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INFRARED TRANSMISSION STUDIES
FINAL REPORT, VOLUME IV

THE INFLUENCE OF NUMEROUS WEAK LINES ON THE ABSORPTANCE OF A SPECTRAL BAND

12 APRIL 1963

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UNITED STATES AIR FORCE
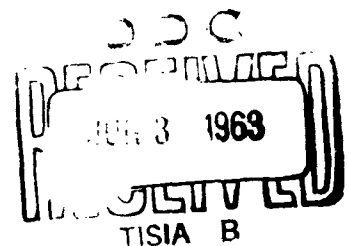
INFRARED TRANSMISSION STUDIES

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THE INFLUENCE OF NUMEROUS WEAK LINES ON THE

ABSORPTANCE OF A SPECTRAL BAND

G. N. Plass

12 April 1963

Prepared for

ABSTRACT

        The influence of numerous weak spectral lines on band
absorption is investigated. It is shown that a region of validity
always exists for the weak line approximation. There is almost
always also a region of validity for the strong line approximation,
unless the number of spectral lines increases very rapidly as the
intensity approaches zero. The principal effects of the weak lines
are to introduce points of inflection in the absorptance curves
and to increase the intermediate range of values of pressure and
absorber concentration over which neither the strong nor weak line
approximation is valid. These effects are illustrated by examples.
From a study of the shape of experimentally determined absorptance
curves it is possible to deduce the number of weak lines in the
frequency interval of interest.

CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (Cont'd)

SECTION 1

INTRODUCTION

Four theoretical models of varying degrees of sophistication have been proposed to represent spectral band absorption: (1) the Elsasser model[1] for a band composed of identical, uniformly spaced spectral lines; (2) the statistical model[2,3] for a band composed of spectral lines with an arbitrary intensity distribution and with a random spacing between lines; (3) the random Elsasser model[4,5] for a band composed of several groups of lines each of which individually forms an Elsasser band, but where these groups are superposed with a random spacing; (4) the quasi-random model[6] for a band composed of spectral lines whose actual intensities and variation of spacing from line to line are accurately simulated.

Theoretical work[5,7] based on the first two of these models has shown that regions always exist where the strong and weak line

[1] W. M. Elsasser, Phys. Rev., 54, 126 (1938).

[2] H. Mayer, "Methods of Opacity Calculations", Los Alamos, LA-647, Oct. 31, 1947

[3] R. M. Goody, Quart. J. Roy. Meteorol. Soc. 78, 165 (1952).

[4] L. D. Kaplan, Proc. Toronto Meteorol. Conf. 1953, 43.

[5] G. N. Plass, J. Opt. Soc. Amer. 48, 690 (1958).

[6] P. J. Wyatt, V. R. Stull, G. N. Plass, J. Opt. Soc. Amer. 52, 1209 (1962).

[7] G. N. Plass, J. Opt. Soc. Amer. 50, 868 (1960).

approximations are valid provided that the intensity distribution of the spectral lines can be represented by certain expressions. These approximations have well defined regions of validity[5,7] when either all of the spectral lines are equally intense or when the intensity distribution decreases with increasing line intensity as the negative exponential of the line intensity.

Recent experimental work[8-11] has shown that the region of validity of the strong line approximation is often much less than is calculated from either of these intensity distributions. Furthermore, the shape for the absorptance curves as a function of pressure and absorber concentration does not agree in some cases with a theory based on either of these intensity distributions. The same conclusions were obtained from a study of the transmittance tables[12,13] for H_2O and CO_2 calculated from the quasi-random model and including the effects of numerous weak lines on the absorption.

The major reason for the disagreement between the theory based upon these intensity distributions and the experimental results on the one hand and more elaborate theoretical calculations on the other hand is the contribution to the absorptance from the many weak spectral lines which exist in many spectra. These lines arise either from the numerous transitions of low probability which always occur or from the spectral lines of the rarer isotopes. The effect of these weak lines on the regions of validity of the strong and weak line approximations and on the shape of the absorptance curves is investigated in this report.

[8] D. E. Burch, D. Williams, Applied Optics 1, 473 (1962).

[9] D. E. Burch, D. Williams, Applied Optics 1, 587 (1962).

[10] D. E. Burch, D. A. Gryvnak, D. Williams, Applied Optics 1, 759 (1962).

[11] D. E. Burch, W. L. France, D. Williams, Applied Optics 2 (in press, 1963).

[12] P. J. Wyatt, V. R. Stull, G. N. Plass, Applied Optics 2 (in press, 1963).

[13] V. R. Stull, P. J. Wyatt, G. N. Plass, Applied Optics 2 (in press, 1963).

SECTION 2

CONTRIBUTION OF NUMEROUS WEAK LINES TO THE ABSORPTANCE

The total absorption by a single spectral line over a frequency interval $\Delta \nu$ is given by

$$W_{s\ell,i} = \int_{\Delta\nu} (1 - e^{-uS_i b_i}) \, d\nu, \tag{1}$$

where $W_{s\ell,i}$ is the equivalent width of the ith spectral line, u is the absorber concentration measured in mass per unit area, S_i is the total intensity of the line, and b_i is the line shape factor normalized to unity. For the Lorentz line shape

$$b_i(\nu) = \alpha_i / \left\{ \pi \left[(\nu - \nu_{oi})^2 + \alpha_i^2 \right] \right\}, \tag{2}$$

where α_i is the half-width of the line whose center is at ν_{oi}. Usually the frequency interval $\Delta\nu$ is assumed to be sufficiently large so that there is no absorption outside of the interval due to the line whose center is within the interval.

When Eq. (2) is substituted into Eq. (1) the resulting integral can be solved exactly[14] for the equivalent width to obtain

$$W_{s\ell,i} = 2\pi\alpha_i \, f(x_i) , \tag{3}$$

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[14]R. Landenberg, F. Reiche, Ann. Physik <u>42</u>, 181 (1913).

where

$$x_i = S_i u/2\pi\alpha_i \tag{4}$$

and

$$f(x) = xe^{-x}\left[I_0(x) + I_1(x)\right], \tag{5}$$

where I_0 and I_1 are the Bessel functions of imaginary argument.

The equivalent width of a group of nonoverlapping spectral lines in the interval $\Delta\nu$ is

$$W_{s\ell} = 2\pi\sum_i N_i \alpha_i f(x_i), \tag{6}$$

where N_i is the number of lines having the particular values α_i and x_i for the parameters α and x.

The influence of the weak lines on the absorptance can be studied best by considering the case of nonoverlapping lines. The particular features introduced into the absorptance curves by the weak lines can be seen most clearly in this limit. These features are only modified somewhat but not changed in their essential character by the overlapping of the lines. Thus much of the following discussion is devoted to the region in which the lines do not overlap. Later the effect of overlapping is considered by using the statistical model and assuming that there are a sufficient number of spectral lines so that[2,3,5,6]

$$A = 1 - \exp(-W_{s\ell}/d), \tag{7}$$

where d is the mean line spacing.

A. Band of Nonoverlapping Spectral Lines

The absorptance of a band of nonoverlapping spectral lines is equal to the equivalent width $W_{s\ell}$ as given by Eq. (6) divided by

a frequency interval $\Delta \nu$. It is assumed that the interval $\Delta \nu$ is sufficiently large so that there is virtually no absorption outside of the interval from the lines whose centers lie within the given interval. Let $x_{i,max}$ represent the largest value of x which occurs in the interval $\Delta \nu$. Consider the two cases when $x_{i,max}$ is much smaller and much larger than one.

Case I. $x_{i,max} << 1$. In this case[7],

$$f(x) = x , \qquad x << 1 , \qquad (8)$$

for all values of x which occur in Eq. (6). From Eqs. (6) and (8) it is found that the equivalent width is

$$W_{s\ell} = u \sum_i N_i S_i . \qquad (9)$$

Thus, for sufficiently small values of the absorber concentration and sufficiently large values of the pressure such that the largest value of x_i which occurs in the interval $\Delta \nu$ is much less than unity, the absorptance always varies linearly with the absorber concentration and is independent of the pressure. This result is always true regardless of the intensity distribution of the spectral lines in the band.

Case II. Assume that there exists a smallest value $x_{i,min}$ for the spectral lines which occur in the interval $\Delta \nu$ and that in addition $x_{i,min} >> 1$. Since[7]

$$f(x) = (2x/\pi)^{\frac{1}{2}} , \qquad x >> 1 , \qquad (10)$$

it follows from Eq. (6) that

$$W_{s\ell} = 2u^{\frac{1}{2}} \sum_i N_i \alpha_i^{\frac{1}{2}} S_i^{\frac{1}{2}} , \qquad (11)$$

since the value of x for every spectral line occurs in the strong line region. Thus, for sufficiently large values of the absorber concentration and sufficiently small values of the pressure so that $x_{i,min} >> 1$, the absorptance increases as the square-root of both the path length and the pressure. This result is always true regardless of the

intensity distribution of the spectral lines in the band, provided only that a smallest value of x_i exists for the lines in the interval $\Delta\nu$.

This requirement might appear unrealistic since spectral lines weaker than any predetermined amount occur in many cases due to either very weak transitions or rare isotopes. However, these very weak lines with $x_i \ll 1$ can be neglected if their contribution in Eq. (6) is small compared to the strong lines with $x_i \gg 1$. The relative contribution of each of these groups can be evaluated approximately by classifying all of the lines as either weak or strong depending on whether x_i is less than or greater than unity. Thus if

$$\sum_{i=1}^{\varkappa-1} N_i \alpha_i x_i \ll 2\pi^{-\frac{1}{2}} \sum_{i=\varkappa}^{i_{max}} N_i \alpha_i x_i^{\frac{1}{2}}, \qquad (12)$$

where $\varkappa$ is the value of i which most closely makes $x_i = 1$, then the weak lines can be neglected compared to the strong lines and the results of Case II are still valid.

This brief analysis shows that the weaker lines can influence the absorption in only two ways: First, a sufficient number of weak lines increases the range of u and p over which neither the linear nor the square-root approximation is valid. Secondly, there may be no region in which the square-root approximation is valid if the number of weak lines increases sufficiently rapidly as the line intensity decreases. However, it has been shown that there must always be a region where the linear approximation is valid. Furthermore, there is also a range of u and p where the square-root approximation is valid unless there is an exceedingly rapid increase in the number of very weak lines. This point is examined in more detail in the examples which follow.

The influence of a large number of weak lines on the absorption can best be illustrated by considering several examples. For convenience, the half-width of all the spectral lines are assumed to be equal in the following examples. For the first example consider the absorption from an interval $\Delta\nu$ which contains one spectral line of intensity S_0 and 10^N spectral lines of intensity $10^{-4} S_0$. The equivalent width $W_{s\ell}$ as a function of $x_0 = S_0 u/2\pi\alpha$ at constant pressure is shown in Fig. 1. The numerical values were calculated from Eq. (6) using the exact expression for $f(x)$ given by Eq. (5). Curves are given
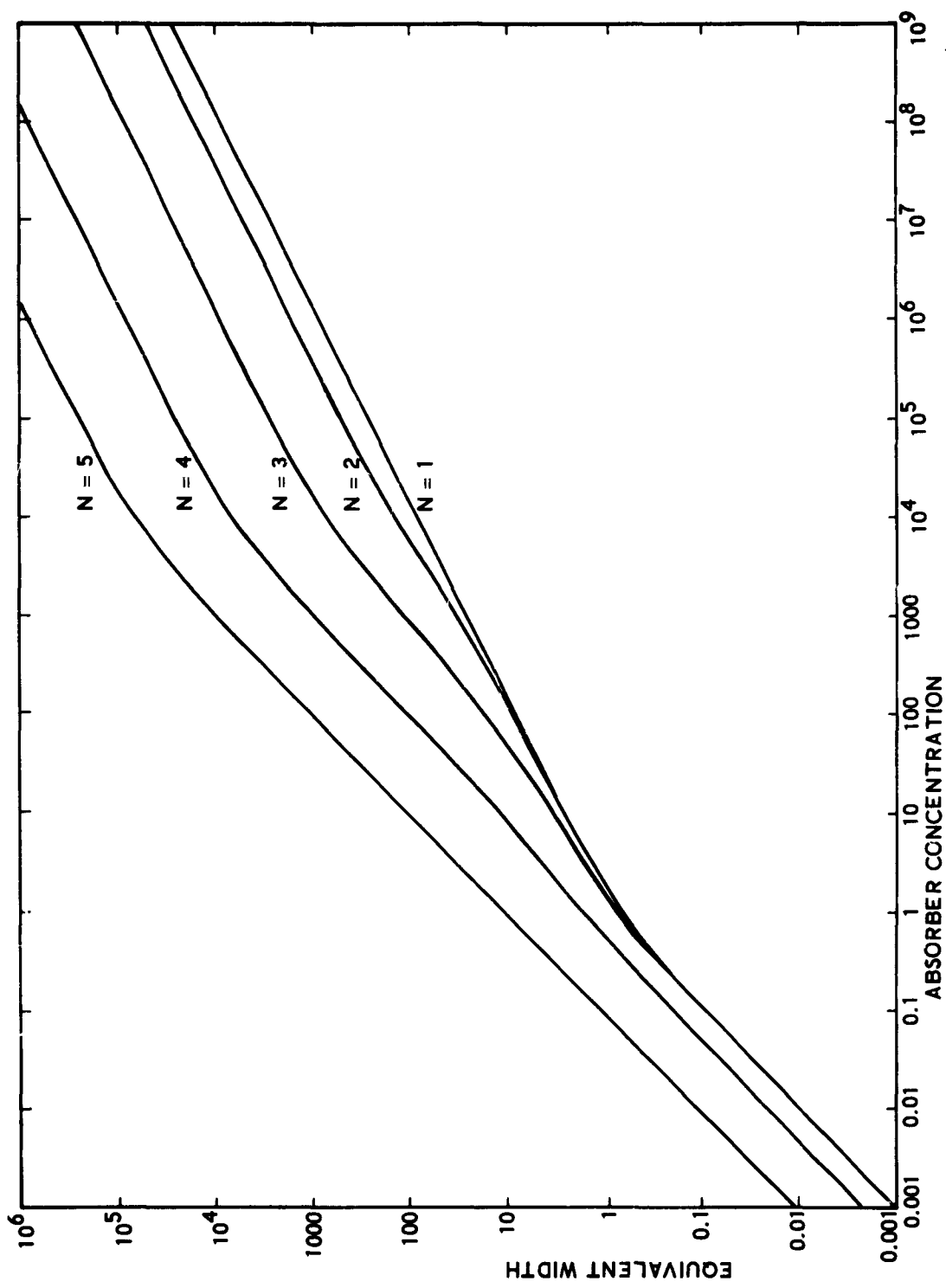
FIG. 1. The equivalent width at constant pressure as a function of absorber concentration. The ordinate is $W_{s\ell}/2\pi\alpha$ and the abscissa is $x_o = S_o u/2\pi\alpha$. The absorption is calculated for a nonoverlapping group composed of one spectral line of intensity S_o and 10^N spectral lines of intensity $10^{-4} S_o$. Curves are shown for $N = 1,2,3,4,5$.

for N = 1,2,3,4,5. The curve for N = 1 is virtually the same on this scale as the curve for a single line of intensity S_o, since there are not sufficient weak lines to absorb significantly.

The equivalent width varies linearly as a function of x_o when $x_o \ll 1$ for all of the curves shown in Fig. 1. In this case all of the spectral lines are in the region where the linear approximation, Eq. (9), is valid. On the other hand when $x_o \gg 10^4$, all of the curves in Fig. 1 vary as the square-root of x_o. In this region both the single strong line of intensity S_o and the weak lines of intensity $10^{-4} S_o$ are in the region where the square-root approximation is valid and satisfy Eq. (11).

The most interesting region of Fig. 1, $1 < x_o < 10^4$, occurs when the strong lines are in the square-root region and the weak lines are in the linear region. The change in the shape of the curves for equivalent width is a function of x_o as the number of weak lines increases can be seen by comparing the curves for different values of N. When N = 1 the slope of the curve on a log-log plot is unity for small values of x_o and changes to one-half in a region which is centered around $x_o = 1$. Most of the absorption is due to the single line of strength S_o which itself changes from a linear to a square-root dependence around $x_o = 1$.

When N = 2 there is no significant difference from the previous curve for $x_o < 0.2$, since 100 weak lines of strength $10^{-4} S_o$ still do not make an appreciable contribution to the absorption in the linear region. The square-root approximation is valid even for these weak lines when $x_o > 2 \times 10^4$. In this region the weak lines make a larger contribution relative to the single strong line because of the square-root factor. In this particular example, the absorption from the weak lines is equal to that of the single strong line when $x_o > 2 \times 10^4$, but is only 10^{-2} of the single strong line when $x_o < 0.2$. This illustrates the general principle that the relative contribution of weak lines is always more important in the region where the square-root approximation is valid for all of the lines.

When N = 3, the slope of the curve on the log-log plot of Fig. 1 is nearly unity when $x_o < 0.2$. As x_o increases the slope decreases to approximately 0.6 at $x_o = 10$. The slope then increases again to approximately 0.9 at $x_o = 1000$ as the relative contribution of the weak lines to the absorption increases. Finally, the slope decreases to nearly 0.5 when $x_o > 2 \times 10^4$. When N = 4 the single strong line of strength S_o and the 10^4 weak lines of strength $10^{-4} S_o$ contribute equally to the absorption in the linear region. When both

sets of lines are in the square-root region, the weak lines absorb
100 times more radiation than the single strong line. The slope of
this curve is fairly close to unity until $x_0 > 2,000$. When $N = 5$
the absorption is due almost entirely to the numerous weak lines and
the curve is nearly identical to one for lines of strength 10^{-4} S_0
only.

The variation of the equivalent width as a function of the
pressure for constant absorber concentration is shown in Fig. 2 for
the same values of N which were used for Fig. 1. The slope of these
curves on a log-log plot varies from one-half to zero as the pressure
increases. When the absorption is largely due to spectral lines of
a single intensity the slope decreases continuously to zero as the
pressure increases. However, this is not true when spectral lines
of different intensities make an important contribution to the
absorption, as is the case when $N = 2,3,4$ in this example. As the
pressure increases, the slope decreases from one-half to a value of
nearly zero and then increases again before finally approaching zero.
Of course with more complicated intensity distributions even more
fluctuations in the slope could be introduced. When experimental
measurements indicate that the slope increases and then decreases
again as the pressure decreases, this may be due to the effect of
weak lines instead of the Doppler effect as is usually assumed. In
fact it seems very likely that in some reported measurements the Doppler
effect is not responsible for the decrease in the slope of the curves
as the pressure decreases as stated by the authors. Rather weak lines
are changing the shape of the absorptance curves.

These curves illustrate the shape of the absorptance curves
when there are a finite number of spectral lines. However, in an
actual spectrum there may be some lines with an intensity smaller than
any predetermined amount. The study of two additional examples will
clarify the behavior of the absorptance curves in this case.

Divide the spectral lines into intensity decades and count
the number of spectral lines in each decade. In Example A, assume
that there is one spectral line in each intensity decade, i.e. one line
with each of the intensities S_0, 10^{-1} S_0, 10^{-2} S_0, 10^{-3} S_0, ...
The variation of the equivalent width with x_0 at constant pressure for
this example is shown in Fig. 3. The curve is qualitatively similar
to the curve for a single line of intensity S_0. The only significant
difference is that there is a slightly larger transition domain between
the linear and square-root regions. In this example where the number
of spectral lines in each intensity decade is constant, there are not
sufficient weak lines to change appreciably the character of the
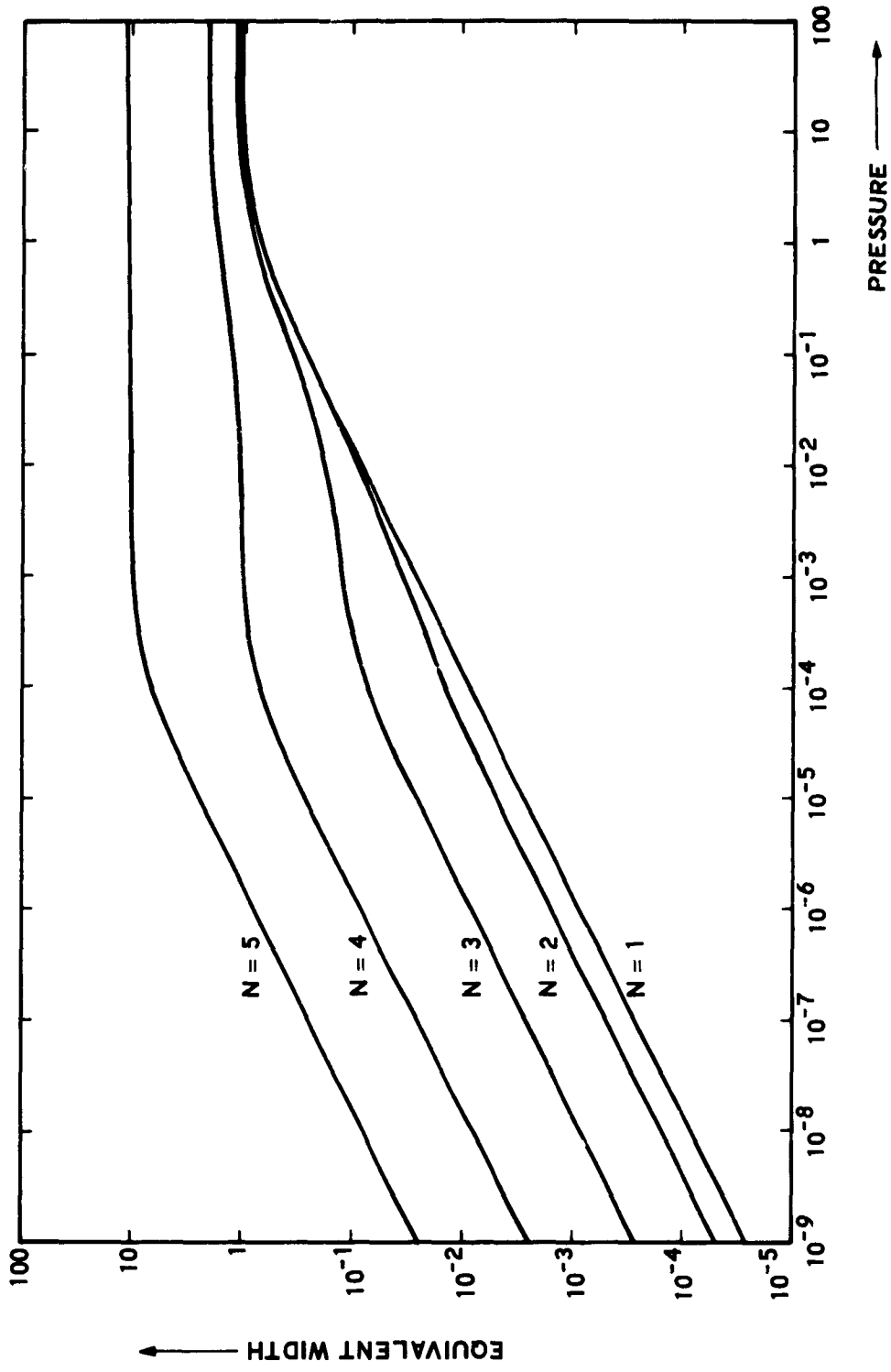
FIG. 2. The equivalent width at constant absorber concentration as a function of the pressure. The ordinate is $S_{ou} W_{s\ell}$ and the abscissa is $2\pi\alpha/S_{ou}$. The absorption is calculated for a nonoverlapping group composed of one spectral line of intensity S_o and 10^N spectral lines of intensity $10^{-4} S_o$. Curves are shown for $N = 1,2,3,4,5$.
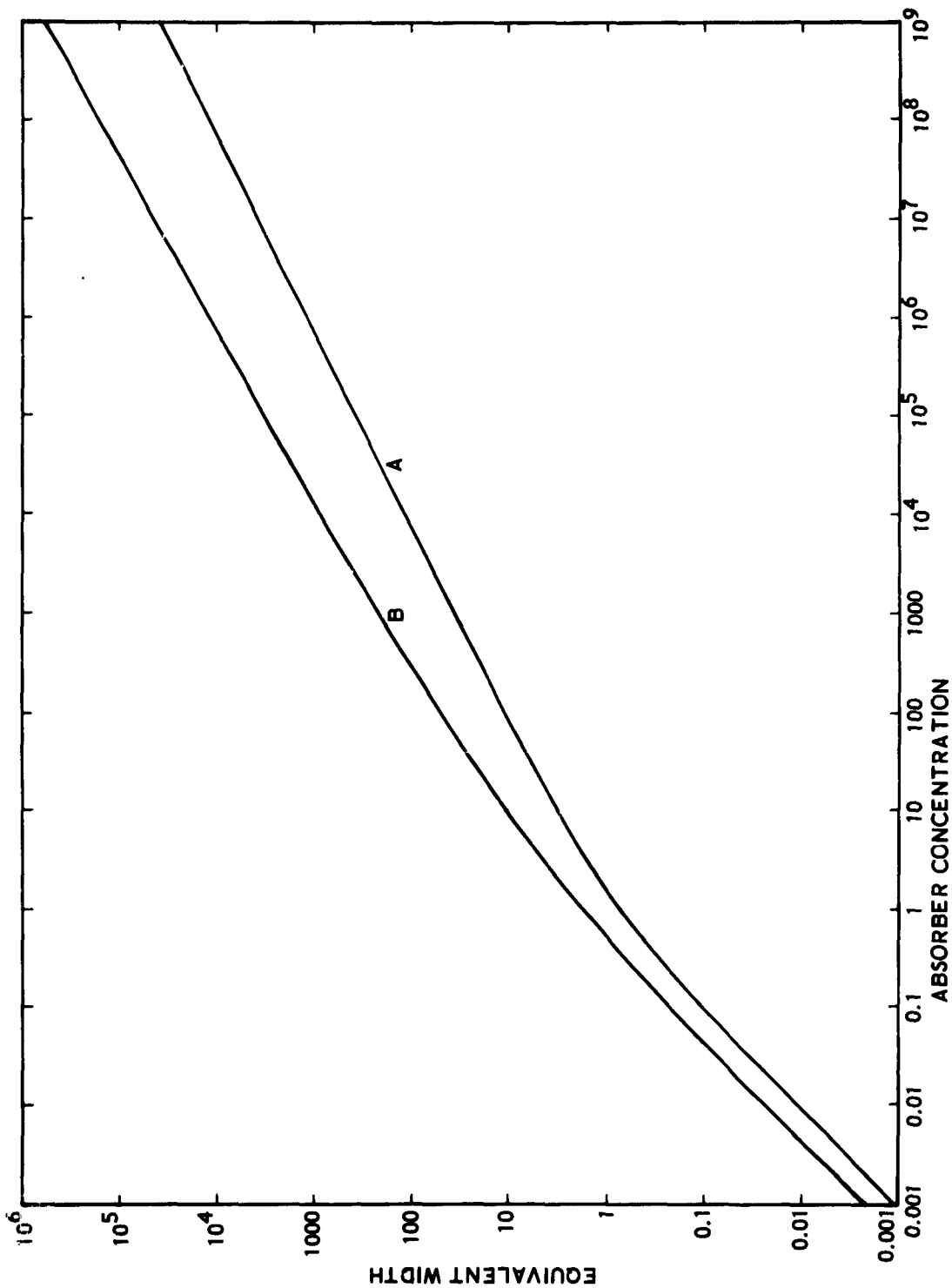
FIG. 3. The equivalent width at constant pressure as a function of absorber concentration. The ordinate is $W_s \ell / 2\pi\alpha$ and the abscissa is $x_o = S_o u / 2\pi\alpha$. The absorption is calculated for a nonoverlapping group composed of N_o lines of intensity S_o, N_1 lines of intensity $10^{-1} S_o$, N_2 lines of intensity $10^{-2} S_o$, etc. For Curve A, all $N_i = 1$. For Curve B, $N_o = 1$, $N_1 = 10$, $N_2 = 10$, $N_3 = 10C$, $N_4 = 100$, $N_5 = 1000$, $N_6 = 1000$, etc.

absorptance curves in either the linear or square-root regions.

There is a limit to the rate at which the number of spectral lines in an intensity decade can increase as the intensity approaches zero. This limit is set by the physical requirement that the equivalent width must be a finite number. Thus, for example, the number of lines in the intensity decades S_0, $S_1 = 10^{-1} S_0$, $S_2 = 10^{-2} S_0$, ... , $S_i = 10^{-i} S_0$, ... , cannot increase indefinitely as rapidly as the series 1, 10, 100, ... , 10^i, ... , since the sum in Eq. (9) would not converge when all of the lines are in the linear region. Since there is a maximum intensity, a sufficiently short path length can always be found so that all of the lines are in the linear region.

Example B illustrates a very rapid increase in the number of weak spectral lines that does not lead to physically unreasonable conclusions. Let the number of lines N_i in the intensity decades $10^{-1} S_0$ be $N_0 = 1$, $N_1 = 10$, $N_2 = 10$, $N_3 = 100$, $N_4 = 100$, $N_5 = 1000$, ... Note that the series given in Eq. (11) would not converge if all these lines were in the strong line region, but there are always some weak lines in the linear region for any given value of x_0. The variation of the equivalent width with x_0 at constant pressure is shown in Fig. 3 as Curve B. This curve increases linearly with x_0 for $x_0 < 0.2$ and has a slope of unity on a log-log plot. As x_0 increases still further, the slope decreases at first fairly rapidly, but eventually very slowly. At $x_0 = 10^4$ the slope is approximately 0.65 while at $x_0 = 10^8$ it is 0.56. As x_0 becomes indefinitely large, the slope approaches the limiting value 0.5.

In Example B each intensity decade which is in the square-root region makes an approximately equal contribution to the absorptance. The summation in Eq. (6) converges only because there are always groups of weaker lines which are still in the linear region. A study of the numerical calculation of the absorptance in this case shows that the slope on a log-log plot at $x_0 = 10^n$ is given approximately by $0.5 \left\{ \log_{10} \left[10(1 - 0.2n^{-1})^{-1} \right] \right\}$ when $n > 2$. This expression approaches one-half as n becomes large.

It is difficult to imagine how the number of weak lines per intensity decade could increase much more rapidly as the intensity decreases than in Example B. If the increase were much more rapid, the summation in Eq. (9) would not converge. Thus, Example B may be considered as a rather extreme example of numerous weak lines. Even in this case the square-root approximation becomes more and more accurate as x_0 increases. However, there is a large intermediate region where neither the linear nor square-root approximation may be used.

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Of course, it would be extremely difficult to obtain experimental data over a sufficiently wide range to follow an absorptance curve such as that in Example B from the linear to the square-root region. The curve appears to have an almost constant slope over a considerable region. For example, the slope is 0.56 ± 0.02 from $10^6 \leq x_o \leq 10^{11}$. An experimental curve obtained in this region would appear to have a constant slope greater than one-half.

The variation of the equivalent width with pressure at constant absorber concentration for Examples A and B is shown in Fig. 4. The transition from a slope of zero to one-half as the pressure decreases occurs over a wider range of pressure than when the lines all have the same intensity. The slope of Curve B only approaches one-half very slowly as the pressure decreases.

B. Band of Overlapping Spectral Lines

The influence of numerous weak spectral lines is best illustrated by considering first the absorption by a band of non-overlapping lines. However, any practical measurements on a band include a range of pressure and absorber concentrations where the lines will overlap. In order to illustrate the effect of overlapping when there are numerous weak lines, the absorptance was calculated from Eq. (7) when there is one spectral line of intensity S_o and 10^3 spectral lines of intensity $10^{-4} S_o$. A random spacing between these lines is assumed in the derivation of Eq. (7). This exponential form should not be used[5,6] for accurate work when there is only a single line of intensity S_o, but it is sufficiently accurate for the present purpose of showing the shape of the absorptance curves when the weak lines are making a significant contribution to the absorption.

Absorptance curves at constant pressure are given in Fig. 5 for this case. When the absorptance is plotted against $\beta^2 x_o$, where $\beta = 2\pi\alpha/d$ (d is the mean line spacing), the limiting curve is the strong line approximation[5,7]. In this particular example the curves do not converge on the strong line approximation nearly as rapidly as if the weak lines were not present. However, in spite of the unusual bends in some of the absorptance curves there still is a definite region of validity for the strong line approximation where the curves approach the uppermost curve of slope one-half in the figure. In this case the pressure and absorber concentration is such that both the single strong line and the relatively weak lines are in the strong line region.

PRESSURE ⟶

EQUIVALENT WIDTH ⟵

A

B

100   10   1 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9}

100   10   1 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5}

FIG. 4. The equivalent width at constant absorber concentration as a function of the pressure. The ordinate is $S_O u\, W_s \ell$ and the abscissa is $2\pi\alpha/S_O u$. The absorption is calculated for a nonoverlapping group composed of N_O lines of intensity S_O, N_1 lines of intensity $10^{-1}\, S_O$, N_2 lines of intensity $10^{-2}\, S_O$, etc. For Curve A, all $N_i = 1$. For Curve B, $N_O = 1$, $N_1 = 10$, $N_2 = 10$, $N_3 = 100$, $N_4 = 100$, $N_5 = 1000$, $N_6 = 1000$, etc.
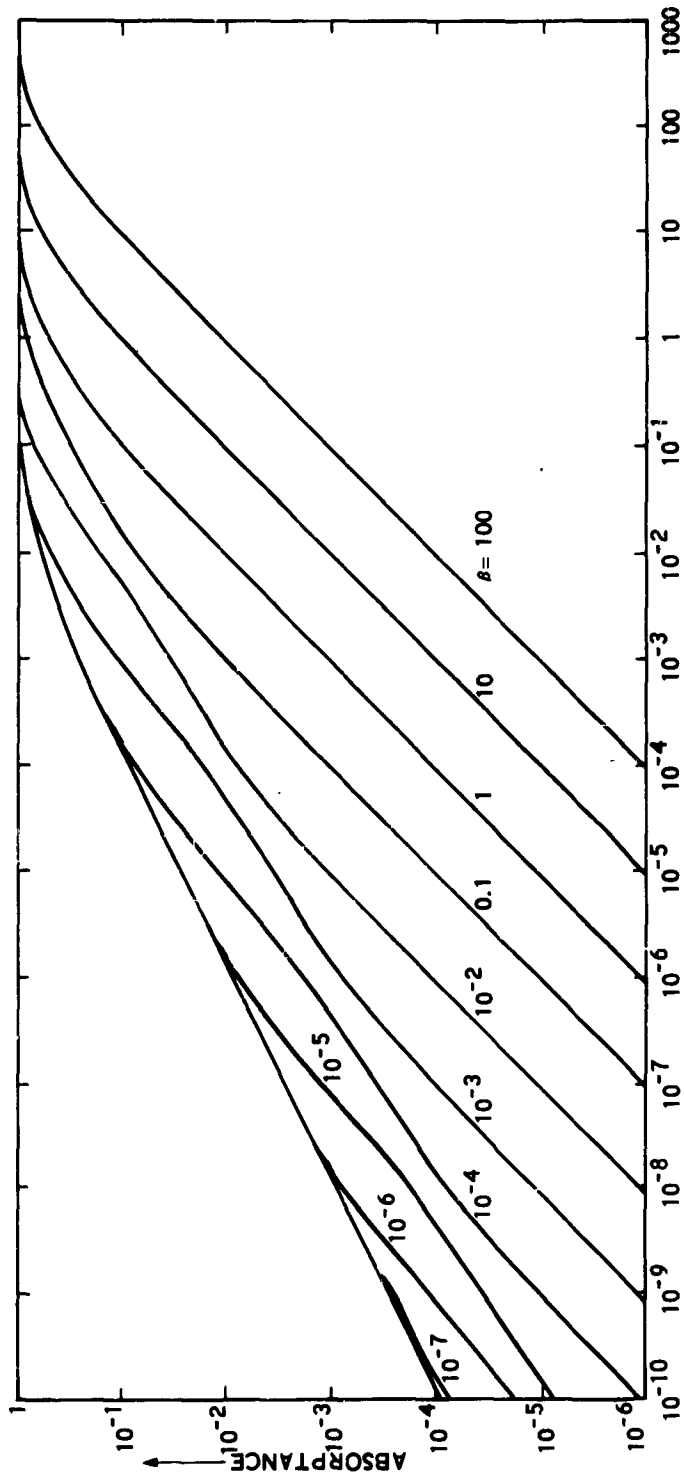
-14-

FIG. 5. The absorptance at constant pressure as a function of $\beta^2 x_o = 2\pi x\, S_o u/d^2$ (proportional to absorber concentration at a given pressure) for one spectral line of intensity S_o and 1000 spectral lines of intensity $10^{-4}\, S_o$. The overlapping of the lines is assumed to be described by the statistical model. The upper limiting curve is the strong line approximation.

In the example just discussed, there are no spectral lines weaker than $10^{-4} S_0$. About the most extreme example which can occur of larger and larger numbers of weak spectral lines as the intensity decreases is the case discussed in connection with Curve B of Figs. 3 and 4. The absorptance curves at constant pressure for this case are shown in Fig. 6. As the parameter β becomes very small, the absorptance curves have long regions where the slope is nearly constant. This slope is somewhat greater than one-half for the cases shown in Fig. 6 and only approaches one-half very slowly as β becomes still smaller. There also is no limiting strong line curve evident in this figure although the curves do crowd closer together as β decreases. Thus in this rather extreme example with rapidly increasing numbers of very weak lines there is no region where the strong line approximation is valid except in a somewhat approximate sense.

The number of weak lines in a spectral region can be determined by experimental measurements of the absorptance curves. First the effects due to overlapping of the spectral lines are separated from those due to the absorption by the weak spectral lines. This is done[5,7] by making a plot of the absorptance divided by the pressure as a function of the absorber concentration divided by the pressure. The limiting curve obtained from such a plot represents the equivalent width of the lines in the nonoverlapping line approximation. This is illustrated in Fig. 7 for the same intensity distribution used for Fig. 5. Each curve represents the absorptance at some fixed value of the pressure. The envelope of these curves is identical with the equivalent width curve for this case in the nonoverlapping line approximation as given in Fig. 1. Note that the unusual variations in the limiting curve between $0.2 < x_0 < 2000$ are clearly brought out by this method.

Once the effects due to the overlapping lines are eliminated by the method illustrated in Fig. 7, the experimental curves define a unique equivalent width curve for the spectral band under study. From the slope of this curve it is possible to reach at least qualitative conclusions about the number of weak lines in that portion of the spectrum. In principle if this curve could be determined accurately enough, the intensity distribution in the spectrum could be determined quantitatively. If $x_0 = S_0 u/2\pi\alpha$, where S_0 is the strongest line in the spectrum, the equivalent width curve must have a slope of nearly unity for $x_0 < 0.2$. The slope must start to decrease around $x_0 = 1$. If the slope is virtually one-half for $x_0 > 2 \times 10^n$, then there is no appreciable contribution to the absorption from weak lines with intensities less than $10^{-n} S_0$. If there is a relative maximum in the slope of the curve, there are a large number of weak lines at
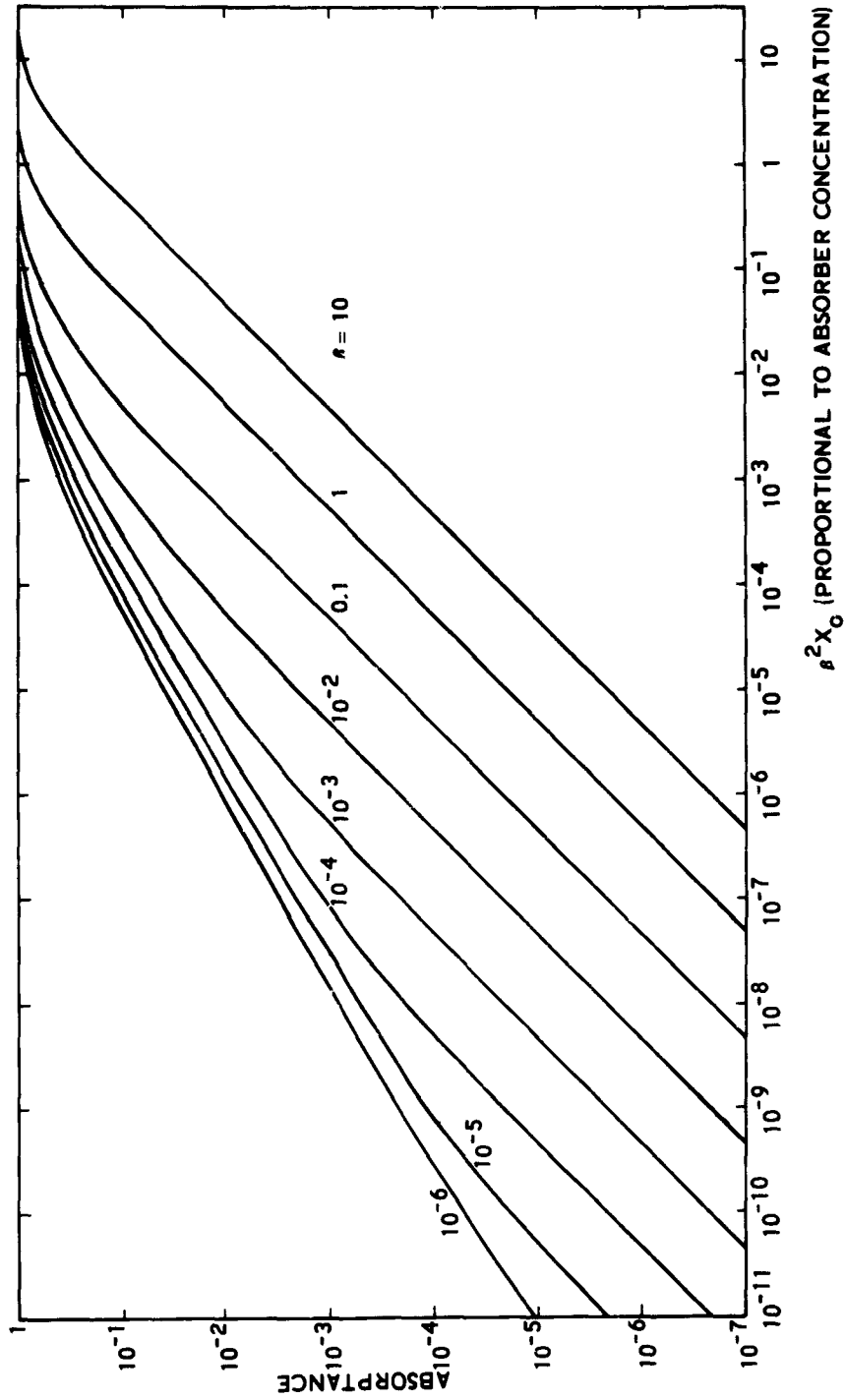
FIG. 6. The absorptance at constant pressure as a function of $\beta^2 x_0 = 2\pi\alpha S_0 u/d^2$ (proportional to absorber concentration at a given pressure) for a group of lines which has the intensity distribution given for Curve B in Fig. 3. The overlapping of the lines is assumed to be described by the statistical model.
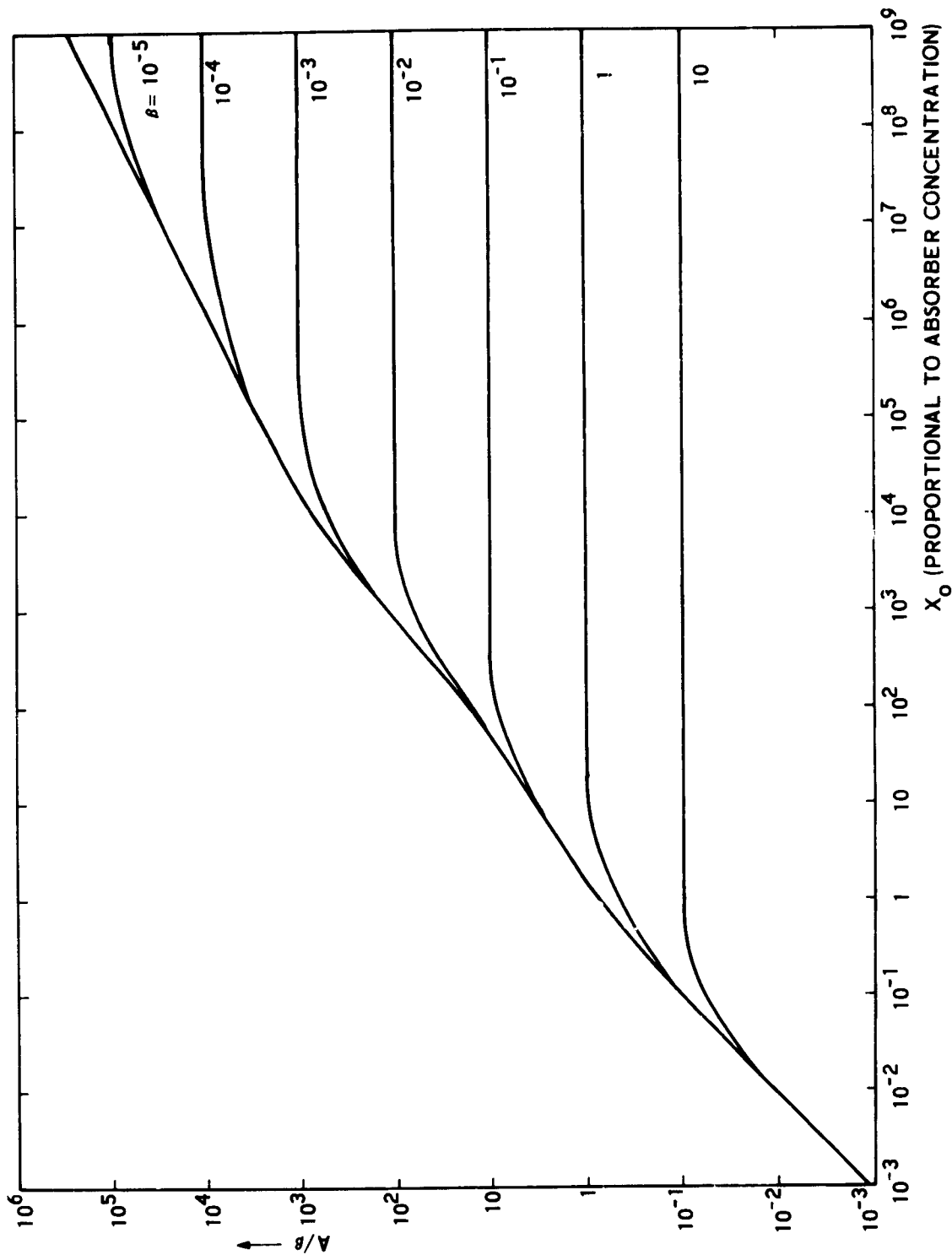
FIG. 7. The absorptance divided by β as a function of $x_o = S_ou/2\pi\alpha$ (proportional to absorber concentration at a given pressure). Curves are given for various constant values of β. The band is assumed to be composed of one spectral line of intensity S_o and 1000 spectral lines of intensity 10^{-4} S_o. The overlapping of the spectral lines is assumed to be described by the statistical model. The upper limiting curve is the nonoverlapping line approximation.

the corresponding intensity. For example, the slope of the equiva-
lent width curve in Fig. 7 has a relative maximum around $x_0 = 10^4$.
From this fact it follows immediately that there are a large number
of weak lines of intensity $10^{-4} S_0$.

A more quantitative analysis of the problem can be made
when the data warrants. The first step in this procedure is to plot
the experimental data as explaired in connection with Fig. 7. The
ordinate is chosen as the absorptance divided by the pressure and the
abscissa as the absorber concentration divided by the pressure. The
limiting curve in the nonoverlapping line approximation as determined
from such a plot of the experimental data can be written as

$$A = p \, g(u/p) , \tag{13}$$

where the function g is determined by the experiment.

However, in the nonoverlapping line approximation, the
absorptance must be given by the equivalent width divided by the mean
line spacing. For simplicity let us make the customary assumption
that all of the line widths are equal. Then from the expression for
the equivalent width given by Eq. (6) and the absorptance given by
Eq. (13), it is found that

$$g(\frac{u}{p}) = \frac{2 \pi \alpha_0}{d p_0} \sum_i N_i \, f \left(\frac{S_i p_0}{2 \pi \alpha_0} \frac{u}{p} \right) , \tag{14}$$

where $\alpha = (p/p_0) \, \alpha_0$, and α_0 is the value of the half-width at
some particular pressure p_0.

If the function g has been determined experimentally at M
different values of u/p and if M arbitrary values of the line intensity
S_i are chosen, then Eq. (14) can be inverted to obtain the number N_i
of spectral lines with each of these intensities. It should be noted
that a unique solution cannot be obtained if the function g has only
been determined in the linear region or only in the square-root region.
Some points must be determined in both of these regions for all of
the line intensities included in the analysis. A line of a particular
intensity S_i changes the shape of the absorptance curve only when x_i
is of the order of unity.

SECTION 3

CONCLUSION

The functional dependence of the absorptance on pressure and absorber concentration can be altered significantly if an appreciable number of weak spectral lines are included in the frequency interval in question. However, for sufficiently high values of the pressure and low values of the absorber concentration there exists a region where the weak line approximation is valid. In this region the absorptance varies linearly with the absorber concentration and is independent of the pressure.

Similarly, for sufficiently low values of the pressure and high values of the absorber concentration a region where the strong line approximation is valid almost always exists. In this region the absorptance is a function only of the product of pressure and absorber concentration. In Example B of Section II a case is given where the number of weak lines increases so rapidly that no region of validity exists for the strong line approximation. However, this is a somewhat unusual case which seldom occurs in practice. It is physically impossible for the number of weak lines to increase as the intensity approaches zero at a rate appreciably greater than that in this example. Furthermore, if the rate of increase is appreciably less than in this example, a region of validity for the strong line approximation exists.

The principal effect of numerous weak lines is to change the nature of the absorptance curves in the intermediate region between the regions of validity of the weak and strong line approximations. First, these weak lines may greatly increase the range of

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pressure and absorber concentration over which neither the weak nor
the strong line approximation is valid, as illustrated in Figs. 1,
3, 5, and 6. Second, the absorptance curves may no longer have a
derivative which increases or decreases continuously along the curve
as is the case for the familiar absorptance curves for spectral lines
all of which have the same intensity. Instead the weak lines may
introduce points of inflection in the absorptance curves as illustrated
in Figs. 1, 2, 5, and 7. From the shape of the experimentally
determined absorptance curves it is possible to deduce the number of
weak lines of various intensities which make a significant contribu-
tion to the absorption.

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