EFFECTS OF FOREIGN GASES ON THE TOTAL ABSORPTION
OF ENTIRE BANDS IN THE INFRARED

DISSERTATION

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Absorption band spectra originate when a molecule is raised from a lower energy state to a higher energy state by the absorption of radiation. The energy of a molecular state in general can be written as the sum of energies due to vibrational and rotational motions of the atoms within the molecule plus energy due to the electrons associated with each atom. Spectra arising from transitions between the electronic energy levels lie in the visible or ultraviolet region of the spectrum.

The energies associated with rotation and vibration are interdependent and so-called band spectra in the near-infrared originate when a molecule in a given rotation-vibration energy state absorbs radiation and is raised to a higher energy state.

The frequency of the radiation which produces an absorption event is given by the Bohr frequency relation as

$$\nu = \frac{E' - E''}{hc}$$

where \(\nu\) is the frequency in \(\text{cm}^{-1}\), \(E'\) and \(E''\) are the energies of the upper and lower states respectively, \(h\) is Planck's constant and \(c\) is the velocity of light.
If a transition between the vibrational energy levels of a diatomic molecule could occur without a change in rotational energy, the quantum mechanics of the simple harmonic oscillator approximating the molecule would yield, for this transition, absorption at a single frequency, $\nu_0$. The quantum mechanics of an anharmonic oscillator more realistically approximating the diatomic molecule shows there are overtones of this fundamental frequency, $\nu_0$, occurring at approximately $2\nu_0$, $3\nu_0$, \ldots with decreasing intensities. The frequencies of this fundamental and its overtones occur in the near-infrared region of the electromagnetic spectrum. If this region is examined with a high resolution spectrometer it is found that on either side of the frequency representing the fundamental vibrational transition frequency there are many "fine-structure" lines. This fine structure on either side of $\nu_0$ occurs because the vibrating molecule is also rotating and the energy state of the molecule must necessarily be a function of both the vibrational and rotational energies. A transition between vibrational levels may be accompanied by a simultaneous quantized change in rotational energy yielding an absorbed radiation frequency either greater or less than $\nu_0$, depending on the rotational energy in the initial and final energy state.
If radiation power, \( P_0 \), in a frequency interval \( \nu_1 \) to \( \nu_2 \) is incident on a gas sample which absorbs energy in this region one finds the transmitted power, \( P \), is reduced in magnitude. The difference in power is given up in raising the absorbing molecules to higher energy states. If one defines the total absorption over the interval \( \nu_1 \) to \( \nu_2 \) as \( \int A(\nu) d\nu \) where \( A(\nu) \) is the fractional absorption at frequency \( \nu \), it is found experimentally that the total absorption is a function of: (a) the absorber concentration which is equal to the gas density times the optical path length at a given temperature, and is proportional to the product of the partial pressure of the absorbing gas \( p \) and the geometrical path length, (b) the partial pressure of the absorbing gas, (c) the total pressure of the absorbing gas plus any "foreign" non-absorbing gas present in the radiation beam and (d) the absolute temperature.

In an attempt to give this functional relationship in the form of an equation relating these parameters, several "band models" have been proposed. Elsasser\(^1\) has considered

\[^1\text{W.M. Elsasser, "Harvard Meteorological Studies No. 6" Harvard University, 1942.}\]

the case of an infinite array of equally intense, equidistant lines. Because of the periodic nature of this proposed band model the fractional absorption in any period is the same as
the fractional absorption for the entire band. Goody\textsuperscript{2} has postulated a statistical or random model for the band where all arrangements of line positions are equally probable and there is no correlation between line positions and line strengths. Kaplan\textsuperscript{3} has presented a method of constructing a given band from its known lines by considering the contribution of each line to the absorption at a given frequency. Benedict\textsuperscript{4} has attempted to determine transmission functions for simple molecules from experimental data and has come to the conclusion that it is impossible to derive an adequate "universal" transmission function which may be applied without modification to any given band.

Much experimental data must be collected as a test of existing theories and before a more reliable theory can be developed.

Howard, Burch and Williams\textsuperscript{5, 6} in a study of synthetic

\begin{itemize}
\item \textsuperscript{2} R.N. Goody, Quart. J. Roy. Met. Soc., 78, 165 (1952).
\item \textsuperscript{3} L.D. Kaplan, J. Chem. Phys., 18, 186 (1950).
\item \textsuperscript{4} W. S. Benedict, Symposium on Molecular Structure and Spectroscopy, The Ohio State University, June, 1958.
\end{itemize}
atmospheres, have determined the total absorption for CO$_2$
bands at 15, 5.2, 4.8, 4.3, 2.7, 2.0, 1.6, and 1.4 microns
at absorber concentrations from 1 to 8600 atmos cm. An
atmos cm is a measure of the amount of gas contained in a
column of arbitrary length, pressure and temperature and is
defined as the path length in cm which would contain the
same number of molecules if the gas were at standard tem­
perature and pressure. Water vapor bands at 6.3, 3.2, 2.7,
1.87, 1.38, 1.1 and 0.94 microns were examined at absorber
concentrations of 0.004 to 3.8 cm of precipitable water.
Centimeters of precipitable water gives the thickness of
the layer of liquid water that would be formed if all the
water vapor transversed by the light beam were condensed
to a column of liquid whose cross-sectional area is the same
as that of the beam.

The results of this work include an extensive accumu­
lation of data relating, in tabular form, the total absorp­
tion, absorber concentration, partial pressure of absorber
and total pressure where nitrogen was used as the foreign
gas. The total pressure range was from 1 mm Hg to one atmos­
phere and the temperature remained constant.

From these data, the authors report two types of empiri­
cal relations which fit the data in different regions of
total absorption. For small values of total absorption
for large values of total absorption,

\[ \int A(\nu) d\nu = C + D \log w + K \log (P + p) \]  

where \( w \) is the absorber concentration, \( p \) is the partial pressure of the absorber, \( P \) is the total pressure and \( c, k, C, D \) and \( K \) are empirically determined constants. Qualitative arguments were advanced to justify the form of equations (1) and (2).

In the present work are presented additional data on total absorption of various bands in the infrared. The total absorption of selected bands of five different absorbing gases has been determined for a range of total pressure from 10 mm Hg to more than 3000 mm Hg. Eight non-absorbing foreign gases were used in combination with the absorbers, although not all combinations of absorber plus foreign gas were possible. The absorption cell path length was fixed at 6.3 cm and \( w \), the absorber concentration, was thus restricted to values in general lower than those of Howard, Burch and Williams. It has been possible to develop empirical equations which relate total absorption to total pressure at constant \( w \) and constant temperature over many of the pressure ranges reported. The functional relationship
between total absorption and the absorber concentration, partial pressure and total pressure, at constant temperature, are presented in tabular form along with the values of total absorption determined from the empirical equations.
Lambert's Law

The law governing the absorption of radiation by homogeneous absorbing materials was discovered by Lambert almost two centuries ago. Lambert found that when a parallel beam of monochromatic radiation passed through a homogeneous absorbing material of optical thickness or absorber concentration \( w \), the fraction of radiation removed from the beam during passage through \( dw \) could be expressed as

\[
\frac{dI(\nu)}{I(\nu)} = -k(\nu)w
\]

where \( I \) is the intensity of the beam and \( k \) is a positive constant called the absorption coefficient of the material. Integration leads to the familiar form of Lambert's law,

\[
I(\nu) = I_o(\nu) e^{-k(\nu)w}
\]

where \( I_o(\nu) \) is the intensity of the incident radiation. The fraction of radiation absorbed by the material is defined as

\[
\text{fractional absorption } A(\nu) = \frac{I_o(\nu) - I(\nu)}{I_o(\nu)}
\]
Deviations from Lambert's law in the infrared were first observed by Angstrom\(^7\) in 1892 in a low resolution study of the effects of foreign gases on the absorption by CO\(_2\). On the basis of his observations, Angstrom surmised the presence of individual absorption lines in the infrared, as then unobserved. On the basis of present understanding of band structure, a simple qualitative explanation of deviations from Lambert's law in low resolution infrared is possible. The frequency interval passed by the spectrometer yields a recorded fractional absorption \(A'(\nu)\). This absorbed energy is due entirely to the several rotational lines present within the interval. If the number of absorbing molecules in the radiation path increases, the rotational lines absorb more radiation approximately according to Lambert's law. However, the recorded fractional absorption, \(A'(\nu)\), increases more slowly than Lambert's law predicts because the observed frequency interval contains "spaces" between the lines which are unaffected by the increase in absorber concentration. Nielsen, Thornton and Dale\(^8\) have

\(^7\) K. Angstrom, Phys. Rev., 1, 597 (1892).

published a comprehensive review of these early studies in infrared absorption.

**Slit Width Effects**

A spectrometer, if set to transmit radiation at a nominal frequency, $\nu$, actually transmits a range of frequencies on either side of $\nu$. For a given dispersion, this frequency interval depends on the geometrical width of the entrance and exit slits (which are usually kept equal), diffraction in the aperture of the dispersive system, aberrations in the optical path, and energy distribution in the radiation source. Of these several causes of finite frequency interval, slit widths are the most easily varied to suit the problem under study. The character of the frequency interval passed by the spectrometer is described in terms of a so-called slit function. This function is usually a symmetrical distribution of frequencies about the spectrometer setting, $\nu$, and depends on the slit width. In cases in which it is not necessary to know the exact form of the slit function it is denoted by $f (\nu - \nu', d)$, where $d$ is the common effective width of entrance and exit slits.

If an absorption cell which contains a gas having an absorption coefficient $k(\nu)$ for radiation of frequency and optical thickness $w$ ($w = \text{gas density} \times \text{path length}$) is placed before the entrance slit of a spectrometer, one ob-
serves the fractional absorption, $A'(\nu)$, over the frequency interval passed by the spectrometer. The observed fractional absorption at frequency setting $\nu$ is defined to be

$$A'(\nu) = \frac{I_0'(\nu) - I'(\nu)}{I_0'(\nu)} = 1 - \frac{I'(\nu)}{I_0'(\nu)}$$

(5)

where $I_0'(\nu)$ is the "background" intensity transmitted when the cell is empty and $I'(\nu)$ is the intensity transmitted when the cell contains the absorbing gas. If $f(\nu)$ represents the energy distribution of the radiation reaching the entrance slit through the empty cell, $A'(\nu)$ is given by the expression

$$A'(\nu) = 1 - \frac{I'(\nu)}{I_0'(\nu)} = 1 - \frac{\int f(\nu) e^{-\frac{\nu}{\nu} \nu} f(\nu') \, d\nu}{\int f(\nu') \, d\nu}$$

(6)

It is usually the case that the frequency interval transmitted by the spectrometer is so narrow that $f(\nu)$ may be considered a constant over the interval and removed from under the integral. If one is interested in total absorption rather than fractional absorption the integral of $A'(\nu)$ over the band limits becomes important. Equation (6) then becomes
\[ \int_{\nu_1}^{\nu_2} A'(\nu) \, d\nu = \int_{\nu_1}^{\nu_2} \left[ 1 - \frac{\int_{0}^{\nu} e^{-k(\nu)w} f(|\nu - \nu'|,d) \, d\nu'}{\int_{0}^{\nu} f(|\nu - \nu'|,d) \, d\nu} \right] \, d\nu' \]

Nielsen, Thornton and Dale \(^3\) have shown that under certain conditions the integral

\[ \int_{\nu_1}^{\nu_2} A'(\nu) \, d\nu \]

becomes independent of slit width and

\[ \int_{\nu_1}^{\nu_2} A'(\nu) \, d\nu = \int_{\nu_1}^{\nu_2} \left(1 - e^{-k(\nu)w}\right) \, d\nu = \int_{\nu_1}^{\nu_2} A(\nu) \, d\nu. \] \(^8\) (8)

The conditions which allow total band absorption to be measured by \[ \int_{\nu_1}^{\nu_2} A'(\nu) \, d\nu \] and to be independent of slit width are that \(\nu_1\) and \(\nu_2\) be close together so that \(S_1\) and \(S_2\) may be regarded as equal and at the same time \((\nu_2 - \nu_1) \gg d\).

Howard, Burch and Williams \(^9\) have shown data illustrating the

\(^3\) Op. cit.

\(^8\) Op. cit.

\(^9\) Howard, Burch and Williams, Scientific Report 1, Contract AF 19(604)-516, Ohio State University Research Foundation, December, 1954.
Ladenburg and Reiche: Lorentz Lines

In 1913 Ladenburg and Reiche\textsuperscript{10} undertook a theoretical investigation of the total absorption of a Lorentz-shaped individual rotational line. In a Lorentz-shaped line the absorption coefficient is given by

\[ k(\nu) = \frac{S}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2}, \quad (9) \]

where \( \alpha \) is the half-width at half maximum \( k(\nu) \) and \( S \) is the line strength. The line strength is defined to be the integrated absorption coefficient

\[ \int_{-\infty}^{+\infty} k(\nu) d\nu = S \quad . \quad (10) \]

Ladenburg and Reiche initiated the property of the total absorption of a line being independent of slit width and when using their treatment one measures

\[ \int_{\nu_i}^{\nu_f} A'(\nu) d\nu \]
where \( \nu_1 \) and \( \nu_2 \) are the frequency limits of the line. Equation (8) can be written

\[
A(\nu) = 1 - e^{-k(\nu)}w
\]

where the absorption coefficient, \( k(\nu) \), is given by equation (9). If equation (9) is substituted in equation (11) and integrated over the frequency limits, Ladenburg and Reiche have shown

\[
\int A(\nu) d\nu = 2\pi\alpha f(x),
\]

where

\[
x = \frac{S_w}{2\pi\alpha},
\]

and

\[
f(x) = \left[ J_0(ix) - iJ_1(ix) \right],
\]

and \( J_0(ix) \) and \( J_1(ix) \) are the Bessel functions of order 0 and 1, respectively. A table of \( f(x) \) has been prepared by Stover and published as part of a paper by L.D. Kaplan and Eggers\(^{11}\) on intensities and line width in the 15 micron \( \text{CO}_2 \) band.

For very weak and very strong absorption lines, the integral has the limiting form:

$$\int A(\nu) d\nu = Sw \quad \text{(for weak lines)} \quad (13)$$

$$\int A(\nu) d\nu = 2\sqrt{S} a w \quad \text{(for strong lines).} \quad (14)$$

The total absorption of the line "grows" with increasing absorber concentration and total pressure. A "curve of growth" is obtained if one plots $\int A(\nu) d\nu$ versus $w$, the absorber concentration. For weak absorption lines $\int A(\nu) d\nu$ versus $w$ yields the so-called "linear region" of the growth curve in which the slope determines the line strength, $S$, in equation (13). If, for stronger absorption lines, $\int A(\nu) d\nu$ is plotted versus $w^{1/2}$, at constant total pressure, the so-called "square root region" of the growth curve is obtained. In this region the slope of the straight line is $2\sqrt{Sa}$ from equation (14). If $S$ has been determined from the linear region, $a$ is thus determined. Since the slit function is generally symmetrical, $\nu_0$, the frequency of the center of the absorption line is relatively easy to determine. Ladenburg and Reiche's treatment of the Lorentz-shaped spectral line then determines $\nu_0$, $S$, and $a$ without the need of corrections made necessary by finite slit width.
The line strength $S$ has been found to be nearly independent of total pressure except for gases at extremely high pressures. However, $\alpha$, the half-width, is found to depend on both temperature and pressure. It is found$^{9}$ that

$$\alpha = \alpha_0 \frac{P}{P_0} \sqrt{\frac{T_0}{T}}.$$  \hspace{1cm} (15)

Total Absorption of Individual Lines

Detailed studies of the strength, shape, width and total absorption of individual lines in molecular band spectra have been made by many workers in infrared spectroscopy. Shaw and France$^{12}$ have investigated individual rotational lines in the 4.7 micron fundamental CO band, and their study indicates that the Ladenburg and Reiche treatment is valid within the experimental error. Complete growth curves were
obtained, including the transition region between the linear and square root regions. This study indicated that the half-width depends somewhat on the nature of the foreign gas broadener.

Benedict, Herman, Moore and Silverman\textsuperscript{13} have published a comprehensive paper on the general theory of the strength, width and shape of infrared lines. They give a general survey of some theoretical relations and three types of measurements, independent of slit width, which combine to yield strength, width and shape. The first of their methods is the measurement of total line absorption. A second type of measurement of isolated lines can be made at absorber concentration which produce high absorption at the line center. The apparent breadth, \( b' \), of such a line at any particular value of \( k(\nu) \) can be measured directly from the recorder tracing and is related to the product of line strength and half-width. A third type of measurement involves measuring the absorption in the "trough" between the lines. For appreciable absorption to occur between lines it is necessary to use high absorber concentrations as in the second type measurement. In these trough measurements, corrections for slit width and line width have opposite signs, and for many

\textsuperscript{13} Benedinct et al., Canad. J. Phys., 34, 830 (1956).
cases all corrections may be neglected. Through measurements yield directly the product $S \alpha$. In a following paper\textsuperscript{14}

\textsuperscript{14} Benedict et al., Canad. J. Phys., 34, 850 (1956).

the same authors describe the application of these methods to a study of rotational lines of HCl. It is shown that at frequency intervals greater than $\sim 1.5 \text{ cm}^{-1}$ from the line centers, the absorption is greater than that given by the Lorentz shape. In the wing of the lines the absorption is better represented by a line shape which varies as $(\nu - \nu_0)^{-\lambda}$, where $\lambda \sim 1.8$.

Broadening of Spectral Lines and Bands

Early in the development of spectroscopy, workers were aware that spectral "lines" were not infinitely narrow but even under the best resolution had a finite width. Classical and quantum mechanical explanations of absorption show that even under infinite resolving power one would expect a "line" of a given "frequency" to have a finite width. The factors contributing to the finite widths of lines can be divided into three general categories: (1) "natural" width, (2) the Doppler effect, and (3) the external influences exerted on the absorbing molecule by external
electric and magnetic fields. Line broadening due to fields associated with neighboring molecules is called "pressure broadening" or "collision broadening."

Natural line width can best be explained in terms of the Heisenberg uncertainty principle. This principle states that if a molecule has a lifetime of $\Delta t$ in a given energy level, then this level has an uncertainty in energy of $\Delta E$, such that

$$\Delta E \Delta t \approx \hbar$$

When a quantum of energy is absorbed, the transition takes place between energy levels which are not infinitely narrow. When many absorption events occur the spectral "line" is broadened. It can be shown that at room temperatures, $\alpha_N$, the natural half-width of an infrared absorption line is of the order of $10^{-4} \text{ cm}^{-1}$.

The broadening of an infrared spectral line because of the Doppler effect occurs as a result of thermal motions of the molecules. This phenomenon is of considerable importance at low pressure where other broadening phenomena are less effective. At room temperature and $10^{-2} \text{ mm Hg}$ pressure, $\alpha_D$, the Doppler half-width of an infrared absorption line is of the order of $10^{-3} \text{ cm}^{-1}$. 
Pressure broadening is a phenomenon which may be described qualitatively in classical terms. If one assumes that the collision effect takes place during the time in which radiation is being emitted, the coherency of the wave-train is interrupted. A Fourier analysis of this non-coherent wave-train reveals an intense radiation at the frequency of the original coherent wave-train and less intense radiation at frequencies near the original frequency. This results in a broadened spectral line.

From the quantum-mechanical standpoint, pressure broadening involves the broadening of the energy levels of a molecule or atom by fields produced by neighboring molecules. The predominant effects are associated with electric fields and are satisfactorily accounted for in Condon's theory of the Stark effect in molecules.15 The half-width

15 E.V. Condon, Phys. Rev., 41, 759 (1932)

of a pressure broadened infrared spectral line under standard conditions is of the order of 0.1 cm⁻¹.

The influence exerted on an absorbing molecule by its neighboring molecules is the type of line broadening of fundamental importance to this study. In the Introduction it was stated that the total absorption of an entire band in the infrared was found to be a function of total pressure
where a given partial pressure of an absorbing molecule was raised to a higher total pressure by the addition of a non-absorbing gas. Collisions between the absorbing molecules themselves and between the absorbing molecules and the non-absorbing gas molecules produce "self-broadening" and the "foreign gas broadening," respectively, of the rotational lines which is observed as an increase in total absorption of the band. The term "broadener" is used to designate the non-absorbing molecule in such a collision.

Optical Collision Diameters

The concept of collision between molecules as an agent which causes a spectral line (or band) to be broadened immediately poses the question of just what constitutes a "collision" between molecules. Does the classical picture of perfectly elastic collisions between "billiard ball" molecules adequately explain the experimentally observed broadening effects? This "impact" theory assumes that a "hard" collision between molecules destroys the coherency of the radiation during the absorption process. The impact theory has been generalized to include the effects of weaker collisions which do not entirely interrupt the radiation but which, if a sufficient number occur, can cause incoherence. The impact theory has been modified somewhat by
Margenau into a statistical theory that treats the idealized physical situation in which all the molecules around the absorbing one are at rest and cause a static perturbation of the energy levels of the absorbing molecule. Various attempts have been made by Anderson\(^{17}\) and Tsao and Curnutte\(^{18}\) to obtain a general theory which would lead to the statistical and impact theories in the correct limits. Anderson's theory, based on impact considerations and assumptions about intermolecular forces, is an attempt to clarify the relationship between the statistical and impact theories. Tsao and Curnutte gave an elaboration of Anderson's work.

Regardless of the state of the theory of collision broadening it is possible, experimentally, to determine the relative "collision diameters" of the molecules involved by examining the relative "broadening ability" of the various broadening gases on the absorbing molecules. The collision diameter is defined to be the sum of the "radii" of the colliding molecules and the relative broadening


ability is defined as the relative ability of the foreign gases to affect, by collision processes, the absorption of radiation by an absorbing molecule. In the present study the broadening ability thus defined is measured in terms of the ratio of the partial pressures of the foreign gases at constant total absorption.

Whether the broadening process is one of collision or one of perturbation, if the molecules are in a state of thermal motion, it is safe to assume that the process is in some way a function of the "collision frequency" of the molecules. From kinetic theory it is shown that the

\[ F_{ab} = n_b \frac{\nu D_{ab}^2}{4} (\frac{v_a^2}{\nu_a} + \frac{v_b^2}{\nu_b})^{\frac{1}{2}}, \]  

where \( D_{ab} \) is the sum of the radii of the colliding molecules. The mean speed \( \bar{v} \) can be expressed as

\[ \bar{v} = 2 \left( \frac{2R M}{\nu M} \right)^{\frac{1}{2}}, \]  

---

where $R_N$ is the gas constant for one gram molecule, $T$ the absolute temperature and $M$ the molecular weight. Substituting equation (17) into equation (16) yields

$$F_{ab} = \bar{v}_a n_b \frac{\pi}{4} D_{ab}^2 \left( 1 + \frac{M_a}{M_b} \right)^{\frac{1}{2}}$$

(18)

If more than two types of molecules are present, equation (18) can be generalized to read

$$F_{ij} = \frac{\pi}{4} \bar{v}_i \sum_j n_j D_{ij}^2 \left( 1 + \frac{M_i}{M_j} \right)^{\frac{1}{2}}$$

(19)

If one increases the total pressure for a given concentration of absorber $a$ with foreign gas $b_1$ and then with foreign gas $b_2$ and observes that the broadening effect of $b_1$ and $b_2$ is different even if their partial pressures are the same, our assumption concerning the collision frequency would lead one to believe that the collision frequencies for the two broadeners must be different. Conversely, if the broadening effect is observed to be the same when $b_1$ and $b_2$ are at two different pressures, then the collision frequency must be the same. By using the latter concept, we equate $F_{ab1}$ and $F_{ab2}$, and equation (19) yields
where $\frac{P_{b1}}{P_{b2}}$ is the ratio of the partial pressures of broadeners $b_1$ and $b_2$ and may be used in place of $\frac{n_{b1}}{n_{b2}}$, the ratio of the densities of the broadeners as would be given by equation (19).

Because all evidence leads one to believe that pressure broadening interactions do not occur at one fixed distance, the ratio of optical collision diameters derived from the above expression do not measure a simple geometrical quantity, but instead they yield an indication of the average strength and range of the interactions between the various broadening and absorbing molecules.

It can be seen from equation (20) that the ratio of the collision diameters is proportional to the product of the pressure ratio at constant total absorption, representing the broadening ability, and a velocity "normalization" term. The collision interaction, which is a molecular property not directly measured, is thus distinguished from the observed broadening ability which is weighted by a term which depends on molecular weight.

Several procedures have been used by earlier investigators to observe relative broadening ability. Cross and Daniels, by using a low resolution spectrometer with a
thermopile-galvanometer circuit, compared the observed maximum absorption $A'(\nu)$ max. by $N_2O$ in the region of 4.5 microns, with He, A, O$_2$, N$_2$, C$_2$H$_6$, CO$_2$, and H$_2$ as broadening agents. Some measurements were also made in the 4.66 micron region of CO. Coggeshall and Saier$^{21}$ used a low resolution spectrometer with more modern detectors to examine the absorption of pressure broadened methane at 7.65 microns and CO$_2$ at 4.3 and 14.8 microns. D.F. Smith$^{22}$ has developed a method of evaluating the ratio of foreign gas to self-broadening efficiencies of the resolved rotation vibration lines of the HF fundamental vibration band in the 2.5 micron region. The method depends on the measurement of the absorption at the line peak for a sample of pure HF followed by the measurement of the absorption when the foreign gas is added to the sample. Benesch and Elder$^{23}$, using a high

\[\text{20} \quad \text{P.C. Cross and F. Daniels, J. Chem. Phys., 2, 6 (1934).}\]

\[\text{21} \quad \text{N.D. Coggeshall and E.L. Saier, J. Chem Phys., 15, 65 (1947).}\]

\[\text{22} \quad \text{D.F. Smith, "Conference on the Broadening of Spectral Lines," University of Pittsburgh, September, 1955.}\]

\[\text{23} \quad \text{Benesch and Elder,}\]
resolution spectrometer, measured the line height, as observed on the recorder, as a measure of the half-width of the $J = 2 \rightarrow 3$ line of the HCl band at 3.46 microns and the $J = 4 \rightarrow 5$ line of the CH$_4$ band at 3.25 microns. They used twin absorption cells containing identical samples of HCl (or CH$_4$) and measured the pressure ratio when both samples, broadened with different broadening gases, yielded a predetermined line height.

Present Study

In the present study, the relative broadening ability of foreign gases on the total absorption of entire bands in the infrared has been examined. The total absorption, $\int A(\nu) d\nu$, of a band has the unique characteristic of being independent of spectrometer slit width. Once the total absorption has been specified in reciprocal centimeters its value is free of restrictive conditions and may be determined independently by other investigators. For a given vibrational band and absorber concentration, growth curves of total absorption versus total pressure (absorber plus foreign gas broadener) have been obtained. From these growth curves the relative broadening ability of the several
foreign gases on the absorber is determined directly by observing the relative total absorption found at the same pressure of each foreign gas.

The relative optical collision diameters are found for each foreign gas relative to \( N_2 \). These collision diameters are found from equation (20) by using the molecular weights of the absorber and broadening gases and the ratio of the pressures which produce an equal total absorption. The relative optical collision diameters have been determined for each set of gases over a wide pressure range and have been examined to determine variations in the ratio over the range of \( \int A(\nu)\,d\nu \), the change in the ratio for the same band at different absorber concentrations, the change in the ratio for different bands of the same absorber and the change in the ratio for different absorbers and the same broadeners.

Because of the general interest of this laboratory in the field of atmospheric infrared spectroscopy, most of the gases used in this study will be found as atmospheric constituents. Table 1 lists the gases used, the absorption bands studied, and pressure range through which the data were taken.
TABLE 1

Collision Diameter Elements

<table>
<thead>
<tr>
<th>Absorber</th>
<th>Band</th>
<th>Broadeners</th>
<th>Pressure Range</th>
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<tr>
<td>N₂O</td>
<td>4.5 μ</td>
<td>N₂, O₂, He,</td>
<td>10 - 3000 mm Hg</td>
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<td>A, H₂</td>
<td></td>
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<td></td>
<td>{8.57 μ}</td>
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<td></td>
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<tr>
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<td></td>
<td></td>
<td>H₂, CH₄</td>
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<tr>
<td></td>
<td></td>
<td>CO₂, He</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>3.3 μ</td>
<td>N₂, A, He, CO₂</td>
<td>.50 - 3000 mm Hg</td>
</tr>
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</table>
Spectrometer

The spectrometer used in this study was a Perkin-Elmer Model 21 Double Beam Spectrophotometer, using a Nernst glower source, a sodium chloride prism, and a thermocouple detector. Detailed descriptions of the instrument are available from the manufacturer, but the double beam, null principle upon which it operates can be given here as a general description of the instrument.

In a conventional single beam infrared spectrometer, the radiation from the source is recorded as a varying function of frequency. This curve approximates that of a black body radiation curve, but is modified by the atmospheric water vapor and carbon dioxide absorption, by reflection losses in the optical system, and by dispersion characteristics of the prism material. If an absorbing gas is placed in the optical path, its spectrum will be superposed on this background radiation curve. If the fractional absorption at frequency $\nu$ is given by equation (5), a plot of fractional absorption versus wavelength is considered to be the absorption spectrum of the sample. Two independent scanning runs are necessary to determine transmittance in the single beam instrument. One run is
made without the sample in the beam. This determines the background radiation curve. A second run with the sample absorber in the beam gives the superposed spectrum, and a point by point calculation of fractional absorption enables one to replot the absorber spectrum versus wavelength.

The double beam instrument computes the fractional absorption automatically and continuously and the Perkin-Elmer Model 21 has the added feature of recording this fractional absorption linearly in frequency.

In the optical system, shown in Figure 1, the radiation flux is split symmetrically into two beams after the source. One beam passes through the sample cell containing the absorbing gas and the other "reference" beam passes through an identical cell which has been evacuated. The two beams are then recombined by a rotating mirrored shutter, M7 in Figure 1, which allows one beam and then the other to enter the monochromator section of the spectrometer. If any difference in intensity of the two beams occurs, the detector "sees" an alternating signal. This alternating signal, after amplification, is used to move an optical attenuator in or out of the reference beam to balance or "null" the difference in intensity of the two beams. The position of the attenuator is mechanically transmitted to the pen of the recorder. The accuracy of the measurement then depends on the linearity of the attenuator. If the attenuator is
Figure 1. Optical diagram of double beam spectrometer.
linear from 0 to 100 percent transmission, its null position is a measure of the transmission of the sample.

In the Perkin-Elmer Model 21, the optical attenuator is in the form of a multiple wedge-type diaphragm. Figure 1 shows this wedge not to scale but illustrates the following characteristics: There are six separate apertures in the wedge. These multiple apertures serve to reduce the effects of non-uniform intensity in the beam. Near the closed end the wedge openings become parallel at the width where diffraction effects might cause some of the beam to diverge from the optical path and fall beyond the limits of the prism. Each aperture is then tapered to zero successively so that the average open area is linearly proportional to the distance from the open end. Undesirable end effects at the closed end occur at less than 2 percent transmission even with the widest possible slits.

Random variations in the source output, slit width, and amplifier gain affect both beams equally and therefore do not affect the balance or null position.

In the Littrow type of monochromator the spectrum is scanned by rotating the Littrow mirror, $M_{12}$ in Figure 1. If the Littrow mirror is rotated clockwise as seen from above in Figure 1, with a uniform angular velocity, the transmitted radiation moves toward lower frequencies but is nonlinear in frequency. This nonlinearity is due to the
nonlinear variation of the index of refraction of the prism material with wavelength. In the Perkin-Elmer Model 21 the Littrow mirror is rotated by means of a lever arm fastened to the mirror shaft. This lever follows a cam which is constructed from known dispersion characteristics of the prism material and which rotates the Littrow mirror with a non-uniform angular velocity so chosen that the recorded spectrum is linear in frequency.

Gas Handling System

Figure 2 is a schematic diagram of a gas-handling system which was constructed for use in this work. A system which would allow several gases to be mixed in the absorption cell at pressures ranging from a few mm Hg to four atmospheres absolute was needed. The body of the gas handling system was constructed from AISI 316 stainless steel. The stainless steel would not only accommodate the pressure range required, but would allow the future use of many gases which are corrosive to carbon steel and non-ferrous metals. A packless type miniature valve, also constructed from 316 stainless steel, provided excellent control over gas flow.

Figure 2 shows three valves located on each side of the gas-handling system through which gases could be admitted to the system. One of the outlet valves on the left in the figure was connected to the sample cell and one to
Figure 2. Schematic diagram of gas-handling system.
the reference cell. After the entire system had been evacuated the reference cell valve could be turned off and gas admitted to the remainder of the system through any one of the four remaining outlet valves. The pressure in the system was recorded by one of four different gauges available, three of which are shown in Figure 2. Not shown is a McLeod gauge which was fastened to one of the outlet valves through a vacuum hose and was used to determine the lowest pressure to which the vacuum pump would take the system. A low pressure of several microns was satisfactory in this application to complete sufficiently the removal of gas from the sample cell. In the pressure range of 0 to 50 mm Hg a Wallace and Tiernan absolute pressure gauge was used. This gauge is calibrated from 0 to 50 mm absolute pressure in units of 0.2 mm and has an accuracy of one part in 300. A simple "U" tube manometer served to measure pressures from 50 mm Hg to two atmospheres and an Ashcroft "Duragauge," bourdon tube-type pressure gauge, calibrated from 0 to 100 pounds per square inch in units of one pound per square inch was used in the higher pressure ranges. The Ashcroft gauge was also constructed from 316 stainless steel.
Absorption Cell

A specially constructed absorption cell was used which could withstand both vacuum and pressure applications. The body of the cell was constructed from 1 3/4" diameter brass rod, 6 cm in length. A 1" diameter hole was made concentric with the longitudinal axis of the rod and the ends of the rod machined to receive 1 1/2" O.D. "O" rings. Polished rock salt windows one-half inch thick seated against the "O" rings and were held in place by one-quarter inch hard aluminum plates which clamped the entire assembly together with six 3/16" diameter brass rods threaded and bolted. Gases entered the cell through a brass tube silver soldered into the side of the cell body. A packless diaphragm type of valve opened and closed the cell to the gas-handling system. With the cell valve closed, the cell itself would remain evacuated indefinitely and pressures up to 60 pounds per square inch gauge could be maintained for a time completely adequate for the present purposes. The reference cell, since it would not be subject to high pressures, was a simple 6 cm glass cell to which one-half inch rock salt windows were fastened. Thus the sample beam and reference beam both passed through identical optical paths with the exception of the absorbing gas in the sample cell.
Calibrations and Corrections

Three adjustments are provided within the spectrometer to calibrate the prism and correct for any errors that may occur in the prism assembly. The lever which rotates the Littrow mirror may be adjusted in length to correct for any dimensional errors in the system. The adjustment is factory-set for the prism and cam for which it is to be used and required no further adjustment. The frequency setting of the spectrometer is indicated by a counter which is geared to the cam through a gear box and flexible shaft. An error in the counter produces a linear error in frequency, and corrections can be made at the junction of the counter with the flexible shaft. The Littrow mirror angle adjustment is the most critical adjustment in the system. Error in this adjustment will be most pronounced in the region where the prism dispersion is the lowest. For NaCl this occurs at about 3 microns. Calibration points given by the absorption spectrum of a polystyrene film, were sufficient to make any adjustments necessary to correct the Littrow mirror angle. In the present study, extreme accuracy in frequency setting was not necessary, since no attempt was being made to identify unknown bands.

Some randomly scattered radiation reached the detector and prevented the optical wedge from recording zero percent transmission even when it was known that the absorbing gas
was "blacking out" the radiation at a particular frequency. The scattered radiation produced an indicated one percent transmission at all frequency ranges which were used; rather than to undertake the task of locating and isolating the source of scattering, it was decided to increase the measured areas of the absorption bands by 1 percent to correct for scattered radiation.

The double beam instrument produces, in theory, a "background curve" which remains at 100 percent transmission and eliminates the need for reinterpreting the recorded spectrum in terms of a recorded background curve. In the present study, however, some difficulty was encountered in a background "drift" which in some cases amounted to 2 percent from 100 percent transmission over the frequency interval of the band. In these cases it was necessary to replot the spectrum in the frequency interval where the background drift occurred so that the replotted spectrum had 100 percent transmission as its background over the entire band. A Gerber variable scale was used in the replotting. This scale is a device which may be expanded or contracted to give one hundred divisions between zero percent transmission and background. In several cases of background shift of less than 1 percent in the wings of the band, the replotting could be done by "eye" with as much accuracy as afforded by the Gerber scale.
The gas-handling system, instead of adding the desired mixture of gases to the absorption cell, added the gases independently, and mixing took place within the cell. After the cell had been evacuated and the absorbing gas added, the gas was present at the indicated pressure in all regions of the cell which did not contain the radiation beam. This is just a necessary feature of all cell construction. When the broadening gas was added, it was necessary to know that both gases were at their respective partial pressures in all parts of the cell, since a non-homogeneous mixture would cause a fictitious spectrum to be recorded. In the present study, mixing was accomplished by allowing sufficient time for thermal motion of the molecules to insure a uniform mixture of gases. It was determined experimentally that this mixing and diffusion took place in an approximately exponential manner, with the "time constant" a function of total pressure. After the gases had been introduced into the cell, one-half hour was allowed for mixing to take place if the total pressure was above 740 mm Hg. For total pressures less than 740 mm Hg, 15 minutes wait was sufficient for complete mixing to occur.
Atmospheric CO₂ Absorption

The study of infrared absorption by CO₂ presents a special problem in instrumentation because of its presence in the air within the spectrometer. The double beam instrument used in the present study partially corrects for this by the very nature of its double beam principle; however, instruments of this type fail to record accurately the absorption of the CO₂ in the sample cell if CO₂ is present within the instrument in quantities present in the atmosphere. In Section II, the effect of finite slit width in low resolution spectroscopy was discussed. It is this finite slit width which causes the spectrometer to record inaccurately the CO₂ spectrum. Figure 3 is an illustration of conditions pertaining to the following argument.

Figure 3
Consider an idealized rotational line as a rectangle one "unit" wide with width representing units of frequency and 4 units in length representing 100 percent absorption. These idealized lines are separated by "spaces" also one unit wide. If the spectrometer slit passes 2 lines and 3 spaces between the lines, then the frequency interval observed by the spectrometer contains $5 \times 4 = 20$ units of radiation. If the gas in the sample cell has caused each line to have absorbed 50 percent of the radiation available at its own frequency a total of 4 units of radiation would have been absorbed from the interval. In an evacuated double beam instrument the optical wedge would move into the path of the reference cell and would record $4/20$ or 20 percent of the radiation absorbed. If the spectrometer is open to the atmosphere and if we assume a number of CO$_2$ molecules in the optical path equal to the number of CO$_2$ molecules in the sample cell, the sample beam would have absorbed from it an additional two units of radiation representing atmospheric CO$_2$ lines absorbing 50 percent of the radiation available to them after absorption in the sample cell. Thus 14 units of radiation reach the detector from the sample beam. In the reference beam four units of radiation are absorbed by atmospheric CO$_2$ and the optical wedge must then remove $2/16$ or 12.5 percent of the re-
remaining radiation to bring the instrument to a null reading. The spectrometer then has recorded 12.5 percent of the radiation absorbed from the interval in contrast to 20 percent removed from the same interval in the evacuated instrument.

In the present study of CO₂ absorption, the entire instrument was flushed with dry nitrogen until a single beam test showed 95 percent of the incident radiation in the reference beam reached the detector at the point of maximum atmospheric CO₂ absorption. With the concentration of CO₂ used in this report it was determined that the CO₂ remaining in the spectrometer had negligible effect on the recorded spectra and no corrections were needed.

Errors and Accuracy

In any study such as this, there are many possible sources of error. These errors may, in general, be divided into four categories: (a) errors in filling the sample cell to the desired pressure, (b) errors caused by the spectrometer recording the spectrum inaccurately, (c) errors in interpreting correctly the position of the background curve and (d) errors in measuring the area of the spectrum.

The pressure gauge used in filling the sample cell to the desired absorber concentration could be read to ± 1 percent for the lowest concentration used. An error of 1 percent in absorber concentration could produce, at most,
an error of ± 1 percent in the measured total absorption. As the total pressure is increased with a foreign gas, the rate of increase of total absorption with total pressure decreases. For total pressures up to two atmospheres the pressure was read on a mercury manometer which could easily be read to 1 mm. This represents only 1 percent error in the smallest total pressure regions and less than 0.1 percent error near two atmospheres. The bourdon tube pressure gauge was accurate to ± 25 mm Hg and was used from 1500 to 3800 mm Hg. This represents, at most, ± 1.7 percent error in pressure which would yield less than ± 1 percent error in measured total absorption. The over-all error due to inaccurately reading the pressure gauges must certainly be less than or equal to ± 1 percent for all values of absorber concentration and total pressure.

Errors in drawing the background for each spectrum can occur through faulty instrument operation and through misinterpretation of the apparent background location. Errors of this sort are particularly noticeable in spectra with low total absorption and are estimated to be ± 5 percent for total absorption less than 10 cm$^{-1}$. As the total absorption increases, the percentage of error decreases and is estimated at ± 2 percent at values of total absorption above 10 cm$^{-1}$. This is undoubtedly the largest single source of error.
The area under the spectra was measured with a compensating polar planimeter. Repeated measurements indicate that a careful operator is easily capable of measuring the area with less than ± 1 percent variation.

It is estimated that the over-all error is less than ± 4 percent if the total absorption is greater than 10 cm\(^{-1}\) and approximately ± 7 percent if the total absorption is less than 10 cm\(^{-1}\).
IV EXPERIMENTAL RESULTS

The 4.5 Micron $N_2O$ Band

The band spectra shown in Figure 4A are low resolution absorption spectra of $N_2O$ in the region of 4.5 microns. Percent transmission is recorded versus wave-number. Eight spectra are shown superposed to illustrate the growth of this band as an initial absorber concentration of $w = 0.075$ atmos cm of $N_2O$, which is equivalent to 10 mm Hg pressure of $N_2O$ in the sample cell, is increased in total pressure to 3053 mm Hg with helium. The increments of total pressure are indicated in the figure. The background spectrum which would result from scanning the same region with the sample cell evacuated is, in each spectrum, the line representing 100 percent transmission. The band limits, or frequencies outside of which this band has negligible absorption, are determined by the apparent intercept of the recorded spectrum with this background curve.

The spectrum in Figure 4A showing the smallest total absorption was recorded when the sample cell contained 10 mm Hg of $N_2O$ alone. Helium was added to bring the total pressure to 51 mm Hg and the frequency interval resampled to record the next larger value of total absorption. This process was continued in pressure increments indicated in the figure.
Figure 4

A 4.5 μ N₂O band broadened with He.
B 4.5 μ N₂O band broadened with H₂.
C 4.5 μ N₂O band broadened with CH₄.
D 4.5 μ N₂O band broadened with N₂.
The total absorptions are given by the areas under the absorption curves or above the transmission curves and were determined by measuring the curves with a Keuffel and Esser compensating polar planimeter. The areas, in cm$^2$ thus obtained were normalized to read in cm$^{-1}$ by the following method.

\[
\text{total absorption} = \frac{\text{area in cm}^2}{\text{frequency limits of band in cm}^{-1}} \times \frac{\text{area between frequency limits of band in cm}^2}{\text{frequency limits of band in cm}^{-1}}
\]

These areas, subject to corrections given in the previous section, are listed in the Tables for each band as Observed $\int A(\nu) d\nu$.

Figure 4B is the 4.5 micron band of N$_2$O showing the growth of this band when the total pressure is increased from an initial absorber concentration of $\tilde{w} = 0.075$ atmos cm to 3058 mm Hg with hydrogen. The increments of total pressure are indicated in the figure. Figure 4C shows this band broadened with CH$_4$. Other gases used as foreign gases were N$_2$, A, and O$_2$. These spectra are qualitatively similar in appearance to Figures 4A, 4B, and 4C and are not shown. The data, including concentration, total pressure and total absorption, for all the 4.5 micron N$_2$O spectra are presented in Table 5.
Figure 5. Total absorption versus total pressure - 4.5 µ N₂O band.
The relationships between $\int A(\nu) d\nu$ and total pressure for the 4.5 micron $\text{N}_2\text{O}$ band broadened with He, $\text{H}_2$, $\text{CH}_4$, $\text{N}_2$, $\text{A}$ and $\text{O}_2$ are shown graphically in Figure 5. In the figure one reads directly from the relative total absorption at constant total pressure that at total pressures of less than 1000 mm Hg, the relative broadening ability of the foreign gases on the band are He, A, O$_2$, N$_2$, CH$_4$, and H$_2$ in increasing order of effectiveness. At total pressures above 1000 mm Hg the curves all approach an asymptotic value of total absorption of about 57 cm$^{-1}$. In the 4.5 micron $\text{N}_2\text{O}$ band the rotational lines are approximately 0.8 wave-numbers apart. As pressure broadening continues, the half-width of the lines increase to the point where overlapping occurs and further increases in pressure of the broadening gas would produce little further absorption. Figure 5 indicates that at pressures above 1000 mm Hg total pressure the approach to this asymptotic value of total absorption has become such that the relative broadening ability as determined from the curves has become indeterminant.

In the lower part of Figure 5, the log-log plot of total absorption versus total pressure shows a region between 14 and 37 cm$^{-1}$ total absorption in which all the gases yield a straight line relationship. In this region the total absorption and pressure are related by
\[ \int A(\nu) d\nu = k P^m \] (21)

where the total absorption \( \int A(\nu) d\nu \) is given in terms of total pressure and empirically determined constants \( k \) and \( m \). These constants have been determined and are given in Table 2.

| Table 2 |
|---|---|---|
| | \( k \) | \( m \) |
| He | 4.35 | .364 |
| Ar | 4.69 | .353 |
| O\(_2\) | 4.62 | .362 |
| N\(_2\) | 4.44 | .387 |
| CH\(_4\) | 4.41 | .389 |
| H\(_2\) | 4.77 | .382 |

In the range of total absorption from 37 cm\(^{-1}\) to the asymptote an empirical equation of the form

\[ \int A(\nu) d\nu = C_0 + C_1 \log P + C_2 (\log P)^2 + C_3 (\log P)^3 \] (22)

was fitted to the curves. In this equation \( C_0, C_1, C_2, \) and \( C_3 \) are constants which are evaluated from the smooth curve considered to be the curve of best fit through the experimental points. The units for the constants are cm\(^{-1}\). The values of these constants for absorber concentration \( w = 0.075 \) atmos cm are given in Table 3.
In Table 5 values of total absorption calculated from the appropriate empirical equation for this band are listed together with observed total absorption.

The 4.5 micron $\text{N}_2\text{O}$ band was also examined at a partial pressure of $p = 20$ mm Hg, corresponding to an absorber concentration of $\tilde{w} = 0.15$ atmos cm, with foreign gases $\text{CH}_4$, $\text{H}_2$ and $\text{N}_2$. Figure 4D shows the growth of the band with $\text{N}_2$ as the broadener. The data for these spectra and those for $\text{CH}_4$ and $\text{H}_2$ are listed in Table 6.

The upper part of Figure 5 shows graphically the relationship between $\int A(\nu) d\nu$ and total pressure. One reads directly from the curves the relative broadening ability of the foreign gases as $\text{N}_2$, $\text{CH}_4$ and $\text{H}_2$ in increasing order of effectiveness except in a region above 1000 mm Hg total pressure where the curve for $\text{CH}_4$ is seen to rise slightly above that of $\text{H}_2$.

An empirical relationship of the form given in equation (22) was chosen to fit the smooth curve through the experimental points. The constants $c_0, \ldots, c_3$ are found from

<table>
<thead>
<tr>
<th>Band</th>
<th>$c_0$</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$c_3$</th>
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<tr>
<td>$\text{H}_2$</td>
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<td>98.38</td>
<td>-14.30</td>
<td>0.00</td>
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</table>
the curves and the value of these constants for \( w = 0.15 \text{ atmos cm} \) are given in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>( c_0 )</th>
<th>( c_1 )</th>
<th>( c_2 )</th>
<th>( c_3 )</th>
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<td>( \text{H}_2 )</td>
<td>41.97</td>
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<td>39.93</td>
<td>-5.87</td>
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</table>

In Table 6 values of total absorption evaluated from the appropriate empirical equation for this band and partial pressure are listed together with observed total absorption.

Let us assume in this case that the relative broadening ability of two foreign gases acting on the same absorber at the same conditions of absorber concentration and total pressure is measured by the relative total absorption under these conditions. We also assume that the total absorption is a function of the collision frequency between molecules. From equation (16) we see that this function may be expressed as

\[
\int A(\nu) d\nu \sim F_{ab} \sim n_b \frac{D_{ab}}{v_a + v_b^2} \frac{v_a^2}{v_b^2}.
\]

where \( a \) represents the absorbing molecule, \( b \) represents the broadening molecule, \( n \) is the density which may be
replaced by \( P \) the partial pressure of \( b \), \( D \) is the sum of the diameters of \( a \) and \( b \), and \( \overline{v} \) is the velocity.

Suppose one measures the relative broadening ability, thus defined, of two different foreign gases, \( b_1 \) and \( b_2 \), acting on the same absorber. If the experiment is done at a single value of \( P \), one can write

\[
\frac{F_{ab_1}}{F_{ab_2}} \sim P'_{b_1} D_{ab_1} (\overline{v}_a + \overline{v}_{b_1})^{\frac{1}{2}}
\]

\[
\frac{F_{ab_2}}{F_{ab_2}} \sim P'_{b_2} D_{ab_2} (\overline{v}_a + \overline{v}_{b_2})^{\frac{1}{2}}
\]

Since \( P'_{b_1} = P'_{b_2} \),

\[
\frac{F_{ab_1}}{F_{ab_2}} = \frac{D_{ab_1} (\overline{v}_a + \overline{v}_{b_1})^{\frac{1}{2}}}{D_{ab_2} (\overline{v}_a + \overline{v}_{b_2})^{\frac{1}{2}}}
\]

Assume in this case that it is observed that \( F_{ab_1} \) > \( F_{ab_2} \). If the experiment is performed again at a higher value of \( P' \), one can write as before

\[
\frac{F_{ab_1}}{F_{ab_2}} = \frac{D_{ab_1} (\overline{v}_a + \overline{v}_{b_1})^{\frac{1}{2}}}{D_{ab_2} (\overline{v}_a + \overline{v}_{b_2})^{\frac{1}{2}}}
\]

Assume that at this higher value of \( P' \) one observes that \( F_{ab_1} < F_{ab_2} \). Since the velocity portion of the ratio is independent of pressure, one can only assume that the ratio of the collision diameters have changed and thus the collision diameter must itself be a function of pressure.
TABLE 5
Total absorption of the 4.5 μ N 2 O band

\[ \tilde{\omega} = 0.075 \text{ atmos cm} \]

\[ p = 10 \text{ mm Hg} \]

Calculated values of \( \int A(\nu) d\nu \) are based on equations (21) and (22) discussed in the text.

<table>
<thead>
<tr>
<th>Broadening Gas</th>
<th>Chart No.</th>
<th>Total Pressure ( \text{mm Hg} )</th>
<th>Observed ( \int A(\nu) d\nu ) ( \text{cm}^{-1} )</th>
<th>Calculated ( \int A(\nu) d\nu ) ( \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>475</td>
<td>10</td>
<td>11.6</td>
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Total absorption of $4.5 \mu m$ N$_2$O band

$w = 0.15$ atmos cm
$p = 20$ mm Hg

Calculated values of $\int A(\nu)d\nu$ are based on equation (22) discussed in the text.

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The 7.78 and 8.57 Micron Bands of $\text{N}_2\text{O}$

The 7.78 and 8.57 micron absorption bands of $\text{N}_2\text{O}$ occur so close together in the spectrum that some overlapping of the wings of the bands occurs at either high absorber concentrations or lower absorber concentrations at high total pressure. For this reason the spectra of these two bands were recorded on the same tracing under the same conditions of absorber partial pressure and total broadened pressure. Figure 6A shows the growth of these spectra as recorded when the total pressure is increased from an initial absorber concentration of $\bar{\omega} = 0.75$ atmos cm, corresponding to 100 mm Hg initial pressure of $\text{N}_2\text{O}$, to over 3000 mm Hg with helium. The increments of total pressure are indicated in the legend of the figure. In Figure 6B the same $\text{N}_2\text{O}$ bands are shown broadened by nitrogen. Other gases used as broadening agents for the 7.78 and 8.57 micron $\text{N}_2\text{O}$ bands were $\text{A, H}_2\text{CO}_2$, $\text{O}_2$ and $\text{CO}$. These spectra are qualitatively similar in appearance to Figure 6 and are not shown.

Figures 6A and 6B both show the slight overlapping which occurs from 1210 to 1220 cm$^{-1}$. Because of this overlapping it is difficult to know the exact shape of the wings of the band in this region. For purposes of measuring total absorption, however, it is not necessary to know this shape and the spectra were divided by a vertical line drawn from
Figure 6 A 7.78 and 8.57 μN₂O bands broadened with He.
B 7.78 and 8.57 μN₂O bands broadened with N₂.
the recorded tracing to the background (100 percent transmission) at 1215 cm\(^{-1}\) as the "dividing" line. The data, including absorber concentration, total pressure and total absorption for all the 7.78 micron \(\text{N}_2\text{O}\) spectra are presented in Table 8. Similar data for the 8.57 micron \(\text{N}_2\text{O}\) band are presented in Table 9.

The relationship between total absorption and total pressure for the 7.78 and 8.57 micron bands broadened with He, \(\text{N}_2\), A, \(\text{H}_2\), \(\text{CO}_2\), \(\text{O}_2\) and CO is shown graphically plotted on a log-log scale in Figure 7. The figure shows the relative broadening ability of these foreign gases on the 7.78 micron \(\text{N}_2\text{O}\) band to be He, \(\text{O}_2\), A, CO, \(\text{N}_2\), \(\text{CO}_2\) and \(\text{H}_2\) in increasing order of effectiveness. The figure also indicates that the total absorption of the band increases rapidly with increased total pressure until the total pressure reaches approximately 1000 mm Hg, then approaches an asymptotic value of about 67 cm\(^{-1}\).

The empirical equation (22) was chosen to represent this "growth" curve. For \(w = 0.75\) atmos cm these constants have been determined and are listed in Table 7. In Table 8 values of total absorption calculated from the above empirical equation for this band are listed together with observed total absorption.
Figure 7. Total absorption versus total pressure - 7.78 & 8.57 μm N₂O bands.
For the 8.57 micron band the total absorption is less than 9 cm$^{-1}$ for the highest total pressure used. The estimated error for total absorption less than 10 cm$^{-1}$ is given in Section III as $\pm$ 7 percent. The data for the 8.57 micron band lie within this estimated error but scatter among the data makes it difficult to draw reliable curves through points representing the different foreign gases. In Figure 7 two curves are shown for the 8.57 micron band. The lower curve is an apparent best fit through the points for He. The upper curve is an "average" curve through all the data points to show the general growth of the band with total pressure. No attempt has been made to establish an empirical equation for these curves. The data are presented in Table 9.

For the 8.57 micron band the total absorption is less than 9 cm$^{-1}$ for the highest total pressure used. The estimated error for total absorption less than 10 cm$^{-1}$ is given in Section III as $\pm$ 7 percent. The data for the 8.57 micron band lie within this estimated error but scatter among the data makes it difficult to draw reliable curves through points representing the different foreign gases. In Figure 7 two curves are shown for the 8.57 micron band. The lower curve is an apparent best fit through the points for He. The upper curve is an "average" curve through all the data points to show the general growth of the band with total pressure. No attempt has been made to establish an empirical equation for these curves. The data are presented in Table 9.
TABLE 8

Total absorption of the 7.78 μ N₂O band

\[ \text{w} = 0.75 \text{ atmos cm} \]
\[ \text{p} = 100 \text{ mm Hg} \]

Calculated values of \( \int A(\nu) d\nu \) are based on equation (22) discussed in the text.

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The 4.7 Micron CO Band

The band spectra shown in Figure 8 are low resolution absorption spectra of CO in the region of 4.7 microns. The spectrum showing the smallest total absorption in the figure was recorded when the sample cell contained 100 mm Hg of CO alone corresponding to $\bar{\omega} = 0.75$ atmos cm. Figure 8A then shows this spectrum as helium was added to the CO to increase the total pressure to over 3000 mm Hg, as indicated in the legend of the figure. Figure 8B shows the 4.7 micron band of CO and the growth of this band when nitrogen was added to increase the total pressure from 100 mm Hg initial pressure of CO to over 3000 mm Hg total pressure. Other gases used as broadeners of the CO band were CH$_4$, A, and H$_2$. These spectra are qualitatively similar in appearance to Figures 8A and 8B and are not shown. The data, including absorber concentration, total pressure and total absorption, for all the 4.7 micron CO spectra are presented in Table 11.

The relationships between total absorption and total pressure for the 4.7 micron CO band broadened with He, N$_2$, CH$_4$, A, and H$_2$ are shown graphically, plotted on a log-log scale, in Figure 9. The figure shows the relative broadening ability of these foreign gases on the 4.7 micron CO band to be He, A, H$_2$, N$_2$ and CH$_4$ in increasing order of
Figure 8 A 4.7 μ CO band broadened with He

B 4.7 μ CO band broadened with N₂
Figure 9. Total absorption versus total pressure - $4.7 \mu$ CO band
effectiveness. Figure 9 also shows that the band is still in a rapid state of growth even at the highest total pressure used. The rotational lines of CO are approximately 4 wavenumbers apart, compared with 0.8 wavenumbers for the 4.5 micron N₂O band and thus overlapping of the rotational lines apparently has not begun to limit the absorption at the highest total pressures available in this study.

The equation chosen to represent these growth curves is of the form (22). The empirical constants are given in Table 10.

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In Table 11 values of total absorption calculated from the above empirical equation for this band are listed together with observed total absorption.
TABLE 11

Total absorption of the 4.7 \( \mu \) CO band

\[
\begin{align*}
\text{w} &= 0.75 \text{ atmos cm} \\
\text{p} &= 100 \text{ mm Hg}
\end{align*}
\]

Calculated values of \( \int A(\nu)\,d\nu \) are based on equation (21) discussed in the text.

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<th>Broadening Gas</th>
<th>Chart No.</th>
<th>Total Pressure in mm Hg</th>
<th>Observed ( \int A(\nu),d\nu ) cm(^{-1})</th>
<th>Calculated ( \int A(\nu),d\nu ) cm(^{-1})</th>
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The 4.2 Micron CO₂ Band

The band spectra shown in Figure 10 are low resolution absorption spectra of CO₂ in the region of 4.2 microns. The spectrum showing the smallest absorption in the figure was recorded when the sample cell contained 50 mm Hg of CO₂ alone corresponding to \( w = 0.375 \) atmos cm. Figure 10 then shows this spectrum as N₂ was added at several values of total pressure as indicated in the figure. Other gases used as broadeners of the 4.2 micron CO₂ band were He, O₂, H₂, and A. These spectra are qualitatively similar in appearance to Figure 10 and are not shown. The data including absorber concentration, total pressure and observed total absorption for all the 4.2 micron CO₂ spectra are recorded in Table 13.

The relationship between total absorption, \( \int A(\nu) d\nu \), and total pressure for CO₂ with N₂, He, O₂, A and H₂ as non-absorbing gases are shown graphically, plotted on a semi-logarithmic scale in Figure 11.

At an initial pressure of CO₂ of 50 mm Hg the figure shows the relative broadening ability of these foreign gases on the band to be He, A, O₂, N₂ and H₂ in increasing order of effectiveness. At 200 mm Hg partial pressure of CO₂, corresponding to \( w = 1.5 \) atmos cm, the absorption has become so great that the observed difference in pressure broadening effects by the various gases has been
Figure 10. $4.2 \mu \mathrm{CO}_2$ band broadened with $\mathrm{N}_2$. 

$w = 0.375 \text{ ATMOS CM}$

$P = 50 \text{ mm Hg}$

200

400

740
Figure 11. Total absorption versus total pressure - 4.2 μ CO₂ band.
reduced to the point that the data no longer yield relative broadening abilities.

For \( w = 0.375 \) atmos cm the logarithmic series of the form of equation (22) was chosen to fit the smooth curves drawn through the experimental points with the constants listed in Table 12.

**TABLE 12**

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<th>( c_3 )</th>
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</table>

For \( w = 1.5 \) atmos cm a single curve whose equation is

\[
P = 0.0214 \times (1.101)^P \int A(v)dv \tag{23}
\]

or

\[
\int A(v)dv = \frac{\log P - \log 0.0214}{\log 1.101}
\]

yields a straight line on the semi-logarithmic scale of Figure 11. All of the experimental points recorded for \( w = 1.5 \) atmos cm lie within \( \pm 2 \) percent of this curve which is within the estimated experimental error.
TABLE 13

Total absorption of the 4.2 μ CO₂ band

\[ w = 0.35 \text{ atmos cm} \]
\[ p = 50 \text{ mm Hg} \]

Calculated values for \( \int A(\nu) d\nu \) are based on equation (22) discussed in the text.

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<th>Broadening Gas</th>
<th>Chart No.</th>
<th>Total Pressure in mm Hg</th>
<th>Observed ( \int A(\nu) d\nu ) cm(^{-1} )</th>
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TABLE 14

Total absorption of the $4.2 \mu$ CO$_2$ band

\[ w = 1.5 \text{ atmos cm} \]
\[ p = 200 \text{ mm Hg} \]

Calculated values of $\int A(\nu)\,d\nu$ are based on equation (23) discussed in text.

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The 3.36 Micron Band of \( \text{C}_2\text{H}_6 \)

The low resolution absorption spectrum of \( \text{C}_2\text{H}_6 \) in the region of 3.36 microns is not a simple single vibration-rotation band, but is a superposition of 5 infrared vibration-rotation bands.\(^{24}\) Two vibrational modes, \( \nu_5 \) and \( \nu_7 \) appear as fundamentals and the others as the following overtone, combination and combination-overtone bands: \(( \nu_3 + \nu_9 + \nu_{11} ), (2 \nu_4 + \nu_8 + \nu_{12} ), ( \nu_2 + \nu_3 + \nu_9 ), ( \nu_8 + 2 \nu_9 ), ( \nu_3 + \nu_9 + \nu_{12} ), ( \nu_6 + 2 \nu_9 ), ( \nu_8 + \nu_{11} ), ( \nu_2 + \nu_6 ) \) and \(( \nu_3 + 2 \nu_9 ) \).

Figure 12 shows the growth of this band as 10 mm Hg partial pressure, corresponding to \( w = 0.075 \) atmos cm, has nitrogen added to a total pressure of more than 3000 mm Hg. The increments of total pressure are indicated in the figure. Other gases used as broadeners of the 3.36 micron \( \text{C}_2\text{H}_6 \) band were He, A, CO\(_2\) and N\(_2\)O. Their spectra are essentially similar in appearance and are not presented in figures.

Figure 12. 3.36 μ C₂H₆ band broadened with N₂.
The relationship between total absorption and total pressure for the band broadened with He and N₂ is shown graphically, plotted on a semi-logarithmic scale, in Figure 13. The extremely slow rate of growth coupled with the very small total absorption led to a situation where scattering in the data partially obscured any quantitative results. The great number of individual rotational lines which make up the 3.36 micron "band" of C₂H₆ probably preclude any large pressure broadening effects, since overlapping of the lines probably begins at very low pressures. Figure 13 contains points determined from all gases used as broadeners, but curves were drawn only through points representing total absorption versus total pressure of helium and nitrogen. The relative broadening ability of nitrogen was greater than that of helium as has been the case with all other bands studied. No attempt was made to determine an empirical fit for the curves. The data, including absorber concentration, total pressure, and observed total absorption are presented in Table 15. The band is observed to grow rapidly with increasing absorber concentration. It would be interesting to have data for this band taken with a higher absorber concentration. Errors inherent in measuring small absorber concentrations could be minimized and more reliable results obtained.
Figure 13. Total absorption versus total pressure - 3.36 μ C₂H₆ band.
TABLE 15

Total absorption of the 3.36 μ C₂H₆ band

\( w = 0.075 \text{ atmos cm} \)

\( p = 10 \text{ mm Hg} \)

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The 3.3 Micron CH$_4$ Band

The bands shown in Figure 14 are low resolution absorption spectra of CH$_4$ in the 3.3 micron region. The spectrum with the smallest total absorption was recorded when the sample cell contained 50 mm Hg of CH$_4$ alone, corresponding to $w = 0.375$ atmos cm. Figure 14 then shows the growth of this band as nitrogen was added to the total pressure in pressure increments indicated in the figure. Other gases used as broadeners of the 3.3 micron CH$_4$ band were A, He, and CO$_2$. These spectra are essentially similar in appearance to Figure 14 and are not shown. The data, including absorber concentration, total pressure and observed total absorption for all the 3.3 micron CH$_4$ spectra are recorded in Table 17.

The relationship between total absorption and total pressure for CH$_4$ using N$_2$, A, He and CO$_2$ as non-absorbing gases with which to increase the total pressure is shown graphically plotted on a log-log scale, in Figure 15. The figure shows the relative broadening ability of these foreign gases on the band to be He, A, N$_2$ and CO$_2$ in increasing order of effectiveness.

In the region between 100 and 3000 mm Hg total pressure the data yield a straight line relationship on the log-log scale of Figure 15. In this region the total
Figure 14. 3.3 μ CH₄ band broadened with N₂.
Figure 15. Total absorption versus total pressure - 3.3 μ CH₄ band.
absorption and total pressure are related by a simple relation of the form of equation (21) with the constants given in Table 16.

**TABLE 16**

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In Table 17, values of total absorption calculated from the appropriate empirical equation for this band are listed together with the observed total absorption.
TABLE 17

Total absorption of the 3.3 μ CH₄ band

\[ w = 0.35 \text{ atmos cm} \]
\[ p = 50 \text{ mm Hg} \]

Calculated values for \( \int A(\nu) d\nu \) are based on equation (21) discussed in the text.

<table>
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<tr>
<th>Broadening Chart No.</th>
<th>Total Pressure in mm Hg</th>
<th>Observed ( \int A(\nu) d\nu ) cm⁻¹</th>
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The experimental determination of molecular collision diameters from infrared band measurements can be accomplished in the present study by reference to equation (20)

\[
\frac{D_{ab2}}{D_{ab1}} = \left[ \frac{P_{b1}'}{P_{b2}'} \right]^{1/2} \left[ \frac{m_{b2}(m_a + m_{b1})}{m_{b1}(m_a + m_{b2})} \right]^{1/2}
\]

and Figures 5, 7, 9, 11, 13 and 15 relating total absorption versus total pressure for the several absorption bands under consideration. Equation (20) was derived from kinetic theory considerations of collision frequencies and the assumption that pressure broadening effects and hence total absorption are a function of these collision frequencies. For example, Figure 5 shows the relation between \( \int A(\nu) d\nu \) and total pressure for the 4.5 micron \( \text{N}_2\text{O} \) band broadened with \( \text{N}_2, \text{H}_2, \text{He}, \text{A}, \text{O}_2 \) and \( \text{CH}_4 \). At a total absorption of 30 cm\(^{-1}\) the total pressure of \( \text{N}_2\text{O} \) plus He is 200 mm Hg. The partial pressure of the \( \text{H}_2 \) and He alone are then 115 and 190 mm Hg respectively. Thus for hydrogen to produce a total absorption of 30 cm\(^{-1}\) requires a partial pressure of hydrogen almost 40 percent less than that required for helium to produce the same total absorp-
tion. This high relative broadening ability of hydrogen is because the velocity and thus the collision frequency of hydrogen is higher than that of helium. From the relative velocities of H₂ and He we see,

\[ \text{velocity of } H_2 = \sqrt{2} \times \text{velocity of He} \]

which is very close to 40 percent. In equation (20) the bracketed term to the \( \frac{1}{2} \) power is a velocity "normalization" term which modifies the pressure ratio representing the broadening ability. Thus

\[ \frac{D_\text{N₂O} - H_2}{D_\text{N₂O} - H_\text{e}} = 1.1 \]

from equation (20) and the collision diameter of hydrogen plus N₂O is only 10 percent greater than the collision diameter of helium plus N₂O.

In the previous example hydrogen and helium were chosen as broadening gases because they showed the greatest difference in broadening ability. In the present study nitrogen was chosen as the broadening gas to which all others would be compared.

The ratio \( \frac{D_\text{N₂O} - H_2}{D_\text{N₂O} - N_2} \) can be calculated from equation (20) and Figure 5 for a range of values of total absorption and yields an indication whether or not the relative collision diameter changes for a given band.
and broadening gases at different regions of total pressure. It can be seen from Figure 5, however, that because of the asymptotic character of the curves in the higher pressure regions it becomes increasingly difficult to read the pressure ratio from the curves in these regions. In Table 18 the collision diameters for the 4.5 micron N₂O band, \((D_{N₂O} - b)\), where \(b\) is He, O₂, A, H₂ or CH₄, are listed relative to \(D_{N₂O} - N₂\) with the pressure range over which the curves were found to yield values of the pressure ratio to ± 1.0 percent and an indication of the constancy of this ratio over the range is given by the mean deviation from the mean value of the ratio over the pressure range and the percent of the mean deviation from the mean.

In a similar manner the relative collision diameters were calculated for the 4.6 \(\mu\) CO, 4.2 \(\mu\) CO₂, 3.3 \(\mu\) CH₄ and 3.3 \(\mu\) CH₄ bands with several broadening gases and are listed together with the 4.5 \(\mu\) N₂O band in Table 18.
<table>
<thead>
<tr>
<th>Total Pressure Range</th>
<th>Absorber</th>
<th>Broadener</th>
<th>( \frac{D_{ab}}{D_{aN_2}} ) (mean)</th>
<th>Mean Deviation from Mean</th>
<th>Percent of Mean Deviation from Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 to 1000 mm Hg</td>
<td>He</td>
<td>O₂</td>
<td>0.581</td>
<td>0.008</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>C₂H₂</td>
<td>H₂</td>
<td>0.928</td>
<td>0.016</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>H₂</td>
<td>0.641</td>
<td>0.016</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>0.945</td>
<td>0.005</td>
<td>0.50</td>
</tr>
<tr>
<td>40 to 800 mm Hg</td>
<td>H₂</td>
<td>H₂</td>
<td>0.690</td>
<td>0.009</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>1.025</td>
<td>0.011</td>
<td>1.11</td>
</tr>
<tr>
<td>130 to 1000 mm Hg</td>
<td>He</td>
<td>O₂</td>
<td>0.569</td>
<td>0.009</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>C₂H₂</td>
<td>H₂</td>
<td>0.635</td>
<td>0.004</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>H₂</td>
<td>0.867</td>
<td>0.025</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>1.148</td>
<td>0.017</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂</td>
<td>0.997</td>
<td>0.004</td>
<td>0.43</td>
</tr>
<tr>
<td>200 to 3000 mm Hg</td>
<td>He</td>
<td>O₂</td>
<td>0.564</td>
<td>0.004</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>C₂H₂</td>
<td>H₂</td>
<td>0.920</td>
<td>0.017</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>0.956</td>
<td>0.005</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂</td>
<td>0.978</td>
<td>0.002</td>
<td>0.49</td>
</tr>
<tr>
<td>70 to 700 mm Hg</td>
<td>He</td>
<td>O₂</td>
<td>0.521</td>
<td>0.011</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>C₂H₂</td>
<td>H₂</td>
<td>0.919</td>
<td>0.012</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>A</td>
<td>0.624</td>
<td>0.010</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>0.927</td>
<td>0.019</td>
<td>2.05</td>
</tr>
<tr>
<td>50 to 1000 mm Hg</td>
<td>He</td>
<td>O₂</td>
<td>0.366</td>
<td>0.025</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>C₂H₂</td>
<td>H₂</td>
<td>0.505</td>
<td>0.025</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>A</td>
<td>0.562</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 to 2500 mm Hg</td>
<td>He</td>
<td>O₂</td>
<td>0.562</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₂</td>
<td>H₂</td>
<td>0.927</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Total pressure range over which the average value of \( \frac{D_{ab}}{D_{aN_2}} \) was calculated.

(1) 4.5 μ, p = 10 mm Hg, w = 0.075 atmos cm
(2) 4.5 μ, p = 20 mm Hg, w = 0.15 atmos cm
(3) 7.78 μ, p = 100 mm Hg, w = 0.75 atmos cm
(4) 4.7 μ, p = 100 mm Hg, w = 0.75 atmos cm
(5) 4.2 μ, p = 50 mm Hg, w = 0.37 atmos cm
(6) 5.36 μ, p = 10 mm Hg, w = 0.075 atmos cm
(7) 5.3 μ, p = 50 mm Hg, w = 0.37 atmos cm
In Section II the work of Cross and Daniels\textsuperscript{20} was discussed along with their experimental method which led to the determination of molecular collision diameters. Their values of collision diameter ratios measured at 4.5 microns for \textit{N}_2\textit{O} and 4.66 microns for CO are listed in Table 19 for several foreign gases which were used in common with the present study. It must be emphasized again that Cross and Daniels' values are given for a single frequency representing the center of the small frequency interval passed by the spectrometer, and thus for reproducibility, are highly dependent on spectrometer slit width. The values of collision diameter reported from the present study are given from data on the total absorption of entire bands and are independent of slit width.

In contrast to determining molecular collision diameters by measuring total absorbed areas in low resolution, Benesch and Elder have used a high resolution spectrometer and observed a quantity proportional to the line width of an individual rotational line. They determined that the observed recorder deflection was a highly sensitive measure of line width if the spectrometer slit width was larger
than the line width and in addition if the line was essentially black at its center. Using kinetic theory collision frequency arguments similar to those in this study, they reported the broadening ability and the collision diameters based on the \( J = 2 \rightarrow 3 \) line of HCl and the \( J = 4 \rightarrow 5 \) line of \( \text{CH}_4 \). Table 20 is a comparison of the results of Benesch and Elder with the results of the present study as far as is applicable. In the table the broadening ability of a given gas is related to that of helium and the collision diameter, \( D_{ab} \), is arbitrarily normalized to \( D_{a \text{He}} = 2.0 \).

**TABLE 19**

Comparison of Collision Diameters

<table>
<thead>
<tr>
<th>( \frac{D_{ab}}{D_{a \text{N}_2}} )</th>
<th>( a = \text{N}_2 \text{O} )</th>
<th>( a = \text{CO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b )</td>
<td>Cross &amp; Daniels</td>
<td>Present Study</td>
</tr>
<tr>
<td>He</td>
<td>0.63</td>
<td>0.581</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>0.70</td>
<td>0.641</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>0.97</td>
<td>0.931</td>
</tr>
<tr>
<td>A</td>
<td>0.98</td>
<td>0.928</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>1.00</td>
<td>1.000</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_6 )</td>
<td>1.09</td>
<td>-</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>1.23</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE 20
Comparison of Broadening Ability and Collision Diameters

Broadening Ability *

<table>
<thead>
<tr>
<th>b</th>
<th>Benesch &amp; Elder</th>
<th>Present Study</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCl</td>
<td>CH₄</td>
</tr>
<tr>
<td>He</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>A</td>
<td>1.87</td>
<td>1.39</td>
</tr>
<tr>
<td>O₂</td>
<td>1.79</td>
<td>1.47</td>
</tr>
<tr>
<td>N₂</td>
<td>2.35</td>
<td>1.73</td>
</tr>
<tr>
<td>CO</td>
<td>3.76</td>
<td>1.60</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.56</td>
<td>1.73</td>
</tr>
<tr>
<td>CH₄</td>
<td>5.48</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Collision Diameters **

<table>
<thead>
<tr>
<th>b</th>
<th>D_HCl-b</th>
<th>D_CH₄-b</th>
<th>D_N₂O-b</th>
<th>D_N₂O-b</th>
<th>D_CO-b</th>
<th>D_CH₄-b</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>A</td>
<td>3.57</td>
<td>3.24</td>
<td>3.19</td>
<td>3.37</td>
<td>3.26</td>
<td>3.31</td>
</tr>
<tr>
<td>O₂</td>
<td>3.92</td>
<td>3.62</td>
<td>3.20</td>
<td>3.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N₂</td>
<td>4.61</td>
<td>2.28</td>
<td>2.21</td>
<td>2.34</td>
<td>1.96</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>5.58</td>
<td>3.82</td>
<td>3.44</td>
<td>3.53</td>
<td>3.54</td>
<td>3.56</td>
</tr>
<tr>
<td>CO₂</td>
<td>6.13</td>
<td>3.51</td>
<td>-</td>
<td>3.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>7.12</td>
<td>3.70</td>
<td>-</td>
<td>4.05</td>
<td>-</td>
<td>4.11</td>
</tr>
</tbody>
</table>

*Broadening Ability normalized to $P_{r He}'/P_{He}' = 1.00$

**Collision Diameter normalized to $D_{a-He} = 2.00$
Relative collision diameters have also been reported from studies in atomic spectroscopy. From experimental values of the absorption of mercury vapor in the presence of foreign non-absorbing gases, Zemansky\textsuperscript{25} has evaluated the half-widths of the collision broadened line and plotted these half-widths as a function of the pressure of each gas used as a broadener. The curves of half-width versus pressure yield the effective collision diameter for each foreign gas molecule plus mercury from a calculation similar to applying equation (20) in the present study. Zemansky assumes that, in the collision process, the mercury atom has a constant radius equal to the gas-kinetic radius ($1.8 \times 10^{-8}$ cm) and Table 21 gives his values of the effective radius of each foreign gas used. Füchtbauer has reported similar findings using very high foreign gas pressures and these results are discussed by Zemansky in relation to those reported in his own work. Table 21 also lists the effective radii of the foreign gases reported by Füchtbauer.

With a notation similar to that used in the present study these radii are listed in Table 21 as "$R_b$". A comparison with the results of the present study can be made.
by constructing $D_{ab}$ from the values of $R_b$ listed in Table 21 where the absorbing gas, $a$, in the present study, has been used as a broadening gas $b$ for the mercury vapor. $D_{ab} = R_b' + R_b$ where $b'$ is an absorber in the present study which was used as a broadener by Zemansky or Flüchtbauer. Nitrous oxide was not used by either Zemansky or Flüchtbauer and comparison must be made by assuming a value for the radius of $N_2O$. Table 22 gives the values of relative collision diameter obtained from the present study, taken from Table 18, and values of the collision diameter constructed from the effective molecular radii reported by Zemansky and Flüchtbauer.

It must be emphasized that $D_{ab}/D_{aN_2}$ constructed from atomic and molecular effective radii and compared with a similar quantity determined as a single parameter from the present work can not be compared in the sense that, if a difference occurs, one or the other is in error. In view of the looseness of the concept of "effective radii," it is perhaps remarkable that the comparison is as close as it is.
TABLE 21
Effective Collision Radii

<table>
<thead>
<tr>
<th>Broadener b</th>
<th>Zemansky $R_b$ (x10^-8 cm)</th>
<th>Flüchtbauer $R_b$ (x10^-8 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.08</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>3.15</td>
<td>3.47</td>
</tr>
<tr>
<td>CO</td>
<td>4.88</td>
<td>-</td>
</tr>
<tr>
<td>N₂</td>
<td>5.35</td>
<td>6.25</td>
</tr>
<tr>
<td>A</td>
<td>6.05</td>
<td>7.64</td>
</tr>
<tr>
<td>NH₃</td>
<td>6.65</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>4.71</td>
<td>-</td>
</tr>
<tr>
<td>C₂H₈</td>
<td>6.78</td>
<td>-</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>9.40</td>
</tr>
<tr>
<td>H₂O</td>
<td>-</td>
<td>6.48</td>
</tr>
<tr>
<td>O₂</td>
<td>-</td>
<td>6.27</td>
</tr>
</tbody>
</table>
## TABLE 22
Comparison of Collision Diameters

<table>
<thead>
<tr>
<th>Absorber</th>
<th>a</th>
<th>b</th>
<th>(D_{ab}) Present Study</th>
<th>(D_{ab}) Zemansky</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_2O)</td>
<td>He</td>
<td>0.581</td>
<td>0.64</td>
<td>0.06</td>
<td>Assume</td>
</tr>
<tr>
<td>4.5</td>
<td>O(_2)</td>
<td>0.931</td>
<td>-</td>
<td>-</td>
<td>(D_{N2O} = D_{CH_4})</td>
</tr>
<tr>
<td>p=10 mm</td>
<td>H(_2)</td>
<td>0.928</td>
<td>1.07</td>
<td>0.15</td>
<td>from Zemansky</td>
</tr>
<tr>
<td></td>
<td>CH(_4)</td>
<td>0.943</td>
<td>1.00</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>p=20 mm</td>
<td>H(_2)</td>
<td>0.690</td>
<td>0.78</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH(_4)</td>
<td>1.025</td>
<td>1.00</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.02</td>
</tr>
<tr>
<td>(N_2O)</td>
<td>He</td>
<td>0.569</td>
<td>0.68</td>
<td>0.12</td>
<td>Assume</td>
</tr>
<tr>
<td>7.78</td>
<td>H(_2)</td>
<td>0.635</td>
<td>0.79</td>
<td>0.16</td>
<td>(D_{N2O} = D_{CO})</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>0.957</td>
<td>1.06</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(_2)</td>
<td>0.867</td>
<td>-</td>
<td>-</td>
<td>from Zemansky</td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
<td>1.148</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>He</td>
<td>0.564</td>
<td>0.68</td>
<td>0.12</td>
<td>Zemansky</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>0.920</td>
<td>1.06</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(_2)</td>
<td>0.556</td>
<td>0.79</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH(_4)</td>
<td>0.978</td>
<td>0.94</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.04</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>He</td>
<td>0.521</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(_2)</td>
<td>0.919</td>
<td>1.00</td>
<td>0.08</td>
<td>Fichtbauer</td>
</tr>
<tr>
<td></td>
<td>H(_2)</td>
<td>0.624</td>
<td>0.82</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>0.927</td>
<td>1.08</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>CH(_4)</td>
<td>He</td>
<td>0.562</td>
<td>0.68</td>
<td>0.12</td>
<td>Zemansky</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>0.931</td>
<td>1.07</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
<td>1.154</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
VII SUMMARY AND CRITIQUE OF WORK

If one wishes to study the effect of foreign gases on a molecule which absorbs energy in the infrared region of the spectrum, it would seem that the present method of measuring total absorption by entire bands offers certain advantages not found in previously reported work. Two cases must be considered: In one case low resolution equipment is used which smooths out the detailed rotational lines and examines the fractional absorption in a frequency interval. In the second case high resolution equipment enables one to examine one rotational line at a time in some detail.

In low resolution work the profile of the band is obtained when one scans the entire frequency range of the band. An examination of this profile offers the opportunity to observe the general effect of the foreign gas broadener on the shape of the band. For example one portion of a complicated band may not show effects of pressure broadening due to overlapping of rotational lines in this region. If the total absorption of the band increases with increasing total pressure, the increase in total absorption is because of pressure broadening in some other region of the band. Effects of the foreign gas are thus observed in both total absorption and fractional ab-
sorption of different frequencies within the band. Total absorption has the additional quality of being independent of spectrometer slit width and thus more easily reproducible. In the present study total absorption by N$_2$O bands at 4.5, 7.78 and 8.57 microns, the CO band at 4.7 microns, the CO$_2$ band at 4.2 microns, the C$_2$H$_6$ band at 3.36 microns and the CH$_4$ band at 3.3 microns has been reported in tabular form as a function of the absorber concentration, $w$, partial pressure of absorber, $p$, and total pressure $P$. The total pressure is the sum of the partial pressure $p$ of the absorbing gas and the partial pressure, $P$, of a non-absorbing gas which is added to the absorber to observe its effect on total absorption. In the present study several non-absorbing gases have been used with each band studied to observe their different effects on the total absorption. Empirical equations representing the functional relationship between these quantities are given with no attempt to attach to the equations any physical significance.

Pressure broadening of a rotational line and hence of the entire band is considered to be a function of the collision frequency between molecules. Using this assumption it is possible to calculate relative molecular collision diameters from the data presented. These collision di-
ameters are reported as the sum of the diameters of the absorber plus the non-absorber relative to the sum of the diameters of the absorber plus the non-absorber relative to the sum of the diameters of the absorber plus nitrogen. With the exception of C$_2$H$_6$ the relative collision diameters thus reported remain constant within ± 3 percent over a range of total pressure somewhat less than the entire total pressure range used. At very low and very high total pressure the curve relating total absorption and total pressure approaches asymptotic values of total absorption. Relative collision diameters calculated from these asymptotic regions have been omitted from consideration, since values of the collision diameter calculated from data in these regions are subject to doubt because of the difficulty in determining the intersection of a nearly asymptotic curve with a line parallel to its asymptote.

The high resolution measurements of the type reported by Benesch and Elder$^{23}$ are possibly a more sensitive measure of broadening effects than the methods used in this study. For a given change in total pressure, measurements of this high resolution type yield, percentage-wise, a greater effect as recorded by the spectrometer. This
greater sensitivity, if scatter can be kept low, allows foreign gas studies to be made over smaller ranges of pressure than the low resolution work would allow. One is limited in the high resolution case to observation of one particular rotational line at a time, and care must be taken not to interpret the results as pertaining to the molecules involved in a general manner. All results pertaining to foreign gas broadening by all workers lead to one predominant conclusion: It is impossible, with the present state of knowledge, to predict relative collision diameters. Care must be taken to specify conditions for which collision diameters are stated and data must be presented for each of these conditions.

It is hoped that the data obtained in the present study along with the empirical equations relating total absorption to total pressure for various absorber concentrations will be useful in providing a basis for further theoretical treatments of absorption. Further experimental work will be necessary. The values of collision diameters reported here are in reasonably satisfactory agreement with values obtained by other methods.
I, Edgar Bryson Singleton, was born in Warren, Ohio, June 17, 1926. I received my secondary school education in the public schools of Warren, Ohio. I completed my undergraduate work at Ohio University and received the Bachelor of Science degree in 1949. By the same university I was granted the Master of Science Degree in 1951. Upon coming to the Ohio State University in October, 1951, I was appointed to the position of teaching assistant in the Department of Physics and Astronomy. I held this position until June, 1957, at which time I became a research assistant while completing the requirements for the degree of Doctor of Philosophy.