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ROTATION LINES IN THE FUNDAMENTAL
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WIDTHS AND STRENGTHS OF VIBRATION-ROTATION LINES
IN THE FUNDAMENTAL BAND OF NITRIC OXIDE

DISSERTATION

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

By

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* * * * *

The Ohio State University
1965

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I. INTRODUCTION

The strength, width, and shape of individual lines in molecular band spectra are quantities of considerable interest. Knowledge of the line widths and shapes can yield information about the intermolecular forces of interacting molecules; determination of the line strengths, which are directly related to the quantum mechanical transition probabilities, give information about the internal forces in the molecule. A knowledge of these parameters is also necessary in meteorology, astrophysics, and other fields in order to study such problems as radiant energy transfer and the abundances of absorbing gases in planetary atmospheres.

In the infrared region of the spectrum many gases have vibration-rotation bands which consist of individual lines whose shapes are determined primarily by collision broadening for samples at pressures greater than a few mm Hg. At lower pressures Doppler broadening of the lines becomes important. Measurements of the spectral parameters of these vibration-rotation lines are frequently needed in radiation transmission studies. Most infrared spectrometers, however, have insufficient resolution to enable direct measurement of the line contours. Hence, measurements are difficult and only limited amounts of data have been obtained in this region.

Benedict, Herman, Moore, and Silverman^{1,2} have obtained good measurements of strength and half width of lines in the fundamental vibration-rotation bands of CO and HCl by applying a curve of growth technique. In these cases the individual lines are sufficiently well separated to allow measurements without troublesome overlapping from neighboring lines. Their results indicate a dependence of the half width on rotational quantum number and a deviation from Lorentzian shape in the distant wings of the lines. Burch, Patty, and Gryvnak³ have also reported different line shapes for different bands in the CO₂ molecule.

The purpose of the present study is to determine the half widths and line strengths of the vibration-rotation lines in the fundamental band of NO near 5.3μ and to obtain a value for the total band strength from the line strength measurements. The study is also intended as an exploration of the feasibility of using the curve of growth technique for the measurement of strengths and widths of self-broadened lines for which strong overlapping occurs.

NO was chosen for the present investigation for several reasons. In the first place, unlike most diatomic molecules, NO has a doublet electronic ground state. For this reason alone, NO is a molecule of interest. The doublet ground state leads to the formation of a band spectrum composed of a series of double "lines" which strongly overlap for an appreciable frequency range. Each of these lines is in turn an unresolved doublet. Thus, the fundamental band of NO affords a formidable test for the curve of growth technique. The investigation of NO

is of further interest since the study of the line strengths enables a value for the band strength to be obtained. At the present time various methods of determining this quantity have yielded results which for standard temperature and pressure vary from $70-145 \text{ cm}^{-2} \text{ atm}^{-1}$.⁴⁻¹¹ The present study is intended to remove the uncertainty in the value of this quantity. Finally, although NO does not appear as an atmospheric constituent in the lower atmosphere of the Earth, it, nevertheless, is believed to be responsible for the creation of the D-layer of the ionosphere.¹² Though the amount of NO present is small and has not been detected spectroscopically the spectral parameters of the 5.3μ NO band are still of interest. The present study is designed to obtain measurements on these spectral parameters.

II. THEORY

Absorption theory

Absorption theory is based on an exponential absorption law proposed by Lambert in the mid-eighteenth century. This law states that when a parallel beam of monochromatic radiation of intensity, $I_0(\nu)$, is incident on a homogeneous absorbing medium, the intensity, $I(\nu)$, of the emerging radiation is given by

$$I(\nu) = I_0(\nu) \exp [-k(\nu) u], \quad (\text{II}, 1)$$

where $k(\nu)$ is the absorption coefficient and u is the optical thickness. In this study ν will be expressed in cm^{-1} . The absorption coefficient of a gas is often a strongly varying function of ν and, for a gaseous absorbing medium, depends on the total pressure, P , the partial pressure of the absorbing gas, p , and the absolute temperature, T . The optical thickness at a given temperature can be expressed in atm-cm by the product of p times L , the length of the absorbing medium. When u is measured in atm-cm, $k(\nu)$ is given in reciprocal atm-cm. By definition, the fractional transmittance, $T(\nu)$, for monochromatic radiation is

$$T(\nu) = \exp [-k(\nu) u]. \quad (\text{II}, 2)$$

It then follows that the fractional absorptance, $A(\nu)$, for

monochromatic radiation is given by

$$A'(\nu) = 1 - \exp[-k(\nu)u]. \quad (\text{II}, 3)$$

For infrared molecular band spectra the absorption coefficient is typically a rapidly varying function of ν with many maxima occurring at discrete frequencies across the band. These maxima correspond to the positions of the many vibration-rotation lines resulting when the numerous discrete rotational energy transitions allowed are superposed on each allowed vibrational transition. Frequently the individual lines overlap sufficiently that several lines contribute to the absorption coefficient at some frequency ν . If $k_i(\nu)$ then represents the absorption coefficient resulting from the i^{th} line alone

$$k(\nu) = \sum_i k_i(\nu). \quad (\text{II}, 4)$$

It is the curve of $k_i(\nu)$ vs ν which designates the shape of an individual spectral line. The half width, α , of the line may be defined as half the width of the $k_i(\nu)$ vs ν curve at half the maximum value of $k_i(\nu)$. The line strength, S_i , is defined by

$$S_i = \int_{-\infty}^{\infty} k_i(\nu) d\nu. \quad (\text{II}, 5)$$

Extending this definition to an entire band one may define the band strength, S_b , as

$$S_b = \int_{-\infty}^{\infty} k(\nu) d\nu. \quad (\text{II}, 6)$$

where only that portion of the absorption coefficient attributed to the lines in the band under consideration is used.

Line broadening effects

The shape and width of an absorption line are determined by the processes responsible for broadening the line. These parameters are then closely related to the intermolecular forces of interacting molecules.

Each spectral line possesses a natural line width independent of effects external to the molecule. This natural width is associated with the Heisenberg uncertainty principle which predicts an uncertainty ΔE in the energy level occupied by the molecule for a lifetime Δt according to the relation

$$\Delta E \Delta t \approx h/2\pi, \quad (\text{II}, 7)$$

where h is Planck's constant. Since an excited state possesses a shorter lifetime than the ground state, the major contribution to the uncertainty in a transition involving the ground state comes from the uncertainty in the excited state. Since $\Delta E = hc\Delta\nu$ the natural line width, α_N , is given by

$$\alpha_N \approx (2\pi c \Delta t)^{-1}, \quad (\text{II}, 8)$$

where c is the velocity of light. For NO the lifetime in the first excited state is of the order of 10^{-3} seconds.¹³ The natural half width is, therefore, about $5 \times 10^{-9} \text{ cm}^{-1}$.

Natural widths are usually small compared with the line broadening caused by the Doppler effect associated with the thermal motions of the molecules relative to the detector. The Doppler broadening, which

depends on the absolute temperature and the frequency of the line, is independent of pressure but becomes significant only at pressures of a few mm of Hg and less. The Doppler half width, α_D , is given by the expression^{14,15}

$$\alpha_D \approx 3.58 \times 10^{-7} (T/M)^{0.5} \nu, \quad (\text{II, } 9)$$

where M is the molecular mass. For lines of the NO fundamental, which occurs near 1876 cm^{-1} , a typical value of α_D at room temperature is $2 \times 10^{-3} \text{ cm}^{-1}$.

Both the natural and Doppler half widths are usually negligible compared with the broadening resulting from the effects of electric fields acting during molecular collisions. Since the frequency of molecular encounters depends on the pressure, the increased breadth resulting from this process is termed "pressure broadening" or "collision broadening." Pressure broadening then encompasses the effects of collision damping, pressure shifts, and Stark effects produced by mutually interacting molecules. These effects occur when the time during a collision is small compared with the time between collisions. Such effects as asymmetry and Stark shifts associated with high pressures where collision times are large compared with times between collisions were not encountered under the conditions of the present study. Moreover, lower pressures for which the contribution of Doppler widths become significant were not used. The present work then deals only with absorption lines whose widths and shapes are determined by collision broadening.

Line strengths

The line strength of a given collision broadened line at a given temperature is a constant which is directly proportional to the quantum mechanical probability of a transition from the initial to the final level. The band strength is likewise a constant at a given temperature and can be found from the individual line strengths in the band. By defining J and v to be the rotational and vibrational quantum numbers, respectively, necessary to specify the lower energy level of a given transition, one may write the band strength of a given vibrational transition as

$$S_v = \sum_J S_{v,J} \quad (\text{II, 10})$$

where the sum is over all the vibration-rotation lines in the band.

The vibrational intensities of diatomic infrared bands have been discussed by Crawford and Dinsmore.¹⁶ They have shown that the line strength, $S_{vJ}^{v'J'}$, for a transition from the energy level v, J to the level v', J' is given by

$$S_{vJ}^{v'J'} = \frac{8\pi^3 N_v}{3hcZ} \nu_{vJ}^{v'J'} A_{vJ}^{v'J'} \left\{ \exp(-E_J/kT) - \exp \left[(-hc \nu_{vJ}^{v'J'}/kT) - (E'_{J'}/kT) \right] \right\} \quad (\text{II, 11})$$

where N_v is the number of molecules in the lower vibrational state v ; k is Boltzmann's constant; Z is the rotational partition function

$$Z = \sum_{J=0}^{\infty} g_J \exp(-E_J/kT), \quad (\text{II, 12})$$

where g_J is the multiplicity of the level; $\nu_{vJ}^{v'J'}$ is the frequency in cm^{-1} of the line; $\nu_v^{v'}$ is the band center frequency; and $A_{vJ}^{v'J'}$ is given by

$$A_{vJ}^{v'J'} = \sum_{mm'} (v', J', m' | p | v, J, m)^2 \quad (\text{II, 13})$$

where p is the dipole moment and m and m' are the z -components of the angular momenta of the upper and lower states respectively. Since $A_{vJ}^{v'J'}$ is proportional to the probability of a transition from the state v, J to the state v', J' , the line strength is directly proportional to this transition probability.

For NO at room temperature the rotational partition function can be written¹⁷

$$Z \approx \frac{kT}{hCB} \quad (\text{II, 14})$$

where B is the rotational constant. Also for these conditions, $\exp(-hc \nu_{vJ}^{v'J'} / kT) \ll 1$ and can be neglected. The validity of assuming a negligible vibration-rotation for NO will be demonstrated later.

Assuming $A_{vJ}^{v'J'} = A_v^{v'} A_J^{J'}$ the line strength may be written as

$$S_{vJ}^{v'J'} = \frac{8\pi^3 N_A}{3hcZ} \nu_{vJ}^{v'J'} A_v^{v'} A_J^{J'} \exp(-E_J/kT). \quad (\text{II, 15})$$

The rotational transition probabilities for the NO fundamental have been calculated by James.⁹ The $A_J^{J'}$ above is found by multiplying these rotational transition probabilities by $2J+1$, the degeneracy term of each rotational level.

Crawford and Dinsmore¹⁶ have also shown that the band strength may be written as

$$S_{\nu}^{\nu'} = \frac{8\pi^3 N_{\nu} A_{\nu}^{\nu'}}{3hc} \left\{ \left[\nu_{\nu}^{\nu'} + (B_{\nu'} - B_{\nu}) (1+Z) \right] \left[1 - \exp(-hc \nu_{\nu}^{\nu'}/kT) \right] \right. \\ \left. + 2 \bar{B} \left[1 + \exp(-hc \nu_{\nu}^{\nu'}/kT) \right] \right\} . \quad (\text{II, 16})$$

where $2 \bar{B} = B_{\nu'} + B_{\nu}$. Again realizing $\exp(-hc \nu_{\nu}^{\nu'}/kT) \ll 1$ for the NO fundamental and neglecting the vibrational dependence of the rotational constants, which introduces less than 1 percent error, the expression for band strength reduces to

$$S_{\nu}^{\nu'} = \frac{8\pi^3 N_{\nu} A_{\nu}^{\nu'}}{3hc} \left[\nu_{\nu}^{\nu'} + 2 \bar{B} \right] . \quad (\text{II, 17})$$

It then follows from equations (II, 15) and (II, 17) that the fractional strength of a rotational line in a given vibrational band is given by

$$\frac{S_{\nu J}^{\nu' J'}}{S_{\nu}^{\nu'}} = \frac{\nu_{\nu J}^{\nu' J'} A_J^{J'} \exp(-E_J/kT)}{Z (\nu_{\nu}^{\nu'} + 2 \bar{B})} . \quad (\text{II, 18})$$

Lorentzian lines

Although the actual shape of a collision-broadened line is not certain, a line shape proposed by Lorentz has been accepted in representing the shape over a wide range of pressures. The expression for the absorption coefficient proposed by Lorentz is

$$k(\nu) = \frac{S}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2} . \quad (\text{II, 19})$$

where ν_0 is the frequency of the line center. Despite the wide acceptance of this shape, however, deviations from the Lorentz line shape in the infrared region of the spectrum have been reported.^{1,2,3,18} The deviations observed occurred in the wings of the line usually of the order of two wave numbers from the line center; near the center of the line the Lorentz shape was considered to be a good representation of the shape. The Lorentz shape should then be expected to hold, at least to a first approximation, provided the pressures do not become high enough that significant absorption occurs in the distant wings.

The half width of a collision-broadened line is proportional to the collision frequency F . It can be shown from kinetic theory of gases¹⁹ that

$$\alpha = \frac{F}{2\pi} = \frac{1}{4\pi} \sum_i N_i (D_{ai})^2 \left[2\pi kT \left(\frac{1}{M_a} + \frac{1}{M_i} \right) \right]^{0.5} \quad (\text{II, 20})$$

where N_i is the number of molecules of the i th type per unit volume, D_{ai} is the sum of the optical collision diameters of the absorbing molecule and a molecule of the i th type, and M_a and M_i are the masses of the absorbing and i th type molecules respectively. If one assumes the collision diameters are temperature independent and the ratio of the partial pressures of the gases to the total pressure are constant, then, for a given mixture of gases, the half width α of a collision-broadened line is given by

$$\alpha = \alpha_0 (P/P_0) (T_0/T)^{0.5} \quad (\text{II, 21})$$

where α_0 is the half width at pressure P_0 and temperature T_0 .

Burch and Williams²⁰ have shown that for a mixture of an absorbing gas and a non-absorbing gas equation (II, 21) may be written in the form

$$\alpha = \frac{1}{4\pi} \left[\frac{2\pi}{kT} \right]^{0.5} C_{a,b} (P_e) , \quad (\text{II, 22})$$

where

$$P_e = P + (B-1)p \quad (\text{II, 23})$$

is the equivalent pressure; B is the self-broadening coefficient of the absorbing gas, the ratio of the "self-broadening ability" of the absorbing gas to the "broadening ability" of the non-absorbing gas; and $C_{a,b}$ is a constant involving the optical collision diameters and masses of the absorbing and broadening gases.

Integrated absorptance

In practice direct measurements of the shape and half width of a spectral line are difficult, for the recorded spectrum is in general significantly different from the $k(\nu)$ vs ν curve. This difference can be attributed to two effects. In the first place any spectrometer must be operated with finite physical slit widths and, therefore, passes a frequency interval $\Delta\nu$ instead of a monochromatic frequency. The fractional transmittance observed, $T(\nu)$, is an "averaged" value for the frequency ranged passed by the spectrometer and is usually different from the true fractional transmittance, $T'(\nu)$. Secondly, even when $T(\nu)$ is equal to $T'(\nu)$ and a linear frequency scale is assumed across the recorded line, the recorded curve, $A'(\nu)$ vs ν , is not often of the

same shape as the $k(\nu)$ vs ν curve. Equation (II, 3) may be rewritten, by expanding the exponential as

$$A'(\nu) = k(\nu)u - \frac{1}{2} [k(\nu)u]^2 + \frac{1}{6} [k(\nu)u]^3 - \dots \quad (\text{II, 24})$$

It is then seen that the recorded curve only approximates the $k(\nu)$ vs ν curve when $k(\nu)u \ll 1$. Thus to make direct measurements of spectral line parameters from recorded spectra, one usually needs to apply corrections for the observed line distortion from the true line shape. Such corrections for certain types of line shapes have been discussed by Bass and Kostkowski.²¹

Another method of measuring spectral line parameters is by the curve of growth technique. This method, which does not require corrections for instrumental broadening of the lines, employs measurements of the integrated absorptances of the lines. The integrated absorptance, or equivalent width as it is sometimes termed, is given by

$$W = \int_{\nu_1}^{\nu_2} A(\nu) d\nu \quad (\text{II, 25})$$

where ν_1 and ν_2 are chosen so the integration is over the entire line. Both Nielsen²² and Babrov²³ have given a theoretical discussion which shows that the integrated absorptance over a line measured by a spectrometer with finite resolving power is equal to the true integrated absorptance of the line provided I_0 , the incident intensity, is slowly varying over the region of interest. Thus, the integrated absorptance is independent of the physical characteristics of the spectrometer and is just the value which would be obtained on a spectrometer with infinite

resolving power. This result has been verified experimentally by Howard, Burch, and Williams.²⁴

Ladenburg and Reiche²⁵ have performed the integration of the expression

$$W = \int (1 - \exp [-k (\gamma) u]) d\gamma \quad (\text{II, 26})$$

for a Lorentz line and find that W can be given exactly by

$$W = 2 \pi \alpha f(x) \quad (\text{II, 27})$$

where

$$x = Su / (2 \pi \alpha) , \quad (\text{II, 28})$$

and

$$f(x) = x \exp(-x) [J_0(ix) - J_1(ix)] . \quad (\text{II, 29})$$

J_0 and J_1 are Bessel functions of order 0 and 1, respectively.

In the limiting cases of large and small x , Elsasser²⁶ has made two approximations to equation (II, 27):

$$W = S u \quad \text{for small } x \quad (\text{II, 30})$$

$$W = 2 \sqrt{S \alpha u} \quad \text{for large } x \quad (\text{II, 31})$$

The regions of validity of these approximations are the "linear" and "square root" regions, respectively.

For the case of mixtures of absorbing and broadening gases at a given temperature, α can be given by equation (II, 22) and the Elsasser approximations may be written as

$$W = S u \quad \text{for small } x \quad (\text{II, 32})$$

$$W \propto \sqrt{S P_e u} \quad \text{for large } x \quad (\text{II, 33})$$

In the linear region the integrated absorptance of a line depends only on u for this case and is independent of the presence of non-absorbing molecules.

For the special case of a single absorbing gas at a given temperature with no admixture of other gases, $p = P$ and α can be given by equation (II, 21). Applying the definition of optical thickness, the approximations become

$$W = SPL \quad \text{for small } x \quad (\text{II, 34})$$

$$W \propto P \sqrt{SL} \quad \text{for large } x. \quad (\text{II, 35})$$

For pure samples it then follows that the linear and square root regions for a line can only be distinguished by varying L .

The above discussions of integrated absorptance have been concerned with a single Lorentz line with no overlapping by other spectral lines. The equivalent width due to two overlapping lines has been discussed by Sakai and Stauffer.²⁷ Plass²⁸ has commented on this study and has suggested a modified expression to represent the integrated absorptance of the two lines together. For two overlapping Lorentz lines of equal strength, S , and equal half width, α , this expression may be written as

$$W = 2 \pi \alpha \left\{ 2f(x) - D^{-1} [2f(x) - f(2x)] \right\} \quad (\text{II, 36})$$

where

$$D = 1 + \left[(\nu_{01} - \nu_{02}) f(x) / (2\alpha x) \right]^2 \quad (\text{II, 37})$$

and ν_{01} and ν_{02} are the frequencies of the two line centers. The integrated absorptance of the overlapping lines is seen to be less than

that of the two lines if they were well separated with the exception of the case of absorption occurring in the linear region. For this case $f(x) \approx x$ and W is independent of the overlapping. For pure absorbing samples, $\alpha \propto P$ and it follows that for a given cell length the values of W/P for a line arising from absorption outside the linear region decreases with increasing pressure since $D^{-1} [2f(x) - f(2x)]$ can not be neglected.

Curve of growth

For pure absorbing samples at a given temperature equations (II, 27) and (II, 28) for a single line may be rewritten as

$$W_0 = 2 \pi \alpha_0 f(x) \quad (\text{II, 38})$$

and

$$x = \frac{S L}{2 \pi \alpha_0} \quad (\text{II, 39})$$

where $W_0 = W/P$ is the integrated absorptance at standard pressure for the given temperature and α_0 is the half width under these conditions. For a given Lorentz line at a given temperature and a given cell length, both x and W_0 are independent of pressure. Also from equations (II, 38) and (II, 39) one obtains

$$\frac{W_0}{S L} = \frac{f(x)}{x} . \quad (\text{II, 40})$$

A curve of W_0 vs L for a given line is then seen to have the same shape as the curve of $f(x)$ vs x . This curve, which can be tabulated theoretically from equation (II, 29), is the Ladenburg and Reiche curve. The

curve of growth may be obtained by fitting the Ladenburg and Reiche curve to the experimentally determined values of W_0 plotted as a function of L .

An expression for the strength of an individual line, obtained from rearrangement of equation (II, 40), is given by

$$S = (W_0/L) (x/f(x)) . \quad (\text{II, 41})$$

A value of line strength can be determined from this expression if the ratio of x to $f(x)$ can be found. A tabulation of $f(x)$ for a given x has been given by Kaplan and Eggers.²⁹ Thus, if α_0 can be found one can determine $f(x)$ by equation (II, 38) and subsequently find S . When S is determined from data near the linear region of the curve of growth the ratio of x to $f(x)$ is very close to one and an error in the determination of α_0 results in an even smaller error in S .

The half width can be found graphically from the curve of growth. The Elsasser approximations given in equations (II, 30) and (II, 31) represent the growth curve in the limiting cases of large and small x . Simultaneous solution of these equations then reveals that the half width is related to $(W_0)_{\text{int}}$, the value of W_0 at the point on the curve of growth plot for which the asymptotes to the curve intersect, by the expression

$$4 \alpha_0 = (W_0)_{\text{int}} . \quad (\text{II, 42})$$

NO fundamental band

Nitric oxide is an interesting diatomic molecule, for not only does it possess a $^2\Pi$ electronic ground state but it is also sufficiently

stable chemically that its spectrum can be studied with relative ease. For NO, the quantum number Λ specifying the component of electronic orbital angular momentum along the internuclear axis has the value unity and an internal magnetic field in the direction of the internuclear axis results. The $^2\Pi$ ground state arises from the two possible values of Σ , the quantum number specifying the component along the internuclear axis of the angular momentum due to electron spin, which occur when the resultant electron spin precesses in the internal magnetic field. Since Σ can have values of $1/2$ and $-1/2$, the quantum number specifying the resultant electronic angular momentum about the internuclear axis, specified by $\Omega = |\Lambda + \Sigma|$, takes on the values $1/2$ and $3/2$. Thus, the electronic ground state actually consists of two levels designated as $^2\Pi_{3/2}$ when Σ is aligned parallel to Λ and $^2\Pi_{1/2}$ when Σ is antiparallel to Λ . The energy separation of these two levels is about 120 cm^{-1} .

The spectrum of the fundamental vibration-rotation band of NO differs from that of most diatomic molecules. Because of the $^2\Pi$ ground state its spectrum consists of two subbands, each with an R, P, and Q branch. The effective rotational and vibrational constants of the two subbands are almost the same causing the bands to be nearly coincident. The resulting spectrum is a series of double lines. Near the centers of the bands the double lines of the R and P branches become very close together with their frequencies differing by only a few hundreds of a wave number; further out in the wings of the bands the separation is of the order of two wave numbers.

For the case when the interaction of the nuclear rotation with the electronic motion is weak, Λ and Σ remain good quantum numbers. The total angular momentum $\underline{J}$ is then the resultant of the electronic angular momentum $\underline{\Omega}$ and the angular momentum $\underline{N}$ of nuclear rotation. This mode of coupling is referred to as Hund's Case (a). In this case J , the quantum number specifying the total angular momentum, can take on the values, $J = \Omega, \Omega + 1, \Omega + 2, \dots$. Levels with $J < \Omega$ do not occur. For NO the lower rotational energy levels are well represented by Hund's case (a). Thus, the level for $J = 1/2$ is missing in the ${}^2\Pi_{3/2}$ component and the $R(1/2)_{3/2}$, $P(1/2)_{3/2}$, $Q(1/2)_{3/2}$ lines do not occur.

For higher rotational levels the resultant electron spin gradually becomes uncoupled from the internuclear axis and Σ is no longer a good quantum number. This situation is termed Hund's Case (b). For NO the mode of coupling may be described as intermediate between Hund's Case (a) and Hund's Case (b).

Since Λ is different from zero for the NO fundamental, each of the double lines in the vibration-rotation spectrum is again split into two components by Λ doubling. The separation of the two components in the R and P branches is too small to be observed with the resolution available. From microwave data, the Λ doubling separation of the ${}^2\Pi_{1/2}$, $J = 1/2 \rightarrow 3/2$ line has been determined^{30,31} to be 0.012 cm^{-1} . To a first approximation this splitting should be independent of J . The splitting in the ${}^2\Pi_{3/2}$ subband should be much smaller^{32,33} except at high J values. Further discussion of the Λ doubling in the NO fundamental is given by James.^{9,34}

III. EXPERIMENTAL METHODS

A. Description of the experiment

Various techniques can be used to obtain spectral line parameters. If high enough resolution is available one can measure the half widths of the lines directly from the spectra recorded at high pressures and short path lengths of absorbing media. For these conditions the Lorentz half widths are much greater than the spectral slit width and also $k(\nu)u \ll 1$ so the recorded spectra closely approximate the $k(\nu)$ vs ν curve; thus, instrumental errors are minimal. The strengths can be subsequently found by integrated absorptance measurements. In this study preliminary attempts were made to measure the half widths of the lines directly at a cell length of 0.025 cm and at pressures up to five atmospheres of pure NO. The measured half widths varied with slit width, however, which indicated that significant distortion of the observed line shape from the true one had occurred. Moreover, at the narrowest slit widths the noise level limited the accuracy of the half width measurements. Rather than apply corrections for instrumental broadening the curve of growth technique was selected for the line parameter determinations.

The determination of line strengths and half widths by the curve of growth method has been discussed by Benedict, Herman, Moore, and Silverman.¹⁴ The theory of the particular approach used in this study

was discussed in the previous chapter. In order to plot a curve of growth for a self-broadened line it is necessary to obtain the integrated absorptance of the line at a number of different cell lengths and preferably at a number of different pressures.

Four cells of lengths 0.200, 1.00, 7.62, and 40.0 cm respectively have been used in this study. Still shorter absorption path lengths were usually required, however, to extend the curves of growth into the linear region. This was best achieved by broadening NO with N_2 in a 2.54 cm cell. Ford¹⁰ has found the self-broadening coefficient, B , of NO relative to N_2 for the range of pressures used in this study to be 1.00 ± 0.02 . With this information, equation (II, 23) reveals the equivalent pressure is just the total pressure. By selection of the proper optical thickness and adjustment of the total pressure by addition of N_2 , mixtures of NO and N_2 were used in the 2.54 cm cell to obtain "effective pure sample" lengths of 0.025 and 0.077 cm. Data for each individual curve of growth plot then came from at least four and usually five cells each of different length.

The pressures used were those for which the integrated absorptances could be measured with reasonable accuracy but for which the fractional absorptances in the "troughs" between lines were essentially zero at some point so the background curves could be placed on the spectrum accurately. The pressures which could be used varied from line to line but were always between 14 mm Hg NO and 760 mm Hg NO.

B. Apparatus

Spectrometer and auxiliary equipment

A 2.5 meter single-pass Ebert spectrometer with a 300-line/mm, 25.4 cm wide Bausch and Lomb replica grating as a dispersing element was used to obtain the data. A schematic diagram of this instrument is shown in Figure 1. Shaw and McCaa³⁵ have discussed the spectrometer in detail and only the general features will be described here. A photograph of the spectrometer is shown in Figure 2. The tank on the right is a 2 meter White absorption cell not used in this study.

The source of radiation was a Nernst glower located in sample tank. This tank also housed the sample cell traversed by the radiation before entering the spectrometer tank via the entrance slit to the fore-prism optics. At this slit the radiation was "chopped" with a mechanical chopper at a frequency of 450 c.p.s. A CaF_2 prism served as the fore-prism to separate overlapping orders; selection of the desired order was achieved by adjustment of the Littrow mirror. The radiation from the entrance slit to the grating section was collimated onto the grating by the Ebert Mirror which also focused the dispersed radiation onto the exit slit. The emerging radiation was detected in the detector tank with a cooled PbSe detector.

The cooling of the detector was achieved by mounting the detector on the end of a solid copper rod which was connected to a liquid nitrogen reservoir within the detector tank. This reservoir was linked to the exterior of the detector tank by two copper tubes which were insulated

EBERT GRATING SPECTROMETER

Fig. 1 - Optical diagram of the Ebert spectrometer

Fig. 2 - View of the Ebert spectrometer and auxiliary equipment

from the tank at the point of penetration. Through one tube liquid nitrogen from a 25 liter dewar was forced into the reservoir with N_2 from a commercial cylinder; the second tube served as a vent. In this manner the reservoir was continuously kept filled.

The detected signal was amplified by a Baird Atomic 450 cycle amplifier and phase sensitive rectifier. The amplified signal was displayed on a Leeds and Northrup double pen strip chart recorder by one of the pens. Since scanning was achieved by rotating the grating table on a cone bearing by driving the grating table arm with a precision screw, rough calibration was achieved by sending an electrical pulse to the second pen on the recorder at regular rotational positions of the driving screw.

One special feature of the spectrometer is noteworthy. The entire optical path traversed by the radiation is evacuable. This feature allowed data to be obtained in the P branches of the NO fundamental where absorption by atmospheric water vapor would otherwise obscure the NO lines.

Absorption cells

The 2.54, 7.62, and 40.0 cm absorption cells were of conventional design. The first two, respectively, were brass cells with NaCl windows. Their design has been described by Gryvnak and Shaw.³⁶ The latter cell was constructed of stainless steel with KBr windows.

The 2 mm and 1 cm cell lengths were achieved by use of a variable length cell. A sketch of this cell is shown in Figure 3. The brass endplates of the cell were soldered to an adjustable brass bellows.

Fig. 3 - Design of the variable length absorption cell and spacers

The NaCl windows were spaced an accurately known distance apart by teflon spacers. The shape of these spacers and the orifices cut in them to allow gas penetration into the cell are also shown in Figure 3. The cell length was adjusted, with the windows and the desired spacer in place, by compressing the bellows with the four adjustment screws connecting the endplates until the O-rings in the endplates were sealed against the windows. The double endplate on one end allowed access to the window and spacer. Three symmetrically placed 1/8 inch rods mounted in the fixed endplate held the windows and spacer in place during mounting.

Pressure chamber

In use, the variable length cell with a non zero pressure in it, was positioned in the evacuated sample tank. The difference in the pressures internal and external to the cell caused some compression of the O-rings and consequently the windows were not in all cases seated firmly against the spacer. This compression caused a change in the cell length with varying pressures which became significant in the case of the 2 mm cell. In order to eliminate such uncertainty in cell length, data for this length of cell were taken with the cell in a "pressure chamber." This chamber allowed the pressure internal and external to the cell to be kept equal by introducing the proper amount of non-absorbing nitrogen to the chamber. In this manner the chamber, which was simply a steel box with NaCl entrance and exit windows, allowed a constant absorption cell length equal to the thickness of the teflon spacer to be maintained as the pressure was varied.

Gas handling system

A schematic diagram of the gas handling system is shown in Figure 4. The gauges, vacuum pump, and gas bottles were controlled by six Veco brass bellows valves. Two Whitey brass forged body valves were used to control the sample cell and pressure chamber.

The valves to the cell and chamber were located at the exterior surface of the sample tank. In this position the valves were easily accessible and the contents of the cell and chamber could be accurately controlled. Such valve positioning, however, meant that the sample cell had to be connected to its valve by about a 50 cm length of 1/4 inch copper tubing. Because of this design feature care was required to ensure that uniform mixing of the gases was achieved when the NO sample was foreign-broadened. The procedure for ensuring uniform mixtures is discussed below.

Pressure measurement

Pressures between 1-20 mm Hg were measured with a Dubrovin absolute pressure gauge. Between 20-200 mm Hg pressure measurements were made with a U-tube mercury manometer. A layer of silicon oil was floated on the mercury column of each side of the U-tube to help prevent chemical reaction between the NO and the Hg. Higher pressures were measured with a Wallace-Tiernan absolute pressure gauge. Pressures greater than 50 mm Hg could be measured to an accuracy of 1 percent on these gauges. For pressures lower than 50 mm Hg the measured pressures were somewhat less accurate.

Fig. 4 - Schematic diagram of the gas handling system

C. Experimental procedure

Before recording any spectra the system was tested to check that the recorded signal varied linearly with a change of the intensity of the radiation incident on the detector. Two tests were performed. First, a known signal was introduced into the amplifier from an audio frequency microvolter used in conjunction with an audio oscillator and compared with the output signal of the recorder. The amplifying and recording systems tested in this manner were linear at all amplifier gain settings and for the entire output range of the recorder to within the accuracy of the test, which was about one percent. Secondly, the peak fractional absorptances of several water vapor lines of different intensities were observed at a constant amplifier gain setting in the 5μ region for various intensities of incident radiation. This variation was achieved by inserting different transmission screens of wire grid into the optical path. The fractional absorptance at the center of each line remained constant for differing incident radiation intensities to within several percent, the accuracy of the test. This indicated the detection, amplification, and recording systems were linear.

The stability of the amplification and detection systems was tested by recording the fractional transmittance for a fixed grating position. This curve varied by less than two percent full scale deflection when recorded over a 20 minute interval. This was the time required for one "run," a continuous scan of about a dozen lines during which no zero check could be made.

The spectral frequencies scanned during a given run comprised a "region." The fundamental band of NO was divided into seven regions. These regions and the range of frequencies they cover are shown in Table 1. For the 5μ region effective slit widths of about 0.1 cm^{-1} were used with a signal to noise ratio of about 50.

Before spectra of a given region were recorded, scans of the transmission curves at fixed frequencies in the troughs between lines were made at various points throughout the region as the pressure of the absorbing gas in the sample cell was varied. This was done for each of the cell lengths used. In each case for a fixed frequency ν such that $(\nu - \nu_0) \gg \alpha$ for all lines of the band, $\ln T \propto P^2$ for pressures up to one atmosphere. For a given cell length and a given region, only those pressures for which the observed fractional absorbance was zero at some frequency between each of the double lines of NO present were used for integrated absorbance measurements. This was to facilitate the placement of the background curves on the spectrum. The cell lengths and pressures used for each region are also shown in Table 1.

Nitric oxide of 98.5 percent purity produced by the Matheson Company was used to obtain the spectrum. Before introduction to the cell the gas was passed through Ascarite to remove some of the NO_2 present as an impurity in the commercial NO. No further purification was employed since at the pressures and path lengths of this study no absorption lines due to impurities were observed.

Table 1

Conditions for Spectra Recorded from Each Region

(For cell lengths less than 0.2 cm the equivalent pure sample pressures and cell lengths listed below were obtained with NO-N₂ mixtures in a 2.54 cm cell.)

Region	Frequency Range (cm ⁻¹)	Range of Index Number m	Cell length (cm)	Pressure (mm Hg of NO)			
				14	50	200	760
I	1798-1810	-37/2 to -41/2	0.077				x
			0.200			x	
			1.00		x	x	
			7.62		x	x	
			40.0	x			
II	1810-1829	-27/2 to -35/2	0.077				x
			0.200		x	x	
			1.00		x	x	
			7.62	x			
III	1829-1852	-15/2 to -25/2	0.025				x
			0.077			x	x
			0.200		x	x	
			1.00		x	x	
			7.62		x		
IV	1852-1876	-3/2 to -13/2	0.025				x
			0.077			x	x
			0.200		x	x	
			1.00		x	x	
			7.62		x		
V	1876-1902	3/2 to 15/2	0.025				x
			0.077			x	
			0.200		x	x	
			1.00		x	x	
			7.62		x		
VI	1902-1928	17/2 to 33/2	0.025				x
			0.077				x
			0.200		x	x	
			1.00		x	x	
			7.62		x		
VII	1928-1944	35/2 to 45/2	0.077				x
			0.200			x	
			1.00			x	x
			7.62		x	x	

For self-broadened samples the cell was prepared for a run in the usual manner. The cell was evacuated, flushed several times with NO, and filled to the desired pressure. For the 2 mm cell the procedure was more extensive as the pressure chamber was used. The absorption cell was first filled in the manner described above as the pressure of NO inside the cell had to be maintained greater than or equal to the pressure of N₂ in the chamber at all times to ensure no leakage of N₂ into the absorption cell. The cell valve was closed and the chamber and gas handling systems were flushed with N₂ before filling the chamber to the desired N₂ pressure. As the nitrogen was added to the chamber the resulting net inward force on the absorption cell windows caused a change in their positions and a corresponding increase in the NO pressure within the cell. The chamber valve was then closed and the gas handling system flushed with NO before readjusting the NO pressure in the cell to the desired amount. This procedure allowed a reproducible path length to be obtained at all pressures used.

For the foreign-broadened samples in the linear and near-linear regions, the procedure of cell filling was also the usual one. Since samples did not remain in the cell for more than a couple hours adsorption-desorption effects were not as important as for cases when the sample must remain in the cell several days. The procedures suggested by Burch and Williams,²⁰ therefore, to decrease these effects when longer periods of time were required to obtain the data were not important. The cell was, therefore, flushed with NO and filled to the desired partial pressure of NO. The cell valve was closed, the system

flushed with N_2 , and the system N_2 pressure brought to a value higher than the NO pressure in the cell. The cell valve was opened and nitrogen was introduced into the cell until the desired total pressure was achieved. As indicated previously the tubing between the cell and the cell valve was about 50 cm in length; this caused the time for uniform mixing by thermal motions to be longer than for a valve mounted near the cell. For the 2.54 cm cell, the only one used with mixed samples, uniform mixing was found to occur in 30 minutes. All foreign-broadened samples were carefully "aged" before the spectra were recorded.

Once the cell had been prepared, the run was obtained. An opaque shutter was placed in the optical path and a zero energy line was recorded on the chart. The grating drive was then started and a scan of the desired region was made. The shutter was again switched into the beam and the zero energy line recorded to ensure no significant change during the run. Such a run required about 20 minutes and included a spectral interval about 25 cm^{-1} in length.

Three such runs of a region were recorded for each cell filling. The cell was then filled to a new pressure and the process repeated. After the conclusion of this process similar spectra at a different cell length or in a different region were recorded.

IV. RESULTS

In the present study spectra of 17-20 lines in each of four branches, the R and P branches of each subband, have been studied. From the data the half widths and line strengths of over 70 lines in the NO fundamental have been obtained and the total band strength determined. Some typical spectra at various conditions of pressure and cell length are shown in Figures 5 to 10.

A. Determination of integrated absorptance

Background determination

In order to analyze a run the location of the background, the 100 percent transmission curve corresponding to $I_0(\nu)$, had to be ascertained and positioned on the spectrum. Since this curve varied smoothly and changed but a tenth of the full scale deflection of the recorder during the scan of a region, the variation of $I_0(\nu)$ across a double line consisting of two vibration-rotation lines of like J value from different subbands, or a single line when the doublet was well separated, was essentially linear with chart distance. The background position problem, so familiar in absorption spectroscopy, was met, therefore, by linearly connecting the spectral curve between two points, each of which lay near the middle of the trough on either side of the line or lines being measured, for which the fractional absorptances were known to be zero from previous measurements. In practice there was a

Fig. 5 - Spectra of the $P(11/2)$ and $P(13/2)$ lines at a cell length of 1.0 cm

Fig. 6 - Spectra of the $P(11/2)$ and $P(13/2)$ lines at an equivalent cell length of 0.077 cm

Fig. 7 - Spectra of the $P(21/2)$ and $P(23/2)$ lines at a cell length of 1.0 cm

Fig. 8 - Spectra of the $P(21/2)$ and $P(23/2)$ lines at an equivalent cell length of 0.077 cm

Fig. 9 - Spectra of the $R(11/2)$ and $R(13/2)$ lines at a cell length of 1.0 cm

Fig. 10 - Spectra of the $R(11/2)$ and $R(13/2)$ lines at an equivalent cell length of 0.025 cm.

range of points in the troughs for which the fractional absorptance was essentially zero. The background curve was consistently positioned by bisecting the peak to peak noise at these points with the line drawn onto the chart. Such a procedure of background positioning was found to be satisfactory.

Dispersion and area measurements

The frequencies of the lines in the NO fundamental have been measured by James³⁴ and Shaw³⁷. Using these known frequencies of the NO lines, one could measure the distance Δd on the spectrum between two points whose corresponding frequency separation was $\Delta \nu$ and obtain the linear dispersion, $(\Delta d / \Delta \nu)$, at any point on the recorded spectrum. Once the backgrounds were drawn onto the spectrum the area, a , between the recorded curve and the background was measured with a compensating polar planimeter. The distance, h , between the background and zero was then measured. Since h and $(\Delta d / \Delta \nu)$ are constant across a given spectra line, the integrated absorptance is given by

$$W = \left[a (\text{cm}^2) / h (\text{cm}) \right] (\Delta \nu / \Delta d) (\text{cm}^{-1} / \text{cm}). \quad (\text{IV}, 1)$$

Doppler effect on integrated absorptance

The integrated absorptances for each line were obtained as above for all lines for which the Doppler contribution to W could be neglected. Plass and Fivel³⁸ have discussed the integrated absorptances of lines for which the Doppler contribution can not be neglected. Their expressions reveal that when absorption occurs outside of the linear region

where x is large, the ratio of the observed equivalent width W to that expected for a truly Lorentzian line W_L is given by

$$\begin{aligned} (W/W_L) = 1 + (3/16) a^{-2}x^{-1} + (45/512) a^{-4}x^{-2} \\ - (15/128) a^{-2}x^{-2} + \dots \end{aligned} \quad (\text{IV, 2})$$

where $x = (S u)/(2 \pi \alpha)$, $a = (\alpha/\alpha_D) (\ln 2)^{0.5}$, and α_D is the Doppler half width which is given by equation (II, 9). In order to estimate the conditions for which Doppler contributions to W were not important, only equation (IV, 2) needed to be considered since all linear region data were at high enough pressures that Doppler contributions were known to be small. By estimating S and α from the curve of growth technique as discussed later but using only high enough pressures that the lines were certainly nearly Lorentzian one could use equation (IV, 2) to select those pressures for which the Doppler contributions contributed less than one percent to the integrated absorptances. This was usually for pressures of 50 mm Hg and higher.

Wing effects on integrated absorptances

The recorded spectral lines were measurable over the noise for a frequency range less than the actual extent of the wings of the lines. Thus, there was an additional area under the wings of the lines which was not measurable. Assuming a Lorentz line shape, Benedict, Herman, Moore, and Silverman¹¹ have shown that if the measurement of area is carried out to a distance g (cm^{-1}) on each side of a line and yields the integrated absorptance W' the true integrated absorptance W is given by

$$W \approx W' [1 + 2\alpha/(\pi g)] \quad (\text{IV, 3})$$

for lines in the linear region and

$$W \approx W' \left[1 + W' / (2\pi g) \right] \quad (\text{IV, 4})$$

for lines in the square root region. Application of these expressions to several NO lines on several spectra revealed that W was usually less than 3 percent larger than W' with the larger difference occurring for linear region lines. Since the error introduced by neglecting the additional area under the wings was small compared with other errors, no wing corrections were made.

B. Effects of line overlap on integrated absorptance

Subband overlap

A convenient method of labeling the lines is by the index number m of the line where $m = -J$ for the P branch and $m = J+1$ for the R branch. This method is preferable to the J specification since there is some evidence of like values of half width for like values of $|m|$ in the R and P branches of diatomic molecules.^{1,2} Thus, by specifying $|m|$ one can refer to two lines simultaneously.

For lines of $|m|$ value between $5/2$ and $15/2$ lines of each subband with the same $|m|$ value overlapped so that the fractional absorptance between them did not drop to zero. In these cases the recorded spectrum and the background curve formed a closed area containing both lines together. In order to separate the absorption due to each line the following procedures were used. If the lines were well resolved, the center of each line was ascertained and the wing of each line in the

internal trough was drawn onto the spectrum such as to be symmetric about line center with the well defined "external" wing. Figure 11 shows the "internal" wings dotted onto the spectrum in this manner for the lines $R(13/2)_{3/2}$ and $R(13/2)_{1/2}$ at $L = 1$ cm and $P = 200$ mm Hg. Because the line separations were greater in the P branches measurements could be made in this manner on all lines; in the R branches the lines with m equal to $5/2$ and $7/2$ were not sufficiently resolved to allow line center determinations and this procedure could not adequately be performed on these lines.

Overlap due to Λ doubling

Each of the double lines in the NO spectrum resulting from the near superposition of the subbands is in turn split by Λ doubling. Although the amount of splitting is too small to be resolved it does cause the shape of the unresolved doublets to be non-Lorentzian and influences the integrated absorptances of these doublets. Each component of the Λ doublet should be represented by the Lorentz line shape to a first approximation. There is also no reason to believe that the half widths of the two components should be significantly different. Then from equation (II, 19), $k(\nu) = S\alpha / [\pi ((\nu - \nu_0)^2 + \alpha^2)]$, it follows that for the special case of the two components occurring with no splitting the combined line is also Lorentzian with the same half width and a strength equal to that of the sum of those of the two components. In order to consider the case for which the components are not exactly superposed one can assume that the components have equal

Fig. 11 - A typical spectrum of subband overlap for the case of the $R(13/2)$ lines showing the method of selecting the internal wing positions

strengths and refer to equation (II,36), $W = 2 \pi \alpha \left\{ 2 f(x) - D^{-1} [2 f(x) - f(2x)] \right\}$, where $D = 1 + [(\nu_{01} - \nu_{02}) f(x) / (2 \alpha x)]^2$. For absorption in the linear region where $2 f(x) \approx f(2x)$, W reduces to $W \approx 2 \pi \alpha f(2x)$ where x for each component is given by $x = S u / (2 \pi \alpha)$. By equation (II, 27), $W = 2 \pi \alpha f(x)$, the value of W for the Λ doublet is just that expected for a single Lorentz line with the same half width as each of the Λ components but of twice the strength. Since strength measurements are made from essentially linear region data the measured strengths should be to a good approximation just twice that of each component. For absorption in the square root region, however, D depends on pressure since α does. Then the term $D^{-1} [2 f(x) - f(2x)]$ is pressure dependent when D^{-1} is between 0 and 1, the values obtained for the limiting cases of $(\nu_{01} - \nu_{02}) \gg \alpha$ and $(\nu_{01} - \nu_{02}) \ll \alpha$, respectively. Thus W is not linear in pressure and $W_0 = W/P$ is not constant. For NO the half width at one atmosphere is about 0.055 cm^{-1} and for the lines considered the largest splitting should be about 0.015 cm^{-1} . For pressures less than 200 mm Hg, therefore, the largest splitting would be of the order of magnitude of α . Some dependence of W_0 on pressure might be expected in the square root region then. Nevertheless, the curve of growth was applied to each line neglecting the Λ doubling.

C. Analysis of data

W_0 was calculated for each line at each cell length since the value of $W_0 = W/P$ was expected to be constant for a given self-broadened line at a given cell length. When mixed samples were used they were

chosen to give the same integrated absorptances as pure samples at shorter path lengths; thus W_0 was also expected to be constant for mixed samples representing the same effective pure sample lengths. The values of W_0 calculated are for 300°K.

A complete summary of the results obtained for a few lines is given in Tables 6 to 9. Included in each table are the equivalent cell length, the equivalent pressure, and the integrated absorptance at one atmosphere W_0 . Each table represents lines from one branch of one of the subbands.

D. Discussion of data

The values of W_0 for a spectral line at fixed cell length, which were found in the above manner, consistently decreased with increasing pressure when the absorption occurred outside the linear region. This decrease amounted to as much as 15-20 percent for the range of pressures used. No such consistent change was noted for linear region data. Qualitatively, this result would be just that predicted by equations (II, 36), $W = 2 \pi \alpha \left\{ 2f(x) - D^{-1} [2f(x) - f(2x)] \right\}$ where $D = 1 + \left[(\nu_{01} - \nu_{02}) f(x) / (2 \alpha x) \right]^2$, if separation of the Λ doublets occurs. In this case D^{-1} would increase with pressure for a given splitting and W would decrease. That this is indeed the case is indicated by the following argument. For low $|m|$ values the Λ splitting is less in the $\Omega = 3/2$ subband than in the $\Omega = 1/2$ subband. The value of x is also less for a line in the $\Omega = 3/2$ subband than for the line of corresponding m in the $\Omega = 1/2$ subband because of the difference in strengths of the two lines. Thus $[2f(x) - f(2x)]$ is smaller for lines in

the $\Omega = 3/2$ subband since x is more nearly equal to $f(x)$ here. Hence there should be less variation with pressure at least at low values of $|m|$ in the $\Omega = 3/2$ subband than for $\Omega = 1/2$. The data substantiate this. Quantitatively variations in W_0 with pressure of the order of magnitude 15 percent were found from equation (II, 36). This agrees favorably with the 15-20 percent variations observed. Uncertainty of the size of the splitting, however, limited this approach. The pressure dependence of W_0 for a given line and given cell length seems, therefore, to result from the neglect of the Λ doubling.

Nevertheless, when the mean values of W_0 obtained for lines at given cell lengths but different pressures are plotted as a function of the cell length, the Ladenburg and Reiche curve can be fitted to the experimental points well, and it was decided to use this method for strength and half width determinations. It should be pointed out that since the strength measurements come from data in the linear and near linear region of the curve of growth these strengths will only be influenced slightly by the Λ doubling effect. The half width measurements, however, are determined from the data in the square root region and consequently, could be affected more by this effect.

Typical plots of the dependence of the mean values of W_0 on the cell length for the $R(13/2)_{1/2}$ and $R(13/2)_{3/2}$ lines are shown in Figure 12. Here the Ladenburg and Reiche curve has been fitted to the experimental points. From the values of W_0 at the points of intersection of the asymptotes the values of α_0 were obtained by equation (II, 42), $4\alpha_0 = (W_0)_{\text{int}}$.

Fig. 12 - Plots of the mean value of W_0 at a given cell length versus the equivalent cell length for the $R(13/2)$ lines with the Ladenburg and Reiche curve fitted to the experimental points. The dotted lines indicate the positions of the asymptotes.

E. Half widths

The values of α_0 for all of the lines analyzed were obtained in the above manner. In Figure 13 the values of α_0 from the R and P branches of each subband are plotted vs $2|m|$. These values are tabulated in Table 2. Although the data show considerable scatter there is a consistent decrease of half width with increasing $|m|$. The most accurate values of α_0 are those of intermediate $|m|$ value between $|m| = 7/2$ and $33/2$. At lower $|m|$ the overlapping of the lines causes increased uncertainty in the values of W and consequently in α_0 . At higher values of $|m|$ the strengths are much weaker and the areas measured for determining W are smaller and can not be measured as accurately. Still a least squares fit yields the straight line shown in Figure 13.

Although there is no consistent difference between the half widths at like values of $|m|$ in the R and P branches of a given subband, one might conjecture a different dependence of α_0 on $|m|$ in the two subbands. If such a difference occurs, however, it is smaller than the experimental error and no such conclusion can be reached. Consequently, the mean value of α_0 was obtained for lines of like $|m|$ from the four branches considered. These mean values are shown in Table 2. Figure 14 shows the dependence of these values on $2|m|$. The straight line is obtained by a least squares fit. Again the measured values of α_0 which deviate the most from the straight line given by the least squares fit are those for the lines with $|m| = 5/2$ and $7/2$ where the largest overlap occurs and those for $|m| = 43/2$ and $45/2$ where the weakest measured strengths occur. Moreover, in the former case only measurements from the

Fig. 13 - Plot of α_0 versus $2|m|$ for lines of the R and P branches of each subband

Table 2

Experimental Half Widths in $\text{cm}^{-1} \text{ atm}^{-1}$ at 300° K

(In most cases the last figure given in the tables below is not significant.)

2 m	$\Omega = 1/2$ Subband		$\Omega = 3/2$ Subband		Average
	R Branch	P Branch	R Branch	P Branch	
3	0.0630	0.0620	-----	-----	0.0625
5	-----	0.0570	-----	0.0570	0.0570
7	-----	0.0575	-----	0.0548	0.0562
9	0.0633	0.0603	0.0618	0.0590	0.0611
11	0.0618	0.0555	0.0625	0.0580	0.0595
13	0.0625	0.0533	0.0625	0.0550	0.0583
15	0.0578	0.0593	0.0578	0.0605	0.0589
17	0.0588	0.0570	0.0625	0.0568	0.0588
19	0.0598	0.0585	0.0588	0.0600	0.0593
21	0.0575	0.0585	0.0575	0.0593	0.0582
23	0.0540	0.0553	0.0585	0.0548	0.0557
25	0.0583	0.0563	0.0585	0.0570	0.0575
27	0.0578	0.0568	0.0560	0.0533	0.0560
29	0.0546	0.0495	0.0546	0.0530	0.0529
31	0.0565	0.0545	0.0549	0.0503	0.0541
33	0.0560	0.0503	0.0547	0.0553	0.0541
35	0.0463	0.0613	0.0485	-----	0.0521
37	0.0413	0.0595	0.0485	0.0588	0.0520
39	0.0450	0.0560	0.0503	-----	0.0504
41	0.0458	0.0580	0.0553	-----	0.0530
43	0.0448	-----	-----	-----	0.0448
45	0.0445	-----	-----	-----	0.0445

Fig. 14 - Plot of the mean value of α_0 for lines of equal $|m|$ value versus $2|m|$

two P branches contributed to the average value of α_0 since R branch measurements were not made due to subband overlap; in the latter case only the lines in the R branch of the $\Omega = 1/2$ subband were of sufficient strength to allow measurements to be made. The dotted curve represents the smoothed curve of half widths James⁹ found from direct measurements of line widths in the R branch of the $\Omega = 1/2$ subband. The agreement between the values of James and those of the present study is seen to be within experimental error.

F. Line strengths

The line strengths can be calculated from the values of W obtained from data near the linear region together with the half widths obtained from the curves of growth. To do this the cell lengths for which the values of W were essentially in the linear region were selected from the curves of growth. These values of L and the corresponding W_0 were used in equation (II, 41), $S = (W_0/L) (x/f(x))$, to determine the line strengths. The ratio of x to $f(x)$ was found from the half widths as follows. Equation (II, 38), $W_0 = 2\pi\alpha_0 f(x)$, allowed the calculation of $f(x)$ for a given W_0 . From a tabulation of the Ladenburg and Reiche function by Kaplan and Eggers,²⁹ x was found and the desired ratio was determined. The ratio of $(x/f(x))$ was usually less than 1.25 and frequently less than 1.10. For a given percent error in α_0 then a much smaller percent error in S resulted. This result is illustrated by the following example. When a typical linear region value for W_0 of $0.10 \text{ cm}^{-1}\text{atm}^{-1}$ is chosen and two quite different values for α_0 of 0.05 and $0.06 \text{ cm}^{-1}\text{atm}^{-1}$ are selected, $f(x)$ is found from equation (II, 38) to be

0.32 and 0.27 respectively. Then $(x/f(x))$ is 1.19 and 1.15 respectively and by equation (II, 41) a 20 percent variation in α_0 results in less than a 4 percent variation in S . The mean value of S for a given line was obtained from those calculated at different cell lengths. This value of S for each line measured is tabulated in Table 3.

For the lines of $2m = 9$ to 15 in the R branches a different technique was employed to determine the strengths. Since the double lines of NO overlapped considerably more here than in the P branches the method of drawing in the internal wings of two overlapping lines in order to obtain the integrated absorptances individually was not sufficiently accurate for strength measurements. The alternate technique used in these cases consisted of measuring the integrated absorptance of the two lines combined. Since the absorption was in the linear region by equation (II, 36), $W = 2\pi\alpha \left\{ 2f(x) - D^{-1} [2f(x) - f(2x)] \right\}$, the W of the two lines together was nearly equal to that of the sum of the W values for each line individually. Assuming equal half widths of the lines the ratio of the integrated absorptances of the lines should be equal to the ratio of their strengths. The theoretical ratios of the strengths were found from equation (II, 18). This procedure will be discussed below. The values of W_0 obtained from the above apportionment were used with the $(x/f(x))$ ratio determined originally to find S from equation (II, 41), $S = (W_0/L) (x/f(x))$.

The line strengths from the R and P branches of each subband are plotted as a function of $2|m|$ in Figure 15. Also shown on this figure are the envelopes obtained by calculating the theoretical strengths assuming no vibration-rotation interaction.

Table 3
Experimental and Theoretical Line Strengths
in $\text{cm}^{-2} \text{ atm}^{-1}$ at 300° K

2m	$\Omega = 1/2$ Subband		$\Omega = 3/2$ Subband	
	S_{exp}	S_{theory}	S_{exp}	S_{theory}
-41	0.317	0.334	-----	0.170
-39	0.425	0.442	-----	0.229
-37	0.536	0.573	0.278	0.299
-35	0.614	0.729	-----	0.383
-33	0.907	0.908	0.474	0.484
-31	1.02	1.12	0.574	0.594
-29	1.36	1.35	0.757	0.709
-27	1.42	1.58	0.879	0.843
-25	1.79	1.81	0.927	0.973
-23	2.03	2.04	1.10	1.10
-21	2.14	2.25	1.16	1.22
-19	2.30	2.40	1.25	1.31
-17	2.37	2.50	1.43	1.36
-15	2.46	2.53	1.37	1.37
-13	2.66	2.47	1.42	1.33
-11	2.33	2.32	1.26	1.22
-9	2.01	2.07	1.10	1.06
-7	1.72	1.72	0.847	0.812
-5	1.36	1.28	0.540	0.489
-3	0.731	0.736	-----	-----
3	0.794	0.758	-----	-----
5	-----	1.29	-----	0.508
7	-----	1.84	-----	0.875
9	2.30	2.26	1.17	1.15
11	2.60	2.59	1.41	1.37
13	2.83	2.81	1.54	1.51
15	2.99	2.93	1.70	1.59
17	2.89	2.95	1.65	1.61
19	2.94	2.89	1.62	1.58
21	2.78	2.76	1.53	1.51
23	2.64	2.57	1.35	1.40
25	2.28	2.32	1.25	1.26
27	2.02	2.04	1.10	1.11
29	1.79	1.78	0.985	0.953
31	1.45	1.52	0.818	0.807
33	1.24	1.26	0.633	0.674
35	1.03	1.02	0.512	0.548
37	0.872	0.822	0.414	0.429
39	0.654	0.647	0.290	0.337
41	0.505	0.500	0.227	0.258
43	0.381	0.377	-----	0.192
45	0.270	0.278	-----	0.143

Fig. 15 - Plots of the line strengths versus $2|m|$ for each branch of each subband. The solid curves are those calculated from theory assuming no vibration-rotation interaction.

The theoretical strengths were obtained from equation (II, 18),
 $(S_{\nu J}^{J'} / S_{\nu}^{J'}) = [\nu_{\nu J}^{J'} A_J^{J'} \exp (-E_J/kT)] / [Z(\nu_{\nu}^{J'} + 2\bar{B})]$. The partition function was represented by the approximate form given in equation (II, 14), $Z \approx kT/(hcB)$. James⁹ has calculated the rotational transition probabilities for the NO fundamental. These probabilities multiplied by the rotational degeneracy $2J + 1$ yield the values of $A_J^{J'}$. The frequencies and rotational constants are also given by James. The energy E_J for the subband under consideration is measured relative to that of the lowest rotational state of the ground state. Therefore E_J is given by

$$E_J = B_{0i} hcJ(J+1) - D_{0i} hcJ^2(J+1)^2 \quad (\text{IV, 5})$$

where the rotational constant D_{0i} is positive. The zero subscript refers to the ground state and the i subscript refers to the subband.

In order to find the band strength of each subband the measured strengths of lines from each subband were summed. From a plot similar to that of Figure 15 smoothed curves were drawn through the experimental strength values and extrapolated so estimates could be made for the strengths of unmeasured lines in the wings of the bands. Estimates were also made of the strengths of the $m = 5/2$ and $7/2$ lines in regions of strong overlap in the R branches and of the $m = -(35/2)$ line in the P branch of the $\Omega = 3/2$ subband where the small amount of strongly absorbing water vapor, which could not be evacuated from the spectrometer tanks, interfered with measurements. These contributions were then added to the sums for the respective subbands. The contributions to the band strengths by the Q branches were estimated as follows. For mixed

samples in the 2.54 cm cell and "effective" pure sample length of 0.025 cm was obtained at one atmosphere pressure. A typical spectrum of the Q branches is shown in Figure 16. A background was positioned onto the spectrum and the area between the spectral curve and the background was planimetered. In this manner the integrated absorptance of the combined Q branches was obtained. From these spectra, the contribution to the band strength from the Q branches was found to be $3.13 \pm 0.19 \text{ cm}^{-2} \text{ atm}^{-1}$. By equation (II, 18) it was found that 26 percent of this contribution should arise from the $1/2$ subband and the remainder from the $3/2$ subband. With these additional contributions the first approximation to the strengths of the subbands were found.

The theoretical strengths of the individual lines were calculated using equation (II, 18) and the estimates of the subband strengths found above. For a second approximation to the band strengths of the subbands, the theoretical instead of graphical strengths of unmeasured lines were used. By adding these contributions to the measured line strengths plus Q branch contributions of each subband, one obtained two new values for subband strengths. The theoretical strengths were calculated repeatedly in this manner in an iterative process until the change in the band strength no longer significantly affected the calculated line strength values. The final values of band strength obtained were $71.5 \text{ cm}^{-2} \text{ atm}^{-1}$ for the $1/2$ subband and $39.4 \text{ cm}^{-2} \text{ atm}^{-1}$ for the $3/2$ subband at 300° K .

The theoretical strengths calculated in the above manner are tabulated along with the measured strengths in Table 3. These strengths

Fig. 16 - A typical spectrum of the Q branches for linear region absorption

are shown as the solid curve in Figure 15. It is seen that the agreement with the measured values is good. Although the measured strengths in the R branches appear to fit the theoretical curves better than those in the P branches, the incident energy from the Nernst is higher in this region allowing the spectrum to be recorded at lower gain settings of the amplifier. The signal to noise ratio of this region is then better and measurements of lines in this region are more accurate. The close fit of the measured strengths to the theoretical curves, even in the wings, substantiates the assumption of a very small vibration-rotation interaction. There is also reasonably good agreement between theoretical and measured values in the wings of the P branches where absorption by N_2O_4 , present in the commercial NO as an impurity and removed by Ascarite, would occur. This would indicate that N_2O_4 has not influenced the measurements.

G. Band strength

The band strength of the NO fundamental was obtained from a weighted average of the measured line strengths. First, the subband band strengths were obtained individually from the four branches by

$$S_i = \frac{\sum_m [(S_{mi_meas}) / (S_{mi}/S_i)]}{\sum_m 1} \quad (IV, 6)$$

where the subscript i denotes the subband and m is summed over the measured strengths of the subband. The ratio (S_{mi}/S_i) is the theoretical ratio calculated previously. This method allowed the measurements to be weighted according to strength with less emphasis placed on the weaker values which were difficult to obtain accurately.

The strength of each subband was obtained in the above manner first from the R branch measurements and then from those of the P branches. The band strengths of the subbands calculated in this manner are shown in Table 4. The values listed are normalized to S.T.P. No consistent differences between R and P branch calculations occur.

Table 4
Band Strengths of the NO Fundamental and Subbands
in $\text{cm}^{-2} \text{ atm}^{-1}$ at 273° K

	$S_{1-0} \frac{1}{2}$	$S_{1-0} \frac{3}{2}$	S_{1-0}
$\Omega = 1/2$ Subband			
R Branch	79.0	----	123.3
P Branch	76.9	----	120.0
$\Omega = 3/2$ Subband			
R Branch	----	43.6	121.3
P Branch	----	44.0	122.2

Although transitions between the $1/2$ and $3/2$ subbands do occur with band centers about 120 cm^{-1} on either side of those of the fundamental band they are "forbidden" transitions with strengths about 10^4 times weaker than the corresponding strengths of transitions within a given subband.⁹ Moreover at room temperature less than one percent of the molecules are outside of the ground vibrational states. Therefore, since the Q branches contribute only a small amount to the total band strength and since the rotational transition probabilities for corresponding transitions in the R and P branches of the two subbands are

comparable,⁹ one can calculate the total band strength by assuming the number of molecules in the ground state of each subband is proportional to the Boltzmann factor. By Boltzmann distribution 64 percent of the molecules were found to be in the 1/2 subband.

A total band strength was obtained from each of the values of subband strength in Table 4 by assuming the strengths of the subbands to be in the ratio of the population of the ground vibrational states of the two subbands. The total band strength values obtained from each of the four branches individually are also shown in Table 4. From the mean value of these measurements the band strength of the NO fundamental is $121.8 \text{ cm}^{-2} \text{ atm}^{-1}$. When the band strength is obtained by averaging those values of total band strength calculated from each of the more than 70 lines individually, one obtains $120.8 \text{ cm}^{-2} \text{ atm}^{-1}$ with a standard deviation of 5.9. This is in good agreement with the weighted average. A good value for the measured band strength of the NO fundamental, therefore, is $122 \pm 6 \text{ cm}^{-2} \text{ atm}^{-1}$.

Table 5 lists the values of NO band strength obtained by other workers. The value obtained in this study agrees reasonably well with those of a number of the other studies. It is strikingly different, however, from those obtained by Penner and Weber, Vincent-Geisse, and Breeze and Ferriso. The values obtained in each of these studies by quite different techniques compare favorably but disagree with those of the present study.

Table 5
 Band Strengths of the NO Fundamental
 in cm^{-2} atm^{-1} at 273°K

Observer	Band Strength	Method
Haven ⁴	121	Dispersion
Dinsmore and Crawford ⁵	145 ± 29	Intensity
Penner and Weber ⁶	70 ± 7	Intensity
Vincent-Geisse ⁷	82	High resolution
Schurin and Clough ⁸	111 ± 7	Intensity
James ⁹	138 ± 6	High resolution
Ford and Shaw ¹⁰	115 ± 9	Curves of growth
Breeze and Ferriso ¹¹	76 ± 7	Shock tube
Present Study	122 ± 6	High resolution

V. ERRORS

In studies of this type there are a considerable number of sources of error. These can be grouped under three categories--sample handling, spectrometer and auxiliary equipment, and data reduction.

A. Sample handling

Pressure measurement

Most pressures measured in this study were 50 mm Hg or more. These pressures could be measured to an accuracy of 1 percent. Measurements below 50 mm Hg were usually of the partial pressures of NO in mixed samples and ranged from 5-25 mm Hg. Measurements of pressure were accurate to 2 percent in these cases.

Purity of the gases

The NO used was produced by the Mathieson Company with a stated minimum purity of 98.5 percent. N_2O was the main impurity but NO_2 and N_2O_4 which have absorption bands near the NO fundamental were also present. Ford¹⁰ has analyzed the NO used and found less than 0.1 percent NO_2 present. The NO was passed through Ascarite before use to remove some of the NO_2 . At the path lengths and pressures used absorption lines of these impurities were not observed so errors resulting from these impurities should be negligible. The N_2 from Liquid Carbonic Division of General Dynamics was 99.9% pure with H_2O being the main impurity.

Gas leakage

In the present system the absorption cells were positioned in the evacuated sample tank during a measurement and sometimes surrounded by the pressure chamber. Three types of leakage could then have caused uncertainty in the sample composition--a direct leak in the cell, an escape of NO from the cell during the introduction of N_2 in the case of mixed samples, and leakage of N_2 into the cell from the pressure chamber should the pressure in the chamber have significantly exceeded that in the cell. Great care was taken to ensure against such leakage. In addition the cell pressure was measured before and after recording the spectra. If a significant change was observed the data were rerun.

Mixing effects

Failure to obtain a uniform mixing of the gases in the absorption cell for the pressure broadened samples could cause a considerable error. Care was taken, however, to allow adequate time for mixing to occur. Since a sample recorded 30 minutes after filling the cell and again after remaining in the cell over night showed no change in the measured value of W , it is believed that this error was negligible. Also, since samples never remained in the cell for more than about two hours, the error introduced by changes in mixtures due to the adsorption-desorption effect on the walls of the cell should have been very small compared with other errors as was discussed in the previous chapter.

Gas decomposition

Should decomposition of the gas occur during a run an error in the measured optical thickness would result. Since three consecutive runs of the same region were recorded for a given cell filling and no consistent changes in the measured integrated absorptances were found, it is felt that the NO was stable. This test also indicated a negligibly small adsorption-desorption effect.

B. Spectrometer and auxiliary equipment

Output fluctuation

The chief source of error associated with the spectrometer is probably the fluctuation in the output introduced by the amplifier and recorder. The detector contributes to this output uncertainty if it is not maintained at a fixed temperature. Variations of the intensity falling on the detector due to maladjustment of the position of the foreprism during a scan can also occur. These combined effects affect the location of the zero percent absorptance curves on the spectrum and cause errors in the measured area that were estimated to be less than 10 percent for samples whose integrated absorptances were less than 0.03 cm^{-1} and 5 percent for samples whose integrated absorptances were greater than 0.03 cm^{-1} . The uncertainty in the output for both the zero and hundred percent absorptance curves also results in an uncertainty in the distance between the two curves which is estimated to be less than 1 percent.

Linearity

An output signal which was not linear with the intensity of the light falling on the detector would result in a false representation of the spectral curve and consequently an erroneous integrated absorptance. As discussed previously the linearity of the system was carefully checked before measurements were made. The output signal is believed to be linear with a changing $I(\nu)$ to within about 1 percent full scale. No zero error was detected.

C. Data reduction

Background determination

One of the largest sources of error in measurements of integrated absorptance is encountered in choosing the position of the zero percent absorptance curve. By recording only those spectra for which the fractional absorptance was essentially zero for a frequency range on either side of the lines in question, one could linearly connect these regions of zero fractional absorptance to obtain a zero percent absorptance curve without actually recording a background curve and fitting it to the spectrum. It is felt that this method of determining the background position gave a more accurate result than by attempting to fit a second curve to the spectrum. Some of the advantage was lost, however, since the areas to measure were smaller on the average than those at higher pressures and, thus, were less accurately measured. By carefully splitting the peak to peak noise in frequency intervals of zero fractional absorptance when drawing in the backgrounds, one could obtain consistent placement of the zero percent absorptance curves.

Measurement of area

The area of the spectral absorption line was measured with a compensating polar planimeter. For integrated absorptances less than 0.03 cm^{-1} the areas could be measured to an accuracy of 5 percent; at larger integrated absorptances the measurements were accurate to 2 percent.

Wing positions

In the case of overlapping lines, the internal wings of the lines had to be drawn onto the spectral lines in the manner previously described. This empirical method could give a poor representation of the true wing position. It is estimated that errors in the area of the absorption line as large as 5 percent could result. Wing corrections which add as much as 3 percent to the area of a line have also been neglected in the present study.

Temperature correction

Temperature fluctuation from run to run about the average room temperature of 27°C were not taken into account in determining W . The extreme variation from the average was 5°C but by far the majority of the data were within 2°C of the average. The values of W determined for 300°K by neglecting the temperature correction, therefore, were affected by less than one percent in most cases.

Influence of water vapor lines

For the spectral frequencies studied about fifteen water vapor lines with peak absorptances of five to ten percent were observed.

These arose from the small amount of strongly absorbing water vapor remaining in the spectrometer tanks after evacuation. All but six of these lines, which were weak compared with the NO lines, were distant enough from the NO lines that no observable overlap occurred. Of the remaining six lines five were sufficiently well separated from the NO lines to allow corrections to be made for overlap. For the $m = -(35/2)$ line in the P branch of the $3/2$ subband, however, measurements would have been significantly affected by a water line and consequently this line was not measured. It is believed, therefore, that water lines have not influenced the width and strength measurements.

Influence of isotopic NO lines

The isotopic bands of $N^{14}O^{17}$, $N^{14}O^{18}$, $N^{15}O^{16}$, $N^{15}O^{17}$, and $N^{15}O^{18}$ occur with band centers at different frequencies throughout the P branches of the subbands of the $N^{14}O^{16}$ fundamental. For the path lengths and pressures used in this study, however, no isotopic lines were observed. The influence of these lines on the width and strength measurements should, therefore, be negligible.

Deviations from Lorentz line behavior

The variation of W_0 with pressure for an absorption line at a fixed cell length amounts to as much as 20 percent for some square root region lines. Then although the individual measurements of W_0 are expected to have an uncertainty of less than 10 percent, the value of W_0 found by averaging values at different pressures may differ from the

true W_0 at a given pressure by up to 15-20 percent in the square root region. This is due to the effect of the Λ doubling.

The total uncertainty in the line strengths, which are found from linear region data, is then estimated to be less than 10 percent. Likewise, the estimated total uncertainty in the half widths, which are found essentially from square root region data is 15-20 percent. The consistency of the data indicates the total random error is less than this. Likewise, because of the number of measurements employed in the determination of the band strength the accuracy of this measurement should be much better than that for the individual strengths.

VI. SUMMARY AND CONCLUSIONS

The half widths and line strengths of individual absorption lines in molecular band spectra are related to the integrated absorbance W of a spectral line, the partial pressure p of the absorbing gas, the total pressure P , the optical thickness u , and the temperature T of the sample. For the case of a self-broadened Lorentzian line, absorption theory predicts a particularly simple relation and the two line parameters can be determined by measurement of the curve of growth of the line. Benedict, Herman, Moore, and Silverman^{1,2} have successfully applied this technique to the fundamental band of CO, which is comprised of single lines separated by about 4 cm^{-1} , and to the fundamental band of HCl, which is comprised of a series of double lines arising from the two isotopic species. The isotopic lines have a separation of about 2 cm^{-1} with the separation between the double lines being about $10\text{-}20\text{ cm}^{-1}$.

The feasibility of applying the curve of growth technique to obtain half widths and line strengths in bands for which the observed lines are not singlets of Lorentzian shape and are less isolated than in the previous studies has been demonstrated in this work. The fundamental band of NO consists of a series of double lines about two wave numbers apart in the wings of the bands but nearly coincident near the band centers. Each of the double lines is composed of an unresolved doublet instead of being a single Lorentzian line. Application of the

curve of growth method to the double lines of the NO fundamental has resulted in the measurement of the line strengths and half widths of over 70 lines from the two subbands.

The half widths measured show a decrease for increasing values of $|m|$. No difference beyond that expected from experimental error is found in the values of half width at a given value of $|m|$ for lines from the R and P branches of each subband. The smoothed curve of the mean values of half width, found by averaging the half widths of like $|m|$ values, ranges linearly with $|m|$ from about $0.062 \text{ cm}^{-1} \text{ atm}^{-1}$ at $|m| = 3/2$ to $0.050 \text{ cm}^{-1} \text{ atm}^{-1}$ at $|m| = 45/2$.

The measured values for the line strengths are in close agreement with those predicted by theory assuming no vibration-rotation interaction. Thus, no anomalies in the strength seem to occur in any branch and the vibration-rotation interaction is quite small.

The band strength of the fundamental was found from the measured line strengths to be $122 \pm 6 \text{ cm}^{-2} \text{ atm}^{-1}$. It is felt that this is one of the most extensive studies undertaken in the determination of this quantity and it is hoped that the value of band strength obtained will help resolve the uncertainty in the measured value of this quantity.

The values of half width found for the NO lines by the curve of growth technique possessed a rather large uncertainty. This uncertainty is believed to arise largely from the Λ doubling. Nevertheless, the values of line strength and band strength should not be appreciably affected by the Λ doubling.

Because of the tedious nature of the methods used here and because of the agreement to within experimental error of the half widths measured in the present study with those found more simply by James⁹ by directly measuring the widths and applying a correction for instrumental broadening, it is believed that the latter technique may in many cases be the preferable one. Line strength and band strength measurements might then be made with the procedure used in this study. In the case of lines comprised of unresolved components, however, the half width uncertainty would be expected to arise in either technique.

Recent investigations of the true spectral shape of pressure-broadened absorption lines has indicated interesting deviations from Lorentzian shape. In order to know the spectral contours predicted according to the Lorentzian absorption coefficient, the strengths and half widths of the individual lines of the band need to be known. It is hoped that the strengths and widths measured in this study will be useful in future line shape studies as well as in other studies of radiation transmission.

Table 6

Data for Typical Lines in the P Branch of the $\Omega = 1/2$ Subband
at 300° K.

(For cell lengths less than 0.2 cm the equivalent pure sample
pressures and cell lengths listed below were obtained with
NO-N₂ mixtures in a 2.54 cm cell.)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_O (cm ⁻¹ atm ⁻¹)
-9	7.62	50	1.82
-9	7.62	50	1.82
-9	7.62	50	1.75
-9	1.00	50	0.714
-9	1.00	50	0.790
-9	1.00	50	0.760
-9	1.00	200	0.688
-9	1.00	200	0.673
-9	1.00	200	0.661
-9	0.200	50	0.319
-9	0.200	50	0.319
-9	0.200	50	0.334
-9	0.200	200	0.255
-9	0.200	200	0.281
-9	0.200	200	0.258
-9	0.077	200	0.129
-9	0.077	200	0.133
-9	0.077	200	0.125
-9	0.077	760	0.139
-9	0.077	760	0.132
-9	0.077	760	0.132
-9	0.025	760	0.045
-9	0.025	760	0.047
-9	0.025	760	0.043
-15	7.62	50	2.16
-15	7.62	50	2.20
-15	7.62	50	2.14
-15	1.00	50	0.790
-15	1.00	50	0.942
-15	1.00	50	0.744

Table 6 (continued)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	$\epsilon_{\text{O}} (\text{cm}^{-1} \text{ atm}^{-1})$
-15	1.00	200	0.718
-15	1.00	200	0.692
-15	1.00	200	0.741
-15	0.200	50	0.334
-15	0.200	50	0.319
-15	0.200	50	0.365
-15	0.200	200	0.300
-15	0.200	200	0.289
-15	0.200	200	0.273
-15	0.077	200	0.144
-15	0.077	200	0.152
-15	0.077	200	0.152
-15	0.077	760	0.153
-15	0.077	760	0.160
-15	0.077	760	0.155
-15	0.025	760	0.061
-15	0.025	760	0.056
-15	0.025	760	0.053
-25	7.62	50	1.79
-25	7.62	50	1.72
-25	7.62	50	1.73
-25	1.00	50	0.699
-25	1.00	50	0.699
-25	1.00	50	0.654
-25	1.00	200	0.597
-25	1.00	200	0.593
-25	1.00	200	0.574
-25	0.200	50	0.289
-25	0.200	50	0.243
-25	0.200	50	0.258
-25	0.200	200	0.236
-25	0.200	200	0.239
-25	0.200	200	0.224

Table 6 (continued)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_0 (cm ⁻¹ atm ⁻¹)
-25	0.077	200	0.122
-25	0.077	200	0.118
-25	0.077	200	0.114
-25	0.077	760	0.119
-25	0.077	760	0.117
-25	0.077	760	0.118
-25	0.025	760	0.040
-25	0.025	760	0.040
-25	0.025	760	0.041
-37	40.0	14	2.61
-37	40.0	14	2.50
-37	40.0	14	2.55
-37	7.62	50	1.06
-37	7.62	50	0.973
-37	7.62	50	0.912
-37	7.62	200	0.817
-37	7.62	200	0.893
-37	7.62	200	0.885
-37	1.00	50	0.380
-37	1.00	50	0.365
-37	1.00	50	0.380
-37	1.00	200	0.315
-37	1.00	200	0.315
-37	1.00	200	0.312
-37	0.200	200	0.106
-37	0.200	200	0.091
-37	0.200	200	0.099
-37	0.077	760	0.037
-37	0.077	760	0.039
-37	0.077	760	0.035

Table 7

Data for Typical Lines in the P Branch of the $\Omega = 3/2$ Subband
at 300° K.

(For cell lengths less than 0.2 cm the equivalent pure sample
pressures and cell lengths listed below were obtained with
NO-N₂ mixtures in a 2.54 cm cell.)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_0 (cm ⁻¹ atm ⁻¹)
-9	7.62	50	1.38
-9	7.62	50	1.38
-9	7.62	50	1.32
-9	1.00	50	0.502
-9	1.00	50	0.562
-9	1.00	50	0.456
-9	1.00	200	0.498
-9	1.00	200	0.486
-9	1.00	200	0.467
-9	0.200	50	0.198
-9	0.200	50	0.167
-9	0.200	50	0.152
-9	0.200	200	0.156
-9	0.200	200	0.175
-9	0.200	200	0.160
-9	0.077	200	0.080
-9	0.077	200	0.072
-9	0.077	200	0.072
-9	0.077	760	0.087
-9	0.077	760	0.079
-9	0.077	760	0.082
-9	0.025	760	0.024
-9	0.025	760	0.028
-9	0.025	760	0.022
-15	7.62	50	1.58
-15	7.62	50	1.63
-15	7.62	50	1.67
-15	1.00	50	0.547
-15	1.00	50	0.593
-15	1.00	50	0.593

Table 7 (continued)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_o ($\text{cm}^{-1} \text{ atm}^{-1}$)
-15	1.00	200	0.505
-15	1.00	200	0.578
-15	1.00	200	0.574
-15	0.200	50	0.198
-15	0.200	50	0.228
-15	0.200	50	0.182
-15	0.200	200	0.194
-15	0.200	200	0.198
-15	0.200	200	0.186
-15	0.077	200	0.091
-15	0.077	200	0.091
-15	0.077	200	0.095
-15	0.077	760	0.090
-15	0.077	760	0.098
-15	0.077	760	0.102
-15	0.025	760	0.032
-15	0.025	760	0.033
-15	0.025	760	0.031
-25	7.62	50	1.35
-25	7.62	50	1.28
-25	7.62	50	1.31
-25	1.00	50	0.426
-25	1.00	50	0.456
-25	1.00	50	0.517
-25	1.00	200	0.433
-25	1.00	200	0.437
-25	1.00	200	0.433
-25	0.200	50	0.198
-25	0.200	50	0.182
-25	0.200	50	0.213
-25	0.200	200	0.148
-25	0.200	200	0.129
-25	0.200	200	0.141

Table 7 (continued)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_O ($\text{cm}^{-1} \text{ atm}^{-1}$)
-25	0.077	200	0.064
-25	0.077	200	0.067
-25	0.077	200	0.062
-25	0.077	760	0.069
-25	0.077	760	0.068
-25	0.077	760	0.068
-25	0.025	760	0.022
-25	0.025	760	0.023
-25	0.025	760	0.020
-37	40.0	14	1.95
-37	40.0	14	1.90
-37	40.0	14	2.01
-37	7.62	50	0.760
-37	7.62	50	0.699
-37	7.62	50	0.714
-37	7.62	200	0.619
-37	7.62	200	0.646
-37	7.62	200	0.657
-37	1.00	50	0.243
-37	1.00	50	0.228
-37	1.00	50	0.243
-37	1.00	200	0.193
-37	1.00	200	0.205
-37	1.00	200	0.220
-37	0.200	200	0.053
-37	0.200	200	0.057
-37	0.200	200	0.053
-37	0.077	760	0.020
-37	0.077	760	0.019
-37	0.077	760	0.021

Table 8

Data for Typical Lines in the R Branch of the $\Omega = 1/2$ Subband
at 300° K.

(For cell lengths less than 0.2 cm the equivalent pure sample
pressures and cell lengths listed below were obtained with
NO-N₂ mixtures in a 2.54 cm cell.)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_0 (cm ⁻¹ atm ⁻¹)
9	7.62	50	2.23
9	7.62	50	2.08
9	7.62	50	2.30
9	1.00	50	0.821
9	1.00	50	0.836
9	1.00	50	0.806
9	1.00	200	0.760
9	1.00	200	0.802
9	1.00	200	0.809
9	0.200	50	0.365
9	0.200	50	0.350
9	0.200	50	0.350
9	0.200	200	0.289
9	0.200	200	0.312
9	0.200	200	0.327
9	0.077	200	0.141
9	0.077	200	0.141
9	0.077	200	0.137
15	7.62	50	2.30
15	7.62	50	2.19
15	7.62	50	2.23
15	1.00	50	0.836
15	1.00	50	0.836
15	1.00	50	0.821
15	1.00	200	0.783
15	1.00	200	0.787
15	1.00	200	0.802

Table 8 (continued)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_0 (cm ⁻¹ atm ⁻¹)
15	0.200	50	0.380
15	0.200	50	0.365
15	0.200	50	0.331
15	0.200	200	0.312
15	0.200	200	0.312
15	0.200	200	0.327
15	0.077	200	0.163
15	0.077	200	0.163
15	0.077	200	0.167
15	0.025	760	0.071
15	0.025	760	0.071
15	0.025	760	0.073
25	7.62	50	1.99
25	7.62	50	1.98
25	7.62	50	2.01
25	1.00	50	0.790
25	1.00	50	0.851
25	1.00	50	0.790
25	1.00	200	0.665
25	1.00	200	0.669
25	1.00	200	0.669
25	0.200	50	0.304
25	0.200	50	0.350
25	0.200	50	0.350
25	0.200	200	0.271
25	0.200	200	0.281
25	0.200	200	0.285
25	0.077	760	0.156
25	0.077	760	0.143
25	0.077	760	0.141
25	0.025	760	0.052
25	0.025	760	0.048
25	0.025	760	0.048

Table 8 (continued)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_O ($\text{cm}^{-1} \text{ atm}^{-1}$)
37	7.62	50	1.16
37	7.62	50	1.12
37	7.62	50	1.16
37	7.62	200	1.01
37	7.62	200	0.999
37	7.62	200	1.07
37	1.00	200	0.365
37	1.00	200	0.369
37	1.00	200	0.369
37	1.00	760	0.325
37	1.00	760	0.330
37	1.00	760	0.339
37	0.200	200	0.137
37	0.200	200	0.125
37	0.200	200	0.125
37	0.077	760	0.061
37	0.077	760	0.060
37	0.077	760	0.061

Table 9

Data for Typical Lines in the R Branch of the $\Omega = 3/2$ Subband
at 300° K.

(For cell lengths less than 0.2 cm the equivalent pure sample
pressures and cell lengths listed below were obtained with
NO-N₂ mixtures in a 2.54 cm cell.)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_0 (cm ⁻¹ atm ⁻¹)
9	7.62	50	1.73
9	7.62	50	1.79
9	7.62	50	1.73
9	1.00	50	0.578
9	1.00	50	0.547
9	1.00	50	0.562
9	1.00	200	0.604
9	1.00	200	0.585
9	1.00	200	0.585
9	0.200	50	0.258
9	0.200	50	0.228
9	0.200	50	0.258
9	0.200	200	0.198
9	0.200	200	0.220
9	0.200	200	0.217
9	0.077	200	0.091
9	0.077	200	0.095
9	0.077	200	0.087
15	7.62	50	1.78
15	7.62	50	1.73
15	7.62	50	1.79
15	1.00	50	0.638
15	1.00	50	0.638
15	1.00	50	0.623
15	1.00	200	0.638
15	1.00	200	0.604
15	1.00	200	0.627

Table 9 (continued)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_0 (cm ⁻¹ atm ⁻¹)
15	0.200	50	0.213
15	0.200	50	0.228
15	0.200	50	0.258
15	0.200	200	0.205
15	0.200	200	0.221
15	0.200	200	0.213
15	0.077	200	0.111
15	0.077	200	0.106
15	0.077	200	0.103
15	0.025	760	0.011
15	0.025	760	0.012
15	0.025	760	0.012
25	7.62	50	1.19
25	7.62	50	1.17
25	7.62	50	1.73
25	1.00	50	0.516
25	1.00	50	0.562
25	1.00	50	0.587
25	1.00	200	0.513
25	1.00	200	0.483
25	1.00	200	0.486
25	0.200	50	0.197
25	0.200	50	0.182
25	0.200	50	0.213
25	0.200	200	0.198
25	0.200	200	0.186
25	0.200	200	0.186
25	0.077	760	0.086
25	0.077	760	0.092
25	0.077	760	0.088
25	0.025	760	0.029
25	0.025	760	0.028
25	0.025	760	0.027

Table 9 (continued)

2m	Equivalent Cell Length (cm)	Equivalent Pressure (mm Hg of NO)	W_0 (cm ⁻¹ atm ⁻¹)
37	7.62	50	0.806
37	7.62	50	0.790
37	7.62	50	0.851
37	7.62	200	0.787
37	7.62	200	0.779
37	7.62	200	0.783
37	1.00	200	0.266
37	1.00	200	0.266
37	1.00	200	0.266
37	1.00	760	0.211 ₄
37	1.00	760	0.233
37	1.00	760	0.224
37	0.200	200	0.072
37	0.200	200	0.065
37	0.200	200	0.072
37	0.077	760	0.030
37	0.077	760	0.031
37	0.077	760	0.032

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