2
This dissertation has been 64-7010
microfilmed exactly as received

FRANCE, Wilbur Leslie, 1925-
TOTAL ABSORPTANCE BY AMMONIA
IN THE INFRARED.

Ohio State University
Ph.D., 1963
Physics, general

University Microfilms, Inc., Ann Arbor, Michigan

TOTAL ABSORPTANCE BY AMMONIA IN THE INFRARED

DISSERTATION

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

By

Wilbur Leslie France, B. S., M. Sc.

The Ohio State University
1963

Approved by

Adviser
Department of Physics

ACKNOWLEDGMENTS

The research reported in this dissertation has been supported in part by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under contract AF 19(604)-6141 with The Ohio State University Research Foundation.

The author wishes to express his appreciation to Professor Dudley Williams for his guidance and suggestions during the course of this research.

CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
LIST OF ILLUSTRATIONS	v
INTRODUCTION	1
THEORY	4
A. Principles of Radiation Absorption	4
B. Lorentzian Lines	5
C. Absorption Bands	8
D. Band Intensities	10
EXPERIMENTAL APPARATUS AND TECHNIQUES	12
A. Spectrograph, Gas-handling System, and Absorption Cells .	12
B. Measurement of Total Absorptance	17
C. Determination of Self-broadening Coefficients	17
D. Units	21
E. Errors and Accuracy	22
TREATMENT OF THE DATA	24
EXPERIMENTAL RESULTS	26
A. The 950 cm^{-1} Ammonia Band	26
B. The 1628 cm^{-1} Ammonia Band	55
C. The 3300 cm^{-1} Ammonia Bands	76
SUMMARY AND DISCUSSION OF RESULTS	91
AUTOBIOGRAPHY	95

LIST OF TABLES

Table		Page
1	Band Frequencies and Slit Widths	25
2	Data for the 950 cm^{-1} NH_3 Band	45
3	Data for the 1628 cm^{-1} NH_3 Band	56
4	Data for the 3300 cm^{-1} NH_3 Bands	77
5	Band Intensities, B Values, and Optical Collision Diameter Ratios	93
6	Comparison of Results	94

LIST OF ILLUSTRATIONS

Figure		Page
1	Schematic diagram of the gas-handling system.....	14
2 - 17	Spectra of the 950 cm^{-1} NH_3 band.....	27 - 42
18	$\int A(\nu)d\nu$ of 950 cm^{-1} NH_3 band vs. P_e for constant w ...	49
19	$\int A(\nu)d\nu$ of 950 cm^{-1} NH_3 band vs. P_e for $w \sim P_e$	51
20	$\int A(\nu)d\nu$ of 950 cm^{-1} NH_3 band vs. w	53
21	$\int A(\nu)d\nu$ of 950 cm^{-1} NH_3 band vs. wP_e	54
22 - 30	Spectra of the 1628 cm^{-1} NH_3 band.....	60 - 68
31	B for the 1628 cm^{-1} NH_3 band.....	70
32	$\int A(\nu)d\nu$ of 1628 cm^{-1} NH_3 band vs. P_e for constant w ..	72
33	$\int A(\nu)d\nu$ of 1628 cm^{-1} NH_3 band vs. P_e for $w \sim P_e$	73
34	$\int A(\nu)d\nu$ of 1628 cm^{-1} NH_3 band vs. w	74
35	$\int A(\nu)d\nu$ of 1628 cm^{-1} NH_3 band vs. wP_e	75
36 - 43	Spectra of the 3300 cm^{-1} NH_3 bands.....	80 - 87
44	$\int A(\nu)d\nu$ of 3300 cm^{-1} NH_3 bands vs. P_e for constant w .	88
45	$\int A(\nu)d\nu$ of 3300 cm^{-1} NH_3 bands vs. P_e for $w \sim P_e$	89
46	$\int A(\nu)d\nu$ of 3300 cm^{-1} NH_3 bands vs. w	90

INTRODUCTION

Present interest in the study of the planets of the solar system and in space exploration has stimulated laboratory investigation of "synthetic atmospheres" in an effort to understand better the transmission of infrared radiation by planetary atmospheres. Problems of long range detection and signaling by means of infrared within the earth's atmosphere can also be related to such studies. Molecular absorption of infrared radiation by N_2O , CO , CH_4 , CO_2 , and H_2O which are constituents of the atmosphere of the earth has been studied experimentally and discussed in various reports.¹⁻⁶ The present study is a

1. R. M. Chapman and J. N. Howard, J. Opt. Soc. Am. 42, 423, 856 (1952).
 2. J. N. Howard, D. E. Burch, and D. Williams, J. Opt. Soc. Am. 46, 186, 237, 242, 334, 452 (1956).
 3. D. E. Burch, E. B. Singleton, and D. Williams, Appl. Opt. 1, 359 (1962).
 4. D. E. Burch and D. Williams, Appl. Opt. 1, 473, 587 (1962).
 5. D. E. Burch, D. A. Gryvnak, and D. Williams, Appl. Opt. 1, 759 (1962).
 6. D. E. Burch, W. L. France, and D. Williams, Appl. Opt. 2, 585 (1963).
-

continuation of research concerning synthetic atmospheres and similar techniques were employed.

Mohler, Goldberg, and McMath⁷ reported evidence of a trace of am-

-
7. O. C. Mohler, L. Goldberg, and R. R. McMath, Phys. Rev. 74, 352 (1948).
-

monia in the atmosphere of the earth. Other investigators⁸ found no

8. M. V. Migeotte and R. M. Chapman, Phys. Rev. 75, 161 (1949).
-

evidence of ammonia in the atmosphere of the earth. Thus studies of ammonia in other planetary atmospheres are more easily accomplished.

Large amounts of ammonia have been reported⁹ in the atmospheres of

9. G. P. Kuiper, ed., "The Atmospheres of the Earth and Planets", 2d. ed.; Chicago: Univ. of Chicago Press, 1951, p. 364.
-

Jupiter and Saturn. The temperature of the Jovian atmosphere is reported to be -140° C.

Although the temperatures for the present study are decidedly different, the techniques should be applicable for determination of the amount of ammonia present in planetary atmospheres. It is hoped that the results may serve as a preliminary step in such a determination.

Infrared radiation is attenuated in planetary atmospheres by particles of dust, fog, haze, and smoke. In addition, in certain spectral regions molecular absorption due to transitions between the vibration-rotation energy levels occurs. The study of infrared absorption by gases is usually accomplished by measuring the relative intensity $I(\nu)$ of transmitted radiation of frequency ν as compared to the intensity $I_0(\nu)$ of radiation incident upon a sample of the gas. The ratio $I(\nu) / I_0(\nu) = T(\nu)$ and is called the measured transmittance which can be expressed as a fraction or percentage. The measured spectral absorp-

tance is then $A(\nu) = 1 - T(\nu)$ and may be expressed as a fraction or percentage.

Experiment shows that the spectral absorptance of a gas sample depends upon the optical density or absorber concentration w which is the total number of absorbing molecules per cross-sectional area of the radiation beam, the partial pressure p of the absorbing gas, the total pressure P which includes the pressure due to nonabsorbing as well as absorbing gases, the absolute temperature T of the sample, and the effective slit width of the monochromator.

Howard, Burch, and Williams² have shown experimentally that the total absorptance of a molecular absorption band of a gas sample where $I_0(\nu)$ is essentially constant throughout the frequency interval of the band is independent of the mechanical slit width of the spectrometer. Babrov¹⁰ has demonstrated theoretically that the total transmittance

10. H. J. Babrov, J. Opt. Soc. Am. 51, 171 (1961).

for a molecular absorption band is independent of the mechanical slit width of the spectrometer provided $I_0(\nu)$ is slowly varying over the region of the band. Since the spectral absorptance at a given frequency ν is $A(\nu) = 1 - T(\nu)$ the total absorptance $\int_{\nu_1}^{\nu_2} A(\nu) d\nu$ for a frequency interval ν_1 to ν_2 which includes the entire band is equal to the true absorptance of the band. Thus the total absorptance of a molecular band can be expressed in terms of w , p , P , and T as defined above.

THEORY

A. Principles of radiation absorption

Absorption of electromagnetic radiation by homogeneous media has been studied for more than two hundred years. Near the beginning of the period Lambert proposed an exponential law for the transmittance of a collimated monochromatic beam of light by a homogeneous absorbing medium. Mathematically the law can be expressed as

$$I(\nu) = I_0(\nu) \exp[-k(\nu)w] \quad (1)$$

where $I_0(\nu)$ is the incident intensity of frequency ν , $I(\nu)$ is the transmitted intensity, $k(\nu)$ is a constant characteristic of the absorbing medium called the absorption coefficient and w is the absorber concentration. The spectral absorptance $A'(\nu)$ is then

$$A'(\nu) = [I_0(\nu) - I(\nu)] / I_0(\nu) = 1 - \exp[-k(\nu)w]. \quad (2)$$

Later, Beer proposed the application of Lambert's law to a mixture of absorbing materials by defining the absorption coefficient for the mixture as the sum of the products of concentration and characteristic constant for each component of the mixture. This application was based on the assumption that the absorption of radiation by a molecule is independent of every other molecule.

For experimental measurement of infrared absorption by gases Beer's law is not valid. The invalidity arises first, as a result of finite slit widths of spectrographs which result in measurements of non-monochromatic radiation in the determination of the absorptance and thus the

experimentally observed absorptance $A(\nu)$ is not the same as $A'(\nu)$ which would result for monochromatic radiation. The problem is further complicated by the fact that the infrared absorption of gases consists of a series of bands composed of many individual lines and thus $A'(\nu)$ has rapid variations with ν . Since, in general, the slit widths of the spectrometer are large compared to the individual line widths of the lines of the bands, $A'(\nu)$ will not be a close approximation of the measured $A(\nu)$.

Secondly, Beer's law fails in that infrared absorption by molecules of a gas is not a process wherein each molecule absorbs independently of every other. The observable broadening of spectral lines with increasing pressure indicates that inter-molecular collisions occur and the independence is negated.

Spectral line widths are the resultant of such factors as natural line width, Doppler broadening, and "pressure broadening". The latter includes collision broadening, pressure shifts, and Stark effects. These last two are encountered at relatively high pressures where the time spent in collisions is large compared to the time between collisions. The present work primarily involves collision broadening.

B. Lorentzian lines

Since a vibration-rotation absorption band of a gas consists typically of many individual lines, the total absorptance of a band can be analyzed in terms of the effect of a single line. Lorentz has proposed a line shape which has been found to approximate satisfactorily actual line shapes over the range of pressures where collision broadening

occurs. The absorption coefficient proposed by Lorentz is given by

$$k(\nu) = \frac{S}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2} \quad (3)$$

where the line strength $S = \int_{-\infty}^{\infty} k(\nu) d\nu$ and α is the half width of the line at half the maximum value of $k(\nu)$. The line strength of a collision broadened line is temperature dependent and related to the transition probabilities and population densities of the initial and final energy levels of the absorbing molecule. The half width of the line is temperature and pressure dependent as well as dependent upon the types of molecules present in the gas sample.

The half width α for a collision broadened line is proportional to the collision frequency F . Kinetic theory gives

$$\alpha = \frac{F}{2\pi} = \frac{1}{4\pi} \sum_i N_i (D_{a1})^2 \left[2\pi kT \left(\frac{1}{M_a} + \frac{1}{M_i} \right) \right]^{\frac{1}{2}} \quad (4)$$

where N_i is the number of particles of the i -th type per unit volume, D_{a1} is the sum of the optical collision diameters of the absorbing molecule and a molecule of the i -th type, k is the Boltzmann constant, T is the absolute temperature, and M_a and M_i are the masses of the absorbing molecule and the i -th type molecule respectively.

Since the partial pressure p_i of the i -th type gas is expressible as $p_i = N_i kT$ and if it is assumed that the collision diameters are temperature independent, one can relate α to total pressure P , which is the resultant of the partial pressures of the components of any mixture of gases, if the ratio of the partial pressures is kept constant. That is, from (4) one can obtain

$$\alpha = \alpha_0 (P/P_0) (T_0/T)^{\frac{1}{2}} \quad (5)$$

where α_0 , P_0 , and T_0 are the values at standard conditions. Thus on the

basis of simple kinetic theory considerations, the value of α should be proportional to the total pressure P .

In the case of a mixture of only two gases, an absorbing gas a and a broadening gas b the summation in (4) yields only two terms; a self-broadening term for $i = a$, and a term for the broadening effects of the broadening gas $i = b$. Thus (4) becomes

$$\alpha = \frac{1}{4\pi}(2\pi kT)^{\frac{1}{2}} \left[N_a(D_{aa})^2 \left(\frac{2}{M_a} \right)^{\frac{1}{2}} + N_b(D_{ab})^2 \left(\frac{M_a + M_b}{M_a M_b} \right)^{\frac{1}{2}} \right] \quad (6)$$

Expression of N_a and N_b in terms of the partial pressures p_a and p_b gives

$$\alpha = \left(\frac{1}{8\pi kT} \right)^{\frac{1}{2}} (p_a C_{aa} + p_b C_{ab}) \quad (7)$$

where C_{aa} and C_{ab} are constants involving the collision diameters and masses of the absorbing and broadening molecules. Since the total pressure $P = p_a + p_b$ one may obtain

$$\alpha = \left(\frac{1}{8\pi kT} \right)^{\frac{1}{2}} C_{ab} [P + (B - 1)p_a] \quad (8)$$

where $B = C_{aa}/C_{ab}$ is the self-broadening coefficient of the absorbing gas, which is the ratio of the "line broadening ability" of the absorbing gas with itself to the "line broadening ability" of the broadening gas with the absorbing gas.

From (8) it is seen that the half width α for a binary mixture of gases can be considered as a function of a single variable called the equivalent pressure P_e , where

$$P_e = P + (B - 1)p_a \quad (9)$$

It should be noted that the above development is for collision broadening processes and is probably not applicable to extremely low pressures or extremely high pressures.

In principle one can evaluate the total absorptance due to a single line by use of (2) and (3) and by integrating over the entire range of absorption. Thus appropriate choice of integration limits leads to $\int A'(\nu) d\nu = \int A(\nu) d\nu$ and experimental and theoretical results may be compared. Ladenberg and Reiche¹¹ have shown that such an evaluation can

11. R. Ladenberg and F. Reiche, *Ann. Physik* 42, 181 (1913).

indeed be made in terms of S , α , and w ; that is,

$$\int A(\nu) d\nu = 2\pi\alpha f(x) \quad (10)$$

where $x = Sw/(2\pi\alpha)$ and $f(x) = x \exp(-x) [J_0(ix) - iJ_1(ix)]$ where $J_0(ix)$ and $J_1(ix)$ are the Bessel functions of order zero and one respectively. To simplify the involved relation in (10) Elsasser¹² has given two ap-

12. W. M. Elsasser, "Harvard Meteorological Studies No. 6", Harvard University, 1942.

proximations which aid in the use of the equation. These approximations are

$$\int A(\nu) d\nu = Sw \quad \text{for small } x \text{ (a weak line)} \quad (11)$$

and

$$\int A(\nu) d\nu \sim 2(S\alpha w)^{\frac{1}{2}} \sim (SP_e w)^{\frac{1}{2}} \quad \text{for large } x \text{ (a strong line)}. \quad (12)$$

For a given temperature the absorber concentration w is proportional to the product of the partial pressure of the absorber and the absorption path length.

C. Absorption bands

In the study of total absorptance for entire bands the line spacings and intensities need to be considered. In general the line spac-

ings of an absorption band are neither uniform nor completely random, and similarly the line intensities vary throughout the band. In addition, if the line spacings are such that neighboring lines overlap, the absorption coefficient must be the sum of the individual coefficients of each of the lines contributing to the absorptance.

Various band models have been proposed. The Elsasser band model¹² assumes equally spaced and equally intense lines and gives relatively good results where the spacing and intensity vary quite gradually throughout the band. Goody¹³ has proposed a statistical model in which

13. R. M. Goody, Quant. J. Roy. Met. Soc., 78, 165 (1952).

the lines are randomly spaced and the intensities vary according to a probability distribution. A random Elsasser model has been discussed by Plass¹⁴ in which a band is composed of several superimposed Elsasser

14. G. N. Plass, J. Opt. Soc. Am., 48, 690 (1958).

bands which result in nearly random line spacing.

In as much as exact theoretical expressions for the above models are rather involved, simplifications or approximations are quite desirable. Plass¹⁵ has offered three approximations for each of the three

15. G. N. Plass, J. Opt. Soc. Am., 50, 868 (1960).

models. The strong-line approximation applies when there is nearly complete spectral absorptance near the centers of the strongest lines of the band. Once the strong-line approximation has been realized, further increases in P_0 or w result only in increased spectral absorp-

tance in the wings of the lines. Thus (12) indicates that the total absorptance is a function of the product wP_0 as well as strength and spacing of the lines of the band. This approximation is valid for large values of w and small values of P_0 .

The weak-line approximation applies for the case in which spectral absorptance is small even at the centers of the strongest lines of the band. This approximation is valid for small values of w and large values of P_0 . In this case the total absorptance is a function of w only, but a linear relation such as indicated in (11) will exist only if there is no overlapping of the lines of the band.

The non-overlapping approximation is for the case of little if any overlapping of individual lines and the total absorptance is only slightly dependent on the line intensity distribution within the band.

Of these three approximations, the strong-line approximation lends itself to experimental testing of the various band models. The other two approximations cannot be used for such testing since for these the total absorptance is practically independent of the line spacing and distribution of line strengths.

D. Band intensities

In molecular spectral studies band strength or band intensity, $\int k(\nu) d\nu$, is of interest. This quantity is analogous to line strength $\sum k(\nu)$ for a band the integration limits are chosen to include the entire band. As in the case of line strength, the band strength is a function not only of transition probabilities but also of temperature and thus related to differences in population density of the energy levels associated with the absorption band.

The band intensity can be evaluated if the value of the product $k(\nu)w \ll 1$ throughout the band. In this case (11) becomes

$$S = \int k(\nu) d\nu = (1/w) \int A(\nu) d\nu \quad (13)$$

and since $\int A(\nu) d\nu$ and w are both measurable the value for band intensity can be determined.

EXPERIMENTAL APPARATUS AND TECHNIQUES

A. Spectrograph, gas-handling equipment and absorption cells

The total absorptance of the various bands was measured by means of a double-beam, single-pass Perkin-Elmer Model 21 spectrometer. This spectrograph is equipped to record spectra on a chart at a linear wave-number scale and a linear percent absorptance scale. The principles of operation of the instrument are given in the instruction manual. For this study a thermocouple detector was used. The dispersive element was a NaCl prism.

The spectrograph is also equipped with Perkin-Elmer dual multiple traversal absorption cells. These cells are about one meter long and employ mirrors, according to the White principle¹⁶, which allow path

16. J. U. White, J. Opt. Soc. Am., 32, 285 (1942).

lengths that are multiples of 4 meters up to a maximum of 40 meters. For shorter path lengths these cells are easily by-passed and shorter cells introduced into the optical paths. Ordinarily one cell is placed in the "reference" beam of the spectrograph and one cell is placed in the "sample" beam to help "balance" the two optical paths. The instrument then registers the "difference" in absorption by the two cells. In this study the reference cell was kept evacuated when the total absorptance of a sample in the sample cell was being measured.

The gas-handling system is made with Hoke Monel Packless Valves, 411 series, connected by 3/8 inch copper tubing. A schematic diagram of the system is shown in Fig. 1. The joints are silver soldered. The gas system was connected by about five feet of 1/4 inch copper tubing to the absorption cells. The joints for this part of the system were soft soldered or made with flare fittings. The sample and reference cells including the multiple traversal cells were controlled by Hoke Miniature Forged Needle Valves, 300 series. The system could thus withstand relatively high pressures, well in excess of the four atmospheres maximum used in this study.

The gauges of the gas-handling system are a Wallace and Tiernan absolute gauge, made of stainless steel, with range 0 to 50 mm calibrated in intervals of 0.2 mm, a mercury manometer used in the range 50 mm to one atmosphere, and an Ashcroft "Duragauge", a Bourdon tube-type pressure gauge made of stainless steel and calibrated in steps of one pound per square inch from 0 to 100 pounds per square inch gauge.

The short absorption cells used in this study are 1.55 cm and 6.35 cm long and are made with thick walled cylindrical brass and stainless steel bodies respectively. The inside diameter of the cells is one inch. The body ends and end plates are machined for rubber "O" rings which prevent metal-to-window contact and provide a vacuum and pressure seal as well as minimize stresses on the windows. These cells could be used for pressures to 60 psig. The cells were equipped with KBr windows although NaCl windows would have been suitable. In the determination of the self broadening coefficients a third cell of length 5.05 cm with

Fig. 1.--Schematic diagram of the gas-handling system.

NaCl windows sealed with beeswax was used in the reference beam while the 6.35 cm cell was used in the sample beam.

The valves closing the absorption cells are welded or threaded directly into the cell body to minimize mixing time when adding the broadening gas. This is desirable since it has been found that a short length of narrow tubing between the cell and the valve necessitated considerable time for completion of mixing by diffusion.

Since ammonia seems especially difficult to remove completely from a system, a separate 1/4 inch copper tube was brought directly from the nitrogen bottle and connected by a tee as near the absorption cell as possible as indicated in Fig. 1. The nitrogen valve was always kept closed except when admitting nitrogen to the system and thus ammonia could not be returned to the system from the nitrogen line and any ammonia in the neighboring lines would, except for the short section of the tube to the cell, tend to be flushed away from the cell and not be added to the sample cell along with the nitrogen.

Mixing of the gases within the short cells was found to be almost instantaneous. This was verified by recording the spectrum of a mixture immediately after the addition of nitrogen and then recording it again after a few minutes. Samples allowed to stand for as long as one hour showed no measurable change in total absorptance. Thus it was concluded that the mixing had been complete before the first spectrum was recorded. In the Perkin-Elmer long-path sample cell a fan is mounted inside to speed the mixing process. It was found that a few seconds of operation of the fan were sufficient for uniform mixing; however, it seemed that a similar time was necessary for turbulence to

subside. Otherwise the indicated total absorptance was not constant.

Although the short cells are provided with grooved end plates to engage the holders on the spectrometer, a more rigid support was found to be necessary. An apparent shift of the 100% transmittance curves of the recorded spectra indicated this need. A support which anchored the cells to the spectrometer base prevented any shifting of the cells when the cell valves were operated. This added support, which prevented shifting of the cells, in turn prevented slight defocusing of the light beams resulting in the apparent shift of the 100% transmittance curves.

Before a spectrum was to be recorded, the gas-handling system and both the reference and sample cells were evacuated and a "background" spectrum recorded. Then with the reference cell closed, ammonia to the desired pressure was admitted to the system and the sample cell. The sample cell valve was then closed and a spectrum recorded. For pure samples of ammonia more of the gas was added to the system and sample cell without evacuating the system. For studies of samples with constant absorber concentration and varying total pressure the initial ammonia sample was obtained as above. After closing the sample cell valve the system was pumped for a few minutes and the pressure reduced to less than 0.1 mm of mercury. Nitrogen was then admitted to the system, by way of the nitrogen valve near the sample cell, to a pressure slightly in excess of that of the initial ammonia sample. The sample cell valve was then opened and more nitrogen was admitted to the desired pressure. The sample cell valve was then closed to prevent any outward diffusion of the absorber. More nitrogen was added by a similar process without evacuating the system.

It was found that for samples of low absorber partial pressure with nitrogen added to a high pressure in successive steps and a similar sample with nitrogen added in one step to the high pressure the observed total absorptance was unchanged. This indicates that little if any of the absorbing gas escaped through the valve during the process of adding the nitrogen in successive steps.

B. Measurement of total absorptance

From the recorder chart tracings, the total absorptance for a given sample was obtained from the area enclosed between the indicated spectral transmittance and the 100% transmittance line obtained with the sample cell evacuated. A compensating polar planimeter was used to measure the area. In principle, the 100% transmittance line for the double beam spectrometer used in this study should be linear but in practice over wide ranges, such as for some of the ammonia bands, one to four percent deviation was observed. Since the total area was usually large and the percent absorptance small where the deviation occurred, replotting was considered to be unnecessary since the error would be quite small.

C. Determination of self-broadening coefficients

Analysis of the data of this study makes use of the equivalent pressure P_e as expressed in (9). The value of P_e depends upon the self-broadening coefficient B . The value of B can be determined experimentally by means of the double beam feature of the spectrometer or by a graphical treatment of the data for total absorptance.

The procedure using the double beam feature of the spectrometer depends upon a study of the radiation transmitted through gas samples of equal absorber concentration w but of different path lengths. A short cell is placed in the reference beam of the spectrometer and contains a pure sample of ammonia at pressure p_{ref} . For this cell $P_{\text{ref}} = p_{\text{ref}}$ and the equivalent pressure according to (9) is

$$P_e = B p_{\text{ref}} \quad (\text{reference cell}) \quad (14)$$

A longer cell is placed in the sample beam of the spectrometer and initially contains a sample of pure ammonia at the partial pressure p which produces an absorber concentration w equal to that in the reference cell; i. e., the product of path length and partial pressure of ammonia for each of the two cells is equal. Since the total and partial pressures in the sample cell are initially less than the pressure in the shorter reference cell, the spectral absorptance is less in the sample cell. Various amounts of nitrogen are then added to the sample cell giving an equivalent pressure

$$P_e = P + (B - 1)p \quad (\text{sample cell}) \quad (15)$$

For the case in which the absorptance in the two cells is equal it is assumed that the equivalent pressures in (14) and (15) are equal. This gives the value of the self-broadening coefficient as

$$B = \frac{P - p}{p_{\text{ref}} - p} \quad (16)$$

where p_{ref} is the ammonia pressure in the shorter reference cell and p and P are, respectively, the partial pressure of the ammonia and the total pressure in the sample cell when the absorptances in the two cells are equal.

The determination of B by graphical treatment of the data for total absorptance uses a graph upon which total absorptance is plotted against total pressure for at least two different path lengths, a shorter "reference" path length and a "sample" path length. For the shorter path a plot of total absorptance against pressure for only pure samples of ammonia is needed. For the longer path a plot of total absorptance against total pressure for ammonia at a given pressure mixed with nitrogen to give a series of higher pressures is needed. By using the partial pressure p of ammonia for a given curve on the graph for the longer path, the absorber concentration is calculated. In turn, by using the shorter path length, the pressure p_{ref} of pure ammonia which gives the same absorber concentration is calculated. From the graph of the shorter path the total absorptance for p_{ref} is noted. The total pressure P of the mixture in the long path which gives equal absorptance is read from the graph. Substitution of these calculated and graphically determined quantities into (16) gives the value of B . A series of such determinations for different absorber concentrations and various path lengths will give sufficient data to derive an "average" value for B for an absorption band.

It is evident from (16) that the value of B is strongly effected by uncertainties in the values of the pressures. These are in turn related to the uncertainties in the values for the path lengths of the uncollimated light beams through the absorption cells. The graphical method of determining B depends upon the observed total absorptance, while the spectrometric double beam method is limited by the ability of the spectrometer to distinguish small differences in transmitted inten-

sities of the reference and sample beams. A further possible complication in the double beam method arises if the detector does not receive exactly the same frequency interval of radiation from both beams. This complication might become evident in case the spectrometer has sufficient resolution to show some rotational or other relatively intense but narrow structure in the spectrum.

Preliminary measurements of total absorptance showed that nitrogen was much less effective in increasing the total absorptance than ammonia. This indicated a relatively large value for B .

The double beam method was used for the preliminary measurements of B . The 1.55 cm and 6.35 cm cells were used and the results indicated a possibility of pressure dependence. These cell lengths were so different that for equal absorber concentration large differences in the ammonia pressures were necessary. Also the value of B seemed to be about 5 or 6 and thus P for equal absorptance was large compared to P_{ref} . The maximum safe pressure for the absorption cells was considered to be four atmospheres. This severely limited the range of partial pressures of ammonia which could be investigated. In addition, if a pressure dependence existed, the variation of B with pressure could not be readily determined since the ammonia pressure in the reference cell was more than four times that in the sample cell for equal absorber concentration.

In view of the above considerations, a 5.05 cm cell was used as the reference cell and the 6.35 cm cell retained as the sample cell. In this manner the pressure difference for equal absorber concentration in the two cells was greatly reduced and in turn the maximum total

pressure required for equal absorptance was similarly reduced. In other words, both the numerator and denominator of the fraction in (16) were reduced.

The range of ammonia partial pressures which could be studied was somewhat limited by the range of absorptance over which the spectrometer can effectively operate; that is, if the sample or reference beam or both have large spectral absorptance or small spectral transmittance, the ratio of the transmittance of the sample cell to the transmittance of the reference cell can become undefined or the signal level reaching the detector can become so low that a true record of the ratio will not be made. To avoid this, values of pressures which gave spectral absorptances between 10% and 80% were used for the determination of the value of B.

Once the value of B is determined, it is possible by means of (6) and (8) to derive a value for the ratio of the sum of the optical collision diameters. From (6) and (8)

$$B = \left[\frac{2M_b}{M_a + M_b} \right]^{\frac{1}{2}} \left[\frac{D_{aa}}{D_{ab}} \right]^2 \quad (17)$$

where the subscripts a and b refer to the absorbing gas and the broadening gas respectively.

D. Units

In this study all values of partial pressure, total pressure and equivalent pressure are given in mm of mercury absolute. Tabulated values of partial pressure are the observed values.

The values of absorber concentration w are expressed as the product of the absorber path length in cm and the partial pressure of the ab-

sorbing gas in atmospheres corrected to standard temperature. The unit for w is thus atm cm.

The experimental data were all recorded at room temperature, which ranged from 24° C to 29° C.

In view of the units indicated above, the units for band intensity are $\text{atm}^{-1} \text{cm}^{-2}$. It should be noted that the intensity values are based on w corrected to standard temperature.

E. Errors and accuracy

The major sources of error in a study such as this are errors in gas sampling, errors in the detection-recording system of the spectrometer, and errors in measuring the total absorptance from the recorded spectra.

Sampling errors include impurities in the gas supplies, adsorption effects, pressure measurement, and mixing of the ammonia and nitrogen within the absorption cell. The last has been discussed in connection with absorption cells and their design. Pressure measurements, with the apparatus indicated earlier, are believed to be accurate within one percent for pressures in excess of 10 mm of mercury. Studies have indicated that adsorption of gases on the walls of a container does indeed occur. This is evidenced by the fact that after an absorption cell containing an absorbing gas has been pumped to a pressure less than 0.1 mm of mercury and then filled with nitrogen to atmospheric pressure or somewhat higher, the recorded spectral absorptance of such a sample shows little if any absorbing gas present if the spectrum is recorded immediately. If the sample is allowed to stand for a number of hours a noticeable increase in spectral absorptance is observed. This indicates

the presence of added absorber within the optical path and seems due to the adsorbed gas being liberated from the cell walls into the optical path. Experiment has shown that the above effect is relatively slow. Since most of the samples used in this study were not allowed to "age" and the spectra for a given absorber concentration could be recorded within an hour, little error is believed introduced by adsorption effects. According to the supplier, impurities in the nitrogen and in the ammonia are considerably less than one percent and thus no correction for impurities is believed necessary.

Errors in the recording of the spectra are due to the normal noise and possibly faulty instrument operation. Since the regions of absorption studied extend over intervals of 600 cm^{-1} or more, a slight error in the 100% transmittance line location could give sizable errors in total absorptance. Such errors are estimated to be $\pm 20\%$ for total absorptance less than 10 cm^{-1} and less for greater total absorptance, perhaps $\pm 3\%$ for total absorptance greater than 25 cm^{-1} .

Measurement of the records should be accurate to $\pm 1\%$ since repeated measurements of any one spectrum with the planimeter showed variations less than this value.

The over-all error is believed to be less than $\pm 5\%$ for total absorptance greater than 20 cm^{-1} and somewhat larger for smaller total absorptance.

TREATMENT OF THE DATA

The choice of values for the spectrometer variables was made by considering the desired results. Since the total absorptance of a band is independent of the spectrometer slit width, a relatively wide slit width was chosen in order to provide a higher signal-to-noise ratio and thus minimize the error in the recorded total absorptance. In addition, such a choice made it easier to measure the total absorptance since wider slits would allow less of the rotational detail of the bands to be indicated. In this study a constant slit width was used for each band except for the rather long 950 cm^{-1} band. For the latter the programmed slit apparatus of the spectrometer was used. This system varies the slit width with frequency so as to maintain an almost constant reference signal to the detector. The slit program was adjusted to give a slit width of 250 microns at 1000 cm^{-1} . Table 1 lists the band frequencies and indicates the bands which overlap and thus were measured over the indicated ranges as a single unit. The slit widths are also listed. For small total absorptances the 5X scale expander was used. This device expands the percent absorptance scale by various factors. In this case the factor 5 was chosen. When the scale expander is used, it is desirable to use wider slits to give a larger signal-to-noise ratio.

After the slit program and other spectrometer variables had been selected, a large number of spectra were recorded to obtain values for total absorptance for wide ranges of absorber concentration w , partial

Table 1. Band Frequencies and Slit Widths.

Identification and band frequencies in cm^{-1} according to Herzberg ¹⁷	Designation in this study	Slit widths in microns	
		Total absorptance spectra	Determination of B and for 5X scale
$\nu_1 \begin{cases} 3335.9 \\ 3337.5 \end{cases}$ $\nu_3 \quad 3414$ $2\nu_4 \quad 3219.1$	3300 cm^{-1}	75	125
$\nu_4 \quad 1627.5$ $2\nu_2 \quad 1922$	1628 cm^{-1}	150	225
$\nu_2 \begin{cases} 931.58 \\ 968.08 \end{cases}$	950 cm^{-1}	Programmed	

17. G. Herzberg, "Molecular Spectra and Molecular Structure. II Infra-red and Raman Spectra of Polyatomic Molecules", New York: D. Van Nostrand Co., 1945, p. 295-6.

pressure p , and total pressure P . Some records were made with pure samples of ammonia.

From the above process, logarithmic plots of total absorptance as a function of equivalent pressure P_e are made for the various values of absorber concentration w . Also logarithmic plots of total absorptance as a function of absorber concentration for various values of equivalent pressure are prepared.

EXPERIMENTAL RESULTS

A. The 950 cm^{-1} ammonia band

The ν_2 fundamental band of ammonia near 950 cm^{-1} has a double frequency due to inversion doubling. At relatively large values of absorber concentration it overlaps slightly the ν_4 fundamental at the high frequency end of the band. The ν_2 band and $2\nu_2 - \nu_2$ band at 629.3 cm^{-1} overlap at the low frequency end of the 950 cm^{-1} region. After observing the spectra for a few samples with high absorber concentration it was decided that 1300 and 660 cm^{-1} were suitable band limits for this study. The symmetry of the bands indicated that the recorded spectral absorbance at these limiting frequencies was approximately 50% due to each neighboring band. The effects of the 667 cm^{-1} band of atmospheric carbon dioxide are believed to be negligible especially since the band lies near the end of this ammonia band.

More than 100 spectra were obtained for this region with absorption cell lengths of 1.55, 6.35, and 400 cm. Different mixtures of ammonia and nitrogen were used to provide absorber concentrations from 0.009 to 47 atm cm and total pressures from 2 to 3000 mm of mercury.

Tracings of many of the recorded spectra are shown in Figs. 2 to 17. Many of the spectra are grouped as they were when recorded, that is for a given absorber concentration and varying total pressure. The total pressure was used to compute the indicated equivalent pressure.

Fig. 2.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 3.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 4.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 5.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 6.--Spectra of the $950 \text{ cm}^{-1} \text{ NH}_3$ band.

Fig. 7.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 8.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 9.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 10.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 11.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 12.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 13.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 14.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 15.--Spectra of the 950 cm⁻¹ NH₃ band.

Fig. 16.--Spectra of the 950 cm^{-1} NH_3 band.

Fig. 17.--Spectra of the 950 cm⁻¹ NH₃ band.

To calculate the equivalent pressure P_e , it is necessary to determine the value of the self-broadening coefficient B . Use of the double beam feature of the spectrometer was attempted for this determination. The resolution of the spectrometer was such that much of the rotational detail was evident in the total absorptance spectra. This relatively rapid variation in intensity of the transmitted radiation with frequency which occurs in both the reference and sample cells leads to wide variations in the signal strength to the detector of the spectrometer. With the gain of the amplifying system set at a value suitable for a desirable signal-to-noise ratio with the cells evacuated or for only slight attenuation in each light path, the sensitivity of the system for regions of strong absorption is greatly reduced and thus the "balance" position of the recorder pen becomes uncertain.

Repeated measurements of B with the double beam technique resulted in decided scatter in the values indicated for any given frequency. For this reason the graphical method was attempted. A determination of B was made for ten different absorber concentrations using data for the three path lengths indicated above. The average of these values was 6.2 and the average deviation from the mean was 1.0. The value of 6.2 was used in calculating the equivalent pressures from the observed partial pressures.

The tracings of the spectra for the larger absorber concentrations indicate that the absorptance is not zero at the end of the measured region. This is as it should be since other absorption bands of ammonia extend into the region of interest. In the case of smaller absorber concentrations, zero absorptance is indicated in these same regions

since the absorptance was not sufficient to be detected and displayed on the recorder of the spectrometer. In some cases, sections of spectral tracings are omitted to prevent over-crowding in the figures. In such cases the spectral absorptance can be estimated by interpolation between the curves shown.

All the experimental results for the 950 cm^{-1} band of ammonia are summarized in Table 2. There the values for w , P_e , and total absorptance are shown along with a figure number indicating where the spectral tracing of each sample is shown. If no figure number is given the tracing is not shown.

The value of the equivalent pressure P_e is computed from the total pressure P and the ammonia partial pressure p by means of (9) which for this case becomes

$$P_e = P + 5.2p \quad (18)$$

Figure 18 shows a logarithmic plot of much of the data of Table 2. Total absorptance is shown as a function of equivalent pressure. Each curve corresponds to a given absorber concentration and shows the effect of increased equivalent pressure by adding nitrogen. The longer curves toward the top of the figure are for data for the 400 cm absorption cell, while the other curves are for the shorter cells. The points indicated with x are for pure samples of ammonia and the other points on a given curve indicate the results for the same amount of ammonia with added amounts of nitrogen. Although some of the curves for long path lengths and large absorber concentrations do not overlap those of shorter path lengths, these curves appear to lie near the expected position if these were extended to cover the gap.

Table 2. Data for the 950 cm^{-1} NH_3 Band

The Fig. No. corresponds to the figure in which the spectrum of each sample is shown. Absence of Fig. No. indicates spectrum is not shown. Uncertainties of the values of $\int A(\nu) d\nu$ are discussed in the text.

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm^{-1}
<u>Path Length = 1.55 cm</u>						
1	2	5.0	5.0	31.0	0.00935	3.48
2		5.0	39.0	65.0	0.00935	4.67
3	2	5.0	104	130	0.00935	5.06
4		5.0	203	229	0.00935	5.42
5		5.0	414	440	0.00935	5.84
6		5.0	817	843	0.00935	6.45
7	2	5.0	1535	1560	0.00935	6.50
8		5.0	3085	3110	0.00935	6.76
9		10.3	10.3	63.8	0.0192	6.32
10		10.3	41.4	94.9	0.0192	7.15
11		10.3	101	155	0.0192	9.52
12		10.3	204	258	0.0192	10.6
13		10.3	401	455	0.0192	12.3
14		10.3	809	863	0.0192	13.3
15		10.3	1535	1590	0.0192	15.2
16		10.3	3085	3140	0.0192	19.7
17	3	20.0	20.0	124	0.0372	13.2
18		20.0	80.0	184	0.0372	15.6
19		20.0	201	305	0.0372	17.6
20		20.0	411	515	0.0372	19.3
21		20.0	816	920	0.0372	21.3
22		20.0	1535	1640	0.0372	23.2
23	3	20.0	3085	3190	0.0372	23.7
24	4	5.2	5.2	32.2	0.00971	3.92
25		10.1	10.1	62.5	0.0189	9.16
26		19.9	19.9	123	0.0372	17.4
27		40.2	40.2	249	0.0753	28.6
28	4	100	100	620	0.188	53.1
29		201	201	1250	0.375	91.6
30		401	401	2485	0.750	156
31	4	800	800	4960	1.50	255
32		1535	1535	11450	2.87	364
33		3085	3085	19130	5.76	462

Table 2. (Continued)

Sample No.	Figure No.	p mm Hg	P mm Hg	P ₀ mm Hg	w atm cm	$\int A(\nu) d\nu$ cm ⁻¹
<u>Path Length = 6.35 cm</u>						
34		5.3	5.3	32.8	0.0405	3.82
35		5.3	21.5	49.1	0.0405	4.51
36		5.3	47.8	75.4	0.0405	6.89
37		5.3	110	138	0.0405	8.42
38		5.3	207	235	0.0405	10.9
39		5.3	410	435	0.0405	12.4
40		5.3	803	831	0.0405	14.1
41		5.3	1535	1565	0.0405	15.0
42		5.3	3085	3115	0.0405	16.5
43	5	10.1	10.1	62.6	0.0772	18.4
44		10.1	40.0	92.5	0.0772	20.3
45		10.1	104	157	0.0772	24.9
46		10.1	205	258	0.0772	28.0
47	5	10.1	414	467	0.0772	31.2
48		10.1	799	852	0.0772	34.4
49		10.1	1535	1590	0.0772	37.3
50	5	10.1	3085	3150	0.0772	41.0
51	6	20.0	20.0	124	0.153	28.2
52		20.0	40.5	145	0.153	31.1
53		20.0	101	205	0.153	37.8
54		20.0	202	306	0.153	40.1
55	6	20.0	406	510	0.153	44.8
56		20.0	802	906	0.153	50.3
57		20.0	1535	1640	0.153	56.3
58	6	20.0	3085	3190	0.153	63.5
59	7	40.2	40.2	249	0.308	51.4
60		40.2	103	312	0.308	57.8
61		40.2	203	412	0.308	65.8
62	7	40.2	412	621	0.308	73.7
63		40.2	802	1010	0.308	83.7
64		40.2	1535	1745	0.308	95.0
65	7	40.2	3085	3295	0.308	104
66	8	101	101	626	0.774	103
67		101	202	728	0.774	109
68		101	408	934	0.774	124
69	8	101	804	1330	0.774	136
70		101	1535	2060	0.774	153
71	8	101	3085	3610	0.774	177

Table 2. (Continued)

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm ⁻¹
72	9	211	211	1310	1.167	182
73		211	410	1510	1.167	190
74		211	813	1910	1.167	209
75		211	1535	2630	1.167	225
76		211	3085	4185	1.167	251
77	10	404	404	2505	3.09	281
78		404	812	2917	3.09	298
79		404	1535	3640	3.09	313
80	10	404	3085	5190	3.09	340
81	11	5.2	5.2	32.2	0.0395	9.29
82		9.9	9.9	61.4	0.0754	14.8
83		20.3	20.3	126	0.154	28.6
84		40.0	40.0	248	0.304	52.0
85		101	101	626	0.768	107
86	11	202	202	1255	1.28	184
87		402	402	2490	3.06	287
88		800	800	4960	6.08	407
89	11	1535	1535	9510	11.7	481
90		3085	3085	19150	23.5	556
<u>Path Length = 400 cm</u>						
91	12	1.2	2.2	8.45	0.769	20.2
92		2.5	3.1	16.1	1.20	24.7
93		1.5	2.8	12.15	0.722	27.0
94		1.5	10.8	20.2	0.722	31.6
95		1.5	29.0	38.4	0.722	43.1
96	12	1.5	50.0	59.4	0.722	48.2
97		1.5	103	112.5	0.722	60.6
98		1.5	203	212.5	0.722	74.8
99		1.5	406	415	0.722	87.5
100	12	1.5	809	818	0.722	108
101	13	4.1	5.0	26.3	1.98	57.6
102		4.1	19.5	40.8	1.98	63.0
103		4.1	40.0	61.3	1.98	74.2
104		4.1	103	124	1.98	92.7
105		4.1	203	224	1.98	116
106	13	4.1	400	421	1.98	139
107		4.1	814	835	1.98	169
108		4.1	1535	1555	1.98	202

Table 2. (Continued)

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm ⁻¹
109	14	10.0	10.0	62.0	4.82	101
110		10.0	74.0	126	4.82	134
111		10.0	199	251	4.82	172
112		10.0	404	456	4.82	205
113		10.0	805	857	4.82	247
114		10.0	1535	1590	4.82	289
115	14	10.0	3085	3140	4.82	336
116	15	20.1	21.0	125.5	9.68	180
117		20.1	59.0	164	9.68	201
118		20.1	100	205	9.68	220
119		20.1	220	325	9.68	259
120		20.1	414	519	9.68	299
121		20.1	820	925	9.68	346
122	15	20.1	1535	1640	9.68	392
123		20.1	3085	3190	9.68	434
124	16	40.4	41.2	251	19.5	297
125		40.4	102	312	19.5	317
126		40.4	202	412	19.5	345
127		40.4	414	624	19.5	386
128		40.4	813	1025	19.5	427
129		40.4	1535	1745	19.5	460
130	16	40.4	3085	3295	19.5	490
131	17	97.0	98.0	602	47.1	454
132		97.0	204	708	47.1	467
133		97.0	408	912	47.1	487
134		97.0	830	1335	47.1	506
135		97.0	1535	2040	47.1	525
136		97.0	3085	3590	47.1	540

Fig. 18.--Total absorptance of the 950 cm^{-1} NH_3 band versus P_e for samples having w constant.

The decrease in slope of the curves of Fig. 18 with increased pressure indicates a decrease in the dependence of total absorptance upon equivalent pressure. This "saturation" can be rationalized by consideration of the change of line shape with pressure. With increased pressure the half-width of a spectral line increases and the absorption coefficient $k(\nu)$ increases at frequencies in the wings of the line but decreases near the line center. For large w and sufficiently high P_e , the half-width increases so that neighboring lines overlap in their wings and the result is almost complete absorption throughout the band so that further increase in pressure results in little if any increase in total absorptance. The approach to saturation is indicated in the spectral tracings for large absorber concentrations and equivalent pressures by the spectral absorptance approaching the 100% value over a considerable portion of the band.

For small values of w , Fig. 18 indicates saturation at lower values of P_e . In this case the increase in P_e causes a decrease in spectral absorptance at the line centers which nearly equals the increase in absorptance in the line wings. Thus little or no change in total absorptance occurs with the increase of P_e .

In Fig. 19 total absorptance of pure samples of ammonia is shown as a function of the equivalent pressure. The absorber concentration is not constant for each curve. In this case the value of w is proportional to P_e . Each curve corresponds to a different absorption path length. These curves indicate saturation, as do those in Fig. 18, for large values of w and P_e . This saturation occurs for smaller pressures

Fig. 19.--Total absorptance of the 950 cm⁻¹ NH₃ band versus P_e for samples whose values of w are proportional to P_e .

for the longer path lengths since the corresponding values of w are greater.

Fig. 20 illustrates the dependence of total absorptance upon absorber concentration w . The values for this figure were taken from Figs. 18 and 19 and plotted on a logarithmic scale. Each curve corresponds to the constant value of equivalent pressure indicated in order from top to bottom. From this figure the value of total absorptance for any sample can be determined if the values for w and P_e are known and fall within the range covered. Interpolation will yield values of total absorptance for values of P_e which lie between the values corresponding to the curves. The plotted points were omitted from the graph in order to make readings from it easier. Each curve is drawn as a solid line over the range of absorber concentrations covered by the data.

The extreme lower portion of the uppermost curve of Fig. 20, corresponding to an equivalent pressure of 3000 mm Hg, is seen to be nearly linear with a slope of approximately one. This indicates a linear dependence on w . Points along the linear portion of the curve are for a large value of P_e and small values of w . These are the conditions for which (13) is applicable. The intensity value so obtained is given in Table 5 in the summary.

Fig. 21 shows total absorptance as a function of wP_e for different values of P_e . The points in this figure are taken from Figs. 18 and 19. Since each curve corresponds to a given value of P_e , it has the same shape as the corresponding curve in Fig. 20 but the relative positions are shifted along the abscissa. Coincidence of the curves

Fig. 20.--Total absorptance of the 950 cm^{-1} NH_3 band versus w .

Fig. 21.--Total absorptance of the 950 cm⁻¹ NH₃ band versus wP_e .

would indicate the total absorptance to be a function of wP_e . The near coincidence of the upper portions of the curves indicates an approach to the wP_e dependence.

The slopes of the linear portions of the curves of Fig. 18 indicate the total absorptance to be proportional to $P_e^{0.34}$. The slopes of the linear portions of the lower curves of Fig. 20 average 0.56 indicating the total absorptance to be proportional to $w^{0.56}$.

B. The 1628 cm^{-1} ammonia band

The ν_4 fundamental band of ammonia at 1627.5 cm^{-1} for large absorber concentrations is overlapped slightly at the low frequency end by the ν_2 fundamental and at the high frequency end by the much less intense $2\nu_2$ band at 1922 cm^{-1} . In this study the total absorptance is measured from 2000 to 1300 cm^{-1} and tabulated as due to the 1628 cm^{-1} band.

The 1595 cm^{-1} band of H_2O overlaps the region of this ammonia band. Since most of the data for this band were taken during the winter and early spring when the relative humidity in the laboratory was low and since the rotational lines of the ammonia do not in general exactly coincide with those of H_2O , it is believed that little error is introduced by overlap and no correction has been made for it.

The total absorptance data were obtained in the same manner as described earlier for the 950 cm^{-1} band and are given in Table 3.

Tracings of many of the spectra are shown in Figs. 22 to 30. The values of w and P_e are indicated in the figures. For large values of w the spectral absorptance at the ends of the band is not zero as a result of overlap of the neighboring bands.

Table 3. Data for the 1628 cm^{-1} NH_3 Band

The Fig. No. corresponds to the figure in which the spectrum of each sample is shown. Absence of Fig. No. indicates spectrum is not shown. Uncertainties of the values of $\int A(\nu) d\nu$ are discussed in the text.

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm^{-1}
<u>Path Length = 1.55 cm</u>						
1		9.6	9.6	54.3	0.0179	2.20
2		9.6	20.2	65.9	0.0179	1.88
3		9.6	43.5	89.2	0.0179	2.66
4		9.6	116	162	0.0179	2.38
5		9.6	212	258	0.0179	2.33
6		9.6	403	449	0.0179	2.58
7		9.6	791	837	0.0179	2.45
8		9.6	1535	1580	0.0179	2.83
9		9.6	3085	3130	0.0179	2.71
10		20.2	20.2	116	0.0377	4.51
11		20.2	44.7	141	0.0377	4.61
12		20.2	109	205	0.0377	4.76
13		20.2	208	304	0.0377	5.06
14		20.2	402	498	0.0377	5.06
15		20.2	829	925	0.0377	5.01
16		20.2	1535	1631	0.0377	5.56
17		20.2	3085	3180	0.0377	5.91
18		39.8	39.8	230	0.0744	8.90
19		39.8	112	302	0.0744	8.76
20		39.8	205	395	0.0744	8.97
21		39.8	408	598	0.0744	9.45
22		39.8	797	987	0.0744	9.37
23		39.8	1535	1725	0.0744	9.80
24		39.8	3085	3275	0.0744	9.92
25	22	114	114	658	0.213	25.9
26	22	246	246	1420	0.459	46.9
27	22	521	521	3005	0.987	91.5
28	22	825	825	4760	1.54	132
29	22	1535	1535	8860	2.86	201
30	22	2310	2310	13300	4.31	256
31	22	3085	3085	17800	5.76	298

Table 3. (Continued)

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm ⁻¹
<u>Path Length = 6.35 cm</u>						
32		10.0	10.0	57.7	0.0761	6.93
33		10.0	25.0	72.7	0.0761	7.38
34		10.0	48.0	95.7	0.0761	7.58
35		10.0	139	187	0.0761	8.62
36		10.0	357	405	0.0761	9.05
37		10.0	807	855	0.0761	9.22
38		10.0	1535	1585	0.0761	9.75
39		10.0	3085	3135	0.0761	10.2
40	23	20.0	20.0	115.5	0.153	14.0
41		20.0	48.0	144	0.153	14.3
42		20.0	113	209	0.153	15.5
43	23	20.0	218	314	0.153	17.0
44		20.0	356	452	0.153	17.4
45		20.0	799	895	0.153	18.3
46	23	20.0	1535	1630	0.153	19.1
47		20.0	3085	3180	0.153	19.9
48		49.8	49.8	287	0.381	34.4
49	24	49.8	124	362	0.381	35.8
50		49.8	295	533	0.381	37.6
51		49.8	742	980	0.381	40.9
52		49.8	1535	1770	0.381	43.5
53	24	49.8	3085	3320	0.381	45.2
54	25	119	119	687	0.911	71.9
55		119	242	810	0.911	74.3
56		119	413	981	0.911	75.5
57		119	816	1385	0.911	80.1
58		119	1545	2115	0.911	83.1
59		119	2310	2880	0.911	85.5
60	25	119	3085	3650	0.911	87.5
61	24	211	211	1218	1.61	113
62		211	427	1435	1.61	117
63	24	211	835	1840	1.61	122
64		211	1535	2540	1.61	128
65		211	2310	3320	1.61	130
66	24	211	3085	4090	1.61	133
67	25	402	402	2320	3.08	180
68		402	837	2755	3.08	185
69		402	1535	3455	3.08	190

Table 3. (Continued)

Sample No.	Figure No.	p mm Hg	P mm Hg	P ₀ mm Hg	w atm cm	$\int A(\nu) d\nu$ cm ⁻¹
70	25	402	2310	4230	3.08	195
71		402	3085	5000	3.08	199
72		805	805	4645	6.13	267
73		805	1277	5115	6.13	270
74		805	2310	6150	6.13	275
75		805	3085	6925	6.13	278
76	26	10.0	10.0	57.7	0.0764	7.46
77	26	20.0	20.0	116	0.153	14.8
78	26	40.0	40.0	231	0.306	26.8
79	26	111	111	640	0.848	66.1
80	26	236	236	1362	1.80	123
81	26	446	446	2580	3.41	190
82	26	820	820	4740	6.27	268
83	26	1535	1535	8860	11.7	348
84	26	3085	3085	17800	23.6	419
<u>Path Length = 400 cm</u>						
85	27	1.5	2.8	12.2	0.722	16.1
86		1.5	10.8	20.2	0.722	23.4
87		1.5	29.0	38.4	0.722	29.0
88		1.5	50.0	59.4	0.722	33.3
89		1.5	103	112	0.722	39.4
90		1.5	203	212	0.722	47.4
91		1.5	406	415	0.722	54.2
92		1.5	809	818	0.722	59.0
93		5.2	5.7	30.5	2.49	44.7
94		5.2	18.3	43.1	2.49	53.2
95		5.2	38.8	63.6	2.49	62.0
96		5.2	106	131	2.49	79.1
97	27	5.2	210	235	2.49	94.7
98	27	5.2	406	431	2.49	115
99		5.2	605	630	2.49	124
100		5.2	888	913	2.49	132
101	28	9.8	10.2	56.9	4.72	82.4
102	28	9.8	28.2	74.9	4.72	90.0
103		9.8	49.8	96.5	4.72	98.4
104		9.8	100	147	4.72	114
105	28	9.8	206	253	4.72	135
106		9.8	310	357	4.72	151
107		9.8	513	560	4.72	170

Table 3. (Continued)

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm ⁻¹
108		9.8	792	839	4.72	185
109		19.2	19.4	111.0	9.30	152
110		19.2	34.8	125.5	9.30	155
111	29	19.2	60.0	151.5	9.30	162
112		19.2	105	197	9.30	175
113		19.2	159	251	9.30	187
114	29	19.2	271	363	9.30	203
115		19.2	407	499	9.30	222
116		19.2	606	698	9.30	239
117	29	19.2	803	895	9.30	250
118	30	39.2	40.0	226	18.8	250
119		39.2	90.0	277	18.8	264
120		39.2	153	340	18.8	279
121	30	39.2	276	463	18.8	294
122		39.2	394	581	18.8	302
123		39.2	614	801	18.8	321
124	30	39.2	801	988	18.8	332
125		59.0	59.0	340	28.4	301
126	28	59.0	97.0	378	28.4	306
127		59.0	155	436	28.4	315
128		59.0	256	537	28.4	328
129	28	59.0	379	660	28.4	340
130		59.0	599	880	28.4	353
131		59.0	808	1090	28.4	363
132	28	59.0	1535	1815	28.4	382
133	27	102	102	589	49.2	372
134		102	152	639	49.2	377
135		102	260	747	49.2	384
136	27	102	413	900	49.2	392
137		102	604	1090	49.2	400
138	27	102	813	1300	49.2	406

Fig. 22.--Spectra of the 1628 cm^{-1} NH_3 band.

Fig. 23.--Spectra of the 1628 cm⁻¹ NH₃ band.

Fig. 24.--Spectra of the 1628 cm⁻¹ NH₃ band.

Fig. 25.--Spectra of the 1628 cm^{-1} NH_3 band.

Fig. 26.--Spectra of the 1628 cm^{-1} NH_3 band.

Fig. 27.--Spectra of the 1628 cm^{-1} NH_3 band.

Fig. 28.--Spectra of the 1628 cm^{-1} NH_3 band.

Fig. 29.--Spectra of the 1628 cm⁻¹ NH₃ band.

Fig. 30.--Spectra of the 1628 cm^{-1} NH_3 band.

The value of the self-broadening coefficient B for this band was determined by use of the double beam feature of the spectrometer. Part I of Fig. 31 shows a typical spectral comparison obtained by this method. The line $T_{\text{sam}}/T_{\text{ref}} = 1.00$ represents the spectrum when both cells were evacuated and indicates the recorder pen position when the two beams were "balanced", that is, the transmittance of the two samples were the same. As the pressure in the sample cell was increased the ratio of the transmittances decreased as would be expected. At some frequencies the spectra occur above the balance line while at others they occur below. Thus the total pressure for balance was not the same for all frequencies and the pressure corresponding to balance for any particular frequency was obtained by interpolation between two adjacent curves which occur on either side of the balance line. This variation of total pressure for balance leads to variation of B with frequency. This variation is indicated in Part II of the figure which shows a plot of a typical set of data for the value of B . A number of such separate determinations of B were made at pressures from 100 to 600 mm Hg in the sample cell.

Since this study deals with total absorptance it is desirable to obtain a nominal value for B for use throughout the entire band. This nominal value was obtained by taking a "weighted average" value of B over the frequency range of the band, with weight adjusted to correspond to the spectral absorptance of the band at the various frequencies. Averaging the values of B obtained from the separate determinations gave the value $5.77 \pm .34$. The values for P_e were calculated using $B = 5.77$.

Fig. 31.--The self-broadening coefficient B for the 1628 cm^{-1} NH_3 band. The same slit width was used for I and III.

A typical absorption spectrum is given in Part III of the figure for comparison with the other parts of the figure.

Figs. 32 and 33 show plots of total absorptance as a function of P_e for nitrogen mixed and pure samples of ammonia respectively.

The slopes of the curves vary in the same manner as those for the 950 cm^{-1} band discussed earlier. It is seen that "saturation" sets in at relatively lower values of P_e .

Fig. 34 shows total absorptance as a function of w for the 1628 cm^{-1} band. Values for this figure were taken from Figs. 32 and 33. The values of P_e are indicated as in the earlier graphs. If w and P_e are known for a given sample, the value of total absorptance for this band can be determined from the figure. Interpolation will yield values of total absorptance for which P_e lies between the values indicated for the curves. The plotted points were omitted to facilitate the use of the graph. The curves are drawn as solid lines over the range covered by the data. The lower portion of the uppermost curve can be used to obtain a value for the intensity of the band by use of (13). The value so obtained is given in Table 5 of the summary.

As in the case of the 950 cm^{-1} band, a plot of total absorptance as a function of wP_e was made. This is shown in Fig. 35. Coincidence of the curves would indicate the total absorptance to be a function of wP_e . The curves converge at the upper right hand side of the graph but do not coincide.

The slopes of the linear portions of the curves in Figs. 33 and 34 indicate that the total absorptance is proportional to $P_e^{0.40}$ and $w^{0.54}$.

Fig. 32.--Total absorbance of the 1628 cm^{-1} NH_3 band versus P_e for samples having w constant.

Fig. 33.--Total absorptance of the 1628 cm^{-1} NH_3 band versus P_e for samples whose values of w are proportional to P_e .

Fig. 34.--Total absorptance of the 1628 cm⁻¹ NH₃ band versus w .

Fig. 35.--Total absorptance of the 1628 cm^{-1} NH_3 band versus wP_e .

C. The 3300 cm^{-1} ammonia bands

The total absorptance by ammonia in the region 3750 to 2900 cm^{-1} is due to the overlapping bands ν_1 , ν_3 , and $2\nu_4$ of ammonia as indicated in Table 1. These bands are of relatively low intensity and the total absorptance is measured for the whole group as a single band. Atmospheric water vapor and carbon dioxide bands which occur near 3700 cm^{-1} overlap the high frequency end of this region. These are relatively weak, and, since most of the data were taken during a period when the relative humidity in the laboratory was low, their effects were considered to be negligible.

The data for total absorptance were obtained as for the previously discussed bands and are tabulated in Table 4. Tracings of many of the spectra are shown in Figs. 36 to 43. Graphs of total absorptance as a function of P_0 for mixed and pure samples of ammonia are shown in Figs. 44 and 45 respectively.

The over-all intensity of this region was too small to obtain satisfactory consistency of experimental values for B by means of the double beam method, and the slopes of the curves were too small to give consistent results by the graphical treatment. Thus the value for B was taken as 6.2 , the value used for the 950 cm^{-1} band.

Fig. 46 shows total absorptance as a function of w for various values of P_0 . As in the earlier cases the points have been omitted from the graph. This graph provides a value for total absorptance over the region for each value of w and P_0 within the range of study.

Since the data for this region are somewhat limited, no attempt was made to compare the results with theory.

Table 4. Data for the 3300 cm^{-1} NH_3 Bands

The Fig. No. corresponds to the figure in which the spectrum of each sample is shown. Absence of Fig. No. indicates spectrum is not shown. Uncertainties of the values of $\int A(\nu) d\nu$ are discussed in the text.

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm^{-1}
<u>Path Length = 1.55 cm</u>						
1		20.0	20.0	124	0.0372	1.55
2		43.0	43.0	266	0.0798	3.56
3		101	101	626	0.188	7.80
4		206	206	1280	0.383	15.6
5	36	401	401	2485	0.745	30.8
6		803	803	4980	1.47	56.5
7	36	1535	1535	9510	2.85	97.5
8	36	3085	3085	19150	5.74	181
9		40.2	40.2	249	0.0753	3.50
10		40.2	105	314	0.0753	3.20
11		40.2	205	414	0.0753	3.30
12		40.2	407	616	0.0753	3.28
13		40.2	817	1025	0.0753	3.35
14		40.2	1535	1745	0.0753	2.75
15		40.2	3085	3295	0.0753	2.95
<u>Path Length = 6.35 cm</u>						
16		20.7	20.7	129	0.158	6.77
17		20.7	42.0	150	0.158	6.90
18		20.7	97.0	215	0.158	7.28
19		20.7	198	306	0.158	7.46
20		20.7	408	516	0.158	6.87
21		20.7	845	953	0.158	7.51
22		20.7	1535	1645	0.158	7.63
23		20.7	3085	3195	0.158	7.41
24	37	47.0	47.0	291	0.358	13.5
25		47.0	120	364	0.358	14.4
26		47.0	276	520	0.358	14.8
27		47.0	699	943	0.358	15.9
28		47.0	1535	1780	0.358	16.1
29	37	47.0	3085	3330	0.358	17.3
30	38	86.0	86.0	533	0.657	24.1
31		86.0	223	670	0.657	24.2
32		86.0	416	863	0.657	25.2
33		86.0	808	1255	0.657	24.4

Table 4. (Continued)

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm ⁻¹
34	38	86.0	1540	1990	0.657	25.7
35		86.0	3085	3530	0.657	26.0
36	38	200	200	1240	1.515	50.7
37		200	400	1440	1.515	51.3
38		200	827	1870	1.515	51.9
39		200	1535	2575	1.515	52.1
40		200	3085	4125	1.515	53.7
41	39	401	401	2485	3.04	87.6
42		401	834	2920	3.04	90.2
43		401	1535	3620	3.04	93.4
44		401	3085	5160	3.04	96.4
45	39	821	821	5090	6.23	158
46		821	1535	5805	6.23	161
47	39	821	3085	7355	6.23	166
48	40	10.0	10.0	62.0	0.0765	3.22
49		20.0	20.0	124	0.153	9.38
50		40.0	40.0	248	0.306	15.8
51		100	100	620	0.765	32.2
52		206	206	1280	1.575	53.6
53		300	300	1860	2.30	72.9
54		557	557	3450	4.26	119
55		800	800	4960	6.11	156
56		1535	1535	9510	11.75	250
57		2310	2310	14300	17.7	322
58		3085	3085	19100	23.6	374
<u>Path Length = 400 cm</u>						
59	41	5.2	5.2	32.2	1.875	33.8
60		5.2	13.6	40.6	1.875	33.8
61		5.2	29.8	56.8	1.875	37.8
62		5.2	55.0	82.0	1.875	40.4
63		5.2	101	128	1.875	43.3
64		5.2	202	229	1.875	48.1
65		5.2	341	368	1.875	51.5
66		5.2	495	522	1.875	52.8
67		5.2	806	833	1.875	56.4
68	42	8.7	9.5	54.0	4.18	59.1
69		8.7	40.0	85.2	4.18	64.6
70		8.7	102	147	4.18	72.5

Table 4. (Continued)

Sample No.	Figure No.	p mm Hg	P mm Hg	P _e mm Hg	w atm cm	$\int A(\nu) d\nu$ cm ⁻¹
71		8.7	203	248	4.18	82.0
72		8.7	400	445	4.18	90.0
73	42	8.7	812	857	4.18	97.5
74		18.1	18.6	113	8.66	106
75		18.1	30.0	124	8.66	108
76		18.1	87.0	181	8.66	119
77	37	18.1	197	291	8.66	133
78		18.1	359	453	8.66	144
79		18.1	738	832	8.66	156
80	37	18.1	935	1030	8.66	160
81	43	31.2	31.2	193	14.93	160
82		31.2	76.0	238	14.93	166
83		31.2	149	311	14.93	176
84	43	31.2	270	432	14.93	189
85		31.2	403	565	14.93	199
86		31.2	626	788	14.93	210
87	43	31.2	850	1010	14.93	217
88	43	48.0	48.0	298	23.2	224
89		48.0	98.0	348	23.2	233
90		48.0	165	415	23.2	242
91	43	48.0	268	518	23.2	252
92		48.0	411	661	23.2	264
93		48.0	603	853	23.2	273
94	43	48.0	833	1080	23.2	282
95	43	117	117	725	46.5	353
96		117	160	768	46.5	359
97	43	117	263	871	46.5	365
98		117	398	1005	46.5	375
99		117	617	1225	46.5	381
100	43	117	832	1440	46.5	388

Fig. 36.--Spectra of the 3300 cm^{-1} NH_3 bands.

Fig. 37.--Spectra of the 3300 cm^{-1} NH_3 bands.

Fig. 38.--Spectra of the 3300 cm^{-1} NH_3 bands.

Fig. 39.--Spectra of the 3300 cm^{-1} NH_3 bands.

Fig. 40.--Spectra of the 3300 cm^{-1} NH_3 bands.

Fig. 41.--Spectra of the 3300 cm^{-1} NH_3 bands.

Fig. 42.--Spectra of the 3300 cm⁻¹ NH₃ bands.

Fig. 43.--Spectra of the 3300 cm^{-1} NH_3 bands.

Fig. 44.--Total absorptance of the 3300 cm^{-1} NH_3 bands versus P_e for samples having w constant.

Fig. 45.--Total absorbance of the 3300 cm⁻¹ NH₃ bands versus P_e for samples whose values of w are proportional to P_e .

Fig. 46.--Total absorptance of the 3300 cm^{-1} NH_3 bands versus w .

SUMMARY AND DISCUSSION OF RESULTS

It is seen from the graphs of total absorptance as a function of w and P_0 for the various bands studied that total absorptance is more strongly dependent upon w than P_0 . In regions where the "strong-line approximation" predicts the total absorptance should be proportional to $(wP_0)^{\frac{1}{2}}$ it was found that the slopes of the curves indicate that total absorptance is approximately proportional to $w^{\frac{1}{2}}$ but not to $P_0^{\frac{1}{2}}$. The near-coincidence of the curves at the upper right of Fig. 21 indicates the strong-line approximation for the Elsasser band model to be relatively appropriate for this region. However, reference to the spectral tracings in Figs. 16 and 17 which correspond to the upper parts of the graphs of Fig. 21 shows almost complete spectral absorptance throughout the band. This would result in the near-coincidence of the curves. Perhaps the data could be fitted to a random Elsasser band model.

It would be possible to derive empirical equations relating total absorptance to w and P_0 for certain limited ranges of the variables. However, it is believed that the graphs shown in this study provide more accurate estimates of total absorptance for various values of w and P_0 . Extrapolations of the data presented in this study should be made with caution since such could result in sizable errors.

The methods of this study provide a means of obtaining band intensities by use of (13). The condition for validity of (13) is that

$k(\nu)w \ll 1$ for all frequencies of the band. This condition is satisfied for sufficiently small values of w and values of P_e large enough that $k(\nu)$ is small even at the centers of the rotational lines.

The convergence of the curves in the graphs of total absorptance versus w for small values of w indicates that the total absorptance is approaching independence of P_e . This is the condition for which the "weak-line approximation" applies and the total absorptance is a function of w and S . The approach of the lower portions of the curves to a slope of unity also indicates that the condition for validity of (13) is satisfied.

The band intensities obtained from the present data are listed along with the values of the self-broadening coefficients and the related ratio of the sum of the optical collision diameters in Table 5. The band intensities were calculated by using (13) and points along the lower portion of the uppermost curve of the graphs of total absorptance versus w or an extrapolation of them to a slope of unity. It should be noted that the intensity indicated for the 3300 cm^{-1} region is the effective intensity of the series of overlapping bands of this region. Also, the values listed are for room temperature which varied from 24° to 29°C . The values used for w are corrected to standard conditions. The optical collision diameter ratios were determined from (17).

By considering the slopes of the linear portions of the graphs of total absorptance versus P_e and w it is possible to express the total absorptance for these regions as a function of $w^m P_e^n$. The slope of the linear portion of the lower curves of total absorptance versus w is the value of the exponent m . Similarly, the slope of the linear portions

Table 5. Band Intensities, Self-broadening Coefficients and Ratios of Optical Collision Diameters.

Band Frequency cm^{-1}	Band Intensity $\text{atm}^{-1} \text{ cm}^{-2}$ $\int k(\nu) d\nu$	Self-broadening Coefficient B	$\frac{D_{\text{NH}_3, \text{NH}_3}}{D_{\text{NH}_3, \text{N}_2}}$
950	790 ± 30	6.2 ± 1.0	2.36 ± 0.20
1628	150 ± 5	5.77 ± 0.34	2.28 ± 0.07
3300	47 ± 3	(from 950 cm^{-1} band)	

of the curves for total absorptance versus P_e , for samples for which the values of w are proportional to those of P_e , is the value of the sum of the exponents $m + n$. The slope of the linear portions of the curves for total absorptance versus P_e , for samples for which the value of w is constant, is the value of the exponent n . The values for m and n obtained for the bands of the present study are tabulated in Table 6. Also shown for comparison are the values of m and n obtained for other molecules by Burch *et al.*⁴⁻⁶ The values for B obtained from the same studies are also shown for comparison.

Of the molecules listed in Table 6, ammonia is the only symmetric top molecule. If the hot bands of CO_2 at 1064 and 961 cm^{-1} are neglected, it is seen that the values of m range from 0.48 to 0.59 which indicates that the total absorptance is very nearly a function of $w^{\frac{1}{2}}$. Again, with the exception of the hot bands of CO_2 , the value of n ranges from 0.22 to 0.44 and gradually decreases in value as the atomic multiplicity of the molecule increases.

Table 6. Comparison of Results.

Band		m	n	Self-broadening Coefficient B
CH ₄	3020 cm ⁻¹	0.55	0.22	1.30 ± 0.08
	1306 cm ⁻¹	0.48	0.30	1.38 ± 0.08
NH ₃	950 cm ⁻¹	0.56	0.34	6.2 ± 1.0
	1628 cm ⁻¹	0.54	0.40	5.77 ± 0.34
	3300 cm ⁻¹	0.59	0.34	
H ₂ O	5332 cm ⁻¹	0.53 ^a		5.0 ± 1.5
	3700 cm ⁻¹	0.49 ^a		
N ₂ O	2224 cm ⁻¹	0.53	0.37	1.12 ± 0.07
CO ₂	3716 cm ⁻¹	}		
	3609 cm ⁻¹			
	2350 cm ⁻¹		0.38	1.30 ± 0.08
	1064 cm ⁻¹		0.40	
	961 cm ⁻¹		0.23	
			0.75	
			0.20	
CO	2143 cm ⁻¹	0.55	0.44	1.02 ± 0.06

^aValues estimated from the lower portion of the curves.

It is hoped that the results of this research may be useful (1) for predicting total absorptance by ammonia over known path lengths and in known mixtures with other gases; (2) as a preliminary to studies to determine the amount of ammonia in planetary atmospheres and (3) to test the various theories offered to explain absorptance phenomena.

AUTOBIOGRAPHY

Wilbur Leslie France

I was born September 8, 1925, near Zanesville, Ohio. I attended McKendree Elementary School and graduated from South Zanesville High School. My undergraduate work was completed at Capital University, where I received the Bachelor of Science degree in 1950. After two years of military service I entered graduate school at The Ohio State University, which granted me the Master of Science degree in 1954. Except for three years of employment, one year of which was as Instructor in Physics at Capital University, I continued graduate study at The Ohio State University. While in graduate school I have held the positions of Teaching Assistant, Research Assistant, Research Associate, and Instructor in Physics.