer. Water vapor nitrogen mixtures were then mixed directly in this system. After filling, the pump was first allowed to run for several minutes to assure proper mixing, then the dew point was measured. Valves A and B were then closed and a measurement was taken. Values obtained by this method were repeatable to within 5 percent.

![Diagram of spectrophone with dew point hygrometer added.](image-url)
The procedure for taking data for a plot such as in Fig. 29 was to first fill the system with a mixture having a large concentration of water vapor, then dilute the mixture for each successive measurement by partially evacuating and refilling to 760 torr with nitrogen.

For several of the water vapor-nitrogen mixtures absorption measurements were made using 8 of the P-branch lines of the CO$_2$ laser from the P(8) line to the P(36) line. Figure 32 shows the results of one of those measurements for a partial pressure near 6 torr broadened with nitrogen to a total pressure of 760 torr. The increase in the absorption at the longer wavelengths is similar to the result obtained by Bignell et al[39] in that the slope is positive with increasing wavelength. Further studies would be necessary to allow a more detailed comparison to be made. However, since the slope seemed quite large an attempt was made to determine if this result was system dependent. The cell was realigned many times, the end windows were changed from NaCl flats at Brewster's angle to NaCl flats normal to the beam, and finally the NaCl flats were replaced with germanium flats which were anti-reflective coated at 10u. The results were consistently of the form shown in Fig. 32.

![Graph showing water vapor-nitrogen absorption](image)

**Fig. 32**--Water vapor-nitrogen absorption for 8 of the P-branch CO$_2$ laser lines.
Another measurement made concerning the water vapor continuum was the observation of the change in absorption coefficient as a function of temperature. Bignell[40] made measurements with a 15 m White cell and a black body source which indicated that a negative temperature coefficient existed for the absorption in this region. His result indicated a 2 percent change per °C at 30°C. The small size of the spectrophone made it appealing as a device for measuring temperature dependence. Further consideration revealed that the temperature variation would not affect the value of the absorption coefficient relative to the pressure sensor signal since the absorption coefficient (Eq. (62)) is proportional to T/P relative to the pressure signal. Thus, only the pressure and temperature at the point of filling the cell need be used in the equation since, \( T_1/P_1 = T_2/P_2 \). Other possible effects of the changes would, of course, have to be taken into consideration; such as pressure broadening, in order to interpret the results. One note in particular is the change in thermal conductivity with temperature.

The approach to this temperature variation measurement was as follows. In the first place the spectrophone cell was already enclosed in a plexiglass box as explained earlier. The cell and the surrounding regions in the box were wrapped with heat tape. Then the box was filled with crumpled cloth to cut down any convection currents which might cause temperature fluctuations. It is important to remember that this device operates on exactly that principle, minute temperature fluctuations, thus it is imperative that a temperature equilibrium exist in order to be able to take measurements. The heat from a person's hand placed on the tubing to the back of the pressure sensor will drive the meter off scale almost instantly when the meter is on the most sensitive scale; placing a hand on the more massive cell itself takes several seconds to cause the same results.

The temperature control was simply a Variac connected to the heating tape. By trial and error, empirical settings on the Variac could be determined which would cause the temperature to equilibrate near the desired value. The total temperature range covered was from 55°C to 29°C. About thirty minutes stabilization time was required between each 3 degree change. Larger steps took longer times.

For a temperature run the gas was put into the cell and an initial signal was measured at room temperature. The cell was then taken quickly to its highest temperature and allowed to stabilize there. Then measurements were taken as the cell cooled to each new temperature, resetting the Variac. Initially this was done with the pure carrier gas to check for outgassing contaminants. The first measurement at 50°C showed a signal 20 times the size of the beginning background signal. Since this was near the size of the expected water vapor signal, it was entirely unacceptable. The cell was
therefore baked under vacuum over night at 75°C. The next measure-
ment showed an increase in contaminant signal over background of only
a factor of 3 for the carrier gas which remained nearly constant for
the entire temperature range (within 5 percent of the average value).
A repeat after the water vapor measurement gave a similar result.
This background level was simply noted rather than subtracted.

Two measurements were made with this rather elementary system.
One at 6 torr of water vapor and one at about 8 torr. For the 8 torr
measurement only the P(20) line was used. At this level of absorption
the contaminant background was sufficiently near the signal that
little can be interpreted from the results other than there does not
appear to be a negative temperature coefficient. For the 8 torr
measurement the absorptions at the P(20) and the P(32) lines were
observed. Here the signal was about 5 times the background signal.
Figure 33 shows the results of the 8 torr measurement.

A visual straight line fit to the data gives a positive tempera-
ture coefficient for the P(20) line of about 0.5 percent/°C. One major
problem for this measurement was the drift of the signal due to
temperature instabilities. Due to the way the computer data program
operates, a general drift upward gives a larger signal and a drift
downward gives smaller signals. The measurements obtained are thus
preliminary and should be taken as such. However, in general the
device looks quite promising as one for studying the temperature
dependence of absorption. For example, sophisticated proportionate
temperature controllers are available and the design of the cell could
be changed to take this special problem into account. Also the
computer program could be modified to remove some of the errors due
to drift. Another necessary improvement would be a more accurate
temperature monitoring system. The one used here was to simply tape
two thermometers to the side of the cell. Undetected temperature
lags due to this setup probably are responsible for some of the scatter
in the data.
Fig. 33.—Temperature dependence of water vapor-nitrogen absorption at 2 of the P-branch CO$_2$ laser lines.
The purpose of this study was to investigate the use of the spectrophone as a spectroscopic tool. The first chapter showed the need for such an instrument which could measure very small absorption coefficients by noting the errors resulting from the usual (IN-OUT)/IN method.

A spectrophone along with a repeatable data taking system was developed which allowed absorption coefficients to be measured which were of the order of 0.01 km\(^{-1}\) using a 1 watt CO\(_2\) laser.

A theoretical calibration formula was developed. An experimental calibration procedure was developed which allowed results to be compared with the theoretical predictions.

Measurements were made of CO\(_2\) absorption in the P-branch of the 10.4 micron band which were used to obtain the self-broadened and foreign-broadened halfwidths of the lines in that branch as a function of the rotational quantum number. The gases used for foreign broadening were nitrogen, argon and helium. These results were found to compare favorably with those of other investigators using different methods.

Absorption measurements of the water vapor continuum in the 10 micron region were made. The resulting measurement at the P(20) line of the CO\(_2\) laser gave absorption coefficients which were higher than those obtained by McCoy[11] in a 50 foot White cell.

A water vapor absorption measurement using 8 of the CO\(_2\) laser lines showed an increase in absorption with increasing wavelength in the 10 micron region. This result is in general agreement with that reported by Bignell et al[39].

Preliminary studies were done investigating the use of the spectrophone as an instrument for measuring the temperature dependence of absorption. The results using water vapor-nitrogen mixtures as the absorber showed the system to be quite promising for this area of investigation.
REFERENCES


26. Laser Engineering Short Course, The Antenna Laboratory, Ohio State University, Columbus, Ohio (1967).


