A SAMPLE MODULATION TECHNIQUE
FOR THE STUDY OF INFRARED
ABSORPTION SPECTRA

DISSERTATION
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I. INTRODUCTION

The absorption of infrared radiation by the various constituents through which it passes in the atmosphere is of considerable importance in a variety of problems. The dependence of gaseous absorption in the infrared on such parameters as pressure, temperature, and concentration has received considerable attention from various investigators. The present study is concerned with the pressure dependence of infrared absorption and its use in the development of an operational technique for the study of weak absorption lines and pressure growth phenomena.

The earliest investigations in the infrared employed techniques which might be termed quasistatic. Herschel, in discovering the infrared in 1800, employed a sensitive thermometer. The discovery of thermoelectricity by Seebeck in 1823 provided the basis for a more quantitative examination of this little-understood spectral region. In 1830 Melloni constructed a sensitive thermopile and used it to investigate the transparency of various substances to infrared radiation, from which investigation he concluded that the invisible infrared rays were of the same nature as visible light. The bolometer principle was first discovered in 1849 by Svanberg, but its application waited until 1881, when Langley rediscovered the principle and employed it in a radiation detector. The late 1800's brought
the radiometer and microradiometer into use as infrared detectors.

The microradiometer as introduced by Boys consisted of a single-turn galvanometer coil, one end of which was completed by a thermocouple. A mirror was mounted to the quartz suspension fiber, and the whole assembly was evacuated. The radiometer detector was devised by Nichols, using a variation of the Crookes "light mill." Instead of permitting the mica vane assembly to rotate freely as in the Crookes radiometer, Nichols opposed the torque of the vanes with the torsion of the quartz suspension fiber. A mirror mounted on the assembly permitted a measurement of the angular displacement.

Absorption spectroscopy in these early days was performed by setting the monochromator to the desired wavelength, then taking the ratio of the detected radiation with and without the absorber in the light path. Drift was a major problem with these methods and it was necessary to check the "dark" deflection of the indicating device frequently.

A significant contribution to spectroscopic instrumentation was Pfund's resonance radiometer of 1929 in which "A single-junction thermopile .. was exposed to radiation at intervals of 0.75 seconds by a pendulum having a period of 1.5 seconds. The thermopile was connected to a low-resistance, underdamped D'Arsonval galvanometer tuned to a period of 1.5 seconds." The deflection of this galvanometer caused deviation of a light beam falling on a second thermopile, this latter actuating a second tuned galvanometer. This system
simultaneously provided tuned amplification and freedom from drift. The modern chopped-beam technique is but a minor variation of Pfund's method, with a motor-driven chopper replacing the pendulum and a tuned vacuum-tube amplifier replacing the tuned galvanometers.

In 1939 Hardy introduced a double-beam spectrometer which permitted simultaneous determination of an absorption spectrum and the background spectrum. This concept has been extended in recent years to permit direct percent-absorption measurements.

All the techniques described above give absorption data at the constant pressure conditions which prevail for any one measurement. Information on the growth of spectral lines and bands can be obtained only by successive measurements, each employing different quantities of the absorbing gas. The technique which forms the basis of this study supplements the absorption data provided by the above methods in that its output is pressure-growth dependent, and greater precision in this type of study is afforded by virtue of its relative independence from variations in source temperature and atmospheric composition. Other characteristics peculiar to the subject of this study include improved positional definition of absorption lines of high J-values and improved band-edge information.
II. SAMPLE MODULATION

A. Definition

It is to be noted that in the above techniques, none of the average parameters of the absorber are intentionally altered during the measurement of absorptions. The detector output is an alternating voltage in the chopped-beam and double-beam methods by virtue of the beam alternately passing through an absorbing and a reference condition resulting from optical diversion of the beam. In contrast with this, consider a technique in which the beam passes constantly through the sample, and some condition of the sample is varied periodically in such a manner as to alter the nature of the absorption phenomenon in accordance with this variation. This may properly be called sample modulation.

B. Radiofrequency Applications of Sample Modulation

The first well-exploited application of sample-modulation was made in 1947 by Hughes and Wilson, in which the Stark effect was employed in their study of the microwave inversion spectrum of ammonia at 1.2 cm wavelengths. Magnetic field modulation has been employed in the study of nuclear magnetic resonance, quadrupole moments, and the absorption of paramagnetic materials.

The half-widths of absorption lines in the microwave region are typically 25 mc (8x10^-4 cm^-1) and lower under the usual measuring
The width of the lines is due to several factors, but the most important of these is collisions of the absorbing molecules with other molecules and with the containing walls. Stark splittings of several line-widths can be conveniently obtained in many molecules with fields of less than 1000 volts/cm. The magnetic field techniques are capable of providing similar perturbations with laboratory fields. It is to be noted that a resolution of about $10^3$ would be sufficient to observe Stark splitting at 1.2 cm wavelengths.

Similar splittings also occur in the vibration-rotation lines of the infrared, but since line half-widths in the infrared are typically $10^{-1}$ cm$^{-1}$, a "splitting" of $10^{-3}$ cm$^{-1}$ would serve only to broaden slightly the line under investigation. Further, in order to observe this, a resolution of $10^6$ or greater would be required. Thus the type of sample modulation employed in radio-frequency regions is not generally applicable to the infrared region, since resolving powers of the order of $10^5$ are realized only in the best infrared spectrometers through the use of gratings and large optical elements.

C. Infrared Sample Modulation

Sample modulation for use in the study of infrared gaseous absorptions has been considered previously by Magnuson and Smith. In their work, two techniques were employed. The first was a continuous-flow system in which air and the absorbing gas were alter-
nately pumped through the cell. The second system employed a cell whose length was sinusoidally varied. A few results were obtained with a prism spectrometer and the project was terminated.

Dickey has reported on a sample modulation technique for the study of infrared emission spectra in flames. He employs a modified burner whose purpose is to produce the emission spectrum of the sample gas by injecting the sample into the flame of an exciting gas. The exciting gas (e.g. methane, hydrogen) is admitted to the burner through the usual inlet, while the sample gas is admitted through a second specially-constructed inlet. A continuously-rotating motor-driven valve is placed in the line to the sample tank, and this serves to interrupt periodically the flow of sample gas to the burner. Thus the radiation incident on the spectrometer always contains the spectrum of the exciting gas, and intermittently a superimposed spectrum of the sample gas. Ideallly the detector output at a given wavelength would consist of a d-c term due to the exciting gas and an a-c term due to the sample gas. Since the amplifier passes only the alternating component, complete suppression of the exciting gas spectrum would be expected. Instability of the flame, however, limited the suppression of the background relative to the desired spectrum to a factor of about 100. Although Dickey's work is perhaps questionably within the earlier definition of sample modulation, it is akin to the pressure modulation study in that both techniques serve materially to reduce the undesired background.
III. THEORY

A. Lines

Infrared absorption in gases is governed by Lambert's law

\[ I = I_0 \exp \left( -k(\nu)l \right) \]

where \( I \) is the intensity remaining from a beam of original intensity \( I_0 \), after traversing the absorber a distance \( l \). The \( k(\nu) \) is called the absorption coefficient for which Lorentz derived the following form based on classical collisions in a Maxwellian gas:

\[ k(\nu) = \frac{S}{\pi} \frac{\alpha}{(\nu - \nu_o)^2 + \alpha^2}. \]

Here \( S \), called the line-strength, is the integral \( \int k(\nu) d\nu \) over the line, \( \alpha \) is the half-width at half-intensity, and \( \nu_o \) is the line-center frequency.

The absorption at a given frequency may be defined by

\[ A(\nu) = \frac{I_o - I}{I_o} = 1 - \frac{I}{I_o} = 1 - e^{-k(\nu)l}. \]

If it were possible to examine absorption lines with a spectrometer of infinite resolving power, the data would depend only on the conditions of the absorbing gas. In practice however, the appearance of the observed spectra is quite dependent on the dispersive system and the slit widths employed. In order to permit a comparison of theoretical predictions with experimental data, the total or integrated absorption \( \int A'(\nu) d\nu \) is widely used. Here \( A'(\nu) \) is
the observed absorption at frequency $\nu$. Neilsen, Thornton, and Dale have shown that over wide limits of resolving power, the integrated absorption is independent of slit function, hence

$$\int A(\nu) \, d\nu = \int A'(\nu) \, d\nu$$

where $A(\nu)$ is the true absorption at frequency $\nu$ as measured with infinite resolution. The indicated integration is carried over the entire interval for which absorption of the line is measurable. The independence of this quantity from slit-width effects has been experimentally verified by Shaw and Howard for lines of CO.

Ladenberg and Reiche utilized Lambert's and Lorentz relations in a direct integration to obtain:

$$\int A(\nu) \, d\nu = 2\pi \alpha \, x \exp(-x) \left[ J_0(ix) - i J_1(ix) \right]$$ (1)

where $x = \frac{S \omega}{2\pi \alpha}$ and $J_0$ and $J_1$ are the zero-order and first-order Bessel functions respectively. The quantity $w$ is called the absorber concentration, which at a given temperature is proportional to the product of the path length $\ell$ and the partial pressure $p$.

By employing series expansions and asymptotic forms, convenient approximations for (1) are obtained in two limiting cases

For weak lines ($S \omega \ll \alpha$) $\int A(\nu) \, d\nu = Sw$

For strong lines ($S \omega \gg \alpha$) $\int A(\nu) \, d\nu = 2(S\alpha w)^{1/2}$ (2)
The dependence of $\int A(\nu) \, d\nu$ on the absorber concentration $w$ has been confirmed experimentally by Shaw and France,\textsuperscript{11} using values of $w$ between $10^{-3}$ and 10 atm-cm. Their work was done on isolated lines of CO at a constant total pressure of 70 cm Hg.

B. Bands

Several attempts have been made to predict the absorption of unresolved bands such as the vibration-rotation bands of the infrared. The earlier theoretical works are due principally to Elsasser,\textsuperscript{12} who chose as his model a uniformly-spaced array of uniform-amplitude lines, and to Goody,\textsuperscript{13} who used a statistical model. Quite recently, King\textsuperscript{14} devised a more general model for bands which includes the above two models as special cases, and Benedict\textsuperscript{15} obtained excellent agreement with observed spectra from a direct summation of the individual absorption lines. Howard, Burch, and Williams\textsuperscript{16-21} conducted a detailed experimental study on the absorption by H$_2$O bands between 6.3$\mu$ and 0.9$\mu$ and by CO$_2$ bands between 15$\mu$ and 1.4$\mu$. Their data on the rather uniformly-spaced CO$_2$ bands fit the Elsasser model very well, and the data on the more complex H$_2$O bands are in excellent agreement with Goody's model. Their results may be summarized by the equations:

For weak bands  $\int A(\nu) \, d\nu = c \, w^{1/2} \, (P+p)^k$

For strong bands  $\int A(\nu) \, d\nu = C + D \log w + K \log (P+p)$
Here \( c, k, C, D, \) and \( K \) are all empirically determined constants and \( w, p, \) and \( P \) are the absorber concentration, absorber partial pressure, and total pressure, respectively. The independence of \( \int A(v) \, dv \) from slit-width effects is demonstrated over wide limits in the work of Howard, et al.\(^{16}\)

C. Extension to Pressure-Modulation Study

If the volume of the closed system containing a gas is isothermally reduced from \( V_o \) to \( V \), the ideal gas law shows that the initial and final pressures are related to the volumes by

\[
\frac{V_o}{V} = \frac{P}{P_o}. \quad \text{Let the gas consist of a partial pressure } p \text{ of an absorbing gas and a partial pressure } P-p \text{ of inert gas, the total pressure of the mixture being } P. \end{equation} \]

The work of Howard, et al.,\(^{16}\) shows that the pressure and temperature dependence of the half-width \( \alpha \) is

\[
\alpha = \alpha_o \frac{P}{P_o} \left( \frac{T_o}{T} \right)^{1/2}. \end{equation} \]

Hence \( \alpha \) is also directly proportional to \( P \) for the isothermal volume change.

Now let infrared radiation traverse some fixed-length portion of the closed system. Using the results (4) and (5) in (2), the
integrated absorption is

For weak lines \( \int A(\nu) \, d\nu = S \frac{\omega_0}{P_0} = C_1 P \)

For strong lines \( \int A(\nu) \, d\nu = 2 \left( \frac{S \alpha}{P_0} \frac{\omega_0}{P_0} \right)^{1/2} = C_2 P \) \hspace{1cm} (6)

Similarly, the band equations (3) can be rewritten in the form

For weak bands \( \int A(\nu) \, d\nu = C \left( \frac{\omega_0 P}{P_0} \right)^{1/2} \left( P \frac{P_0}{P_0} \right)^{k} = C_3 P^{1/2+k} \)

For strong bands \( \int A(\nu) \, d\nu = C + D \log \left[ \frac{\omega_0}{P_0} \right] + K \log \left[ P \frac{P_0}{P_0} \right] \) \hspace{1cm} (7)

\[ = C + \log \left[ \frac{\omega_0}{P_0} \right]^D + \log \left[ \frac{P}{P_0} \right] ^K + \log . P^{D+K} \]

\[ = C_4 + \log P^{D+K} \]

In order to clarify the pressure-dependence concept, a Lorentz line at two total pressures is shown in Figure 1. These are drawn according to the modified Ladenberg and Reiche relation (6) for a given \( S \) and \( \alpha \) and \( P_1/P_2 = 0.63 \). The total absorptions are the areas between the curves and the baseline.

The simple dependence on \( P \) exhibited by the above expressions led to the belief that a technique could be developed which would provide direct pressure-growth information with application to both lines and bands.
D. Preliminary Considerations of Technique

In consideration of the foregoing, a periodic pressure variation would be expected to provide an alternating output voltage from a detector. Figure 2 shows the envelope of the expected output signal when the pressure is periodically varied between total pressures $P_1$ and $P_2$ of Figure 1. For brevity, such a periodic pressure variation in the sample will be referred to as pressure modulation.

If the absorption spectrum of a sinusoidally pressure-modulated gas is taken between pressures $P_1$ and $P_2$ with the same apparatus as used for conventional spectra, then the area under the modulated-absorber curve is expected to be $\pi/4$ times the difference between the areas of Figure 1. This statement is justified in Appendix I. It is found that greater gain is required to obtain satisfactory modulated-absorber spectra than is required for conventional spectra, and also that the detection system response is slightly different at the pressure-modulation frequency than at the beam-chopping frequency. Combination of these factors gives the relation

$$\Delta A = \frac{A_{PM}}{G \cdot R \cdot \frac{\pi}{4}}$$

where $\Delta A$ is the area difference of conventional spectra at pressures $P_1$ and $P_2$, $A_{PM}$ is the area of the modulated-absorber curve for the same line or band, and $G$ and $R$ are the ratios of system gain and response at the two frequencies above.
Figure 1. Illustration of the Dependence of a Lorentz Line on Closed-System Total Pressure

Figure 2. Envelope of Detector Output under Pressure-Modulation between $P_1$ and $P_2$. 
It was recognized early in the course of the investigation that, at frequencies for which vacuum tube amplifiers could be readily obtained, the pressure variation could not be considered isothermal. The behavior of a dynamic closed system in poor thermal contact with its surroundings is described by the adiabatic law $PV^r = \text{constant}$. Combination of the adiabatic law with the ideal gas law $PV = nkT$ introduces the temperature of the gas through the relation

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{r-1}{r}}.$$

Since temperature varies with pressure in the presumably adiabatic system, it is necessary to consider the quantum-mechanical expression for line-strength. This is given for diatomic molecules by

$$S = K \omega \frac{B}{T} (2J + 1) \exp \left[ -J(J+1) \frac{\hbar c B}{kT} \right]$$

where $K$ is a constant for a given vibration-rotation band, $\omega$ is the frequency of the line with initial quantum number $J$, $B$ is the rotational constant, and $T$ is the absolute temperature. In qualitative terms, the effect of increasing the temperature of a sample is to cause a relatively greater population of the higher $J$-levels, resulting in an increase in the line-strengths of high-$J$ lines at the expense of a decrease in the line-strengths of low-$J$ lines. The net effect of this shift in line-strengths on $\int A(v)$ for bands is slight for small temperature variations, but the temperature dependence enters significantly into the explanation of the data on resolved absorption lines.
IV. EXPERIMENTAL APPARATUS AND PROCEDURES

A schematic diagram of the apparatus is shown in Figure 3. The shaft speed of a quarter-horsepower 1725 rpm induction motor is reduced to about 8 rps with pulleys. An eccentric mounted on the 8 rps shaft is connected by an aluminum rod to the center of a circular neoprene diaphragm. This last is edge-mounted to a 3-1/2-inch length of 8-inch i.d. brass tubing. The optical system forms the first image of the Nernst source at the center of the cell, and the second image is formed at the entrance of the spectrometer.

The amplifier is a Perkin-Elmer Model 107 whose output is rectified with a Perkin-Elmer mechanical rectifier driven by the 8 rps shaft. The rectifier is aligned with the eccentric so that only those components of signal in phase with the pressure modulation are integrated in the output filter.

A photograph of the motor-driven reservoir is shown in Figure 4. The eccentric which drives the diaphragm is provided with five steps of eccentricity, specifically, 1/2-inch, 5/8-inch, 3/4-inch, 7/8-inch and 1-inch. However all the data to follow were obtained at the 7/8-inch setting because this was found to provide a satisfactory compromise between large pressure variations and excessive stretching of the diaphragm.
FIGURE 3. BLOCK DIAGRAM OF PRESSURE MODULATION EQUIPMENT
Figure 4. Photograph of the Pressure-Modulation Apparatus
The grating spectrometer data in this presentation were taken between frequencies of 6000 and 2000 cm\(^{-1}\). The data between 6000 and 4000 cm\(^{-1}\) were taken with an uncooled Perkin-Elmer lead sulfide detector, and a Perkin-Elmer thermocouple detector was used for the lower frequencies. The grating spectrometer is of the Pfund type, employing a plane grating with 4500 lines/in\(^2\) blazed at 3000 cm\(^{-1}\). This instrument is described elsewhere.\(^{24}\)

The prism instrument used is a Perkin-Elmer Model 12C, with a LiF prism and a Reeder thermocouple detector.

Some preliminary work showed that the technique was sound, but considerably greater amplifier gain was required to obtain satisfactory spectrograms with the pressure-modulation technique than with the conventional technique. Theory and experiment both showed that the magnitude of signal increased with increasing pressure change, but it was felt that any appreciable increase in the length of the eccentric stroke would materially shorten the lifetime of the diaphragm. In an effort to reduce the system "dead" volume, the hose connecting the reservoir to the cell was shortened, and an aluminum filler block was machined to fill, within practical limits, that volume not occupied by the diaphragm assembly over the modulation cycle. Further, the neoprene diaphragm displayed a tendency to stretch slightly near the center. In order to minimize the degradation of pressure ratio from this cause, the pressure was set at one atmosphere at the minimum volume condition so that the diaphragm is pulled unidirectionally by the eccentric, while the
pressure difference with the atmosphere helps return the diaphragm to the minimum volume position. The modifications in apparatus and procedure produced a more satisfactory pressure variation and they were permanently adopted prior to obtaining the data to be presented.

An expected static pressure ratio is readily calculated by using the following parameters: Reservoir with filler block (diaphragm at center), 81.38 in³; hose, 7.98 in³; cell, 6.14 in³; variation of diaphragm, ±22.54 in³. The pressure ratio $P_{min}/P_{max}$ thus obtained is 0.631, on the assumption that the diaphragm is drawn taut at both ends of the stroke. Because of the elasticity of the diaphragm, an experimental check on these calculations was felt desirable. A mercury manometer was connected to the system in place of the absorption cell with a sufficient length of rubber hose to approximate the volume of the cell. The static pressure ratio was determined to be 0.722 and the average dynamic pressure was 0.864 atm. A brief calculation indicated that reconciliation of these two measured parameters required the assumption that thermal energy is transferred from the containing walls to the sample gas molecules, such that the average temperature over the modulation cycle becomes equal to the ambient temperature. A consideration of the thermal capacities involved and the heavy brass containers serves to make this assumption quite credible. The orifices and hoses between the reservoir and the absorption cell can also be expected to reduce the pressure variation in the
cell. Unfortunately, no pressure-measuring device was available which would follow the 8 cycle/sec modulation frequency, hence no direct determination of the dynamic pressure ratio could be made. The dynamic ratio can be inferred, however, from the experimental data, using the theory already presented.

The filling technique employed was necessitated by the flexible diaphragm. The filling procedure for the high-w data consisted of evacuating the cell and filling it with one atmosphere of dry nitrogen, meanwhile flushing the system with the gas under study. After a thorough flushing, the cell was re-attached and the system closed. The motor was then set in operation to assist the diffusion. Rough checks have shown that a few minutes of "assisted diffusion" produces a uniform mixture. The excess gas was then released to produce one atmosphere at minimum volume, and the high-w conventional and modulated-absorber data were taken.

To reduce the partial pressure, the system was opened to a nitrogen tank, and allowed to fill to one atmosphere at maximum volume, then closed off. The motor was turned on and the added nitrogen diffused with the original gas mixture for several minutes. Then the excess gas was released to restore the system to one atmosphere at minimum volume. Since the ratio of minimum to maximum volumes is 0.631, such a dilution reduced the absorber concentration to 0.631 its original value. This procedure was repeated to a total of five dilutions to produce an expected absorber concentration \((0.631)^5=0.1024\) the original concentration. In some cases, it
was felt that additional information would be provided at even lower absorber concentrations, and the dilution process was repeated five times more to produce an expected concentration \((0.631)^{10}=0.0105\) the original. The original concentration is readily calculated by using the preceding volume parameters and the cell length of 13 cm. Since the hose and reservoir were initially filled with absorber and the cell with nitrogen, the initial absorber concentration was calculated to be 12.25 atmo-cm. The concentrations of the diluted samples were calculated as 1.25 and 0.128 atmo-cm. The dilution factors will later be shown to be in error by a significant margin in a typical case, but the numbers here stated will be retained throughout the discussion as nominal values.

The spectra of the pressure-modulated samples shown in the next section are all accompanied by the conventional absorption spectra taken on the same sample at a total pressure of one atmosphere. In taking the data, the conventional spectrum of the sample in the closed system was obtained first, then the motor was turned on and the spectrum of the pressure-modulated gas was taken. In order to check the system for leakage during operation of the motor-driven reservoir, a few conventional spectra were repeated after the modulated-absorber runs. Excellent agreement with the preceding conventional runs indicated negligible leakage in the system. Periodically, after perhaps twenty hours of running modulation spectra, the neoprene diaphragm developed cracks near the center due to the repeated flexures. These caused gas leakage and the
The mechanical rectifier which demodulates the amplified signal is employed in a synchronous detector circuit and must be properly phased with the signal. For the conventional absorption data, the rectifier is driven synchronously with the beam-chopper. While taking the spectrum of a pressure-modulated sample, as mentioned above, the rectifier is driven by the shaft which actuates the diaphragm. The phasing adjustment is made with the aid of an oscilloscope which permits observation of the rectified waveform before filtering. Because the two detectors used in the grating instrument have significantly different time-constants, it was necessary to readjust the phasing whenever the detector is changed, as shown below.

It was pointed out in Section III that the signal produced by pressure-modulating the sample is calculable from conventional spectra by using Equation (8), which includes the effects of differing system response at the pressure-modulation and beam-chopping frequencies. Both spectrometers used in this study included a beam-chopper operating at 13 cycles/sec, and this could not conveniently be altered to 8 cycle/sec operation. On the other hand, the pressure-modulator could not conveniently be rebuilt for 13 cycle/sec operation. Accordingly, it is necessary in evaluating the experimental data to make an allowance for the difference in amplifier and detector sensitivities at the two frequencies.
A brief consideration of detector time-constants will demonstrate the dependence of the sensitivity and phasing on the modulation frequency, as follows: All detectors employed in the infrared respond exponentially with time to an applied radiation density. Thus a detector is said to have a time-constant \( \tau \), which is that time required for the detector to produce \((1-1/e)\approx 63\%\) of its maximum output for a given radiation. The detectors employed in modulated-beam systems have time-constants from about \(10^{-3}\) sec to about \(10^{-1}\) sec. Let two idealized detectors be identical except for time-constant, the faster having \(\tau = 10^{-3}\) sec and the slower having \(\tau = 10^{-1}\) sec. Figure 5 shows the behavior of these two detectors when exposed to incident radiation chopped at 5 cycles/sec and at 20 cycles/sec. Note that at a chopping frequency of 5 cycles/sec the slow detector produces about 63\% of the maximum output, while the fast detector produces essentially 100\%. At 20 cycles/sec the slow detector produces only about 20\% of the maximum output while the fast detector again provides 100\%. As to phasing, consider the superposition of a "best fit" sinusoidal waveform on the curves of Figure 5. It is clear that the phasing (placement of the sinusoid with respect to the time axis) will vary by almost 90\(^\circ\) in going from the fast detector to the slow detector. This analysis is slightly simplified for brevity, but the conclusions drawn are correct.

No manufacturer's data were available on the time-constant of the lead sulfide cell, but it may be inferred that the time
Figure 5. Illustration of the dependence of phasing and output amplitude on chopping frequency and detector time-constant.
constant is $10^{-3}$ or less. The manufacturer quotes the thermocouple as having "75% of the d-c response at 13 cycle modulation", from which the time-constant is calculated to be $56 \times 10^{-3}$ sec. The response of the lead sulfide detector, as predicted above, is experimentally found to be uniform across the short frequency interval from 8 to 13 cycles/sec. The thermocouple's response at 8 cycles/sec is 1.293 times the response at 13 cycles/sec. These measurements were made under simulated operating conditions, using a beam-chopper whose speed was adjusted with the aid of a General Radio Strobotac to match the modulating frequencies employed in obtaining the spectra.

The amplifier response at a given gain setting is also frequency-dependent. This is a result of intentional bandwidth limiting which is built into the amplifier circuitry to minimize the degradation of weak signals by noise. The amplifier response at 8 cycles/sec is found to be 0.895 times that obtained at 13 cycles/sec. Thus the combination of the thermocouple and amplifier produces at 8 cycles/sec an output 1.157 times that at 13 cycles/sec, while the lead-sulfide detector and amplifier produce an output at 8 cycles/sec of 0.895 that at 13 cycles/sec.

The Perkin-Elmer Model 107 amplifier has a stepped logarithmic gain control. This was calibrated in the region of interest and found to have a voltage ratio of 1.525 per step over a wide range.
V. EXPERIMENTAL SPECTRA OF SEVERAL PRESSURE-MODULATED
SAMPLES: QUALITATIVE INTERPRETATION

A. Discussion

The purpose of this section is to present a qualitative comparison of the pressure-modulation technique with the chopped-beam technique through an examination of the data characteristic of each. A quantitative analysis of a small portion of this data is given in the next section.

In examining the data that follow, several significant aspects should be considered in order to appreciate the additional information afforded by the use of the pressure-modulation technique.

A non-zero ordinate defines a region not only where absorption exists, but also where that absorption is pressure-dependent. Conversely, a zero ordinate implies only that the absorption does not change as the pressure is varied; This can occur either in the total absence of absorption, or when the absorption is complete for all the pressures which occur over the modulation cycle. Since the modulated-absorber runs in this section are taken with a gain of 5.41 times the gain used for the conventional spectra, edge effects near zero absorption and near total absorption are greatly exaggerated, thereby enabling the spectroscopist to define these limits with greater precision than that afforded by conventional techniques. The magnitude of the ordinate is a measure of the
rate-of-growth with pressure and its secondary consequence in this method, temperature, but the ordinate at a point on the curve must be utilized with due regard for the slit function of the spectrometer. The data in this study were taken with the same slit widths for both conventional and modulated spectra, so the ordinate at a point on the modulated-absorber run can be directly related to the variation at the corresponding point on the conventional run.

The spectroscopist is frequently confronted with the problem of spurious absorptions due to atmospheric constituents. Since the spurious absorptions reduce the intensity of the beam incident on the spectrometer in exactly the same way as the intended absorber, there is no unique characteristic of the signal which permits an immediate identification of the spectroscopic data with the absorbing sample. The pressure-modulation technique provides an output only when the absorption varies in phase with the applied pressure variation; hence the constant absorption of the atmospheric constituents is not presented as an output signal.

In assigning numerical values to the various constants which enter into the energy level expressions, it is desirable to have available many lines of a given band in order to permit many line-spacing measurements. The temperature variation produced as a result of the adiabatic behavior of the sample during pressure modulation causes a variation in the relative populations among the various rotational energy levels. The variation is as follows:

During the high-temperature portion of the cycle, the high-J
levels have a greater population than at the ambient temperature, while during the low-temperature portion of the cycle, the high-J populations are less than those at the ambient temperature. The phase of the high-J population shifts is such as to enhance the variation of absorption which would be predicted from pressure variation alone. The low-J levels act in the reverse sense, but since the low-J lines are always well defined at the pressures employed, the small reduction in amplitude due to temperature variation does not interfere with identification of these lines.

The four gases selected for this study were chosen for several reasons: None of the gases exists in significant concentration in the atmosphere; therefore the measurements incidental to a determination of \( \int A(\nu) d\nu \) are not subject to error of spurious absorption. The line-spacing is suited to four reasonably distinct conditions of resolution on the grating spectrometer, namely: \( \text{CH}_4 \), polyatomic, fully resolved; \( \text{CO} \), diatomic, fully resolved with approximately half the line-spacing of \( \text{CH}_4 \); \( \text{N}_2\text{O} \), marginally unresolved but with band-structure effects evident over the entire band; and \( \text{C}_2\text{H}_6 \), not at all resolved, no rotational-line structure detectable. Finally, these gases have absorptions in the region where atmospheric constituents give rise to spurious absorptions, hence the suppression of undesired absorptions can be studied.
B. Prism Spectra

This subsection contains several figures which show conventional and modulated-absorber spectra for four gases CO$_2$, CH$_4$, N$_2$O, and C$_3$H$_8$, in the region 2000 cm$^{-1}$ to 5000 cm$^{-1}$. The prism instrument, as employed to obtain these spectra, provides a resolving power of about 150 in this frequency region; thus several lines of a given band are passed through the spectrometer at a given wavelength setting, and the observed band shape is proportional to the envelope of the absorption lines comprising the band.

In order to appreciate some of the effects entering into the prism data, consider briefly a "detector's eye" view of the radiation incident upon it. For simplicity, let the slit function and the lines be rectangular. Then for a very weak band, the radiation presented to the detector might appear as shown in Figure 6a, where the cross-hatched area is proportional to the energy extracted by the absorber. Under pressure modulation, the lines vary in amplitude and half-width. Figure 6b shows the effect (greatly exaggerated) of increasing pressure upon the lines of Figure 6a. On the other hand, the strong band, in these simplified terms, might appear as shown in Figure 6c. When the pressure of the sample is increased, the absorption lines can only broaden, as shown in Figure 6d. In general, the line-spacing is not uniform across a band. If the lines of the strong band of Figures 6c and 6d are the less closely-spaced lines, the more closely-spaced lines and their variations might appear as shown in Figure 6e. Under a pressure variation
(a) Slit function presentation of a segment of a very weak band

(b) Effect of increasing pressure on the lines of Fig. 6(a)

(c) Slit function presentation of a segment of a strong band

(d) Effect of increasing pressure on the lines of Fig. 6(c)

(e) Effect of increasing pressure on more closely-spaced lines of the band of Fig. 6(d)

Figure 6. Slit function presentation for several sample conditions
which would cause complete opacity of the slit function of Figure 6e, the lines of Figure 6d would still have "room to grow". A further pressure variation would not produce a corresponding increase in the energy variation of the closely-spaced lines, but the wide-spaced lines would show an increase. This partially accounts for the considerable asymmetry which will be evident in the strong bands of the modulated-absorber spectra to follow.

The figures to follow present the conventional spectrum above the modulated-absorber spectrum, with the frequency axes coincident. An approximate frequency (in cm\(^{-1}\)) scale is drawn beneath the conventional spectrum for ease of reference from the text. All these spectra were taken under as nearly identical conditions as possible, with a LiF prism in the Perkin-Elmer spectrometer and slits of 200\(\mu\). A break in the conventional spectrum will be noticed at about 3300 cm\(^{-1}\) in all the figures. At these points, a gain shift of 3.55 (3 steps) is introduced to compensate for the variation in energy output from the Nernst source. The gain-shift point for any one gas is so chosen that it will disturb the data as little as possible. A similar shift is introduced at the corresponding point for the accompanying modulated-absorber run. Common to all the conventional spectra are the intense absorption band of CO\(_2\) at 2350 cm\(^{-1}\) and the bands of CO\(_2\) and H\(_2\)O at 3600-3750\(^{-1}\). The background suppression of the modulation technique can be noted by the absence of these absorption bands in the lower spectra.
Carbon Monoxide. Carbon Monoxide is a diatomic molecule; hence, it has two rotational and one vibrational degrees of freedom. The term values or energy levels is cm⁻¹ are given by the equation

\[ F_J + G_v = J(J+1)B_v + D_J J^2(J+1)^2 + (\nu + \frac{1}{2})^2 \omega_e - \frac{1}{2} \nu \omega_v \left( \nu + \frac{1}{2} \right)^2 + G_o \]

in which \( J \) is the rotational quantum number, \( \nu \) is the vibrational quantum number, \( B_v \) is the rotational constant in the \( v \)th vibrational state, \( D_J \) is the centrifugal distortion coefficient (typically \( 10^{-6} B_v \)), \( \omega_e \) is the vibrational constant (typically \( 10^3 B_v \)), \( \omega_v \) is the anharmonic constant (\( \ll 1 \)), and \( G_o \) is the vibrational reference term value. The selection rules for CO are \( \Delta J = \pm 1 \), \( \Delta \nu = 0 \), \( \pm 1 \), \( \pm 2 \), ... By taking the appropriate differences defined by \( \Delta \nu = +1 \) and \( \Delta J = \pm 1 \), the transition frequencies are obtained as follows:

- P-branch (\( \Delta J = -1 \)) \( \nu = \nu_o - (B_v' + B_v')J^2 + (B_v' - B_v')J^2 \)
- R-branch (\( \Delta J = +1 \)) \( \nu = \nu_o + (B_v' + B_v')J^2 + (B_v' - B_v')J^2 \).

Here \( \nu_o \) is called the band-center frequency, and the single-primes and double-primes refer to the upper and lower states, respectively. It is to be observed that the second-order term is of the same sign in both equations. \( B_v'' \) is generally larger than \( B_v' \), and in this case the second-order term causes a decreasing line-spacing in the R-branch, and an increasing line-spacing in the P-branch, for successively higher values of \( J'' \). Thus the lines in this case tend to bunch together on the high-frequency end of the band, and to spread out on the low-frequency end.
For $^{12}$O$^{16}$ the following parameters are listed\(^{27}\):

\[
\begin{align*}
B_0 &= 1.9225 \text{ cm}^{-1} & B_1 &= 1.90699 \text{ cm}^{-1} & B_2 &= 1.88754 \text{ cm}^{-1} \\
D_0 &= -5.95 \times 10^{-6} \text{ cm}^{-1} & \omega_e &= 2169.81 \text{ cm}^{-1} \\
x^2 \omega_e &= 13.284 \text{ cm}^{-1}
\end{align*}
\]

Figure 7 presents an energy level diagram for the CO molecule for the lowest three vibrational states and the lowest five rotational states. The vertical lines indicate the allowed transitions and the dotted vertical lines represent all transitions of $\Delta J=0$, which are not allowed for this molecule.

Figure 8 gives the data obtained on CO at an absorber concentration of 12 atm-o-cm. The fundamental band at 2170 cm\(^{-1}\) is immediately observed along with the CO\(_2\) band at 2350 cm\(^{-1}\). Less striking but readily detected are the CO\(_2\) and H\(_2\)O bands between 3600 and 3750 cm\(^{-1}\) and the CO overtone band at 4280 cm\(^{-1}\). This last band occurs as a result of transitions between the ground vibration levels and the levels of $v=2$.

With reference to the modulated-absorber spectrum in the lower portion of Figure 8, the fundamental and overtone bands are seen along with the 2350 cm\(^{-1}\) band of CO\(_2\). The appearance of the CO\(_2\) band is due not to a failure of the modulation technique to suppress this band, but rather to a 0.3% impurity of CO\(_2\) in the CO gas sample used in obtaining these data.

Figure 9 shows the same spectra for an absorber concentration of 1.25 atm-o-cm. The reduction in concentration causes the overtone
Figure 7. Elementary Energy Level Diagram and Transitions of CO Fundamental and First Overtone Vibration-Rotation Bands.
Figure 8. Prism spectra of CO at 12 atm-cm.
band to be so weak that it no longer appears in the spectra. Note that in the conventional run the 2350 cm\(^{-1}\) band of CO\(_2\) is now considerably larger than the CO fundamental, but it is completely suppressed by the pressure-modulation technique.

**Nitrous Oxide.** Nitrous Oxide is a linear triatomic molecule with the asymmetric arrangement NNO. Four vibrational modes exist, but since \(\nu_2\) is twofold degenerate, only three fundamental vibrational frequencies are found. These occur at 588.8, 1285.0, and 2223.5 cm\(^{-1}\) for \(\nu_2\), \(\nu_1\), and \(\nu_3\), respectively.\(^{28}\)

The degeneracy of \(\nu_2\) gives rise to \(J\)-type doubling, a splitting of the \(\nu_2\) levels. This has been thoroughly treated elsewhere,\(^{29}\) and need not be considered for purposes of this study. The basic energy level diagram showing those levels which give rise to the fundamental bands is shown in Figure 10; the effects of \(J\)-type doubling are neglected. The heavy line shown as a transition from states of \(\nu_2=0\) to \(\nu_2=1\) is to symbolize all transitions of \(\Delta J=0\), which transitions are permitted for this band because the angular momentum about the symmetry axis can change in this vibrational mode.

Nitrous Oxide, unlike carbon monoxide, possesses multiple vibrational modes. This results in the so-called combination bands which occur when two or more vibrational quantum numbers change essentially simultaneously. Several combination bands are listed in the next paragraph.
Figure 10. Elementary Energy Level Diagram and Transitions of $\text{N}_2\text{O}$ Fundamental Vibration-Rotation Bands.
Figure 11 presents the observed data for N$_2$O at an absorber concentration of 12 atm-o-cm. The bands shown in this spectrum are identified with the vibrational transitions as follows:

<table>
<thead>
<tr>
<th>Band Center Frequency (cm$^{-1}$)</th>
<th>Band Center Frequency (cm$^{-1}$)</th>
<th>Upper Level</th>
<th>Upper Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>2223.5</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2461.5</td>
<td>1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2563.5</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2798.3</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3365.6</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3481.2</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>4419.5</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>4734.7</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

The bracketed pair of bands is just resolved and very little of the combined absorption is due to the weak band at 3366 cm$^{-1}$. The band at approximately 3800 cm$^{-1}$ cannot be reconciled with Herzberg's data for N$_2$O, and is presumed to be due to a small impurity in the gas used. The asymmetry predicted under the slit-function discussion on page 31 for the modulated-absorber spectrum of strong bands is evident in the $\nu_3$ fundamental and the $\nu_1$ overtone, but the weaker combination band at 2461 cm$^{-1}$ displays symmetry in the spectrum of the modulated sample.

Figures 12 and 13 show the N$_2$O spectra obtained at absorber concentrations of 1.25 and 0.128 atm-o-cm, respectively. The bands grow less intense with successive dilutions and the regions of greatest growth shift from the wings toward the band centers in the stronger bands, while the weaker bands have essentially disappeared for these two sets of spectra.
Figure II. Pressure spectrum of N$_2$O at 12 atm.

N$_2$O at 12 atm - CM
Figure 14 is a set of tracings of the three curves obtained in Figures 11, 12, and 13 at the strong $\nu_3$ fundamental band. These are drawn out to a larger scale to permit a closer examination of strong-band behavior. Note that in the 12 atmo-cm curve, the entire central region is sensibly opaque for all pressures encountered over the modulation cycle, while at 1.25 atmo-cm some radiation is transmitted by the sample at the lower pressures of the modulation cycle. It is interesting to note that the frequencies of the maxima of the pressure-modulation curve are approximately the frequencies of half-maximum absorption in a conventional spectrum.

Methane. Methane is a pentatomic molecule with the four hydrogen atoms forming the vertices of a regular tetrahedron and the carbon atom at the center. A total of nine vibrational modes exist, but because of a twofold and two threfold degeneracies, only four fundamental vibrational frequencies occur.\(^{28}\)

In order for a vibrating molecule to interact with an incident electromagnetic field, an oscillating dipole moment must exist. In particular, if any one vibrational mode is to interact with a field independently of the other modes, an oscillating dipole moment must exist in that mode. This point was not mentioned previously because the single vibrational mode of CO and all three vibrational modes of N$_2$O possess oscillating dipole moments, and all of these interact with radiation fields. In CH$_4$, however, two of the four vibrational modes do not possess oscillating dipole moments, and these two fundamentals are described as inactive in the infrared.
Figure 14. Detailed Tracings of 2220 cm$^{-1}$ Band of N$_2$O at Three Absorber Concentrations.
The effects of the two inactive fundamentals are evident in infra-red spectra, however, through combinations with infrared-active modes. Thus the spectrum of CH$_4$ is expected to show many absorption bands because of the large number of combinations which can be formed.

Figure 15 is an elementary energy level diagram showing only the first excited and the ground vibrational levels and the first five rotational levels associated with each vibrational level. The active fundamentals $\nu_4$ and $\nu_3$ are located at 1306.2 and 3020.3 cm$^{-1}$ respectively. The fundamental vibration frequencies of the inactive $\nu_2$ and $\nu_1$ modes are found by Raman spectroscopy to be 1526 and 2914 cm$^{-1}$ respectively.

Figure 16 shows the spectra of methane at an absorber concentration of 12 atm-cm. The identifiable bands and their assignments are as follows:

<table>
<thead>
<tr>
<th>Band Center (cm$^{-1}$)</th>
<th>Upper Level $V_1$</th>
<th>$V_2$</th>
<th>$V_3$</th>
<th>$V_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2600</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>3020.3</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4216.3</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>4313.2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4546</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>5585</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>6006</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

The bracketed terms are three bands which are not resolved in Figure 16. Several additional weak bands are known to exist in this region, but are not listed above because they cannot be detected in the data. There is a fairly obvious impurity of CO$_2$ at 2350 cm$^{-1}$ and the band
Figure 15. Elementary Energy Level Diagram and Transitions of CH₄ Fundamental Vibration-Rotation Bands.
Figure 16. Prism spectra of CH₄ at 12 atm/cm.

CH₄ 12 ATM-O-CM
near 2220 cm\(^{-1}\) is undoubtedly the \(\nu_3\) fundamental of \(N_2O\) due to a remnant of the gas from earlier runs. The small absorption at about 3800 cm\(^{-1}\) is attributed to a trace of \(H_2O\) in the \(CH_4\) sample.

In Figure 16, it is noteworthy that even the weak bands at 2600 and 6000 cm\(^{-1}\) are readily discernible in the modulated-absorber spectrum, while in the conventional spectrum they might very easily be unnoticed in the noise and the spurious absorptions.

Figure 17 presents the \(CH_4\) spectra at an absorber concentration of 1.25 atmo-cm. The \(H_2O\) and \(CO_2\) impurity absorption are gone in these data, but the \(N_2O\) band remains. As anticipated, the weaker bands of \(CH_4\) have disappeared. Note how the asymmetry of the modulated 3020 cm\(^{-1}\) band has changed from the preceding figure. The band is now almost symmetrical. In view of the slit-function discussion above, this observation would tend to indicate that few, if any, of the lines constituting this band are 100% absorbing, except for those in the Q-branch.

Propane. Propane is an eleven-atomic molecule with the grouping \(CH_3 CH_2 CH_3\). It possesses a total of twenty-seven vibrational modes, not all of which have been determined with certainty, and most of which are degenerate. The great number of modes causes a very complex spectrum.

Figure 18 presents the spectra of propane at an absorber concentration of 12 atmo-cm. For the region 2000-5000 cm\(^{-1}\) Herzberg\(^2\) identifies only four moderate-to-strong bands and these are all
Figure 17. Prism spectra of CH₄ at 1.25 atm. cm.
Figure 18. Prism spectra of C$_3$H$_8$ at 12 atm cm$^{-1}$. C$_3$H$_8$ 12 ATM-CM
included in the single unresolved absorption which extends approximately from 2600 to 3300 cm\(^{-1}\). This extremely intense absorption region is due to the vibrations of CH valence bonds in the CH\(_2\) and CH\(_3\) groups. According to Herzberg, strong absorptions around 3000 cm\(^{-1}\) are characteristic of these vibrations, as evidenced in CH\(_3\)Cl (3042 cm\(^{-1}\); very strong), CH\(_2\)Cl\(_2\) (2984 and 3048 cm\(^{-1}\), both strong), CH\(_2\)CH\(_2\) (2989.5 and 3105.5 cm\(^{-1}\), both strong), and others. The absorptions in the region 2200 to 2400 cm\(^{-1}\) are due partially to residual N\(_2\)O and CO\(_2\) in the system.

Figure 19 shows the data obtained from a 1.25 atm-cm sample of CH\(_4\). The intense CH band remains opaque over a considerable region, and once again the peaks of the modulation curve define the width of the conventional band at half-maximum absorption.

C. Grating Spectra

This section presents a few absorption bands as observed under the greatly increased resolution of the grating spectrometer. It has been noted that the bands as observed with the prism spectrometer are formed of a series of unresolved lines resulting from rotational and vibrational energy level transitions in the molecule, each band resulting from a common vibrational transition (or transitions, in the combination bands) and many rotational transitions. With the grating spectrometer some of the bands can be resolved into their constituent lines, and the observed line spacings can be used to determine rotational properties of the molecule.
Figure 19. Prism spectra of C$_3$H$_8$ at 1.25 atm.cm.

C$_3$H$_8$ 1.25 ATM-CM
Since the theoretical interpretation for these data has already been discussed in some detail in Section V, B, the remarks on the grating data to follow are confined primarily to features of the spectra which are unusual, or which serve to point out the characteristics peculiar to the pressure-modulation technique.

As before, the conventional spectrum is placed above the modulated-absorber spectrum with the wavelength axes coincident. No frequency scale is appended as it would not materially assist in discussing the data. For the longer bands, the figures appear in two sections with the band broken at the band center.

**Carbon Monoxide.** Figures 20 and 21 present grating spectra of the fundamental band of CO (2170 cm\(^{-1}\)) at absorber concentrations of 12 and 1.25 atmo-cm, respectively. The band center appears at the left-hand edge of the R-branch, and at the right-hand edge of the P-branch. The value of \(B\) in the first vibrational state is approximately 1.9 cm\(^{-1}\), so the average line-spacing is \(2B = 3.8\) cm\(^{-1}\).

The P-branch displays a series of secondary lines which are reproduced in the modulated-absorber spectrum. These are the lines of \(^{13}\)C\(^{16}\)O, which constitutes approximately 1% of normal CO. The absorption of the stronger lines in the conventional spectrum is observed to reach 100% for both concentrations, in agreement with the earlier hypothesis noted under the prism data. The strong lines of the modulation spectrum at 12 atmo-cm are seen apparently to invert, having zero ordinate over the regions where the absorption is complete, and having non-zero ordinates only in the region
Figure 20. Grating Spectra of CO Fundamental at 12 atm-cm. R-Branch.
Figure 20. Grating Spectra of CO Fundamental at 12 atmo-cm. P-Branch.
Figure 21. Grating Spectra of CO Fundamental at 1.25 atmo-cm. R-Branch.
Figure 21. Grating Spectra of CO Fundamental at 1.25 atm·cm. P-Branch.
between the lines. At 1.25 atmo-cm this effect is reduced and the strong lines of the modulation spectrum have narrow depressions at their centers, rather than broad nulls.

The behavior of the high-J lines near the band edges is particularly significant. Recall that the temperature variation over the modulation cycle results in varying distributions of the populations in the various J-levels, and that these population variations are in such a phase relation with the pressure variation as to enhance the high-J absorption lines. This effect can be readily seen in the weak lines near the band edges in all the data.

The suppression of spurious absorptions can be noted by examining the left-hand edge of the P-branch, where several absorption lines of H\textsubscript{2}O appear. These can be detected by the absence of corresponding lines in the lower spectrum. In a few cases, lines of CO are observed under pressure modulation which are completely masked by the lines of H\textsubscript{2}O in the conventional spectrum. The more closely-spaced lines near the right-hand edge of the R-branch are lines of the 2350 cm\textsuperscript{-1} band of CO\textsubscript{2}, and these are also suppressed in the lower spectra.

Figures 22 and 23 present the grating spectra obtained for the first overtone of CO at 4280 cm\textsuperscript{-1}, for absorber concentrations of 12 and 1.25 atmo-cm respectively. The single baseline in these figures is the zero ordinate for both spectra. This band is considerably weaker than the fundamental, and the isotopic
Figure 22. Grating Spectra of CO Overtone at 12 atmo-cm.
Figure 23. Grating Spectra of CO Overtone at 1.25 atmo·cm.
absorptions of $^{13}O^{16}$ are not appreciable. The suppression of spurious absorptions and enhancement of weak lines are obvious.

**Methane.** Figures 24 and 25 show the grating spectra for the $3020 \text{ cm}^{-1}$ band of $\text{CH}_4$ at absorber concentrations of 12 and 1.25 atmo-cm, respectively. As with CO, these bands are displayed in two sections, with the band center at the right-hand edge of the P-branch and at the left-hand edge of the R-branch. The line-spacing is approximately $9.5 \text{ cm}^{-1}$. Unlike the CO bands above, this band of $\text{CH}_4$ has a strong central maximum, or Q-branch, which is readily observed at the band center in these spectra.

In the 12 atmo-cm data, a great number of weaker absorption lines are detected between the almost-uniformly spaced lines of the $\nu_3$ fundamental band. Since these weaker lines appear in the modulated-absorber spectrum as well as in the conventional spectrum, they are attributed to isotopic bands of methane in this same frequency region.

Figures 26 and 27 show the data for the $\nu_3$ overtone, centered at $6006 \text{ cm}^{-1}$. The single baseline in these figures is the zero ordinate for both curves. The enhancement of the weaker lines in these spectra is less than that noted in the fundamental because the weakest lines detectable here go only to $J$ values of about 15.

**Nitrous Oxide.** The $\nu_3$ fundamental band of $\text{N}_2\text{O}$ at $2223 \text{ cm}^{-1}$ is shown in Figures 28, 29, and 30 for absorber concentrations of 12, 1.25, and 0.128 atmo-cm, respectively. The line-spacing for
Figure 24. Grating Spectra of CH₄ ν₅ Fundamental at 12 atmo-cm. R-Branch.
Figure 24. Grating Spectra of CH$_4$ $\nu_3$ Fundamental at 12 atmo-cm. P-Branch.
Figure 25. Grating Spectra of CH₄ ν₃ Fundamental at 1.25 atmo-cm. R-Branch.
Figure 25. Grating Spectra of CH₄ ν₃ Fundamental at 1.25 atmo-cm. P-Branch.
Figure 26. Grating Spectra of \( \text{CH}_4 \nu_3 \) Overtone at 12 atmo-cm.
Figure 27. Grating Spectra of CH$_4$ $\nu_3$ Overtone at 1.25 atmo-cm.
Figure 28. Grating Spectra of $\text{H}_2\text{O} \nu_3$ Fundamental at 12 atmo-cm.
Figure 29. Grating Spectra of $\text{H}_2\text{O} \nu_3$ Fundamental at 1.25 atm·cm.
Figure 30. Grating Spectra of $\text{H}_2\text{O} \nu_3$ Fundamental at 0.128 atm cm.
this band is about 0.84 cm\(^{-1}\), several times less than that of CO and CH\(_4\), and this spacing is marginally resolved for the conditions under which the grating spectrometer is operated.

The 12 atmo-cm spectra are seen to be opaque practically for the entire extent of the band. The resolved lines on the right edge of the figure are lines of the CO\(_2\) band centered at 2350 cm\(^{-1}\). This impurity was also noted faintly in the N\(_2\)O prism data.

In the 1.25 atmo-cm data, weak structure is detectable over a greater portion of the band. This structure is perhaps slightly better defined in the modulated-absorber spectrum because of the lower average pressure. In these runs the band center appears as a small region of reduced absorption in the conventional spectrum, while in the modulation spectrum it is much more clearly defined as a region in which the absorption varies significantly with the pressure variation.

The 0.128 atmo-cm data show very strikingly the transition from the more widely-spaced CO\(_2\) lines to the lines of N\(_2\)O near the right edge of the figure. The CO\(_2\) lines are also reproduced weakly in the pressure-modulation spectrum, showing clearly that a small quantity of the impurity exists even after the hundred-fold dilution in the sample gas. It is to be noted that under similar conditions, the prism spectra were devoid of any trace of the CO\(_2\) band.

Occasional irregularities can be noted throughout these data, and these are due to the very poor signal-to-noise conditions under which the data were taken. Reduced slits were employed in an effort
to bring out the structure as well as possible, and the gain of the amplifier was increased accordingly in order to obtain reasonably large deflections of the recorder pen. A certain amount of power line pickup is known to exist in the amplifier used, and under high-gain and small detector-signal conditions, the line-frequency pick-up is perhaps ten to twenty times the desired-signal voltage. Under normal conditions, no harmonic relation exists between the line frequency and the modulation frequency, and the integration of the output filter nullifies these effects. However, a short-term variation in line frequency causes the two frequencies to be related harmonically for a short time, with the result that the recorder pen acts briefly in a manner which is negligibly related to the signal from the detector. Some of the most obvious of these irregularities have been redrawn in the data presented here, but some are still detectable.

**Propane.** The grating spectra of the 3000 cm\(^{-1}\) region of \(\text{C}_2\text{H}_6\) are presented in Figure 31. The line-spacing is not known to have been measured in the infrared, but an order-of-magnitude calculation indicates a spacing of 0.4 cm\(^{-1}\), well below the resolution of the spectrometer. Consequently, the appearance of the band is not greatly unlike that obtained with the prism spectrometer.

At the lower concentrations, two distinct bands are detectable. The more intense band is centered at 2968 cm\(^{-1}\) and the weaker at 2960 cm\(^{-1}\). Surprisingly, the 2960 cm\(^{-1}\) band is not readily
Figure 31. Grating Spectra of 3000 cm$^{-1}$ Region of C$_3$H$_5$. 
detectable in the modulated-absorber spectrum at 0.128 atmo-cm, although it is readily detected in the conventional spectrum at this absorber concentration and in the modulated-absorber spectrum at 1.25 atmo-cm.
VI. QUANTITATIVE COMPARISON OF RESULTS WITH THEORY

The preceding section presented a qualitative interpretation of a number of experimental spectra observed with the pressure-modulation technique. The purpose of the present section is to compare quantitatively a few experimental results with the predictions of the theory of Section III, in order to ascertain the validity of the theory.

A. Discussion

It was stated in Section IV that no pressure-measuring device was available which would permit a direct determination of the dynamic pressure ratio in the absorption cell. Equation (8) relates the area under the curves of conventional spectra to the area under the curve of the modulated-absorber spectrum. Through a manipulation of Equation (8), a numerical value for the pressure ratio is deduced from the observed spectra of bands, as obtained with the prism spectrometer. Two independent determinations of the pressure ratio are made, and agreement of the two results serves to confirm the validity of Equation (8).

The value of pressure ratio so obtained is then employed to predict the effects of pressure-modulation on resolved lines. The agreement between experimental and predicted results confirms
the anticipated effect of varying temperature-dependent populations of the rotational energy levels.

In the integrated absorption \( \int A'(\nu) d\nu \), \( A'(\nu) \) is the observed absolute absorption at frequency \( \nu \). Since the spectrum of the incident radiation as "seen" by the detector is reasonably uniform and the frequency scale is reasonably linear for the regions of interest, it is approximately true (at least for comparisons on a given line or band) that the integrated absorption is directly proportional to the observed area under the curve A on the recorder chart.

B. Band Measurements

If one selects a given absorption band and runs conventional absorption spectra of that band at constant temperature and with several values of \( w \), then the integrated absorption \( \int A'(\nu) d\nu \) (or more directly, the area under the absorption curve on the recorder chart) can be measured and plotted as a function of \( w \). This gives a "calibration" curve from which \( w \) of an unknown sample can be determined from \( \int A'(\nu) d\nu \) for the unknown sample. The absorber concentration of an arbitrary sample of this gas at the same temperature can then be determined by taking the conventional spectrum of the given band and locating its area on the calibration curve.

This concept is employed in the determination of the dynamic pressure ratio as follows: A sample is placed in the closed pressure-modulation system and a conventional spectrum taken at a
total pressure of one atmosphere. Comparison of the area of the absorption band with the calibration curve defines the absorber concentration at maximum pressure. Then the modulated-absorber spectrum of the same band is taken with the same sample, and the area of this curve $A_{PM}$ is determined. Equation (8) may now be utilized in the form $\Delta A = A(P_{\text{max}}) - A(P_{\text{min}}) = A_{PM} \sqrt{GR \pi / 4}$. Since the conventional spectrum yields $A(P_{\text{max}})$ and the modulated-absorber spectrum yields $\Delta A$, the difference is the value of $A(P_{\text{min}})$ appropriate to this sample and pressure variation. $A(P_{\text{min}})$ is the area under the conventional curve of the given absorption band if this run were made at the lowest pressure of the modulation cycle. The difference $A(P_{\text{min}})$ is located on the calibration curve and the corresponding absorber concentration at minimum pressure is obtained. Because of the proportionality of absorber concentration and total pressure, the ratio of the values of $A$ at minimum and maximum pressure is the ratio of total pressures $P_{\text{min}}/P_{\text{max}}$.

The bands selected for quantitative comparison are the 2460 and 2563 cm$^{-1}$ bands of $N_2O$. These are used for several reasons: The background in this region is particularly constant for the LiF prism used in the Perkin-Elmer spectrometer. There are no spurious absorptions to introduce significant error in the area measurements. These bands are both "weak" for the absorber concentrations used (12 and 1.25 atmo-cm); hence larger areas are developed under the curves of the modulated-absorber spectra than would be obtained with the logarithmic dependence of the "strong" bands. The single disadvantage of these two bands is that they overlap slightly at
these absorber concentrations; hence the possibility exists that some of the area measured may be attributed to the wrong band.

Calibration for the 12 atmo-cm data was accomplished by filling the absorption cell (detached from the reservoir) with N₂O at pressures of 20, 40, 60, and 80 cm Hg and taking the conventional absorption spectra data at each pressure. The following areas for each absorption band were measured with a polar planimeter:

<table>
<thead>
<tr>
<th>P (cm Hg)</th>
<th>2460 cm⁻¹ band</th>
<th>2563 cm⁻¹ band</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>326 arbitrary units</td>
<td>569 arbitrary units</td>
</tr>
<tr>
<td>41.5</td>
<td>569</td>
<td>929</td>
</tr>
<tr>
<td>59.0</td>
<td>743</td>
<td>1075</td>
</tr>
<tr>
<td>91.0</td>
<td>892</td>
<td>1182</td>
</tr>
</tbody>
</table>

These were plotted as a function of absorber pressure (in this case, the total pressure, P) as shown in Figure 32. The areas are in the arbitrary area units of the polar planimeter. A rather distinct "knee" is exhibited in the upper curve of Figure 32, which shows that this band tends to strong-band behavior at the higher pressures.

The system was then reassembled for pressure-modulated operation and filled to the nominal 12 atmo-cm. Two conventional and two modulated-absorber runs were taken in alternate sequence, and the following mean areas were determined:

<table>
<thead>
<tr>
<th>Type of Spectrum</th>
<th>2460 cm⁻¹ band</th>
<th>2563 cm⁻¹ band</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>824 arbitrary units</td>
<td>1152 arbitrary units</td>
</tr>
<tr>
<td>Modulated-Absorber</td>
<td>594</td>
<td>553</td>
</tr>
</tbody>
</table>
Figure 32. Determination of Dynamic Pressure Ratio at 12 atmo-cm.
The conventional area for each band was then located on the appropriate curve of Figure 32. An absorber pressure of 71 cm Hg was thus obtained at the highest-pressure point for this sample. The areas under the modulated-absorber curve were divided by the gain ratio G (5.41) and the response ratio R (1.157), and the factor \( \pi/4 \) of Appendix I to obtain the following values of \( \Delta A \):

\[
\Delta A = \frac{A_{PM}}{GR \pi/4} = \frac{A_{PM}}{(5.41) \cdot (1.157) \cdot (0.786)} = 0.203 A_{PM}
\]

\[
\begin{align*}
\text{2460 cm}^{-1} \text{ band} & \quad \Delta A = 0.203 \times 894 = 119.5 \\
\text{2563 cm}^{-1} \text{ band} & \quad \Delta A = 0.203 \times 563 = 114.5
\end{align*}
\]

By subtracting these values of \( \Delta A \) from the appropriate values of \( A(P_{\text{max}}) \), the expected areas at minimum pressure \( A(P_{\text{min}}) \) were obtained:

\[
\begin{align*}
\text{2460 cm}^{-1} \text{ band} & \quad A(P_{\text{min}}) = 830 - 119.5 = 710.5 \\
\text{2563 cm}^{-1} \text{ band} & \quad A(P_{\text{min}}) = 1148 - 114.5 = 1033.5
\end{align*}
\]

These values of \( A(P_{\text{min}}) \) were located on Figure 32 to obtain a minimum pressure of 54.5 cm Hg. Thus the dynamic pressure ratio obtained from these calculations is \( P_{\text{min}}/P_{\text{max}} = 54.5/71.0 = 0.768 \).

A corresponding determination was made at the nominal absorber concentration of 1.25 atmo-cm on the same bands. Calibration data were taken at 1, 3, 5, and 8 cm Hg partial pressures of \( \text{N}_2\text{O} \). In order to duplicate the effects of foreign-gas broadening, a partial pressure of nitrogen nine times that of the absorber was added to each sample. (This approximates the absorber to foreign-
gas ratio in the comparison sample.) The total pressures thus obtained were 10, 30, 50, and 80 cm Hg. The conventional spectra were run, the areas measured, and the calibration curves of Figure 33 drawn, using the absorber partial pressure p as abscissa. Then the pressure modulator was reattached to the cell and the comparison data were measured. The following mean areas were obtained:

<table>
<thead>
<tr>
<th>Type of Spectrum</th>
<th>2460 cm(^{-1}) band</th>
<th>2563 cm(^{-1}) band</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>120</td>
<td>345</td>
</tr>
<tr>
<td>Modulated-Absorber</td>
<td>92</td>
<td>274</td>
</tr>
</tbody>
</table>

The maximum partial pressure of the gas sample was determined from the curves to be 4.80 cm Hg. The area differences were 92 x 0.203 = 18.7 area units for the 2460 cm\(^{-1}\) band and 274 x 0.203 = 55.6 area units for the 2563 cm\(^{-1}\) band, thus yielding values of \(A(P_{\text{min}})\) of 130 - 18.7 = 111.3 and 325 - 55.6 = 269.4 area units respectively. The minimum partial pressure was thus determined as 3.80 cm Hg, giving a minimum to maximum pressure ratio of 0.793. This value agrees reasonably well with the value of 0.768 obtained at 12 atmo-cm. The average value of 0.780 is used for the calculations on lines.

C. Line Measurements

The lines chosen for this study are those of the R-branch of the CO fundamental at an absorber concentration of 1 atmo-cm. These lines are well resolved, and little chance of area measurement error exists. The lines of low J approach 100% absorption as
Figure 33. Determination of Dynamic Pressure Ratio at 1.25 atm-cm.
observed on the grating spectrometer, and considerable deflections are obtained in the spectra of the modulated absorber. The first 24 lines of the R-branch have appreciable areas in both conventional and modulated-absorber spectra; hence the effects of varying population distributions are measurable. The H-branch is reasonably free of absorptions resulting from foreign gases or isotopic species.

A brief review applicable to the temperature dependence of line-strengths will serve to introduce the test made on these lines. The integrated absorption \( \int A(\nu) d\nu \) for lines is given by the modified Ladenberg and Reiche relation (6) as
\[
\int A(\nu) d\nu = C_i P
\]
where the subscript \( i \) is now appended to denote the particular line under consideration. For weak lines of a diatomic molecule Equation (9) gives

\[
C_i = \frac{Sw_o}{P_o} = \frac{w_o}{P_o} K W B (2J+1) \exp \left[ -J(J+1) \frac{hc}{kT} \right]
\]

This shows that the anticipated temperature effects are evidenced through the \( a_i \). It has been shown (Appendix I) that the area under the curve of a modulated-absorber spectrum is proportional to the difference of areas of conventional spectra taken at the pressure extremes. Thus the area representing an absorption line of a pressure-modulated sample should be proportional to
\[ A_{PM} \sim C_1 (T_{\text{max}}) P_{\text{max}} - C_1 (T_{\text{min}}) P_{\text{min}} = \frac{w_o \omega K B (2J+1)}{P_o} \cdot \left( \frac{P_{\text{max}} \exp \left[ -J(J+1) \frac{\hbar C B}{k T_{\text{max}}} \right]}{T_{\text{max}}} - \frac{P_{\text{min}} \exp \left[ -J(J+1) \frac{\hbar C B}{k T_{\text{min}}} \right]}{T_{\text{min}}} \right) \]  

where the role of the subscript \( i \) has now been superseded by the more specific \( J \)-value of the line. In line with the philosophy of a system test, it can be seen that the majority of the molecular constants can be eliminated by dividing (10) by the conventionally obtained area of the same absorption line

\[ \frac{A_{PM}}{A_1} \sim \frac{w_o \omega K B (2J+1)}{P_o} \cdot \left[ \frac{P_{\text{max}} \exp \left[ -J(J+1) \frac{\hbar C B}{k T_{\text{max}}} \right]}{T_{\text{max}}} - \frac{P_{\text{min}} \exp \left[ -J(J+1) \frac{\hbar C B}{k T_{\text{min}}} \right]}{T_{\text{min}}} \right] \]

\[ = \frac{P_{\text{max}} T_1}{P_1 T_{\text{max}}} \exp \left[ -J(J+1) \frac{\hbar C B}{k} (\frac{1}{T_{\text{max}}} - \frac{1}{T_1}) \right] - \frac{P_{\text{min}} T_1}{P_1 T_{\text{min}}} \exp \left[ -J(J+1) \frac{\hbar C B}{k} (\frac{1}{T_{\text{min}}} - \frac{1}{T_1}) \right] \]

where the subscripts \( 1 \) now refer to the conditions prevailing for the conventional spectrum. The proportionality of (11) becomes equality on multiplication of the right-hand side by the factors \( R \cdot G \cdot T_{1/4} \).
\[ \frac{A_{PM}}{A_1} = \frac{P_{max}}{P_1} \frac{T_1}{T_{max}} \frac{R \cdot G \cdot \gamma^4}{4} \exp \left[ \frac{-J(J+1) \hbar \omega}{k} \left( \frac{1}{T_{max}} - \frac{1}{T_1} \right) \right] \]

\[ - \frac{P_{min}}{P_1} \frac{T_1}{T_{min}} \frac{R \cdot G \cdot \gamma^4}{4} \exp \left[ \frac{-J(J+1) \hbar \omega}{k} \left( \frac{1}{T_{min}} - \frac{1}{T_1} \right) \right] \]

The pressure ratio \( P_{min}/P_{max} \) was determined from the measurements on bands as 0.780. The adiabatic law gives the temperature ratio \( T_{min}/T_{max} = (P_{min}/P_{max})^{\gamma-1} \). For \( N_2 \) and \( CO \) the value of \( \gamma \) at room temperature is 1.404; thus for the pressure ratio above,

\[ \frac{T_{min}}{T_{max}} = (0.780)^{0.404/1.404} = 0.931 \]

It has been noted previously that the average temperature over the modulation cycle is the ambient temperature. By using 294°K as the ambient temperature and the experimentally determined average pressure over the modulation cycle of 0.864 atm, the following values are assigned for the modulation parameters in the cell:

\[ T_{max} = 304.5°K \quad T_{min} = 283.5°K \quad T_1 = 294°K \]

\[ P_{max} = 0.971 \text{ atm} \quad P_{min} = 0.757 \text{ atm} \quad P_1 = 1 \text{ atm} \]

The comparison data were obtained by filling the system to the nominal 1.25 atmo-cm and making two runs each of conventional and modulated-absorber spectra. The areas of the first 24 lines were measured with a polar planimeter and averages obtained for each line of the conventional and modulation spectra. Table 1 presents
the calculated and experimentally determined values for the ratio $A_{PM}/A_1$ for the first 24 lines, designated by the index 0, 1, 2, ... corresponding to the initial J-level of the transition. Figure 34 is a plot of this data, with $A_{PM}/A_1$ as ordinate and line index as the abscissa. It is worthwhile at this point to restate the measurements and assumptions which enter into the calculated curve. They are:

1. Pressure ratio was determined from band measurements.
2. Temperature ratio was calculated on the basis of a completely adiabatic process.
3. Average temperature was assumed to be the ambient temperature.
4. Average pressure was measured on a mercury manometer.
5. $A(v)$ was assumed to vary sinusoidally over the modulation cycle.
6. Pressure ratio was assumed accurately reproducible.

The pressure ratio determination would be in error by any area measurement error, but the agreement of the two figures on pressure ratio was indicative of good area measurements. Although the temperature variation was presumed to result from an adiabatic process, it must be acknowledged that the adiabatic process is at best only an approximate description of the system's behavior. The pressure ratio obtained for any run was considerably influenced by the condition of the flexible diaphragm. Until the variability of this factor became known, much time was lost in attempting to obtain quantitative agreement of data obtained under dissimilar pressure
Figure 34: Measured (+) and Calculated (solid line) Values of the Ratio $\frac{A_{PM}}{A_1}$. 
ratios. The quantitative data presented here were taken in close time sequence in order that the pressure variation under modulation would be the same for all the runs.

In consideration of the foregoing potential sources of error, the agreement between experiment and theory shown in Figure 34 is considered good.
Table 1. Measured and Calculated Values of the Ratio \( \frac{A_{PM}}{A_1} \)

<table>
<thead>
<tr>
<th>Line Index</th>
<th>Calculated ( \frac{A_{PM}}{A_1} )</th>
<th>Measured ( \frac{A_{PM}}{A_1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.493</td>
<td>0.332</td>
</tr>
<tr>
<td>1</td>
<td>0.497</td>
<td>0.342</td>
</tr>
<tr>
<td>2</td>
<td>0.504</td>
<td>0.544</td>
</tr>
<tr>
<td>3</td>
<td>0.515</td>
<td>0.465</td>
</tr>
<tr>
<td>4</td>
<td>0.529</td>
<td>0.633</td>
</tr>
<tr>
<td>5</td>
<td>0.548</td>
<td>0.674</td>
</tr>
<tr>
<td>6</td>
<td>0.570</td>
<td>0.628</td>
</tr>
<tr>
<td>7</td>
<td>0.597</td>
<td>0.614</td>
</tr>
<tr>
<td>8</td>
<td>0.626</td>
<td>0.700</td>
</tr>
<tr>
<td>9</td>
<td>0.660</td>
<td>0.713</td>
</tr>
<tr>
<td>10</td>
<td>0.696</td>
<td>0.707</td>
</tr>
<tr>
<td>11</td>
<td>0.737</td>
<td>0.818</td>
</tr>
<tr>
<td>12</td>
<td>0.781</td>
<td>0.765</td>
</tr>
<tr>
<td>13</td>
<td>0.830</td>
<td>0.809</td>
</tr>
<tr>
<td>14</td>
<td>0.882</td>
<td>0.874</td>
</tr>
<tr>
<td>15</td>
<td>0.937</td>
<td>0.867</td>
</tr>
<tr>
<td>16</td>
<td>0.997</td>
<td>0.970</td>
</tr>
<tr>
<td>17</td>
<td>1.059</td>
<td>1.033</td>
</tr>
<tr>
<td>18</td>
<td>1.127</td>
<td>1.140</td>
</tr>
<tr>
<td>19</td>
<td>1.195</td>
<td>1.103</td>
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<td>20</td>
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<td>1.164</td>
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<td>21</td>
<td>1.352</td>
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<tr>
<td>22</td>
<td>1.435</td>
<td>1.500</td>
</tr>
<tr>
<td>23</td>
<td>1.521</td>
<td>2.051</td>
</tr>
<tr>
<td>24</td>
<td>1.597</td>
<td>1.531</td>
</tr>
</tbody>
</table>
VII. SUMMARY

This study represents an attempt to establish the basis of a technique to supplement existing methods of studying infrared absorption in gases. This basis is a pressure variation and its associated adiabatic temperature variation, both of which independently produce variations in the absorption of the gaseous sample. As contrasted with the chopped-beam method, the pressure-modulation technique has been shown to reduce the observed effects of spurious absorptions, to improve the positional definition of high-J lines, and to provide a direct method of obtaining information on pressure-growth in bands and lines.

A theory has been developed to predict the information obtainable through the use of the pressure-modulation technique and this information has been interpreted qualitatively and quantitatively from a number of observed spectra. The theory has been shown to correlate well with the observed data. The several assumptions which enter into the formulation of the theory are apparently justified.

The apparatus is admittedly crude and suffers from many shortcomings, most of which are due directly to the use of a flexible diaphragm in obtaining the pressure variation. The inability to obtain accurately reproducible pressure variations over long time intervals constitutes the most severe limitation to the use of the diaphragm.
A new design for the apparatus has been suggested. This design employs concentric cylinders with a mercury seal, so arranged mechanically that the driving motor would effect a telescoping motion of the cylinders to produce an internal pressure variation. The radiation could be permitted to traverse a constant-length path through the sample (thus providing spectra similar to those of the present study), or by passing the radiation through a window in the moving cylinder along the direction of motion, a constant-w path could be provided for studying pure pressure-broadening and temperature effects. This design would permit evacuation of the system and operation at reduced pressures in addition to providing accurate sample handling and reproducible pressure variations.
APPENDIX I

RELATION OF PRESSURE-MODULATED SIGNAL TO CONVENTIONAL SIGNALS

At some pressure $P_1$ and some frequency $\nu$, let the observed absorption be $A_1(\nu)$. The energy incident on the detector of a chopped-beam spectrometer is then a square-wave of amplitude

$\int_0(\nu) \left[ 1 - A_1(\nu) \right]$ for one half-cycle and zero for the other.

A narrow-band amplifier which passes only the fundamental component of the square-wave is usually employed (this is true in the present study). The first Fourier coefficient of a square-wave of amplitude $2B$ is $4B/\pi$. Hence the effective signal presented to the detector is

$\frac{2I_0(\nu)}{\pi} \left[ 1 - A_1(\nu) \right] \sin 2\pi ft$ where $f$ is the beam-chopping frequency. Similarly, the effective signal presented to the detector at pressure $P_2$ and the same infrared frequency $\nu$ is

$\frac{2I_0(\nu)}{\pi} \left[ 1 - A_2(\nu) \right] \sin 2\pi ft$. The difference between the two ordinates at frequency $\nu$ is then proportional to

$\frac{2I_0(\nu)}{\pi} \left[ A_2(\nu) - A_1(\nu) \right]$.

In the pressure-modulation system, the signal incident on the detector at $\nu$, $P_1$, is $I_0 \left[ 1 - A_1(\nu) \right]$ while the signal at $\nu$, $P_2$, is $I_0 \left[ 1 - A_2(\nu) \right]$. If $A(\nu)$ is varied sinusoidally at frequency $f$ between the limits $A_1(\nu)$ and $A_2(\nu)$, then the resulting signal is

$\frac{I_0(\nu)}{2} \left[ A_2(\nu) - A_1(\nu) \right] \sin 2\pi ft$.

Now $A(\nu)$ as seen by the spectrometer is actually weighted average of the absorptions over a small frequency interval centered at $\nu$. The total pressure is the parameter which is altered over
the modulation cycle, and only if $A(\nu)$ is a linear function of $P$ would the waveform be truly sinusoidal. However, a small departure from linearity over the pressure differential produced by the pressure modulation would not be expected to distort seriously the waveform. Hence, approximately, the area under the curve of the pressure-modulated sample is $\pi/4$ times the difference in areas at the two extreme pressures.
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