

**A STUDY OF THE FIRST OVERTONE ROTATION-
VIBRATION BAND OF NITRIC OXIDE IN GAS,
LIQUID AND NITRIC OXIDE - FOREIGN GAS
MIXTURES AT PRESSURES UP TO 20,000 PSI**

CENTRE FOR NEWFOUNDLAND STUDIES

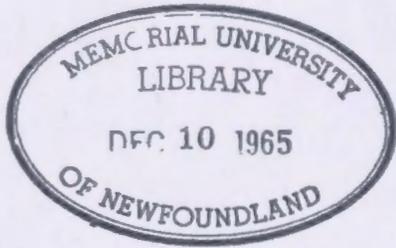
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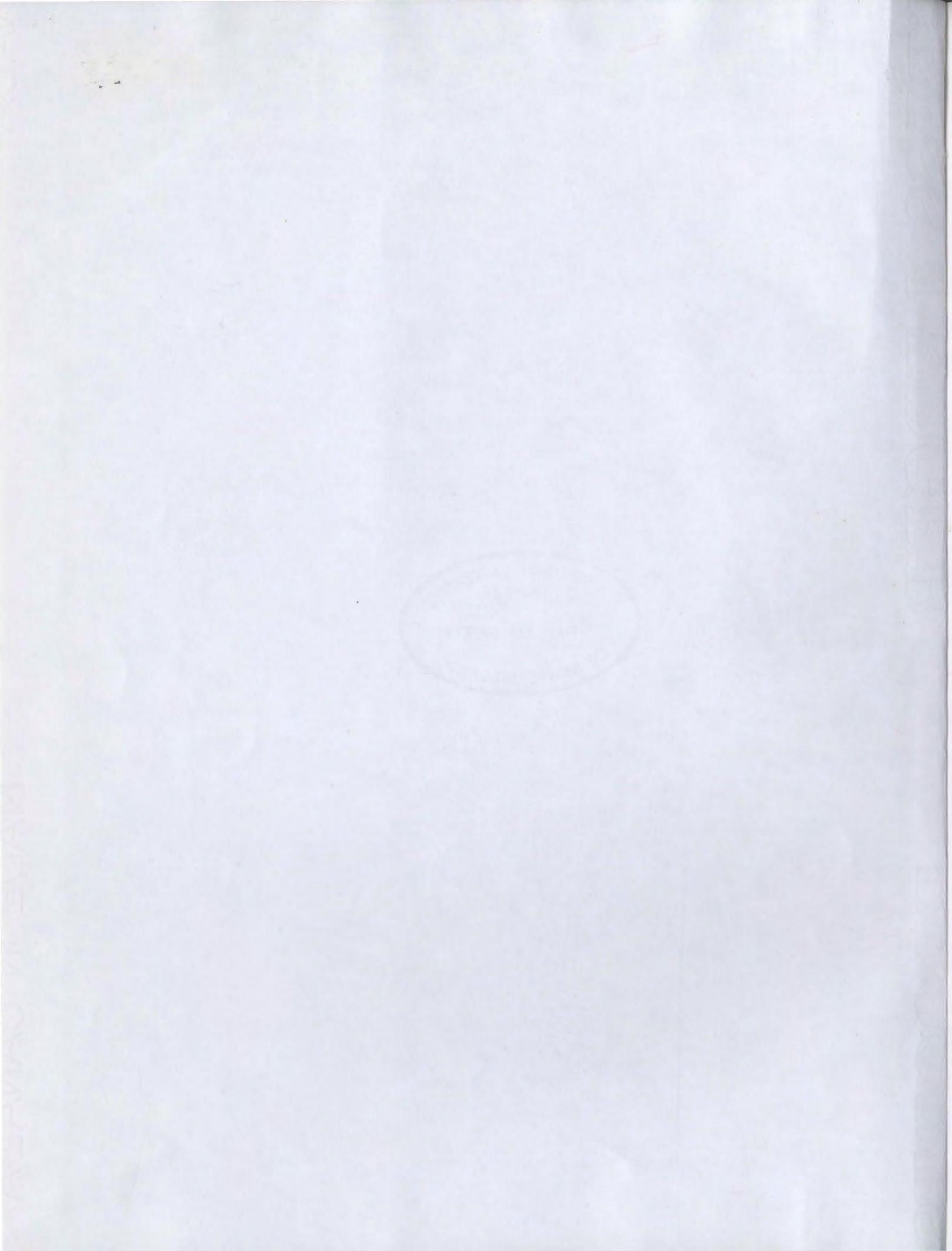
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A STUDY OF THE FIRST OVERTONE ROTATION-
VIBRATION BAND OF NITRIC OXIDE IN
GAS, LIQUID AND NITRIC OXIDE - FOREIGN
GAS MIXTURES AT PRESSURES UP TO 20,000 PSI

by



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A Thesis

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CHAPTER I

INTRODUCTION

The absorption spectra of the nitric oxide molecule have been the subject of a number of investigations, covering the spectral region from the ultraviolet to the microwave. These investigations have been carried out for the gaseous, liquid, and solid phases of nitric oxide in the pure state and also in nitric oxide-foreign gas mixtures at moderate pressures and in liquid mixtures (specific references are to be discussed below). While chemically stable diatomic molecules normally have a ${}^1\Sigma$ as their ground electronic state, the nitric oxide molecule has been found to have a ${}^2\Pi$ electronic state as its ground state (Jenkins, Barton, and Mulliken, 1927). The nitric oxide molecule is therefore paramagnetic and thus different from most of the other chemically stable diatomic molecules with the exception of the oxygen molecule which is also paramagnetic.

Since the nitric oxide molecule possesses a permanent electric dipole moment its rotation-vibration absorption bands arise due to allowed transitions. The fundamental rotation-vibration band of nitric oxide under low pressure was first

observed by Warburg and Leithauser (1908). They were able to obtain the envelope of the fundamental band and located its center at 5.3μ . Since then a number of investigations have been carried out on the fundamental band (Nielsen and Gordy 1939; Gillette and Eyster 1939). The rotational constants of the nitric oxide molecule have been determined by Gillette and Eyster. Although the band had the appearance of a Bjerrum doublet in the low dispersion spectrum, the band observed in high dispersion by Gillette and Eyster (1939) showed a Q branch with a small intensity in addition to the P and R branches. Their analysis of the band confirmed the theoretical prediction that the nitric oxide molecule has the $^2\pi$ as its ground electronic state. The selection rule for the rotational quantum number, J , for a π state is $\Delta J = 0, \pm 1$, which gives rise to P, Q and R branches while it is $\Delta J = \pm 1$ for a Σ state giving rise to P and R branches only.

The first and second overtone rotation-vibration bands of nitric oxide have also been studied in low pressure gas by various investigators (Snow, Rawlins and Rideal 1929; Nielsen and Gordy 1939; Penner and Weber 1952; Nichols, House and Noble 1955). These bands have their origins at 3724 cm^{-1} and 5544 cm^{-1} respectively and have been observed to resemble, in shape, the fundamental band. Recently in our laboratory, Snook (1962)

made a study of the second overtone band at pressures up to 200 atm. The higher overtone bands have also been observed in the near infrared (Nichols, House, and Noble 1955).

On the consideration of the paramagnetism and the thermodynamic properties of the nitric oxide molecules, Rice (1936), was lead to postulate the existence of the associated $(NO)_2$ molecules in liquid nitric oxide. A similar postulate has been proposed for the existence of $(O_2)_2$ complexes in liquid oxygen by Lewis (1924). In the study of the absorption spectra of liquid nitric oxide in the visible and ultraviolet regions, Vodar (1937) has observed two intense continua, one starting at λ 4000 Å and extending towards the ultraviolet, and the other starting at λ 5600 Å and extending towards the infrared. The same continua were also studied by Bernstein and Herzberg (1947). They have suggested that these continua were probably due to the associated $(NO)_2$ molecules. A comprehensive study of the infrared and Raman spectra of liquid and solid nitric oxide has been made by Smith, Keller and Johnston (1951). They have satisfactorily explained the spectra on the basis of the associated $(NO)_2$ molecules, proposing a model of a bent ONNO structure. The "combination bands" of liquid oxygen, (Ellis and Kneser 1933) and some of the infrared absorption bands of

oxygen in liquid and solid phases (Smith, Keller and Johnston 1950; Smith and Johnston 1952), have been also interpreted as due to $(O_2)_2$ complexes.

The pressure-induced absorption

When a pure gas or a gas mixture is subjected to a high pressure, the absorption spectrum has been observed to exhibit two major effects: (i) pressure-broadening (i.e. self-broadening and foreign-broadening), and (ii) the pressure-induced absorption. The self-broadening and foreign-broadening of absorption lines of polar molecules have been extensively studied (e.g. Penner and Weber 1952; Pigott and Rank 1957). It has been observed that broadening of spectral lines takes place without change in the transition probability. When a spectral line, which is not broadened, is recorded by a spectrometer having a finite slit width, the shape of the recorded line will not normally represent the true line shape. In order to observe the true integrated absorption coefficients of the band, it is often convenient to use the method of broadening of spectral lines. Perturbation of molecular rotation-vibration energy levels has also been observed in polar gas-foreign gas mixtures at high pressures (e.g. Rank, Eastman, Birtley and Wiggins 1960; Gebbie and Stone 1963).

The pressure-induced absorption of polar diatomic molecules has been observed in polar gas-foreign gas mixtures at high pressures (Coulon, Oksengorn, and Vodar 1954; Vu and Turrell 1959; Vu 1960; Turrell, Vu and Vodar 1960). It has been observed that a strong Q branch appears in the fundamental rotation-vibration band of polar molecules like CO, HCl and HBr whose ground electronic states are Σ states. The dipole moment selection rules for these molecules allow only transitions corresponding to $\Delta J = \pm 1$. The intensity of the Q branch was found to be proportional to the density of each component of the mixture at moderate densities, indicating that the appearance of the Q branch is due to heterogeneous binary collisions (Turrell, Vu, and Vodar 1960). This indicates that pressure-induced absorption in polar molecules occurs in a similar way as in the pressure-induced absorption observed in homonuclear diatomic molecules (Crawford, Welsh and Locke 1949). The pressure-induced infrared rotation-vibration bands of homonuclear diatomic molecules have been extensively studied, experimentally as well as theoretically, since 1949. The general selection rule governing the pressure-induced absorption is known to be $\Delta J = 0, \pm 2$, giving rise to Q, O, and S branches. Therefore the appearance of a strong Q branch in the fundamental band of polar molecules perturbed by the collisions with non-

polar molecules seems to confirm the selection rule for the pressure-induced absorption although O and S branches have never been observed. According to Van Kranendonk's "exp-4" model (Van Kranendonk and Bird 1951; Van Kranendonk 1957, 1958), the pressure-induced absorption is due to a dipole moment induced by a long range quadrupole interaction and a short range overlap interaction during the process of binary collisions. The theory suggests that the Q branch of the induced fundamental band is due to both the quadrupole and overlap interactions while the O and S branches are due only to the quadrupole interaction.

It seems, therefore, that the nature of NO-NO and NO-foreign gas interactions can be studied from the infrared absorption spectra of pure nitric oxide and nitric oxide-foreign gas mixtures at high densities. In the present investigation the first overtone rotation-vibration band of nitric oxide was studied in pure gas at pressures up to approximately 200 atm and in nitric oxide-foreign gas mixtures at total pressures up to approximately 1500 atm. A study of the infrared absorption spectra of liquid nitric oxide in the region from 1.8 μ to 5.0 μ was also made. A short report on a study in the visible region on the absorption spectrum of the pure gas at pressures up to 180 atm is given in the Appendix.

CHAPTER II
THE FIRST OVERTONE BAND OF NITRIC OXIDE
IN PURE GAS AND NITRIC OXIDE -
FOREIGN GAS MIXTURES

(i) Experimental

The following is a description of the apparatus and experimental procedure used in the study of the first overtone band of nitric oxide in pure compressed gas and nitric oxide - foreign gas mixtures at pressures up to 20,000 Psi.

(a) Purification of nitric oxide gas

In studying the first overtone band of nitric oxide at high pressures, it is important to make sure that the gas used in the experiments does not contain other compounds of N_2 and O_2 . Preliminary experiments with nitric oxide gas used directly from a commercial cylinder indicated the presence of NO_2 and N_2O . This and the reports of other investigators have indicated the necessity of careful purification of nitric oxide supplied in cylinders by commercial firms.

Previous investigators (e.g. Johnston et al 1951; and Vodar 1957) have indicated that the nitric oxide gas obtained

from commercial cylinders may contain other compounds of N_2 and O_2 , such as N_2O_3 , N_2O , NO_2 and also N_2 and CO_2 .

Johnston et al and Vodar have observed that the removal of the N_2O_3 (melting point $-103^\circ C$) from the nitric oxide gas is much more difficult than the removal of the other impurities.

In Fig. 1 is a schematic diagram of the apparatus used in the present investigation for the purification of nitric oxide. Nitric oxide gas from a commercial cylinder was allowed to condense and solidify in a liquid nitrogen trap, A. Trap A was made from a pyrex glass flask having a volume of 250 cc. When a sufficient amount of the solid had been collected in A the stopcock, S_1 , was closed and the trap opened to the vacuum pump for a period of approximately 15 minutes to remove any nitrogen impurity. The colour of the liquid in the trap A before solidification, was deep green. The solid was also green with a reddish brown tinge. This contrasted sharply with the colours of the liquid and solid nitric oxide observed by previous investigators (Johnston et al 1951 and Vodar 1937). They have reported a purple colour for the solid and a blue colour similar to that of liquid oxygen for the liquid.

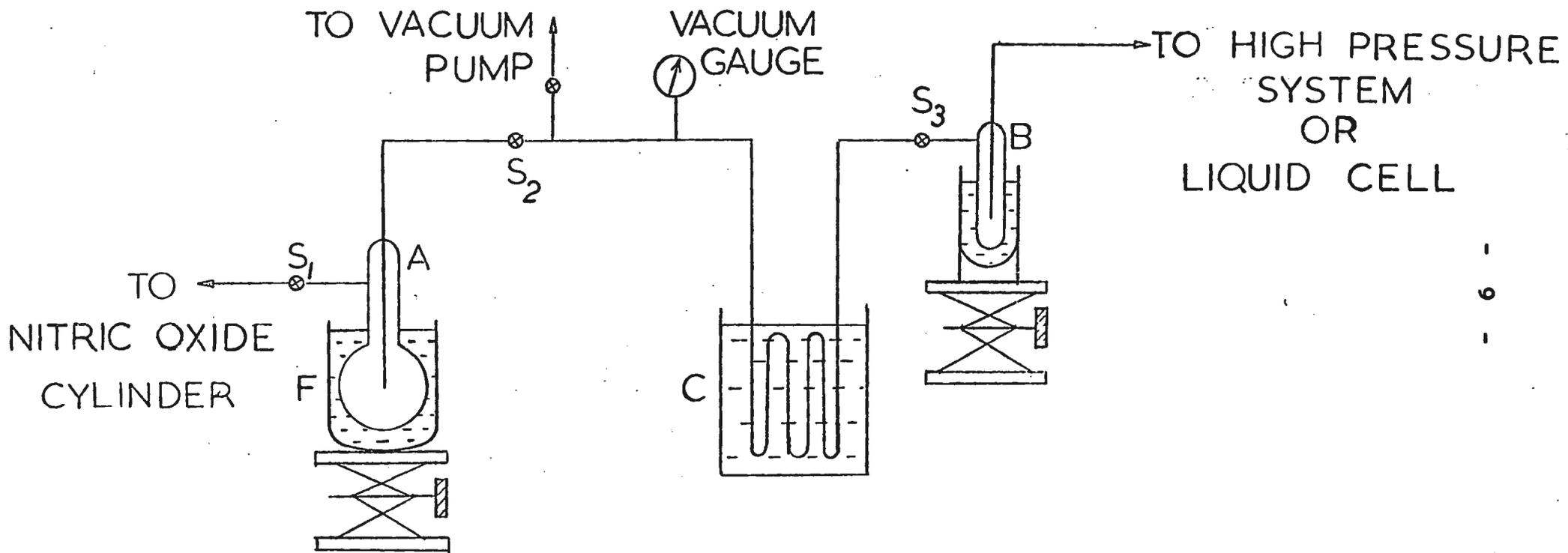


Fig. 1. Nitric Oxide Purifying System

The level of the liquid nitrogen surrounding trap A was then lowered to about 2 inches below the bottom of trap A and the solid allowed to melt. By adjusting the level of the liquid nitrogen bath, the temperature of the liquid in Trap A was kept just below its boiling point. Stopcock S₃ was then adjusted so that there was a slow flow of vapor from Trap A to another liquid nitrogen trap, B, which was made from pyrex glass tubing 3.0 cm in diameter and 10 cm in length. In passing from A to B, the vapor passed through a purifying trap, C. Trap C consisted of several bends of pyrex glass tubing 8 mm in diameter filled with crushed glass and was surrounded by frozen or viscous ethyl alcohol having a temperature range from -110°C to -120°C.

The rate of flow of the vapor from trap A to trap B was adjusted by raising or lowering the surface level of the liquid nitrogen in dewar F. This adjustment was so made that approximately 3 cc of liquid was collected in trap B in one hour.

Since the boiling and melting points of the other compounds are considerably higher than those of nitric oxide, (NO: BP = -151.8°C, MP = -163.6°C; N₂O: BP = -88.49°C, MP = -102.4°C; NO₂: BP = 21.15°C, MP = -11.2°C; N₂O₃: BP = 3.5°C

MP = -102°C and CO_2 : BP = -78.5°C sublime, MP = -56.6°C), the above procedure served as a fractionation process.

The colour of the solid obtained in trap B was found to be white with a slight indication of violet. The colour of the liquid was pale violet-blue similar to that of liquid oxygen. Upon allowing the solid collected in trap C to liquefy it was observed that its colour, as liquid, was quite different from that of the liquid in trap B. The colour of the liquid in trap C was dark blue. Judging from its colour and the temperature of the trap C, the substance collected in trap C was identified to be mostly N_2O_3 . The purification of nitric oxide was now assumed to be complete, and the purified nitric oxide in trap B was then used for the present investigation.

(b) Gas absorption cells

Fig. 2 represents the 12 cm transmission-type high pressure absorption cell used in the pure nitric oxide and nitric oxide - foreign gas mixture experiments. The construction of the cell has been described previously (Clouter 1962; Snook 1962). The absorption cell consists mainly of the cell body, A, which was constructed of stainless steel $3\frac{1}{2}$ inches in

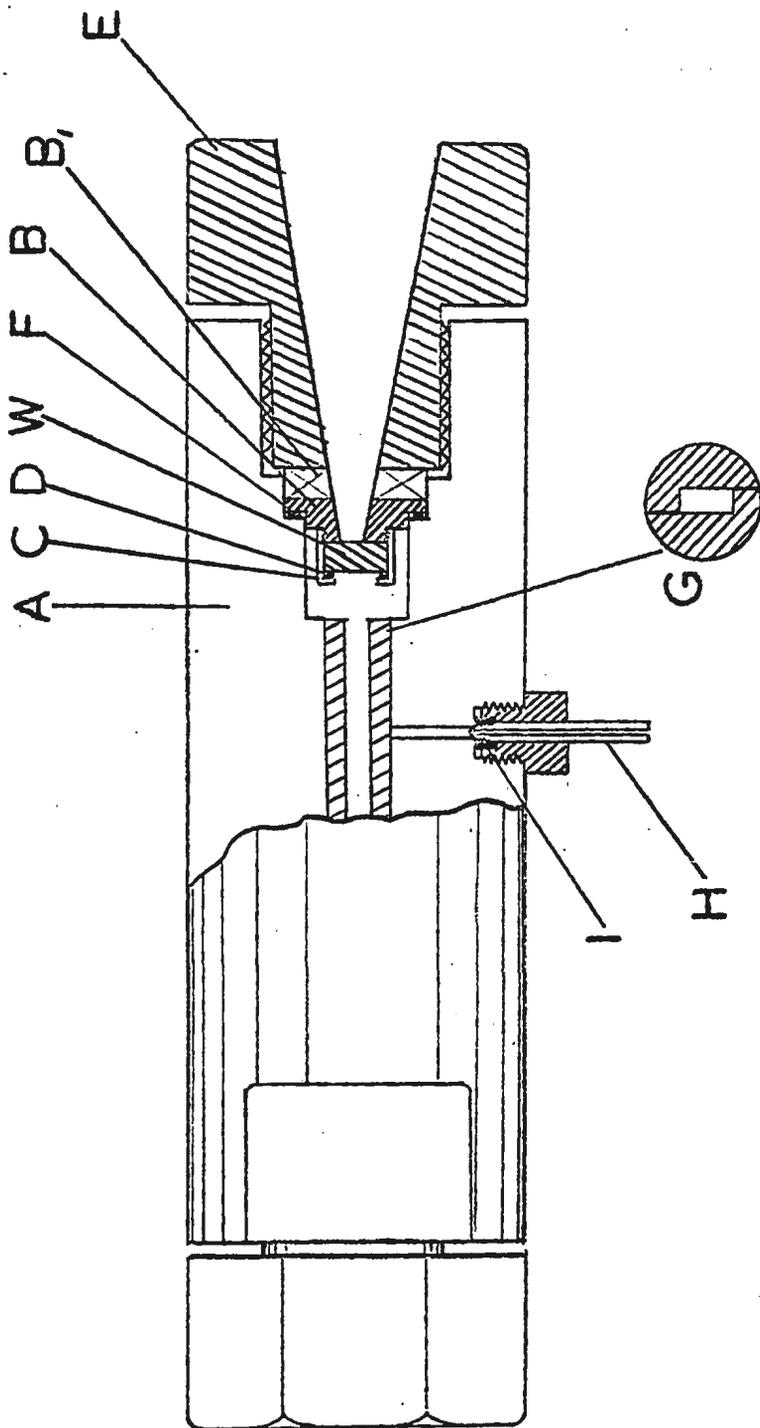


Fig. 2. High Pressure Gas Absorption Cell.

diameter with a bore of 3/4 inches.

A hollow stainless steel cylinder, G, made of two sections, having a central bore of rectangular cross-section 13/16 inch by 13/32 inch served as a light guide; the inside surfaces of the bore being polished to insure a good reflection of light. It was inserted into the bore of the cell body.

The entrance and exit windows, W, were synthetic sapphire plates, 1 inch in diameter and 5 mm thick for the pure gas experiments; the pressure range was from 0 to 4000 Psi. For the high pressure nitric oxide - foreign gas experiments, synthetic sapphire windows, 1 inch in diameter and 10 mm thick were used. They were cemented on to the stainless steel window plates, B, with General Electric Glyptol Cement. The surface of the window plate, on which the window was cemented, was polished optically flat to insure a good pressure seal. The windows were secured by steel caps, C, with teflon washers, D, so that the cell could be evacuated without the windows becoming loose. The apertures in the window plates were rectangular having dimensions 3/8 inch by 3/16 inch.

The absorption cell was held "pressure tight" by means

of heavy steel closing nuts, E, with teflon washers, F, between the window plates, B, and the main cell body, A. The portion, B₁, of the window plates, 3/8 inch thick, was square in shape and fitted into a matched recess in the cell body. This part of the design thus prevented non-alignment of the light-guide and window plate apertures when the nut, E, was tightened. A 1/4 inch diameter steel capillary tube, H, served as a gas inlet to the cell and was connected by means of an "Aminco" fitting I. For the pure gas experiments the effective path lengths was 12.4 cm and for the high pressure nitric oxide - foreign gas experiments it was 11.4 cm.

For the high pressure pure gas experiments a reflection type high pressure absorption cell was used. The cell, obtained on loan from the University of Toronto, has been described by Welsh, Pashler and Dunn (1950). In the present investigation the cell was used with a stainless steel mirror. As the optical arrangement of the cell provided a flexible range of optical pathlengths from 0.5 cm up to 7.0 cm, it was possible to study the absorption band even with small optical pathlengths. An optically flat synthetic sapphire plate, 1 inch in diameter and 5 mm thick, was used as an entrance-exit window.

(c) Experimental procedure

(1) The high pressure gas system:

A high pressure gas system composed of pressure gauges, thermal and gas compressors, and needle valves was used to introduce the nitric oxide gas and perturbing gases to the absorption cell at various pressures. Fig. 3 is a schematic diagram of the high pressure gas system used.

Prior to each pure NO or nitric oxide - foreign gas mixture experiment, the whole system was evacuated for a period of approximately twenty-four hours. About 4 cc of purified nitric oxide liquid, obtained in the purifying system (section (a)), was allowed to condense in a thermal compressor, J, before nitric oxide being admitted to the absorption cell. After nitric oxide was collected in the thermal compressor, the glass purifying system was isolated by means of an Aminco needle valve, A. All other valves shown in Fig. 3 were of the same type as valve A. While a valve, I, was kept closed, valves B and C were then opened, and the liquid nitrogen bath around the thermal compressor was removed, thus allowing the pressure of nitric oxide gas in the cell to reach to a desired value.

For the pure gas experiments a low-pressure gauge, X,

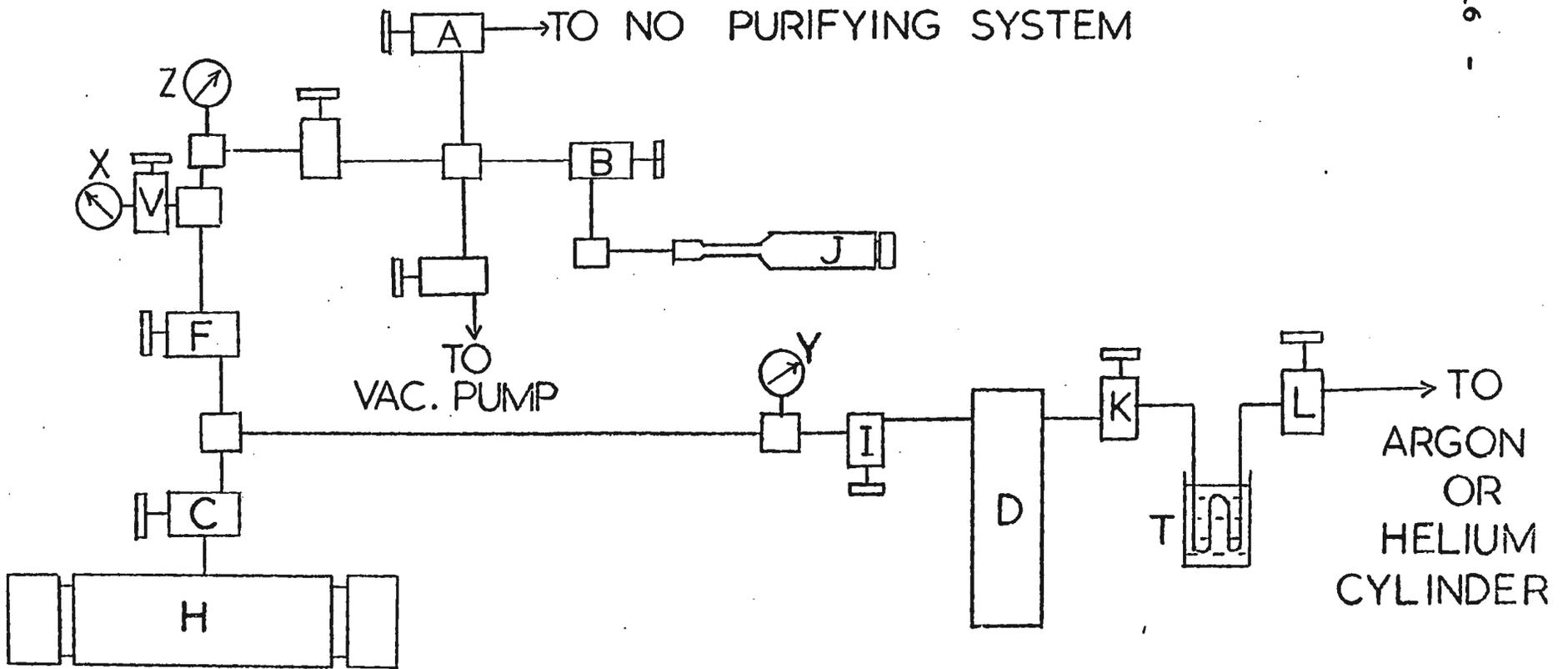


Fig. 3. Arrangement for High Pressure Experiments.

was isolated by means of valve, V, and the gas pressures were measured by a pressure gauge Z. The gauge Z was a Bourdon type having a range of 0 - 5000 Psi.

For the gas mixture experiments, nitric oxide gas at 15 - 120 Psi was first introduced into the absorption cell. Argon or helium gas at a certain pressure was then admitted to the cell using the following method. Having obtained nitric oxide gas at a required pressure, the absorption cell was isolated by means of valve, C. The pressure of NO in the cell was measured by means of the gauge X having a calibrated pressure range of 0 - 160 Psi. The nitric oxide gas in the remainder of the system was then recondensed in the thermal compressor, and to insure the complete removal of NO from the tubings and gauges of the system, the entire high pressure system excluding absorption cell and thermal compressor, was evacuated for about two hours. A perturbing gas, argon or helium, was then introduced to the system, after the valve, F, was closed. The perturbing gas was compressed by means of a 0 - 50,000 Psi gas compressor, D; compression of the gas in the gas compressor was achieved by a column of mercury which was driven by an Aminco oil compressor in conjunction with an Aminco intensifier. Valves I, K, and L were opened and a gas

from a commercial cylinder was admitted slowly to the compressor through trap, T. For argon gas, trap T was surrounded by frozen or viscous ethyl alcohol giving a temperature range of -110°C to -120°C ; and for helium gas liquid nitrogen was used. Valve K was then closed and the gas was compressed to a given pressure before it was admitted to the cell. In admitting the foreign gas to the absorption cell, a pulsing technique had to be used to prevent back diffusion of the nitric oxide already in the absorption cell. Valve C was opened repeatedly for about half a second. This pulsing was repeated several times until the pressure at both sides of valve C was equalized. Valve I was closed during the last few pulsings to isolate the compressor, D. The gas pressure in the cell was then measured on a pressure gauge, Y, of range 0 - 20,000 Psi. The two component gases, NO and the perturbing gas, were then allowed to mix thoroughly before any recordings of absorption spectra were made. The mixing was assumed to be complete when two successive duplicate recordings of spectra were obtained. This took usually about one hour to complete. Using the above procedure various total gas pressures up to 20,000 Psi were achieved for each base pressure of nitric oxide.

The type of tubing used in the high pressure system was $\frac{1}{4}$ inch O.D. stainless steel capillary tubing. Gauges X and Z were calibrated by means of Ashcroft test gauges having ranges of 0 - 400 Psi and 0 - 5000 Psi respectively. Gauge Y was calibrated using an Ashcroft dead weight tester (type 1305B100) of range up to 20,000 Psi.

When the mixture experiments were carried out caution was taken to minimize the error caused by inhomogeneous mixing in the length of capillary tubing between the absorption cell and valve C; the length of the connecting tubing was made as short as possible.

(2) Optical arrangement, etc.

The optical system used with the 12 cm transmission cell is shown in Fig. 4 (a). Infrared radiation from the global source, S, was focused on the entrance window of the cell, H, by means of an aluminized spherical front surface mirror, M_1 . The infrared radiation from the exit window of the cell was then focused onto the slit, S_1 , of the spectrometer, A, by means of a second spherical mirror, M_2 . In order to match the internal optics of the spectrometer, an F/4 light cone was used throughout the external optical arrangement.

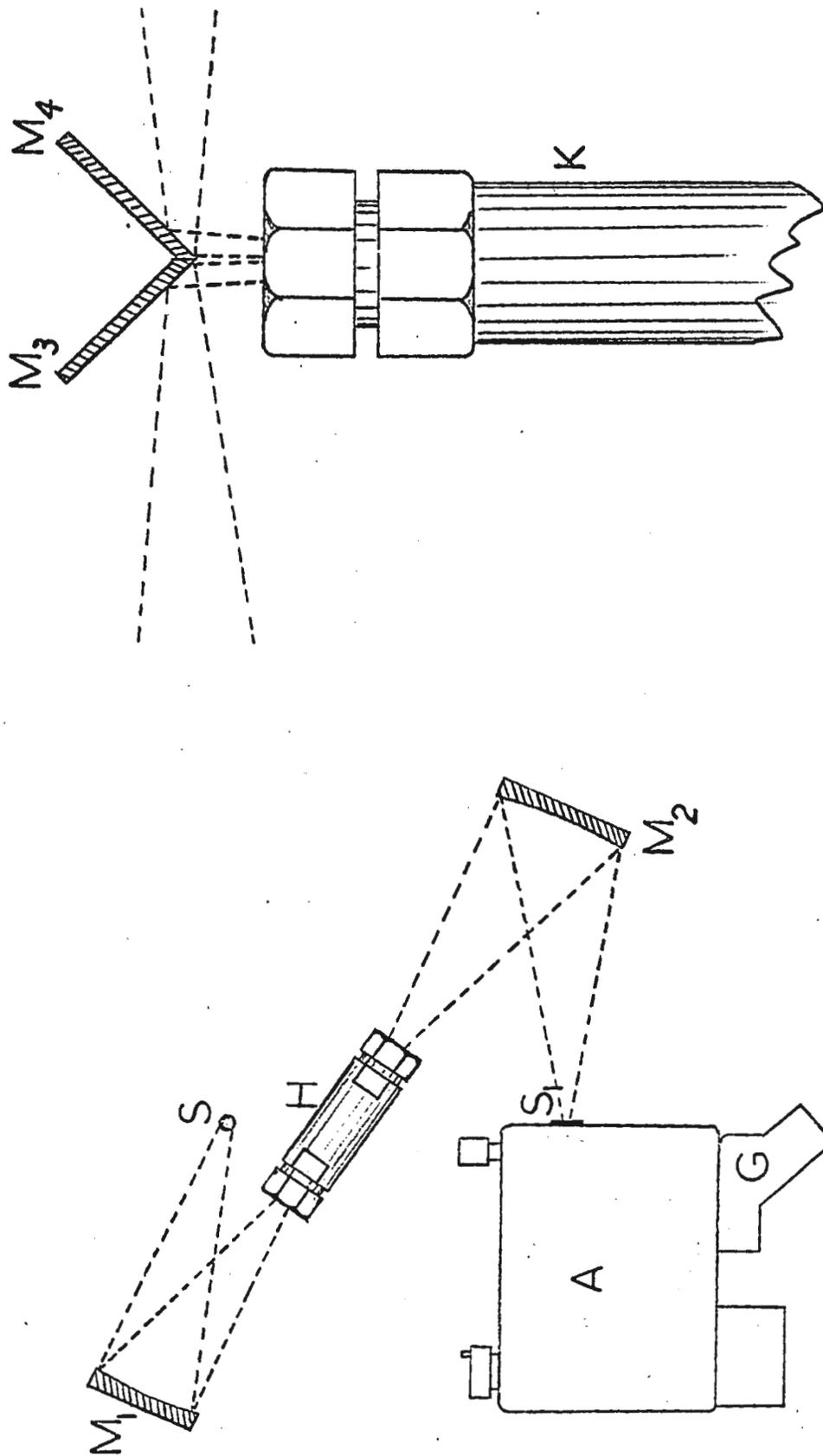


Fig. 4. Optical Arrangements With Gas Cells.

The optical system used with the reflection type cell was similar to that for the transmission cell. The radiation from the Globar source was focused onto the window of the reflection cell, K, (see Fig. 4 (b)) by means of mirror M_1 after it was reflected from a plane front surface mirror, M_3 . The returning radiation, after the reflection from the stainless steel mirror inside the reflection cell, was then focused onto the spectrometer slit by means of mirror M_4 and M_2 . The angle between M_3 and M_4 was set at approximately 90° .

A Perkin-Elmer model 12-C infrared spectrometer with an LiF prism and a Golay pneumatic infrared detector (G in Fig. 4 (a)) was used to record the absorption spectra in the present investigation. A water cooled Globar connected to a Sorenson voltage regulator served as the source of infrared continuum. For the pure gas and nitric oxide - foreign gas mixture experiments a spectral slit width of 15.6 cm^{-1} at 2.7μ was used.

An absorption contour was obtained from a recorded trace of the absorption spectrum by plotting the absorption coefficient, α , at a given frequency, against the frequency in cm^{-1} . Here, the absorption coefficient α is given by $\frac{1}{l} \log_e (I_0/I)$, where I is the intensity of light from a source after the light has passed through an absorbing path length l , and I_0 is the background intensity of the light measured at the same frequency but without the absorbing material in the path. The integrated absorption coefficient of the entire absorption band $\int \alpha \, d\nu$ in cm^{-1}/cm , was thus obtained by computing the area under the absorption contour. For the computation of the densities of nitric oxide gas at various pressures, the isothermal data of Golding and Saye (1951) was used. Their data covered the pressure range up to 2500 Psi. Beyond 2500 Psi the isotherm data for nitric oxide was not available. In calculating the partial densities of component gases in the NO - foreign gas mixtures it was assumed that the partial pressures of the component gases were additive. This was well justified since the partial pressure of nitric oxide in the gas mixtures used were very small (at most 6% of the mixture). The error introduced in making such an assumption was well within the experimental error. Partial densities of the argon and helium gas were obtained from the available

isothermal data (Michels, Wijker and Wijker 1949; Michels and Wouter 1941; and Hare 1955). The densities are expressed in the Amagat unit, which is defined as the ratio of the density at a given pressure and temperature to the density at N.T.P.

In the spectroscopic region where the first overtone rotation-vibration band of nitric oxide is observed, a strong absorption band of water vapor occurs. It was therefore necessary to flush the spectrometer and external optical path with a dry atmosphere in order to eliminate or reduce the influence of the water absorption band from the recorded spectrum. The source, spectrometer and complete external optics were enclosed in a polyethylene plastic bag and then the system was flushed with dry nitrogen. Spectrometer recordings of backgrounds taken indicated that the above arrangement reduced the intensity of the water absorption band to approximately 10% of its original intensity, and the fluctuation in the background during each experimental period was within the noise level of the recording system.

Prior to the mixture experiments, the spectra with ~~with~~ foreign gases were taken at pressures up to 1000 atm in the spectral region of the first overtone band of NO; no change in background intensity was found.

(ii) Results and Discussion

The first overtone rotation-vibration band of nitric oxide was studied in the pure gas at pressures up to 270 atm at 298°K. The study was not extended for the pure gas pressures beyond 270 atm since it was found that a rapid chemical reaction takes place in the nitric oxide gas within the cell at the higher pressures (Ref. Appendix). In the study of the pure nitric oxide gas, the reflection cell with 3.2 cm optical path length and the transmission cell with 12.4 cm optical path length were used to study the band in the pressure ranges of 7 - 270 atm and 1 - 7 atm respectively. In Fig. 5, the observed absorption contours at the low pressure range and those obtained at the high pressure range are reproduced. It is seen that the absorption contours obtained at high pressures show a marked difference from those obtained at low pressures. The low pressure contours have the appearance of Bjerrum doublets while the high pressure contours show broad single peaks. The band origin was calculated from the molecular constants given by Herzberg (1950) and its position is indicated by ν_0 in Fig. 5. The low pressure contours presented in Fig. 5 cannot be considered to be the true absorption contours as they are somewhat distorted. It has been known that the accurate

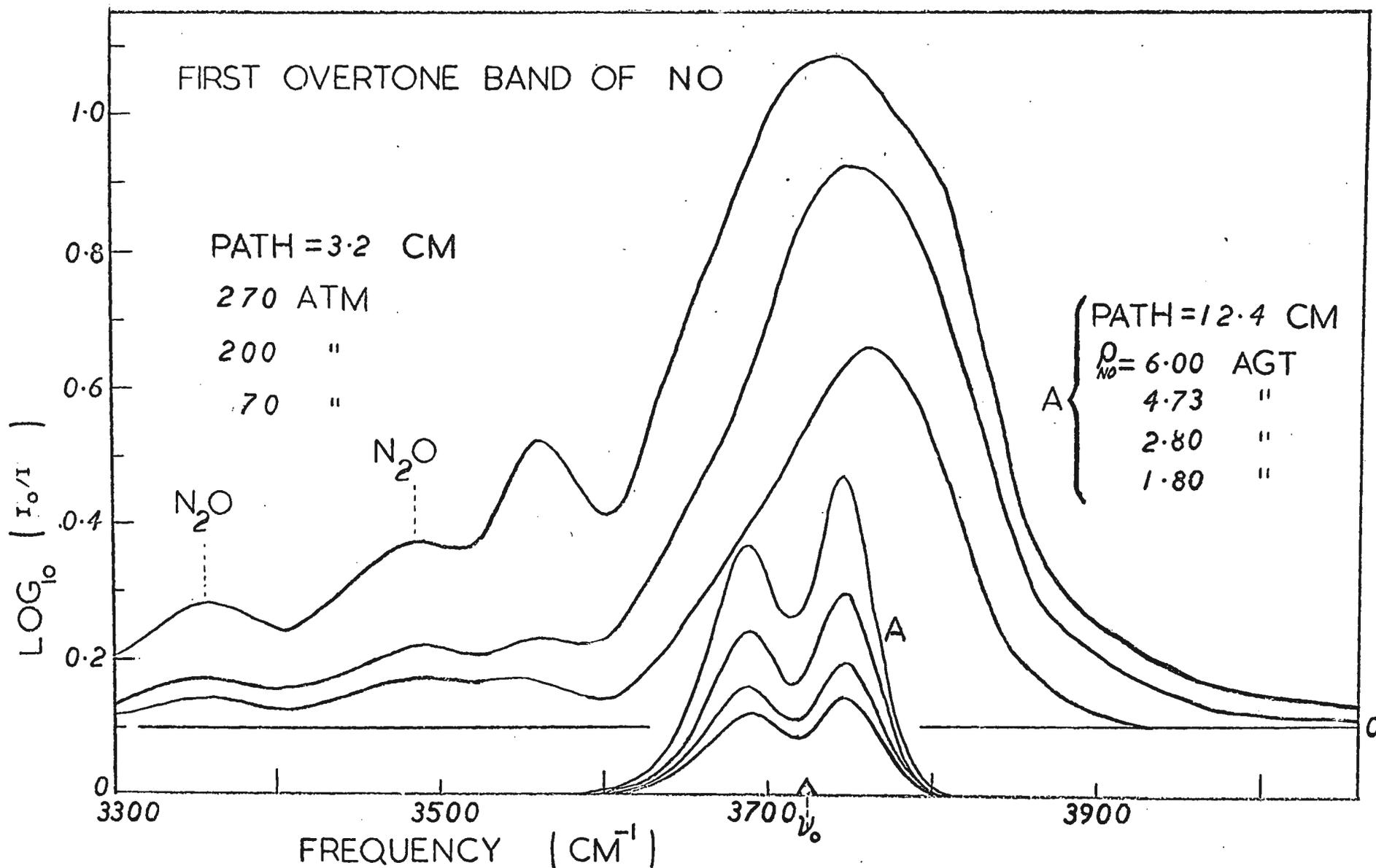


Fig. 5. Observed absorption contours of the 2-0 rotation-vibration band of NO in pure gas at various pressures.

measurements on the intensities of sharp rotational lines, without a sufficient pressure-broadening, in an absorption band cannot be made with a spectrometer having a finite slit width (Wilson and Wells 1946). This effect was studied experimentally in the course of the present investigation by taking several spectrometer recordings of the band at a given pressure, varying the instrumental slit width. At pressures up to 50 atm it was found that the ratio between the peak intensities of the R and P branches and the integrated absorption coefficient of the band increased as the slit width was decreased.

At higher pressures there is no change in the ratio of the peak intensities of the R and P branches and the integrated absorption coefficient remained constant when the slit width was changed from 400 μ to 200 μ . It was therefore concluded that the individual rotational lines of the band have been sufficiently broadened by the "self-broadening" at pressures above approximately 50 atm for an instrumental slit width of 300 μ . A slit width of 300 μ corresponds to a spectral slit width of 15 cm^{-1} at the center of the band, which was used throughout the present investigation.

The integrated absorption coefficients of the band in

pure nitric oxide gas at high pressures are given in Table I.

Table I. The observed integrated absorption coefficients of the 1st overtone rotation-vibration band of nitric oxide at various pressures.

Pressure (atm)	Density* (Amagat)	$\int \alpha d\nu$ (cm ⁻¹ /cm)
68	67.0	63.6
136	137	96.6
204	207	125
272	278	195

*Densities above 170 Agt are extrapolated values.

Since two satellite peaks, which appeared in the band observed at higher pressures and were at 3365 cm⁻¹ and 3481 cm⁻¹, have been identified as due to N₂O molecules (Herzberg 1950), the integrated absorption coefficients given in Table I can be taken as only approximately correct. Another satellite peak which appears approximately at 3560 cm⁻¹, could not be identified with any known transitions. The presence of N₂O molecules in the gas was interpreted as the polymerization of nitric oxide gas at high pressures. In order to obtain the accurate values

of the integrated absorption coefficients of the band in nitric oxide gas at densities below 10 Agt, the method of foreign broadening was used. These results will be discussed below.

The band was studied also in NO-A and NO-He mixtures. The partial density of nitric oxide in the mixtures ranged from 2 to 6 Agt. The total pressure of the NO-A mixtures used was varied up to approximately 1300 atm and that of NO-He mixtures up to approximately 500 atm. The NO-A and NO-He mixtures, with several partial densities of nitric oxide and at the total pressure up to approximately 80 atm, were first used to observe the effect of foreign broadening on the band. The general effects of the foreign broadening thus obtained was found to be of a similar nature as the self-broadening which has been discussed above. It was found, from the variation of the integrated absorption coefficients, that the broadening appeared to be sufficiently large at the partial pressure of the foreign gas above 40 atm to give the true absorption profile of the band. This was true for both the NO-A mixtures and the NO-He mixtures; the foreign-broadening effect being practically the same in both.

Fig. 6 shows the observed absorption contours of the band in NO-A mixtures at various partial densities of argon above

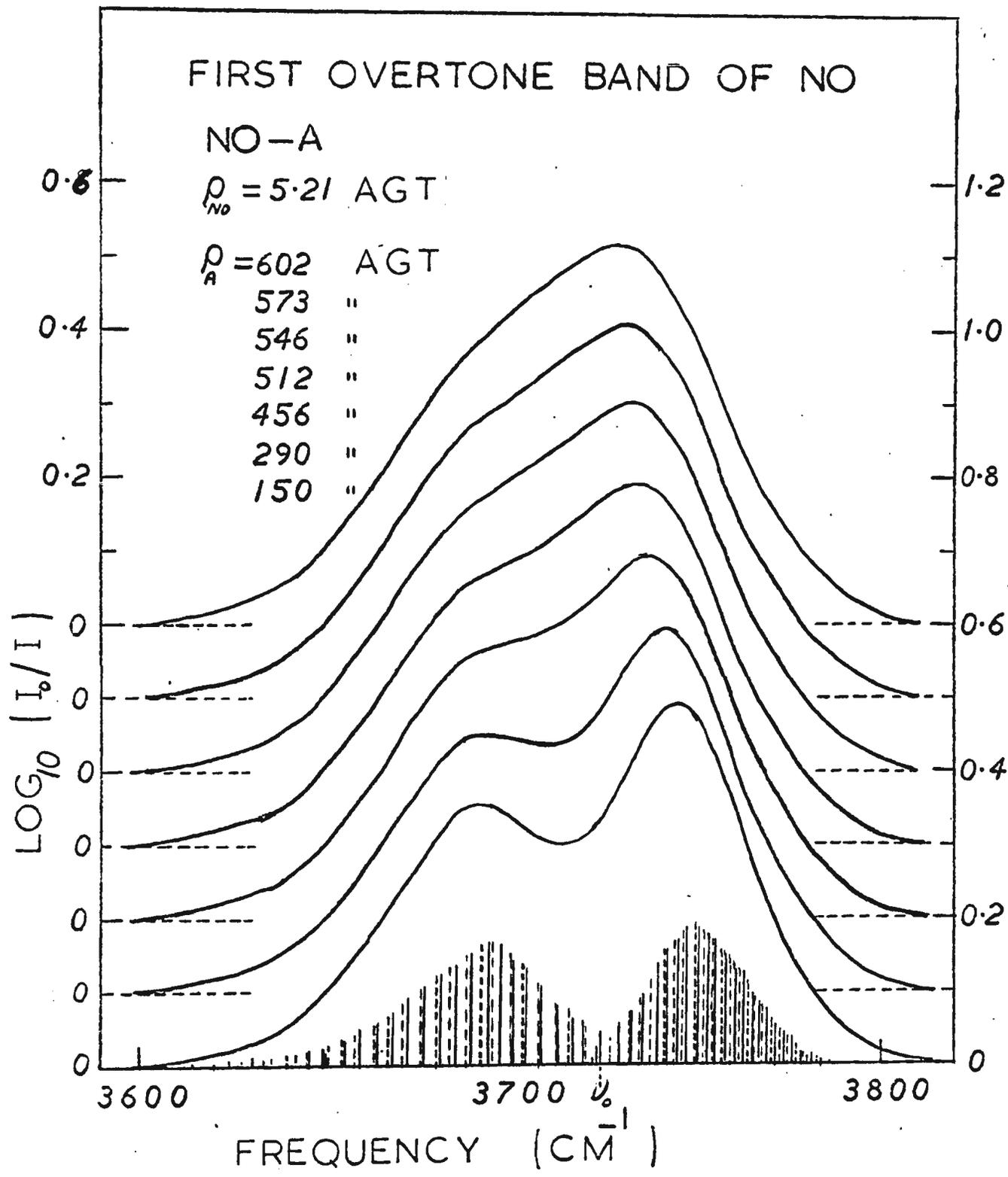


Fig. 6. Observed absorption contours of the 2-0 rotation-vibration band of NO in NO-A mixtures.

150 Agt with a partial density of nitric oxide of 5.21 Agt. It is seen that the peak corresponding to the R branch maximum shifts towards the low frequency side and the two peaks corresponding to the P and R branch maxima become less defined as the partial density of argon is increased. As it will be discussed below, the above change in the absorption profile can be explained as due to the broadening of P and R branches and the increase in the Q branch. Shown also in Fig. 6 are the individual rotational lines of the band. The positions of the rotational lines were calculated using the molecular constants given by Gillette and Eyster (1939); the band origin was indicated by ν_0 . Because the ground electronic state of nitric oxide is a $^2\pi$ state each rotational line in the rotation-vibration bands is a doublet; the solid and broken lines are used in Fig. 6 to indicate transitions in the $^2\pi_{\frac{1}{2}}$ and $^2\pi_{\frac{3}{2}}$ states respectively. The length of each line in the rotational structure of the band is drawn proportional to the transition probability of the corresponding transition in the fundamental band.

In Fig. 7, are reproduced the observed absorption contours of the band in NO-He mixtures at various partial densities of helium with a partial density of nitric oxide of

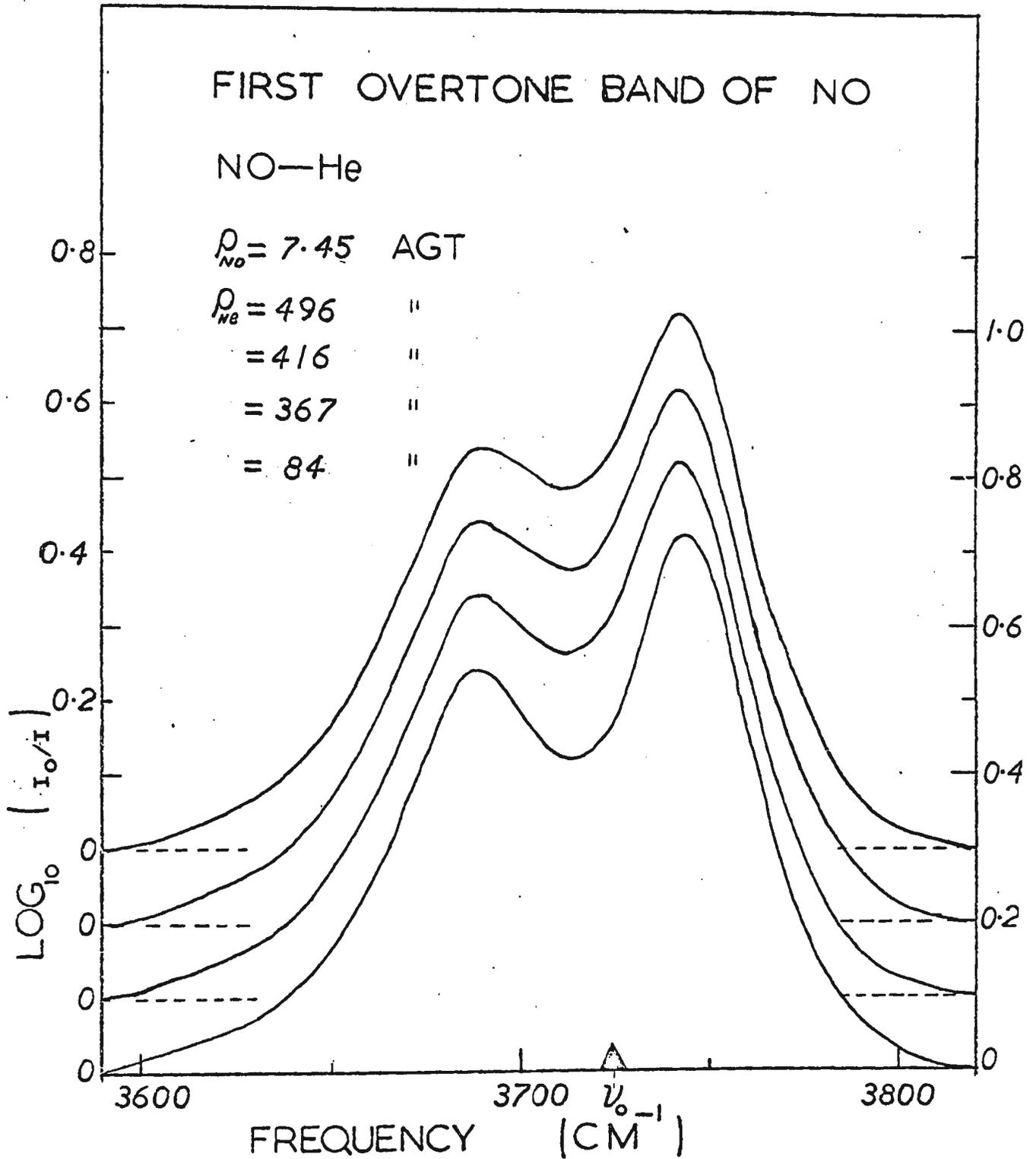


Fig. 7. Observed absorption contours of the 2-0 rotation-vibration band of NO in NO-He mixtures.

7.45 Agt. It is seen that the effects of the helium molecules on the observed profile of the band seem in general to be similar to those of argon molecules observed in the NO-A mixtures, but are not as pronounced.

Integrated Absorption Coefficient

In Figs. 8 and 9, the observed integrated absorption coefficients of the band in the low pressure NO-A and NO-He mixtures are plotted against the partial density of argon and helium respectively. It is seen that the integrated absorption coefficient for the different base densities of nitric oxide in both NO-A and NO-He mixtures becomes virtually constant at a foreign gas density above 40 Agt and below 80 Agt. It has been suggested that the correct value of the integrated absorption coefficient can be obtained by making either $P\ell \rightarrow 0$ or P_T large, where P is the pressure of the absorbing gas, ℓ is the absorption path length, and P_T is the total pressure of a mixture in which the absorbing gas is a component (Wilson and Wells 1946; Penner and Weber 1952). The constant values at various partial densities of nitric oxide were, therefore, taken as true absorption coefficients at corresponding densities of nitric oxide, and these values are plotted against densities of nitric oxide in Fig. 10. The graph represents a straight line

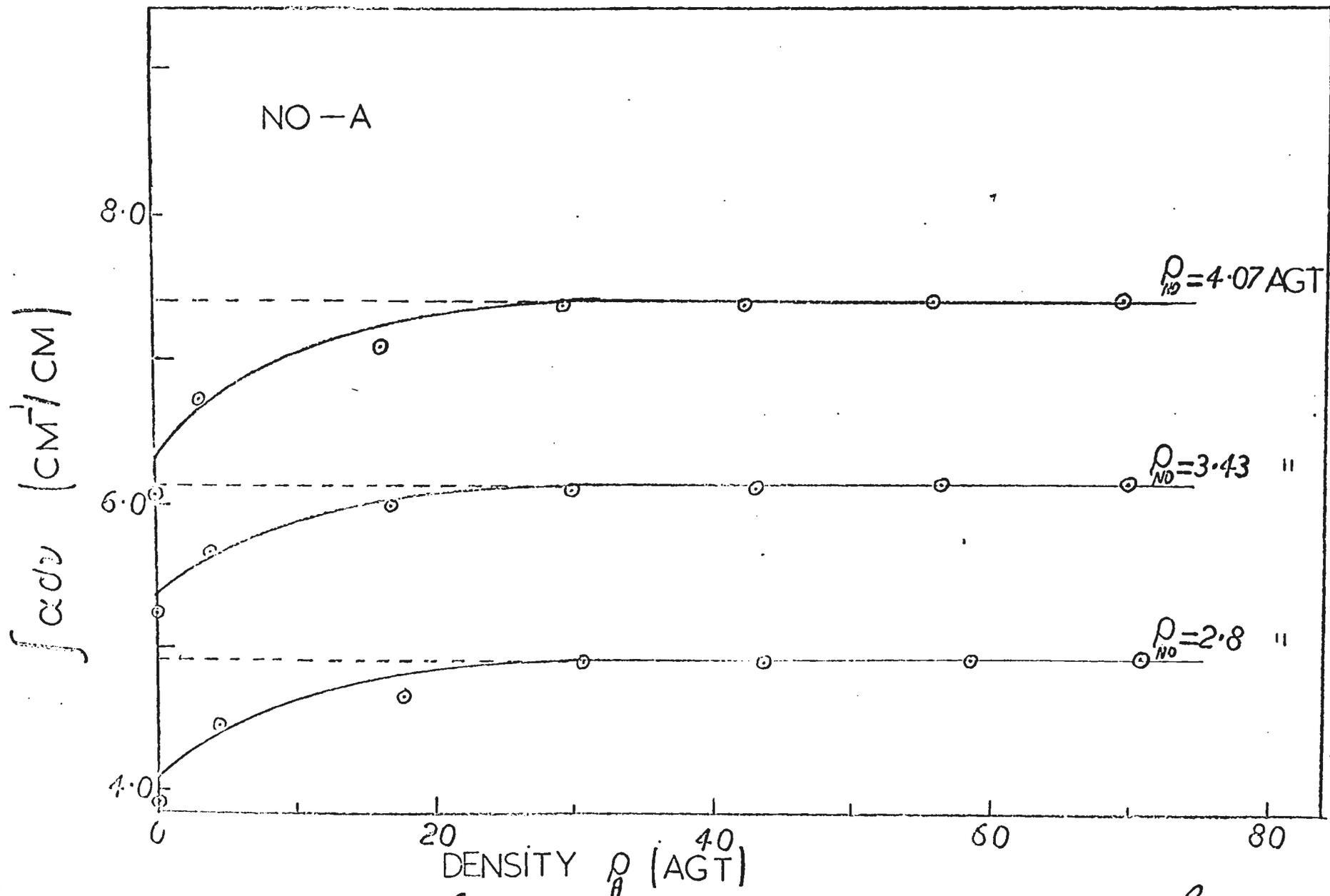


Fig. 8. Dependence of $\int \alpha d\nu$ of the 2-0 rotation-vibration band of NO on ρ_A in NO-A mixtures

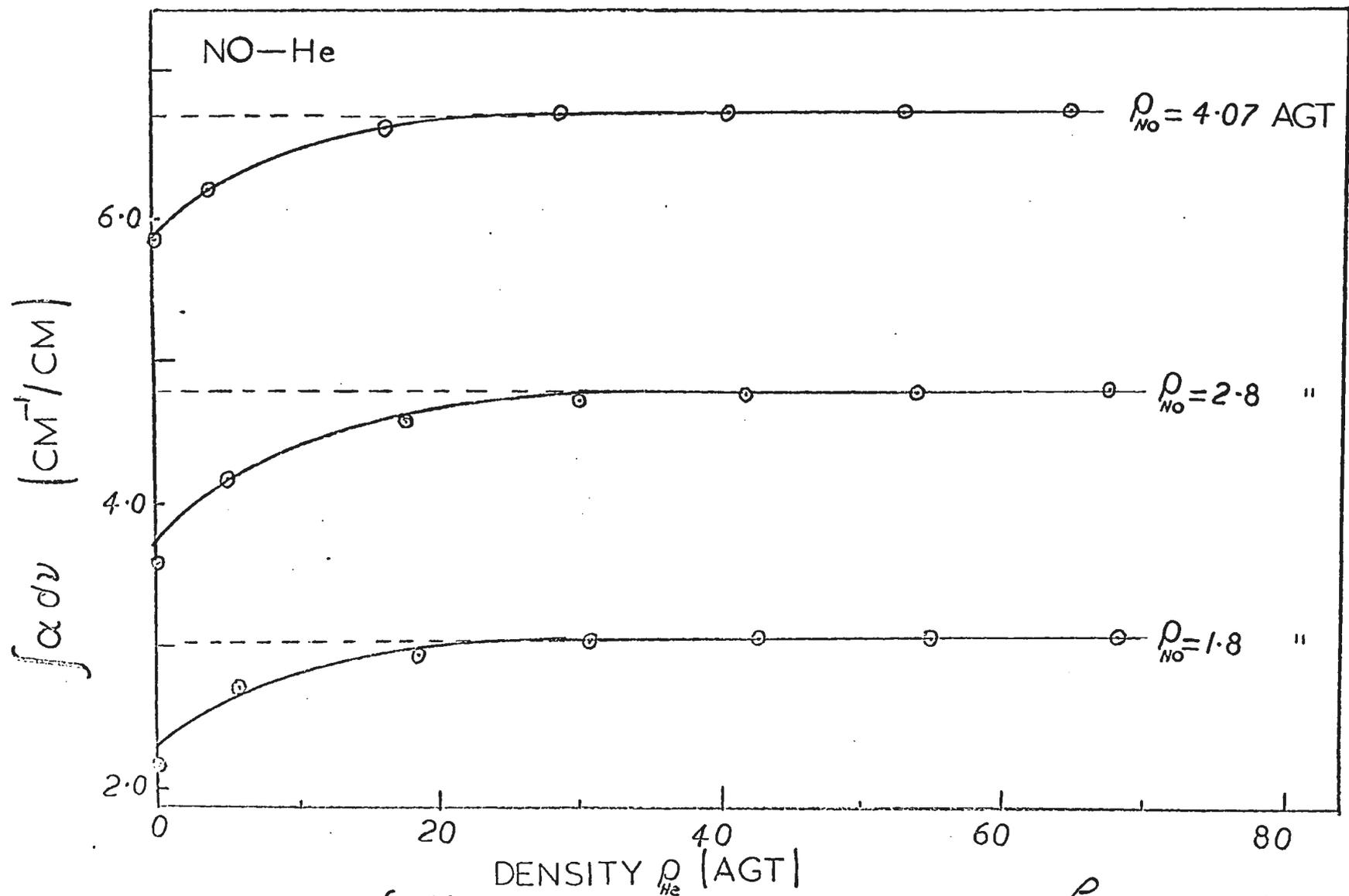


Fig. 9. Dependence of $\int \alpha d\nu$ of the 2-0 rotation-vibration band of NO on ρ_{He} in NO-He mixtures.

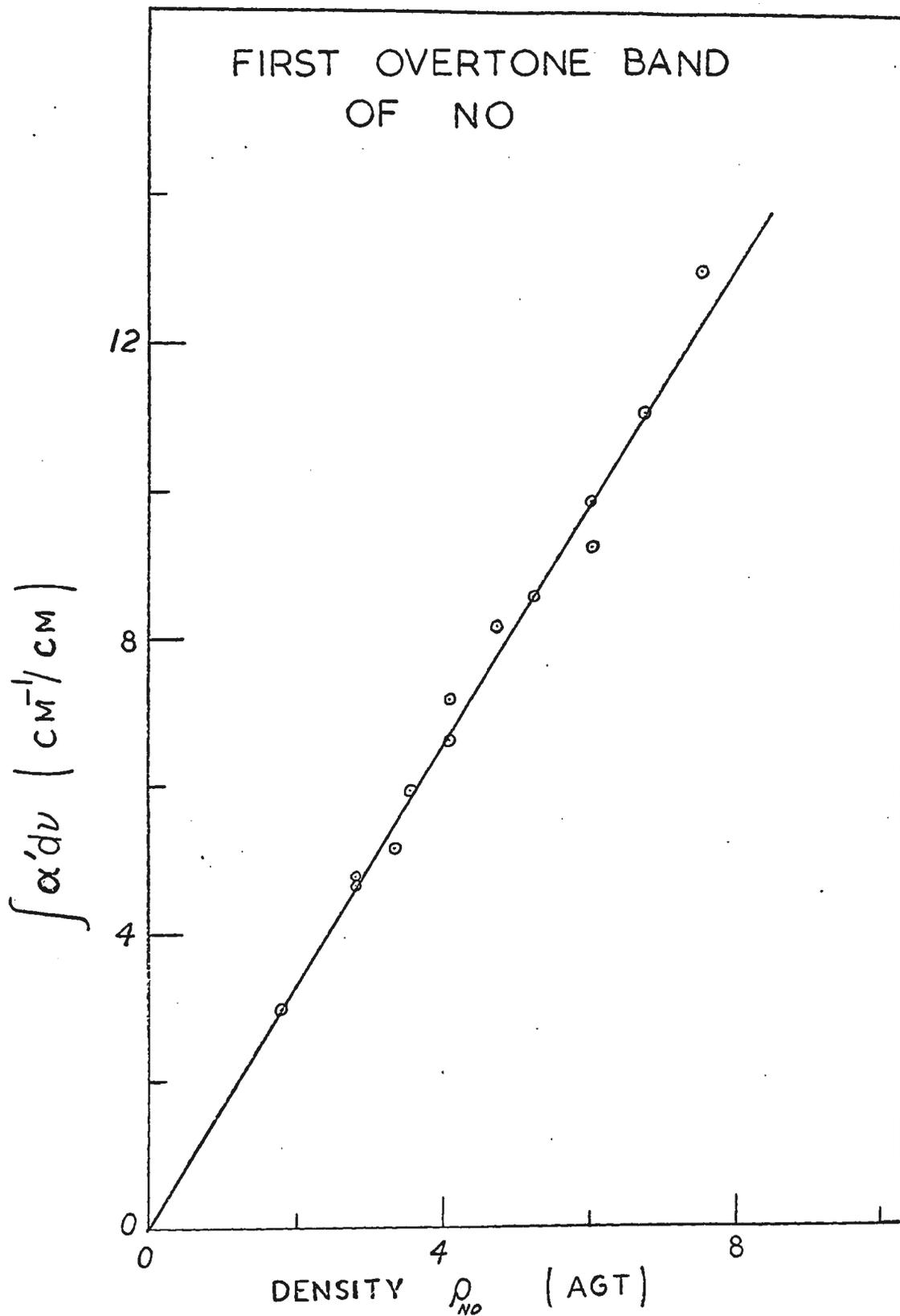


Fig. 10. Dependence of the true integrated absorption coefficients of the 2-0 rotation-vibration band of NO on ρ_{NO}

passing through the origin, thus the true integrated absorption coefficient $\int \alpha' d\gamma$, (in cm^{-1}/cm), is given by

$$\int \alpha' d\gamma = \alpha_0 \rho_{\text{NO}}$$

where ρ_{NO} is the density of nitric oxide in Agt, and α_0 is the "intrinsic" absorption coefficient in cm^{-1}/cm Agt. From the slope of the straight line in Fig. 10, α_0 is given by $\alpha_0 = 1.65 \pm .05 \text{ cm}^{-1}/\text{cm} - \text{Agt}$. The range of error is estimated from the standard deviation of the observed values. No quadratic term of the density of nitric oxide was observable in the integrated absorption coefficient, in the present density range.

In Figs. 11 and 12, the observed integrated absorption coefficients in the higher pressure NO-A and NO-He mixtures are plotted against the partial density of argon and helium respectively. The results are also summarized in Tables II and III.

Because the effects of helium gas on the band, other than the pure foreign broadening, were found to be so small the NO-He mixture experiments had to be limited only for a small range of partial densities of nitric oxide with the present experimental set up.

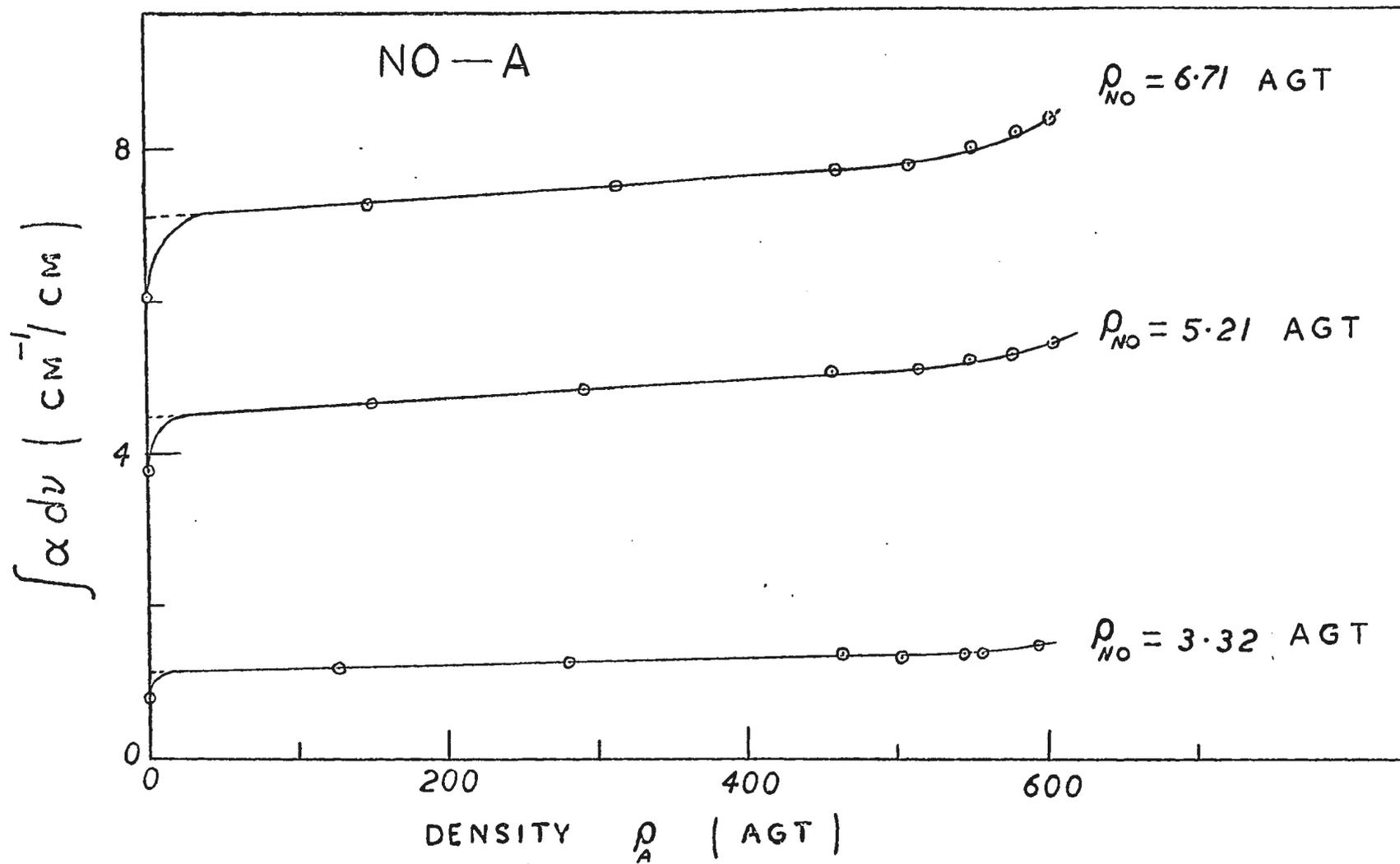


Fig. 11. Dependence of $\int \alpha d\nu$ of the 2-0 rotation-vibration band of NO on ρ_A in NO-A mixtures.

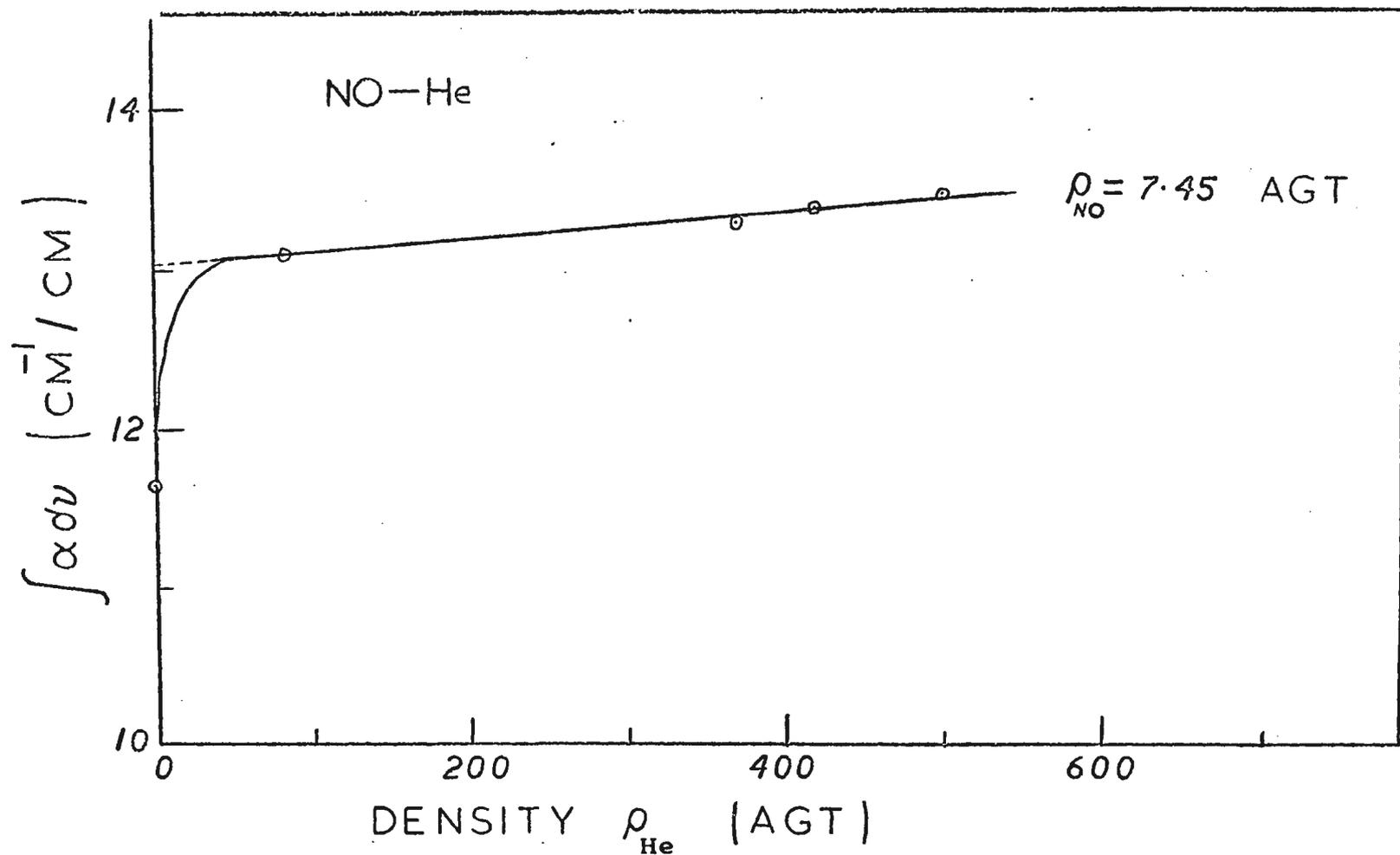


Fig. 12. Dependence of $\int \alpha d\nu$ of the 2-0 rotation-vibration band of NO on ρ_{He} in NO-He mixtures.

Table II. Integrated absorption coefficients of the 1st overtone band of nitric oxide in NO-A mixtures

$\rho_{NO} = 3.32 \text{ Agt}$		$\rho_{NO} = 5.21 \text{ Agt}$		$\rho_{NO} = 6.71 \text{ Agt}$	
ρ_A (Agt)	$\int \alpha d\nu$ (cm^{-1}/cm)	ρ_A (Agt)	$\int \alpha d\nu$ (cm^{-1}/cm)	ρ_A (Agt)	$\int \alpha d\nu$ (cm^{-1}/cm)
0	4.83	0	7.82	0	10.10
125	5.19	150	8.73	148	11.32
282	5.26	290	8.85	312	11.57
463	5.36	456	9.12	457	11.75
502	5.32	512	9.17	506	11.92
545	5.36	546	9.26	546	12.07
556	5.38	573	9.36	576	12.24
594	5.49	602	9.46	600	12.39

Table III. Integrated Absorption coefficients of the 1st overtone band of nitric oxide in NO-He mixtures

$\rho_{NO} = 7.45 \text{ Agt}$	
$\rho_{He} \text{ Agt}$	$\int \alpha d\nu$ (cm^{-1}/cm)
0	11.64
84	13.11
367	13.31
416	13.41
497	13.48

From Figs. 11 and 12, it can be seen that the straight line portions of the graphs show positive slopes, and in NO-A mixtures the deviation from the straight line relationship can also be detected at the higher partial densities of argon. As in the case of the low pressure mixtures, the foreign-broadening effect at the lower partial density of foreign gases is also detectable, and the intercepts of the extrapolated straight lines are again considered as true integrated absorption coefficients of pure gas at the given density. These values are included in Fig. 10. The results for NO-A mixtures were analysed as follows: It was first assumed that the (true) integrated absorption coefficient,

$$\int \alpha d\nu$$

(in cm^{-1}/cm), is given by a power series of

the partial densities P_{NO} and P_{A} of NO and of argon

respectively:

$$\int \alpha d\nu = \alpha_0 P_{\text{NO}} + \alpha_{1a} P_{\text{NO}}^2 + \alpha_{1b} P_{\text{NO}} P_{\text{A}} + \alpha_{2ab} P_{\text{NO}}^2 P_{\text{A}} + \alpha_{2b} P_{\text{NO}} P_{\text{A}}^2 + \dots$$

where the densities are given in Agt, and $\alpha_0, \alpha_{1a}, \alpha_{1b}, \alpha_{2ab}, \alpha_{2b}$

are various absorption coefficients. Using the values for

α_0 ($= 1.65$) and α_{1a} ($= 0$) obtained above, the results may be

further reduced to the form,

$$\left(\int \alpha d\nu - \alpha_0 P_{\text{NO}} \right) = (\alpha_{1b} + \alpha_{2ab} P_{\text{NO}}) P_{\text{NO}} P_{\text{A}} + \alpha_{2b} P_{\text{NO}} P_{\text{A}}^2$$

$$\text{or } (1/\rho_A) (\int \alpha d\nu - \alpha_0 \rho_{NO}) = (\alpha_{1b} \rho_{NO} + \alpha_{2ab} \rho_{NO}^2) + (\alpha_{2b} \rho_{NO}) \rho_A$$

Therefore, when $(1/\rho_A) (\int \alpha d\nu - \alpha_0 \rho_{NO})$ is plotted against ρ_A for each experiment in which ρ_{NO} is kept constant, the straight line

$$y = L + M \rho_A,$$

$$\text{where } y = (1/\rho_A) (\int \alpha d\nu - \alpha_0 \rho_{NO})$$

$$L = \alpha_{1b} \rho_{NO} + \alpha_{2ab} \rho_{NO}^2$$

$$M = \alpha_{2b} \rho_{NO}$$

may yield desired coefficients. The values thus obtained are:

$$\alpha_{1b} = 0 \text{ (} < 10^{-5} \text{ cm}^{-1}/\text{Agt}^2 \text{)}$$

$$\alpha_{2ab} = (2.5 \pm 0.6) \times 10^{-5} \text{ cm}^{-2}/\text{Agt}^3$$

$$\alpha_{2b} = (1.6 \pm 0.6) \times 10^{-7} \text{ cm}^{-2}/\text{Agt}^3$$

The above values were obtained by means of the least square method and the limits of error represent the standard deviations. IBM 1620 of the Department of Mathematics, M.U.N., was used for the calculations. It can be seen that the ternary absorption coefficients, α_{2ab} and α_{2b} , are the only coefficients which give appreciable contribution to the integrated absorption coefficient beside its "intrinsic" absorption coefficient α_0 . The binary absorption coefficients, α_{1a} and α_{1b} , do not seem to have appreciable values for the present range of densities; the absence of α_{1a} is probably due to the low density range of nitric oxide which had to be used in the present work.

The pressure-induced absorption of homonuclear as well as heteronuclear diatomic molecules, has already been studied by a number of investigators (see Chapter I for references). In the case of homonuclear diatomic molecules, where the induced rotation-vibration bands show O, Q and S branches, the induced absorption in a first order approximation is proportional to $\rho_a \rho_b$ in mixtures, where ρ_a is the density of the absorbing gas and ρ_b , the density of the perturbing gas. Hence for homonuclear diatomic molecules, the primary pressure-induced effect in a gas mixture is due to binary collisions between absorbing and perturbing molecules (Crawford, Walsh and Locke 1949). This has been interpreted theoretically by Van Kranendonk (1957; 1958) as due to an induced dipole moment during binary interactions. A number of observations of the rotation-vibration spectra of polar diatomic molecules, in binary mixtures at high pressures, have been made (Turrell, Vu and Vodar 1960). The principal effect which has been observed is the appearance of a Q branch in the fundamental rotation-vibration band of a polar molecule for which the Q branch is normally absent in the spectrum. The intensity of the Q branch appeared to be proportional to $\rho_a \rho_b$, the product of the component densities. As it has been stated above, in the present investigation it was found that the induced absorption

arises primarily due to ternary interactions. The ternary absorption coefficients α_{2ab} and α_{2b} in the expansion (1) can be explained in terms of the following three effects:

(1) The finite volume effect, (2) the ternary collisions, and (3) the change of polarizability of the absorbing molecule with pressure (Hare and Welsh 1958). Among the above three effects, the change of polarizability of the absorbing molecule with pressure, which has been predicted by theoretical considerations (Michels, de Boer, and Bijl 1937; de Groot and ten Seldan 1947), may not be important for the pressure range in the present investigation. It is difficult to estimate the finite volume effect in the present result since the binary absorption coefficients, α_{1a} and α_{1b} , could not accurately be determined in the present range of pressures. However, using the value $1 \times 10^{-5} \text{ cm}^{-2}/\text{Agt}^2$ which has been estimated as the upper limit for α_{1b} , and the value of α_{2b} ($= 1.6 \times 10^{-7} \text{ cm}^{-1}/\text{Agt}^2$), the finite volume effect may be computed using the relationship (Chyisholm and Welsh 1954)

$$\alpha_{2b}/\alpha_{1b} = \frac{4\pi}{3} d^3 N_0,$$

where N_0 is Loschmidt's number, and d is the diameter of the NO molecule and of the argon molecule. The value d thus obtained is approximately 5 \AA , whose order of magnitude compares favorably

with the value 3.3 \AA , average of the diameters given elsewhere (Hirschfelder, et al 1954). The ternary absorption coefficient α_{2ab} , however, is too large to be explained in terms of finite volume effect alone, and, therefore, α_{2ab} may be considered to arise mainly due to the ternary collisions. In this ternary collision effect, the value α_{2ab} may be somewhat too low owing to the "cancellation" effect (Van Kranendonk 1957). The "cancellation" effect in the present case, however, should not be appreciable. In view of the above considerations, it may be concluded that the induced absorption which was observed in the band is mainly due to the ternary collisions of two NO molecules and one A molecule, and the induction due to the binary collision of two NO molecules is at least one order of magnitude smaller than that due to the ternary collisions ($\alpha_{1b} \rho_{NO} \rho_A \sim 5 \times 10^{-4} \text{ cm}^{-1}$, and $\alpha_{2ab} \rho_{NO}^2 \rho_A \sim 6 \times 10^{-3} \text{ cm}^{-1}$ for $\rho_{NO} = 5 \text{ Agt}$ and $\rho_A = 10 \text{ Agt}$).

A similar result has been obtained in the study of the 1 - 0 "infrared atmospheric" absorption bands of oxygen in O_2 - foreign gas mixtures at high pressures (Cho 1958; Cho, Allen and Welsh 1963). While the power series expansion of the integrated absorption coefficient of the 0 - 0 band of the same system show an appreciable value for the binary coefficient, the series

expansion for the 1 - 0 band showed zero (or very small) value for the binary coefficient α_{1b} but a comparatively large value for the ternary coefficient corresponding to the two O₂ and one foreign gas molecule interactions. Judging from the evidence of the "double transition" in the 1 - 0 band obtained in liquid oxygen (Cho 1958), contribution of the ternary coefficient to the total absorption is probably due to the strong double transition in the 1 - 0 band. From the present result, therefore, one might postulate that the induced intensity in the first overtone band of nitric oxide in NO-A mixtures is almost entirely due to the ternary collision of 2 NO - A, and it is mainly of the double transitions of either one or both of the following types: (1) two NO molecules make simultaneous 1 - 0 (fundamental) rotation-vibration transitions in a colliding ternary system; (2) one NO molecule makes a 2 - 0 rotation-vibration transition and another NO molecule makes a pure rotational transition simultaneously in the colliding system.

The above conclusion with respect to the mechanism of the transitions in the first overtone band of NO is interesting in view of the behaviour of the 1 - 0 band of the "infrared atmospheric" band system of oxygen. Both NO and O₂ gases are

paramagnetic, and there have been the postulates of the existence of $(O_2)_2$ and $(NO)_2$ complexes in the liquid states.

Decomposition of the observed absorption profiles

The observed absorption profiles of the first overtone rotation-vibration band of nitric oxide in NO-A and NO-He mixtures were decomposed into the P, Q and R branches using the following method. Examples of such decomposition of the band are shown in Figs. 13, 14 and 15.

In spite of the observations made in the previous section, a preliminary analysis of the absorption contours did not show any evidence of the double transitions, but the induced absorption occurs only at the Q branch position of the band. It was therefore assumed that the induced absorption in the band contributes entirely to an increase in the intensity of the "Q" branch; the word "Q" branch was used merely to indicate a portion of the absorption which occurs approximately at the position of the Q branch of the band. For a given absorption contour obtained in a mixture, this induced Q branch contribution was estimated by subtracting the extrapolated integrated absorption coefficient, at zero partial densities of foreign gas, from the integrated absorption coefficient obtained from the contour. The total intensity of the Q branch of the given contour may then be

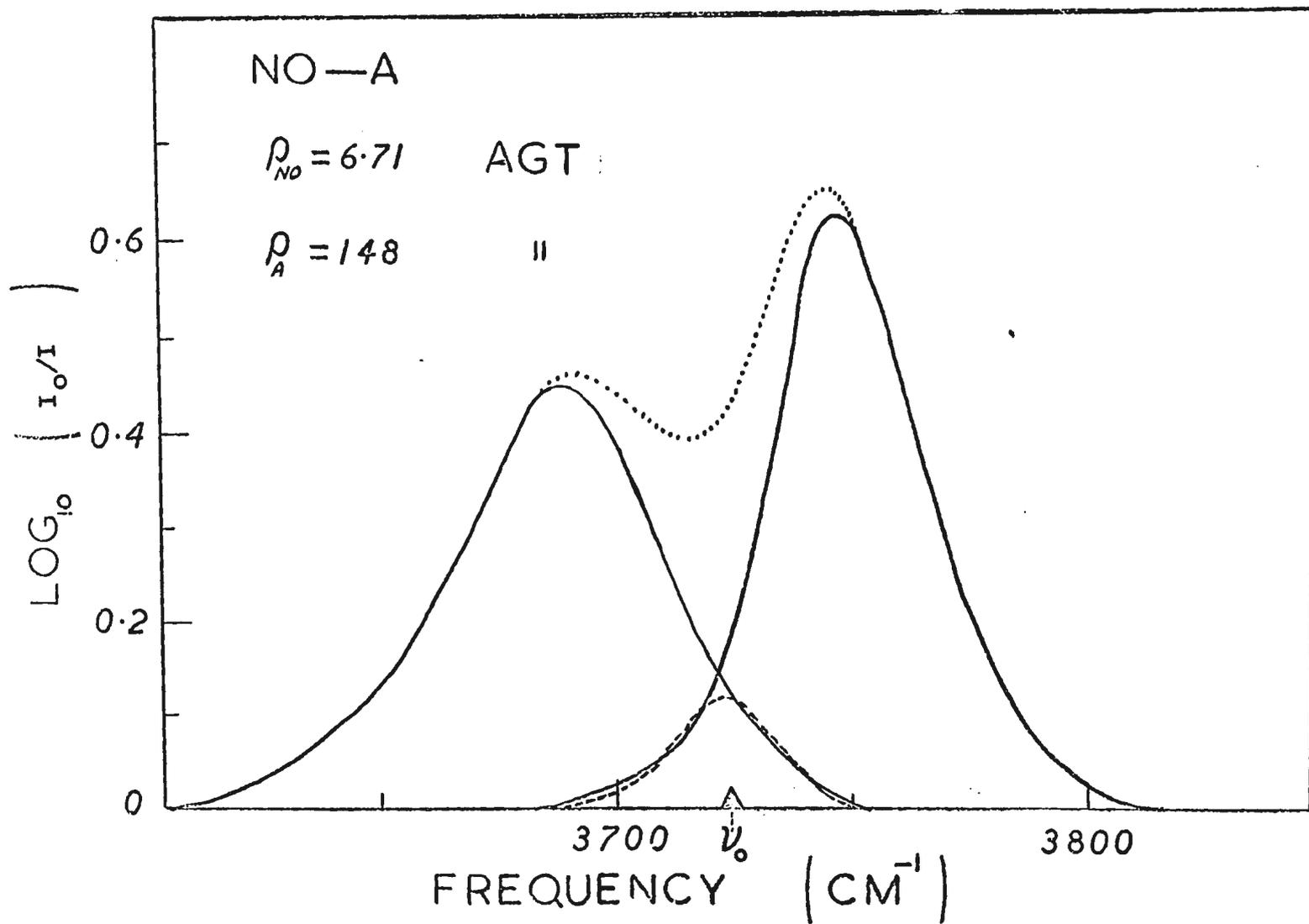


Fig. 13. The constructed P, Q and R branches of the 2-0 rotation-vibration band of NO in a NO-A mixture. The dotted curve indicates the observed contour.

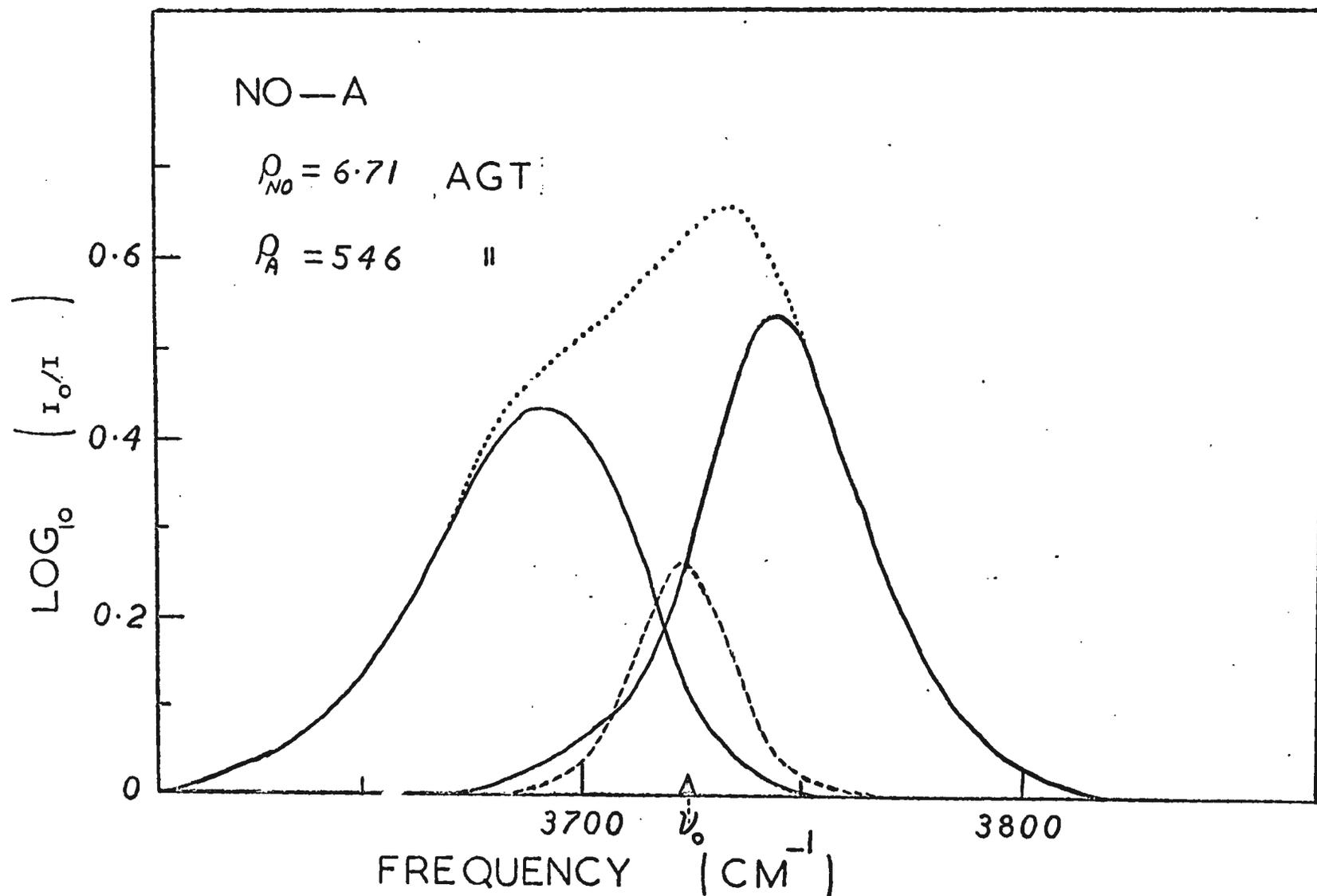


Fig. 14. The constructed P, Q and R branches of the 2-0 rotation-vibration band of NO in a NO-A mixture. The dotted curve indicates the observed contour.

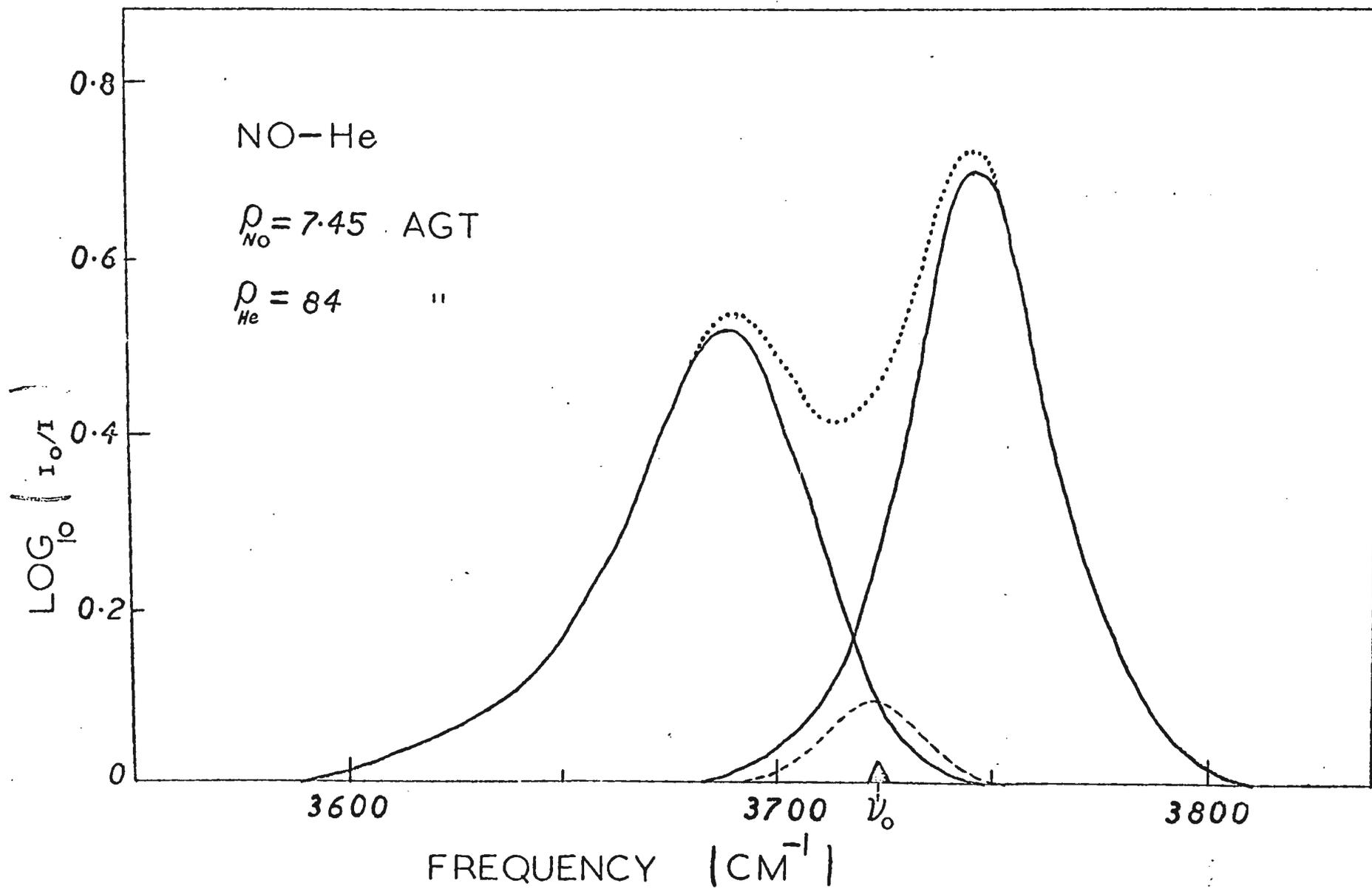


Fig. 15. The constructed P, Q and R branches of the 2-0 rotation-vibration band of NO in a NO-He mixture. The dotted curve indicates the observed contour.

obtained by addition of the intrinsic and induced Q branch intensities, the intrinsic intensity of the Q branch being calculated from the theoretical intensity ratios for P, Q and R branches of the fundamental band of nitric oxide. In order to determine the profile of the Q branch, the absorption contours of the band in two NO-A mixtures; one with approximately 90 Agt of argon and the other with approximately 150 Agt of argon, were compared and by taking the difference in absorption intensities at corresponding frequencies, the profile of the induced Q branch was constructed. The contours at these particular mixtures were chosen since the peak positions corresponding to the P and R branch maxima remained constant between these mixtures, thus indicating that the changes in the P and R branches of the band may be regarded as being very small. It was assumed then that the shape and the position of the Q branch remained constant for all the contours in the mixtures. Such an assumption may not introduce a large error in the decomposition since the contribution of the Q branch to the total absorption contour is small even at the highest pressure (\sim 8% of total intensity). The Q branch profile was then normalized in such a way that the area under the Q branch contour was equal to the estimated total intensity of the Q branch in a given mixture. By subtracting

the estimated Q branch from the total experimental absorption contour the remaining contour was obtained, and was assumed to contain P and R branches only. This remaining contour was then decomposed as follows:

It has been found by Kiss and Welsh (1959) that the shape of a pressure-induced rotational line is asymmetric; the high frequency wing, $I^+(\nu)$, of the line is of the dispersion line shape, i.e.,

$$I^+(\nu) = I(\nu_0) / \left\{ \left[(\nu - \nu_0) / \delta \right]^2 + 1 \right\},$$

where $I(\nu_0)$ is the peak intensity and 2δ is the width of the line at half-intensity, while the low frequency wing, $I^-(\nu)$, follows the relationship

$$I^-(\nu_0 - \Delta\nu) / I^+(\nu_0 + \Delta\nu) = \exp(-\Delta\nu hc/KT),$$

where h is Planck's constant, c is the velocity of light in vacuum, K is the Boltzman constant, and T is the temperature in $^{\circ}\text{K}$. Although the nature of transitions in the present band is quite different from that of the pure induced absorption, the same line shape has been assumed for the construction of the theoretical absorption contour. With a given value of δ , a calculated absorption contour is constructed by assuming the

above line shape for individual rotational lines in the band, using the calculated position and intensities which are shown in Fig. 6. The actual computation was carried out using IBM 1620. The most suitable value of δ was then chosen after comparing the experimental profile of the band in NO-A mixtures with the partial density of argon of approximately 90 atm (which was considered as the true contour without appreciable induced intensity but sufficiently broadened). δ thus chosen was found to be 15 cm^{-1} ; it was found that this value could be chosen easily within an accuracy of $\pm 2 \text{ cm}^{-1}$.

It was then assumed that the high frequency wing of the P branch and the low frequency wing of the R branch of the experimental P plus R contours, which, was obtained above, had the same shape as those of the calculated contour. By the method of trial and error, the positions for P and R branch maxima were chosen. The decomposition of the observed band into the P, Q and R branches was thus assumed to be complete.

In Fig. 13 and 14, the decompositions of two experimental contours in NO-A mixtures with low and high partial densities of argon respectively were presented. It is seen that the above

method of decomposition gives fairly successful separation of the three branches for all the contours obtained in the present NO-A mixtures. In Fig. 15, are shown the individual P, Q and R branches of an observed absorption contour in an NO-He mixture. It can be seen that the method of decomposition is also successful for this contour. In Fig. 16 the decomposed P and R branches of three different NO-A mixtures with constant partial density of nitric oxide are presented for the purpose of comparison. It can be observed that both P and R branches become broader and the positions of their maxima shifts towards the band origin as the density of argon is increased. It has been observed by previous investigators (e.g. Pigott and Rank 1957) that the pressure broadening of individual spectral lines shows a dependence on the rotational quantum number, J , for linear polar molecules. They found that the broadening is maximum for the most intense line. It has been also found that the perturbation of molecular rotation-vibration energy bands takes place when the absorbing polar gas is mixed with high pressure non-polar gases (Rank, Eastman, Birtley and Wiggins 1960). The shift of the positions of rotational lines increases as J increases; giving a "spreading out" effect of the rotational lines. It is therefore concluded that the above

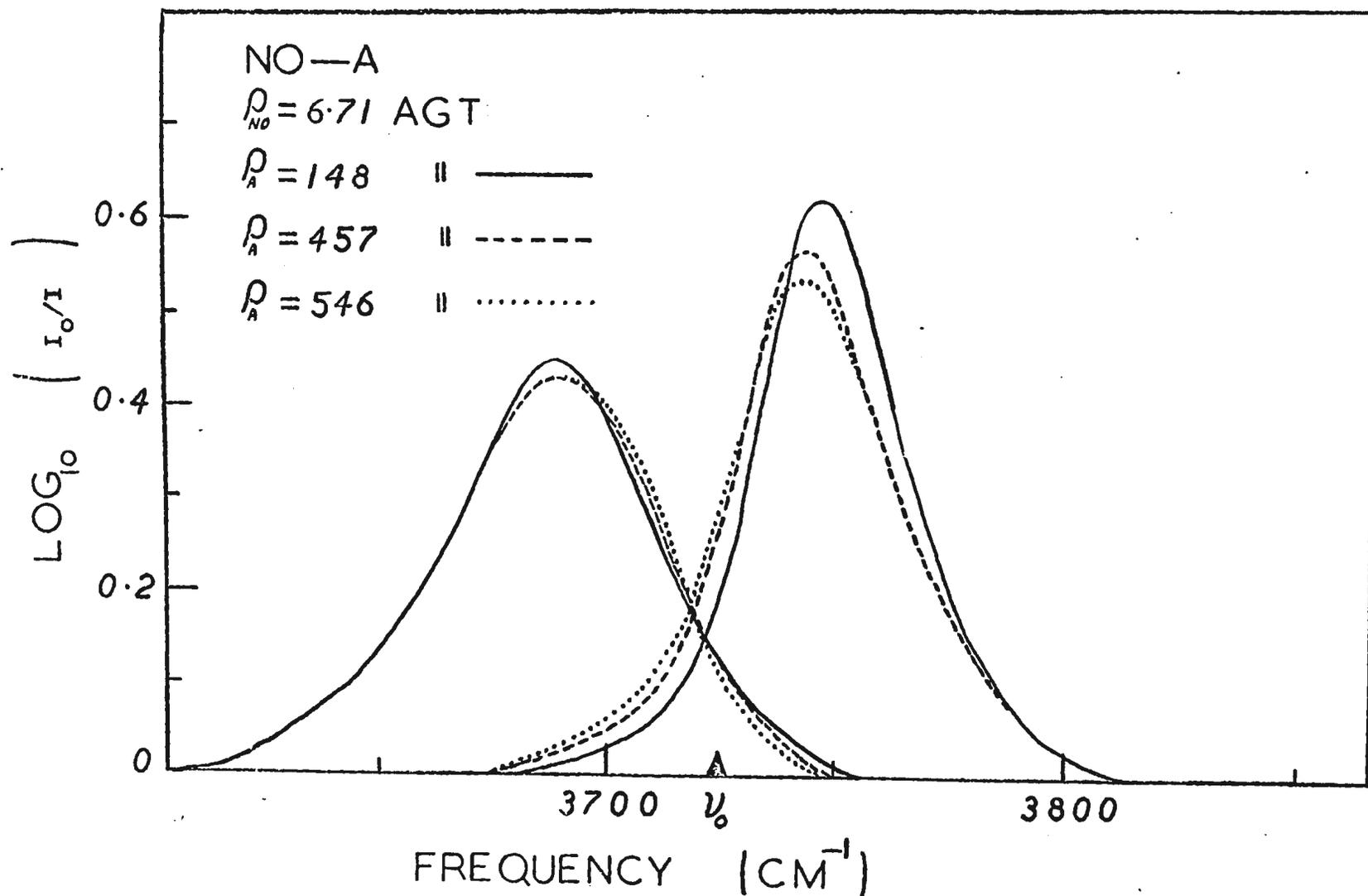


Fig. 16. The P and R branches of the 2-0 rotation-vibration band of NO in three NO-A mixtures.

effect on the P and R branches presented in Fig. 16 may be the result of the combination of the two effects described above.

An attempt was made to calculate the possible double transitions of two colliding NO molecules which may be observed in the region of the first overtone band. If these are to be induced by the collision, the selection rule for each individual molecule should be $\Delta J = 0, \pm 2$ and $\Delta V = 0, +1$ or $+2$. If one designates O, Q and S for $\Delta J = -2, 0,$ and $+2$ transitions respectively, and 0-0, 1-0 and 2-0 for $\Delta V = 0, +1$ and $+2$ transitions respectively, the following possible combinations of transitions would give maximum peaks at the frequencies given below: $Q_{1-0} + Q_{1-0}: 3752 \text{ cm}^{-1}$, $Q_{1-0} + S_{1-0}: 3814 \text{ cm}^{-1}$, $Q_{1-0} + O_{1-0}: 3700 \text{ cm}^{-1}$, $O_{1-0} + S_{1-0}: 3762 \text{ cm}^{-1}$, $Q_{2-0} + S_{0-0}: 3788 \text{ cm}^{-1}$, $O_{2-0} + S_{0-0}: 3736 \text{ cm}^{-1}$. In comparing these frequencies with the observed induced "Q" branch (maximum at 3720 cm^{-1}) it is concluded that there is insufficient evidence of any of the above double transitions in the observed band contour. It may be postulated, however, that the vibrational levels may be perturbed during the collision in such a way that the double transitions may occur in the neighbourhood of the observed "Q" branch.

CHAPTER III

THE INFRARED ABSORPTION OF LIQUID NITRIC OXIDE BETWEEN $\lambda 1.8\mu$ AND $\lambda 5.0\mu$

(i) Experimental

(a) Cryostat and liquid cells

The cryostat used in the experiments with liquid nitric oxide is shown in Fig. 17. Part, A, on which the cell assembly was attached, was constructed from a brass cylinder, 23 cm long and 10 cm in diameter, to which was soldered an inner brass cylinder, 20 cm long and 8 cm in diameter. The inner cylinder served as a liquid nitrogen reservoir. Part B, which served to enclose the cell assembly and to hold the optical windows, was constructed from a brass cylinder 6.5 cm long and 10 cm in diameter. The entrance and exit windows, W, were made of optically polished synthetic sapphire plates, 1 inch in diameter and 2 mm thick, and were cemented to the window adaptors, Q, by means of sealing wax. The parts A and B were connected by means of flanges, N, which held an O-ring, O. A hollow copper post, D, 2 cm in diameter and 4 cm long, was soldered on to the base of the inner cylinder of part A by means of a copper ring, F, 4 cm in diameter and 1 cm thick. The post D supported the cell holder, E, which had a length of 4 cm and inside diameter of 2 cm approximately. A temperature

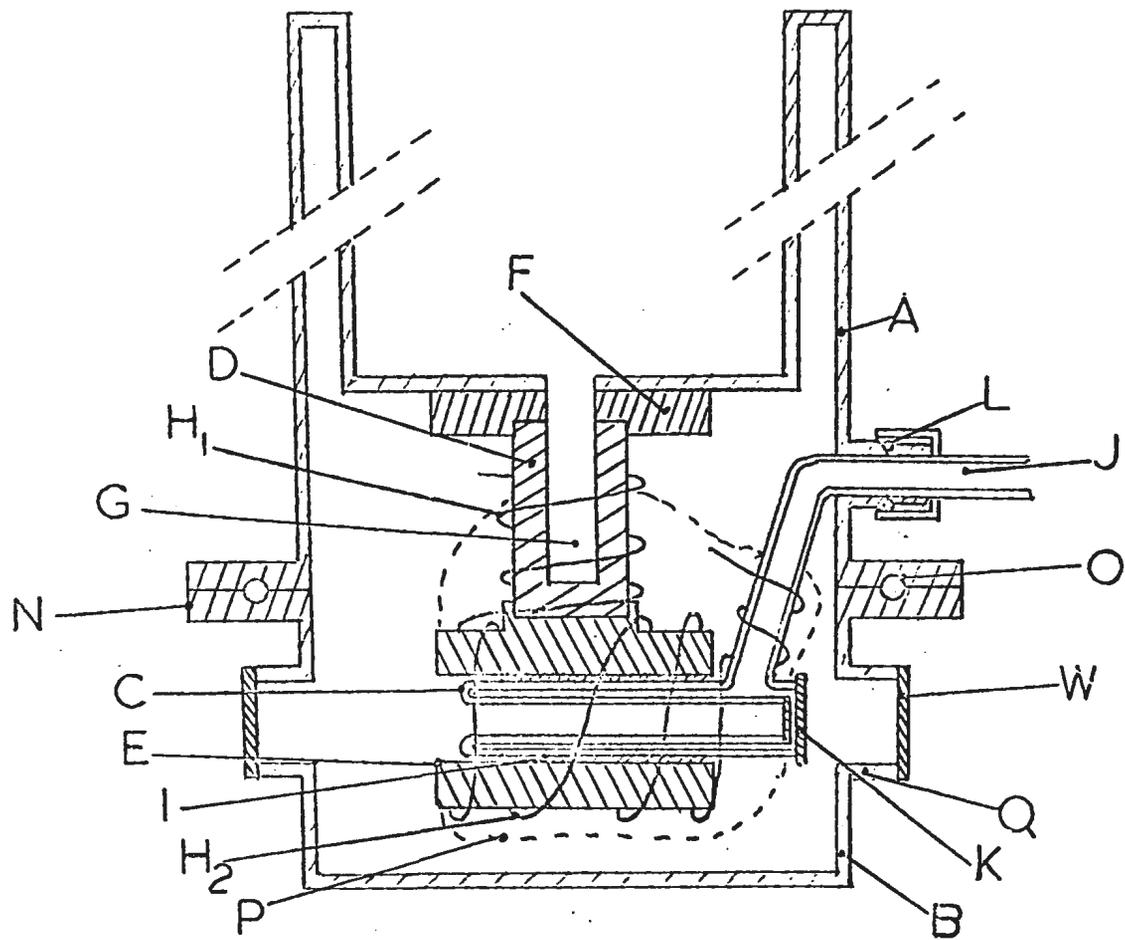


Fig. 17. Liquid nitrogen cryostat with the liquid absorption cell.

gradient along the post D was maintained by means of a heater, H₁; the post D was made hollow to allow liquid nitrogen in the reservoir to fill the central bore, G.

An absorption cell, C, whose description will be given below, was placed inside the holder E. The space between the cell and holder was filled with copper wool, I. A heater, H₂, was wound around the cell holder E and the inlet tube J. An outlet tube, J, was passed through the outer wall of the cryostat by means of an O-ring seal, L. With this design, it was possible to maintain the temperature of the absorption cell at $-160 \pm 2^{\circ}\text{C}$ by passing a requisite amount of electric current through the heaters H₁ and H₂. The temperature measurements were made by means of an iron - constantan thermocouple. The cell holder E and part of the post D were wrapped in an aluminum foil, P, in order to increase the heat conduction of the whole cell.

The type of absorption cell used in the liquid nitric oxide experiments is shown in Fig. 18. The cell was made of two pyrex glass tubings having diameters 2 cm and 1.2 cm which were fused together at one end. The windows, W₁ and W₂, were made from optically flat sapphire discs, 2 mm thick and 1.2 cm and 2.5 cm in diameter respectively. These were cemented to

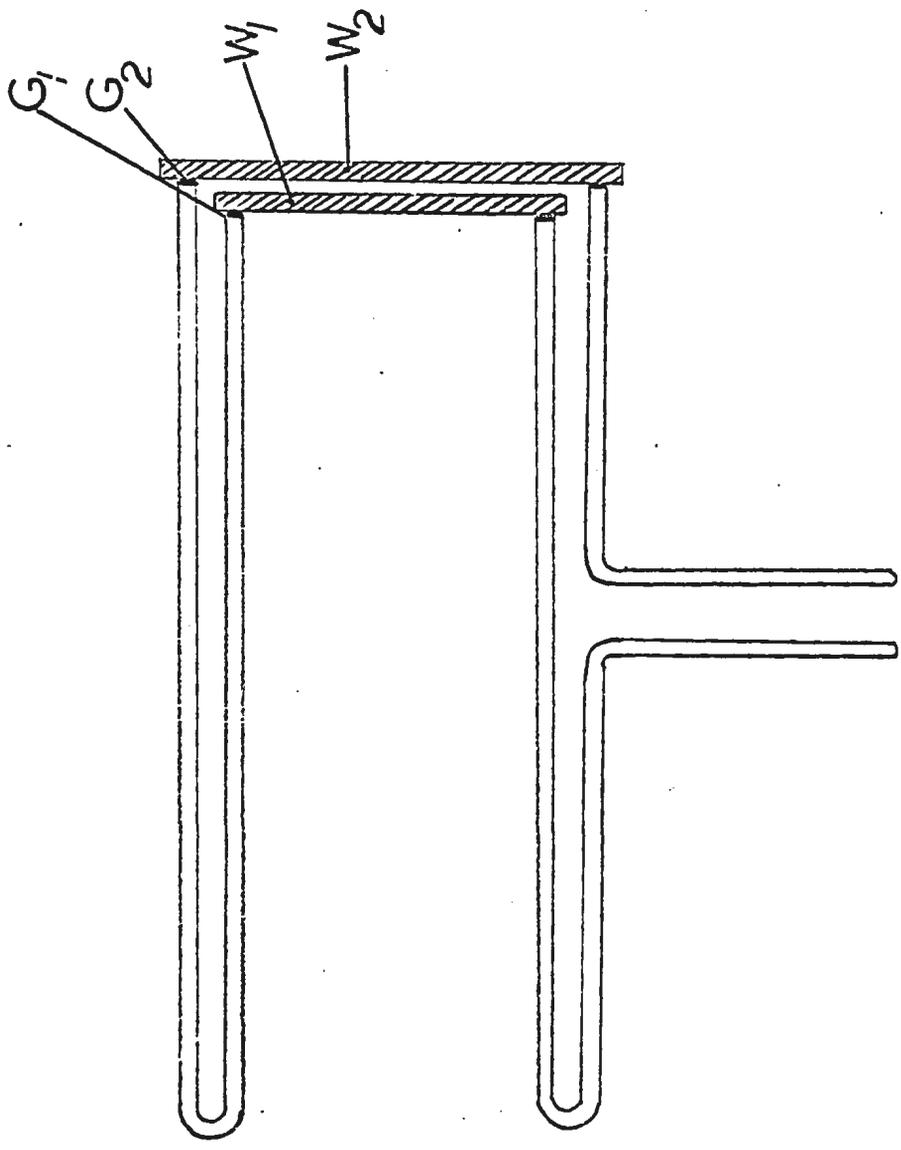


Fig. 18. Liquid Absorption Cell.

the surfaces, G_1 and G_2 , of the cell by means of Hysol cement. The inlet tubing is joined on the outer wall of the cell.

Two cells with path lengths of 0.26 mm and 0.11 mm were used for the present investigation. To obtain these small path lengths the following technique was used in cementing the windows on the cell. The smaller window W_1 was first attached. Iron wire, having the approximate thickness of the required path length was placed between W_1 and W_2 before W_2 was cemented on to the cell. The iron wire was later dissolved in dilute nitric acid, and the spacing between W_1 and W_2 was measured using a travelling microscope.

(b) Experimental method

The infrared absorption of liquid nitric oxide between $\lambda 1.8\mu$ and $\lambda 5.0\mu$ was studied using the liquid cells of path length 0.11 mm and 0.26 mm and cryostat described in the previous section. The optical arrangement used in the present investigation was similar to that used with the 12 cm transmission cell in the investigation of gases which has been described in Chap. II; the absorption cell in Fig. 4(a) being replaced by the liquid cell.

For the study of the absorption band in the liquid nitric oxide the inlet tube of the liquid cell was connected directly to the outlet tube of the purifying system (Fig. 1) and the cell was evacuated for a period of approximately twenty-four hours. Approximately 4 cc of purified liquid nitric oxide was prepared for each liquid experiment. Liquid nitrogen in the reservoir of the cryostat (Fig.17) was used as the refrigerant to obtain the required temperature of -160°C for the liquid cell. Temperature readings were made by means of an iron-constantan thermocouple, and by means of heaters H_1 and H_2 , (Fig.17), the temperature of the cell was held constant at $-160 \pm 2^{\circ}\text{C}$ throughout the duration of the experiment. The nitric oxide previously purified was then allowed to condense slowly into the liquid cell. This process usually required an hour to complete. When it was seen that sufficient liquid nitric oxide had condensed in the cell, several spectroscopic readings of the resulting absorption spectrum for the particular path length of liquid nitric oxide were made. The small variation of the temperature of the cell was also detected by a vacuum gauge attached to the system.

In this investigation the Perkin and Elmer model 12-C

Spectrometer was used with a LiF prism and Golay pneumatic detector. An instrumental slit width of $300\ \mu$ was used over the entire spectral region under study. At the position of the middle of the first overtone band, $\lambda\ 2.7\ \mu$, the slit width represented a spectral slit width of $15.6\ \text{cm}^{-1}$. A Globar, which was connected to a Sorensen voltage regulator, served as the source of continuous infrared radiation. The method of reduction of the absorption contours for the region $\lambda\ 1.8\ \mu$ to $\lambda\ 5.0\ \mu$ was the same as used in the experiments previously described (Chap. II).

(ii) Results and Discussion

The experimental absorption contours of liquid nitric oxide in two different path lengths are presented in Fig. 19. It can be seen that three sharp absorption peaks, whose positions occur in the neighbourhood of the first overtone rotation-vibration band of nitric oxide in gaseous nitric oxide, and two peaks, in the neighbourhood of the second overtone rotation-vibration band of nitric oxide in gaseous nitric oxide, are superimposed on a broad continuum whose maximum occurs at approximately $3500\ \text{cm}^{-1}$. Another peak can be seen at $2032\ \text{cm}^{-1}$. In order to be certain that the observed spectrum is not influenced by impurities in the liquid, several experiments were carried out

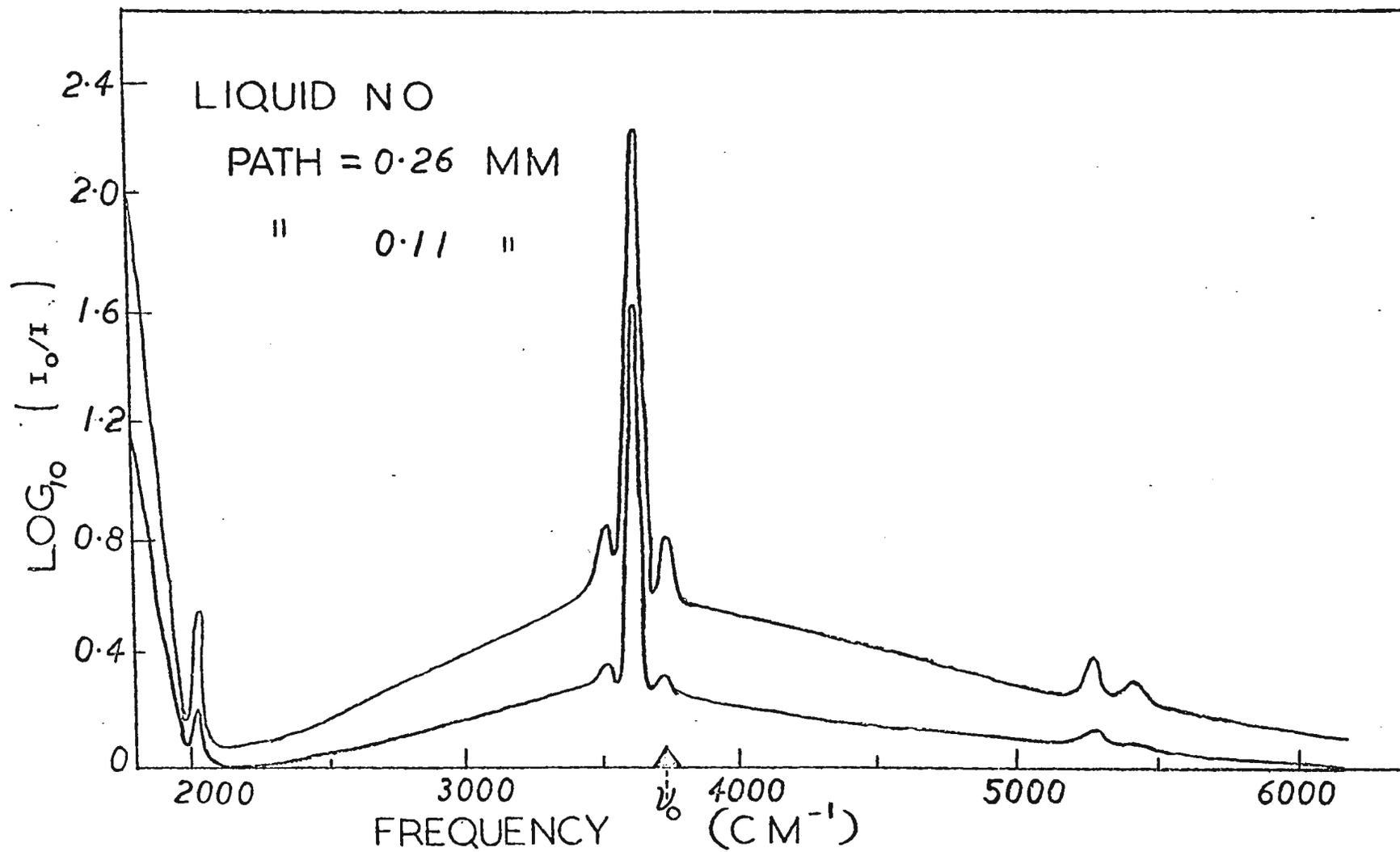


Fig. 19. Observed absorption contours of liquid nitric oxide.

using nitric oxide from the purifying system (Fig. 1) before the purification was considered to be complete. Thus, by comparing the spectra obtained with liquid containing different degrees of impurity it was possible to eliminate absorption peaks which arise due to molecules other than nitric oxide.

A similar investigation of liquid nitric oxide in the region extending from $\lambda 1.0\mu$ to $\lambda 6.0\mu$ was carried out by Smith, Keller and Johnston (1951). A summary of the position of the absorption peaks obtained in the present investigation is given in Table IV,

Table IV. Summary of the frequencies of the observed absorption peaks.

Present investigation Frequency (cm^{-1})	Smith, Keller & Johnston Frequency (cm^{-1})
2025	2032
—	2124
3500	3515
3600	3600
3710	3708
5250	5200
5400	5390

the results of Smith, Keller and Johnston were compared in the same table. The absorption peak, which was observed by the previous investigators at 2124 cm^{-1} was not observed in the present investigation. The peak positions obtained in the present investigation agree well with the previous results.

Following the interpretation given by Smith, Keller and Johnston, all the observed bands in the present investigation may be explained in terms of various combinations of the two observed absorption peaks, 1863 cm^{-1} and 1770 cm^{-1} , obtained by them in the region between $\lambda 5 \mu$ and $\lambda 6 \mu$, and one peak which was observed in the Raman effect spectrum of liquid nitric oxide, 167 cm^{-1} . The above investigators attempted to explain the observed spectrum by postulating the existence of $(\text{NO})_2$ molecules in the liquid in the form of the bent ONNO structure. However, such combination bands have been observed in a number of cases in which the induced absorption was studied. It can therefore be said that the above absorption peaks observed in liquid nitric oxide may be explained in terms of double transitions in two colliding molecules in the liquid. No attempt was made by the previous investigators to explain the possible origin of the continuum whose center position is at approximately 3500 cm^{-1} . One could postulate that this

continuum is probably due to the various types of double transitions in two colliding nitric oxide molecules; these have been discussed in the previous chapter with respect to the first overtone rotation-vibration band of nitric oxide in gaseous mixtures. It is worth-while to note that the maximum of the continuum is observed at a frequency which is close to the frequency of the first overtone band. The continuum is probably due to the double transitions of two colliding nitric oxide molecules, each molecule making the fundamental rotation-vibrational transition. Each rotation-vibration transition would include O, Q and S branches, thus the resulting double transitions will give rise to a very broad band whose maximum would occur at approximately twice the fundamental frequency. The continuum observed in the red region of the visible spectrum of liquid nitric oxide observed by previous investigators, (Vodar 1908; Bernstein and Herzberg 1947; Snook 1962) should be the high frequency wing of the infrared continuum found in the present investigation.

APPENDIX
THE ABSORPTION OF GASEOUS NITRIC
OXIDE AT HIGH PRESSURES IN THE
VISIBLE SPECTRAL REGION

Experimental method

As a preliminary investigation to the study of the infrared spectrum, the absorption spectrum of nitric oxide gas at high pressures was studied in the visible region between λ 3500 Å and λ 6600 Å using a Hilger constant deviation glass spectrograph with a spectral slit width of 7.0 cm^{-1} at 4000 Å. Kodak Super Panchromatic plates were used to photograph the spectrum. As the comparison spectrum for this region an iron arc spectrum was used. The transmission type cell with a 12.4 cm path length was used at pressures up to 700 atm. The investigation was carried out at room temperature. A 750 watt projection lamp operating on 60 cycle power supplied through a Sorensen voltage regulator served as a source of continuous radiation.

Results and observation

In Fig. 20 the absorption spectrogram of gaseous nitric oxide at various pressures are reproduced. A background spectrogram taken with an evacuated absorption cell is also presented in Fig. 20. It is seen that a continuous absorption

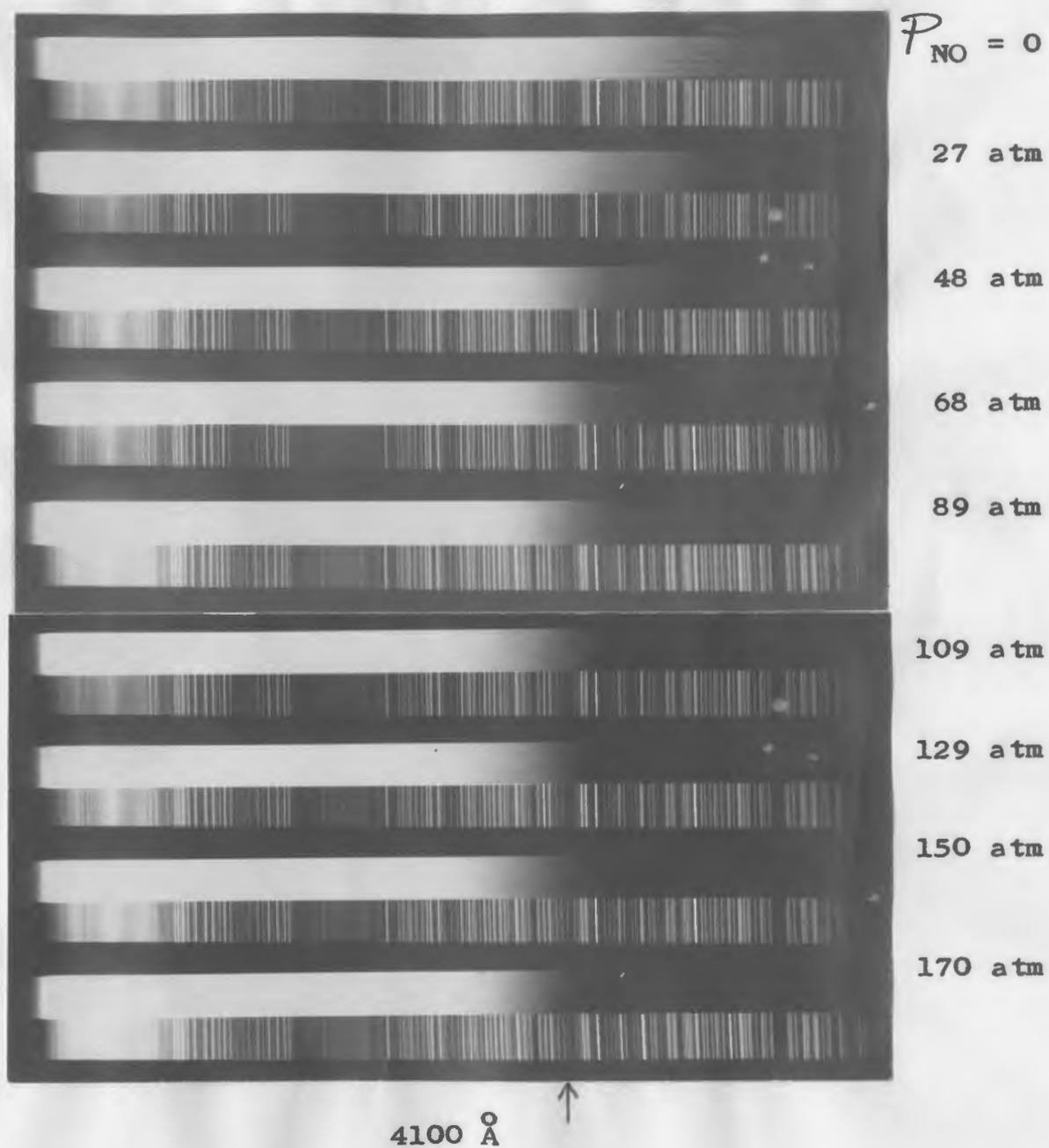


Fig. 20. Absorption spectra of gaseous nitric oxide at various pressures; optical path 12.4 cm

at the violet end of the spectrum starts to appear at a pressure of nitric oxide as low as 20 atm and the extent of the continuum increases towards the long wavelength side with increase in pressure. The continuum appears to reach a limiting cut-off wavelength of approximately 4100 \AA at a pressure of approximately 110 atm. In Figure 21 the absorption spectrogram of the liquid nitric oxide of path length 1.1 cm, which has been obtained by Snook (1962) was presented as spectrogram number (2.) In Fig. 21 a background taken with an evacuated liquid cell is also shown. as (1).

As is seen in Fig. 21 the continuous absorption in liquid nitric oxide, which starts at approximately 4200 \AA and extends towards the shorter wavelengths, resembles the continuum observed in the gaseous nitric oxide at high pressures (Fig. 20). In liquid the continuum has a sharp cut-off whereas in the high pressure gas the cut-off is more gradual and at a shorter wavelength. Another continuum which was observed in the red end of the spectrum of the liquid nitric oxide is absent in the spectrogram of gaseous nitric oxide. The absence of the "red" continuum in the gas is probably due to the absence of the infrared continuum, observed in the infrared absorption spectrum of liquid nitric oxide, but not in the infrared

Background spectrum



Absorption of liquid NO; path = 1.1 cm



Fig. 21. Reproduced spectrum of liquid nitric oxide.
(After Snook, 1962)

absorption of gaseous nitric oxide. The above results indicate that the postulate by Herzberg with respect to the "violet" continuum observed in liquid nitric oxide as due to the existence $(NO)_2$ complexes may not be correct. The above two continua do not obviously behave in a similar way in liquid and high density gas. Concluding from the results obtained in the infrared region where the infrared continuum was directly connected to colliding NO pairs or $(NO)_2$ complexes, the continuum observed in the violet region, both in liquid and high density gaseous nitric oxide may be due to quite different transitions from those postulated by Herzberg.

As the pressure of nitric oxide gas was increased above 200 atm, it was observed that the nature of the gas inside the absorption cell changed gradually. Visual observation showed the appearance of colour in the gas, and the pressure of the gas decreased gradually but steadily. When the pressure of nitric gas was increased up to 700 atm, the colour of the gas changed to dark green and the pressure decreased at a rate of approximately 50 atm/hr until the pressure reached to as low as 100 atm. It was therefore concluded that the rapid chemical reaction took place in nitric oxide gas at pressures above 200 atm. An attempt was made to examine the infrared

absorption of the gas at these high pressures, and many absorption bands corresponding to NO_2 , N_2O , N_2O_5 molecules were obtained.

SUMMARY

The first overtone rotation-vibration band of NO was studied in gaseous NO at pressures up to 750 atm, and in gaseous NO-A and NO-He mixtures at total pressures up to 1300 atm. The range of the partial density of NO used in the mixture experiments was up to 6 atm. The absorption profiles obtained in high pressure NO and in the mixtures show a marked difference from the profile observed in low pressure NO. The observed absorption contours in the gaseous mixtures were decomposed into the P, Q and R branches, and it was found that the P and R branches broaden and the maxima of both branches shift toward the band origin as the partial density of the perturbing gas is increased. A power series expansion of the observed integrated absorption coefficient of the band in NO-A mixtures suggests that a part of the absorption intensity arises due to the induced transitions. It was also found that the induced absorption is primarily due to the ternary interaction of NO - NO-A. The intrinsic absorption coefficient, α_0 and the ternary absorption coefficients α_{2ab} and α_{2b} were determined as $1.65 \pm 0.5 \text{ cm}^{-2}/\text{Agt}$, $(2.5 \pm 0.6) \times 10^{-5} \text{ cm}^{-2}/\text{Agt}^3$, and $(1.6 \pm 0.6) \times 10^{-7} \text{ cm}^{-2}/\text{Agt}^3$ respectively.

The infrared absorption of liquid NO was studied with the path length of 0.26 and 0.11 mm, at -160°C . It appears that all the absorption peaks are "combination" bands, and a broad continuum, whose maximum is approximately at the position of the first overtone rotation-vibration band of NO gas, may be explained as due to double transitions.

BIBLIOGRAPHY

- Bernstein, H.S., and Herzberg, G. J. Chem. Phys. 15,
77 (1947).
- Cho, C.W., Allen, E.J. and Welsh, H.L. Can. J. Phys.
41, 1991 (1963).
- Cho, C.W. Ph.D. Thesis, University of Toronto (1958).
- Crawford, M.F., Welsh, H.L., and Locke, J.L. Phys. Re.
75, 1607 (1949).
- Chisholm, D.A., and Welsh, H.L. Can. J. Phys. 32
291 (1954).
- Clouter, M. M.Sc. Thesis, Memorial University of
Newfoundland (1962).
- Coulon, R., Oksengorn, B., and Vodar, B. Comp. rend.,
239, 964 (1954).
- de Groot, S.R., and ten Seldan, C.A. Physica 13, 47 (1947).
- Ellis, J.W., and Kneser, O. Zeirs. der Phys. 86, 583 (1933).
- Gebbie, H.A., and Stone, N.W.B. Proc. Phys. Soc. 82,
309 (1963).
- Gillette, R.H., and Eyster, E.H. Phys. Rev. 56, 1113
(1939).
- Golding, B.H., and Saye, B.H. Ind. Eng. Chem. 43
160 (1951).
- Hare, W.F.J. Ph.D. Thesis, University of Toronto (1955).
- Hare, W.F.J., and Welsh, H.L. Can. J. Phys. 36, 88 (1958).
- Herzberg, D. Spectra of Diatomic Molecules, 2nd edit.
D. Van Nostrand (1950).

- Hirschfelder, J.O., Curtiss, C.F., and Bird, R.B. Molecular Theory of Gases and Liquids. J. Wiley & Sons (1954).
- Jenkins, F.A., Barton, H.A., and Mulliken, K.S. Phys. Rev. 30, 150 (1927).
- Kiss, Z.J., and Welsh, H.L. Can. J. Phys. 37, 1249 (1959).
- Lewis, C.N. J. Am. Chem. Soc. 46, 2027 (1924).
- Michels, A., and Wouters, H. Physica, 8 (1941).
- Michels, A., and Wijker, Hub., and Wijker, H.K. Physica 15, 627 (1949).
- Neilsen, A.N., and Gordy, W. Phys. Rev. 56, 781 (1939).
- Nichols, N.L., House, C.D., and Noble, R.H. J. Chem. Phys. 23, 59 (1955).
- Penner, S.S., and Weber, D. J. Chem. Phys. 19, 807 (1951).
- _____ J. Chem. Phys. 21, 649 (1952).
- _____ J. Chem. Phys. 17, 1351 (1951).
- Pigott, M.I., and Rank, D.H. J. Chem. Phys. 26, 384 (1957).
- Rank, D.H., Eastman, D.P., Birtley, W.B., and Wiggins, T.A. J. Chem. Phys. 33, 323 (1960).
- Rice, O.K. J. Chem. Phys. 4, 367 (1936).
- Smith, A.L., Keller, W.E., and Johnston, H.L. Phys. Rev. 79, 728 (1950).
- _____ J. Chem. Phys. 19, 189 (1951).
- Smith, A.L., and Johnston, H.L. J. Chem. Phys. 20, 1972 (1952).
- Snook, C. M.Sc. Thesis, Memorial University of Newfoundland (1962).

Snow, C.P., Rawlins, F.I.G., and Rideal, E.K. Proc.
Roy. Soc. 124, 453 (1929).

_____ Proc. Roy. Soc. 126, 355 (1929).

Turrell, G.C., Vu, H., and Vodar, B. J. Chem. Phys.
33, 314 (1960).

Van Kranendonk, J., and Bird, R.B. Physica, 18, 953
(1951).

Van Kranendonk, J. Physica, 22, 825 (1957).

_____ Physica, 24, 347 (1958).

Vodar, B. Comp. rend. 204, 1467 (1937).

Vu, H., and Turrell, G.C. Comp. rend. 249, 2758 (1959).

Vu, H. J. Rech. C.N.R.S. 53, 313 (1960).

Warburg, E., and Leithauser, G. Ber. D. Chem. Ges.
1, 145 (1908).

Welsh, H.L., Pashler, E.P., and Dunn, A.F. J. Chem. Phys.
19, 340 (1951).

Wilson, E.B., and Wells, A.J. J. Chem. Phys. 14,
578 (1946).

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