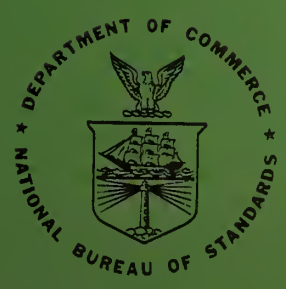# NBS TECHNICAL NOTE

476

Line Emission Sources for Concentration Measurements and Photochemistry

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

● Physics and Chemistry

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $6.00; foreign, $7.25*.

● Mathematical Sciences

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75*.

● Engineering and Instrumentation

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, $2.75; foreign, $3.50*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—*for engineers, chemists, physicists, research managers, product-development managers, and company executives*. Annual subscription: Domestic, $3.00; foreign, $4.00*.

*Difference in price is due to extra cost of foreign mailing.

Order NBS publications from: Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

Federal Information Processing Standards Publications. This series is the official publication within the Federal Government for information on standards adopted and promulgated under the Public Law 89–306, and Bureau of the Budget Circular A–86 entitled, Standardization of Data Elements and Codes in Data Systems.

CLEARINGHOUSE

The Clearinghouse for Federal Scientific and Technical Information, operated by NBS, supplies unclassified information related to Government-generated science and technology in defense, space, atomic energy, and other national programs. For further information on Clearinghouse services, write:

Clearinghouse
U.S. Department of Commerce
Springfield, Virginia 22151

NBS TECHNICAL NOTE 476

Line Emission Sources for Concentration Measurements and Photochemistry

Walter Braun and Tucker Carrington

Physical Chemistry Division
Institute for Basic Standards
National Bureau of Standards
Washington, D.C. 20234

CONTENTS

Line Emission Sources for Concentration Measurements and Photochemistry

Walter Braun and Tucker Carrington[*]

Abstract

When a resonance line is absorbed in its own gas, measurements
of this absorption can be used to derive a value of the
product, nf, of concentration of the absorber and f value of
the transition. This line absorption process is also
important in the study of fluorescence and photochemistry,
where it is possible to produce atoms or molecules in a
single quantum state without otherwise disturbing the system.
The interpretation and success of these applications of line
absorption depend critically on the shape of the line emitted
by the light source. This is strongly influenced by the
optical depth in the emitting region, and by the inevitable
presence of a reversing layer through which the light must
travel on its way out of the lamp. This paper presents a
simple model which can be used to estimate the effects of
these properties of the light source on the threshold and
sensitivity of measurements of nf, and on the power which
can be delivered to absorbing atoms outside the lamp.
Emphasis is on the general principles of lamp design and
diagnosis, rather than on accurate description of a particular
lamp.

Key words: Spectroscopy; photochemistry; analysis; gas;
vacuum ultraviolet; absorption.

INTRODUCTION

In spectroscopic observations designed to determine the concentration
or f value of atoms or molecules forming an absorption line, one can use
either a light source which emits a continuum[1,2] or one which emits
a discrete spectrum.[3] In either case, we want to relate the observed
attenuation of the incident light beam to the product nf of the f value
and number of absorbing atoms traversed by the beam. When a continuum
is used, its intensity can be assumed to be independent of frequency over
the range where absorption is significant, so that the wavelength
dependence of the light source intensity is unimportant. The resolving
power of the spectrometer is however very important in determining the
sensitivity with which absorption by a narrow line can be detected and
measured.[1,4,5] If on the other hand, the light source is not a continuum,

[*]Present address: York University, Toronto, Canada.

but instead emits a relatively sharp line whose center coincides with that of the absorption line, we are freed from the requirement of high resolution of the spectrometer (assuming we are concerned with a single line) but the intensity distribution in the emission line becomes of critical importance. This distribution is strongly influenced by self absorption and reversal in the light source.

This paper illustrates and discusses the effects of the intensity distribution in the emission line on two somewhat different types of absorption measurements. In one case, one measures the fraction of incident light which is absorbed, and relates this to the product, nf, of absorber concentration and f value for the transition, using curves analogous to the curve of growth familiar in connection with continuum light sources. In such measurements, the absolute intensity of the light source may be of little interest. Absolute measurement of the absorber concentration is possible if the f value, or integrated absorption co-efficient of the transition is known.[3,6] If the f value is unknown, empirical calibration curves can be constructed.[7] Absorption measurements can be used to derive f values if the concentration of absorbers can be independently measured.[8-11]

In a second type of absorption measurement, one is primarily inter-ested in maximizing the absolute rate of absorption of energy in a gas irradiated by the lamp in question. An example is the measurement of absorber concentration by measurement of the intensity of re-emission (fluorescence) of the absorbed light. In many cases this method is quite sensitive.[12] Another application is to photochemical or photosensitized processes, where, as in the fluorescence method, one is simply interested in the rate of absorption of energy from a line emission source.[13]

In Section I we define the simple three layer model used to treat a lamp consisting of an optically thick emitter (1) with a separate reversing layer (2) and an external absorbing layer (3). In Section II this model is used to derive a relationship, analogous to a curve of growth, relating total absorption to optical depth in the absorbing layer, assuming Doppler shapes for the absorption coefficients, and different temperatures in each layer. The effect of the reversing layer in the light source on the sensitivity and linearity of the method are illustrated and discussed. Section III discusses effects of parameters of the light source (optical depth of emitting and reversing layers) on the sensitivity of the fluorescence method, i.e. on the rate of absorption of energy in layer 3. A lamp which is optimum in this respect will not, in general, be optically thin. After this discussion of the importance of the optical depth of emitting and reversing layers in the light source, a method of estimating these parameters for lamps emitting multiplet lines is discussed in Section IV. There follows in Section V a brief discussion of the application of these ideas to practical measurements.

I.   THE THREE LAYER MODEL

Figure 1 illustrates the model, an optically thick emitter whose radiation is transmitted through a reversing layer and then through a separate absorbing layer.   A more complicated model, including smooth gradients of concentration rather than separation into layers, has been treated by Hooymayers,[14] for application to flames.   Another continuum model has been treated by Cowan and Dieke[15].   In this reference the general quantitative aspects of the mechanism of self-absorption particularly in arc discharges is discussed in detail.   The specific layer model we adopt here is similar to that suggested by Bleeker.[16]   This model has not been treated by Cowan and Dieke but falls between their two extreme cases (a) where the emitting and absorbing atoms are uniformly distributed in the discharge and (b) where the emitting and absorbing atoms are completely separated.   Since Cowan and Dieke found that the general line intensity distribution depends very little on the particular spatial distribution function describing the emitting and absorbing atoms the simplified layer distribution model adopted here should very adequately describe the end-on type discharges characterized in this paper.

The three layers shown in Figure 1 will in general have different temperatures and optical densities of absorbers.   The lamp is character-ized by the number of emitting atoms (which we assume to be much smaller than the number of absorbing atoms) and by the optical depth (at the center of the line) and temperature in layers 1 and 2.   To write an expression for the intensity emitted from layer 1 we need the path length ℓ, populations of absorber and emitter n and n', statistical weights g and g', and absorption cross section $\sigma(\nu)$.   Subscript numbers refer to the layer in question and the prime denotes the upper level.   The intensity emitted from layer 1 is then[17]

$$I_1(\nu) = B(\nu, T_{ex})J_1(\nu) \ J \ cm^{-2}s^{-1}sr^{-1}(s^{-1})^{-1} \qquad (1)$$

where $B(\nu)$ is the Planck function with temperature T_{ex} defined for the first layer by

$$\frac{n'}{g'}/\frac{n}{g} = exp \ - \ (E'-E)/kT_{ex} \qquad (2)$$

and J_1 is the emissivity,

$$J_1(\nu) = 1 - exp(-\sigma(\nu)n_1\ell_1). \qquad (3)$$

In the usual case, when $n' \ll n$ and ν^3 is nearly constant over the line, we have the proportionality

$$I_1(\nu) \propto \frac{n'}{g'} \ \frac{g}{n} \ J_1(\nu) \qquad (4)$$

3

The intensities transmitted through layers 2 and 3 are then simply obtained from this by multiplying by the factor $\exp(-\sigma(\nu)n\ell)$ for one or both of these layers.

Use of these expressions requires knowledge of the magnitude and frequency dependence of σ. These problems are separated by defining

$$\sigma(\nu) = s(\nu) \int \sigma(\nu)d\nu, \qquad \int s(\nu)d\nu = 1 \qquad (5)$$

The integral of the cross section is then equivalent to the absorption transition probability in its various forms,

$$\int \sigma(\nu)d\nu = \frac{h\nu \, B}{c} = \frac{\pi e^2 f}{mc}. \qquad (6)$$

All integrals are extended over the range $-\infty$ to $+\infty$. The line shape factor $s(\nu)$, in its dependence on ν and T for the three layers, has a profound effect on the absorption in layer 3. In the work presented here we will assume pure Doppler broadening for which

$$s(\nu) = \frac{1}{\sqrt{\pi} \, \delta} \, \exp \, -\left(\frac{\nu - \nu_0}{\delta}\right)^2. \qquad (7)$$

This is appropriate to many low pressure systems with transitions in the ultraviolet, and it is just such systems which are of interest in the measurement of concentrations of ground states of atoms by the line absorption method, and in many photochemical experiments. Lorentz or Voight profiles[18,19] could be used instead of the Doppler form, with some increase in computing time.

We are now in a position to calculate $I(\nu)$ and I, its integral over frequency, for light emitted from each of the three layers. In the first group of calculations we have chosen the Doppler temperatures $T_1 = 700$, $T_2 = 350$, $T_3 = 300$ K, though in most of the following only the ratios are important. With these fixed, $J_1 = \int J_1(\nu)d\nu$ depends only on the optical depth at the center of the line, $D_1 = \sigma_1(0)n_1\ell_1$. J_2, the integral of $J_2(\nu)$, depends on D_2 as well as D_1,

$$J_2 = \int [1 - \exp(-\sigma_1(\nu)n_1\ell_1)] \exp(-\sigma_2(\nu)n_2\ell_2)d\nu \qquad (8)$$

and similarly J_3 depends on all the optical depths,

$$J_3 = \int [1 - \exp(-\sigma_1(\nu)n_1\ell_1)] \exp(-\sigma_2(\nu)n_2\ell_2) \exp(-\sigma_3(\nu)n_3\ell_3)d\nu. \quad (9)$$

Here the $\sigma(\nu)$ functions are expressed in terms of (6) and (7) with the Doppler widths δ appropriate to each temperature. As in Eq. (4), we have the proportionalities

$$I_2 \propto \frac{n'}{g'} \cdot \frac{g}{n} J_2, \quad I_3 \propto \frac{n'}{g'} \cdot \frac{g}{n} J_3 \qquad (10)$$

The calculations reported in this paper were done with the OMNITAB general purpose computer program.[20]

II. INTEGRATED ABSORPTION

The integrated absorption in layer 3, $(I_2-I_3)/I_2$, depends strongly on the characteristics of the lamp, that is on the optical depths in layers one and two. The curves in Fig. 2 show this dependence on optical depth in the reversing layer. The curves have two properties of interest. The smallest D_3 which can be detected (corresponding for example to 1% absorption) depends strongly on D_2. The sensitivity, in this sense of detection limit, is greatly decreased by absorption in the reversing layer. The second important property of these curves is the slope, which is related to sensitivity in the sense of distinguishing one value of D_3 from another. As is to be expected, all the curves have unit slope at sufficiently small D_3, but for the curves corresponding to relatively large D_2, this region of unit slope extends to higher D_3 than for the other curves. This is because the lamp emits relatively little light at the center of the absorption line, so that the effective optical depth in layer 3 is much less than D_3, the optical depth at the center of the line. Since it is only in this region of unit slope that the integrated absorption is simply proportional to D_3, the presence of a reversing layer in the lamp does give a certain advantage in the measurement of large D_3 values. Another way of saying this is that although all the curves in Fig. 2 level off toward unity at sufficiently high D_3, the curves for large D_2 do so more slowly, and thus retain a useful dependence on D_3 up to higher D_3 values.

III. ABSORBED POWER

For fluorescence, and for photochemical applications, the quantity of

5

interest is the absolute rate of absorption of energy in layer 3, I_2-I_3, rather than the normalized absorption $(I_2-I_3)/I_2$ just discussed. The absolute rate of absorption also depends strongly on lamp parameters, as is illustrated in Fig. 3, showing curves of I_2-I_3 for various ratios D_2/D_1. For all cases where $D_2 \neq 0$, the curve goes through a maximum, and the height and width of this maximum decrease strongly as D_2/D_1 increases. Though the presence of a reversing layer is frequently unavoidable in practical light sources, Fig. 3 emphasizes its profoundly detrimental effect on absorbed power, and hence on the intensity of fluorescence or the rate of a photochemical process. The assumption of $D_2/D_1 = const$ with D_1 as independent variable in Fig. 3 corresponds to a type A lamp in which increasing the power input increases the density of absorbing atoms (for example H in a He discharge containing a trace of H_2) in the emitting layer and hence in the reversing layer also, but does not change the excitation temperature. Alternatively, the plot in Fig. 3 also corresponds to the change of I_2-I_3 on increasing addition of an active species, i.e., H_2 to an inert gas discharge, since in this case too, D_2 will be approximately proportional to D_1, in this case I_2-I_3 is proportional, for example, to the rate of absorption of Ly α in layer 3.

In a lamp for which I_2-I_3 is a maximum it will generally be impossible to make $D_2 = 0$, hence it is necessary to be able to predict lamp performance when D_1 and D_2 are not negligibly small.

If one is interested in absorption by a continuum rather than a line, in layer 3, there is no need to worry about matching of emission and absorption line shapes, and one must simply maximize I_2. This criterion can lead to lamps with very large optical depths in the emitter. In the case of Kr, resonance lamps which have been described as optimum[21,22] have optical depths at the center of the line of the order of 10^3 per cm of length in the emitting layer.

<center>IV. MULTIPLET LINES AND
LAMP DIAGNOSIS</center>

Up to now we have discussed only single, isolated lines. We may be concerned instead with an atomic multiplet or with isotope or nuclear spin hyperfine structure. The situation is the same as for a single isolated line only in the limiting case in which the line separation is much less than the width of the shape function $s(\nu)$ for a single line. In this case the shape function is the same as that for a single line, but the integral of the absorption cross section is correspondingly larger. In the opposite limiting case, when the lines are so well separated that they do not significantly overlap, but all are nevertheless transmitted by the spectrometer or filter used with the detector, the results for single lines must be appropriately averaged. In the quantity I_2-I_3/I_2, the weighting factor for each line is just the fraction of the total observed intensity of the multiplet due to that line. If the lines are neither coincident nor well separated, their overlap

<center>6</center>

produces a complex line shape which is the sum of the shape factors for the component lines, suitably displaced and weighted according to the relative intensities. The integral of the composite absorption coefficient is the integral for the weakest line (assigned a relative strength of unity) times the sum of the relative strengths, nf, of all the lines. For multiplets obeying L-S coupling, with populations proportional to degeneracy, these relative strengths, gf, are conveniently tabulated.[23]

The discussion in Sections II and III has emphasized the importance of the parameters D_1 and especially D_2 of the light source. In many cases of practical interest these parameters can be estimated directly in light sources emitting three or more well resolved lines in the same multiplet. If D_1 and D_2 are large enough so that the behavior of the light source differs significantly from that characteristic of the small optical depth limit, the relative intensities of the multiplet lines in emission will differ from the theoretical values (or the limiting values at small optical depth). D_1 and D_2 may be estimated from the observed intensity ratios. For simplicity we will first discuss the case of a triplet with common upper level in which each line is resolved by the spectrometer. We then have two independent observable intensity ratios for use in estimating D_1 and D_2.

In Figure 4, calculations for a two layer model are compared with experimental relative intensities [21,25] of the components of the oxygen I triplet ($^3P_{2,1,0}-^3S$) near 1302Å. In this particular plot the optical depth in the weakest line in the reversing layer is assumed to be one-half its value in the emitting layer. A family of such plots can be constructed for various ratios, N, of this optical depth in the two layers. One procedure in lamp diagnosis is to choose from this family a plot which gives both of the observed intensity ratios at the same value of the abscissa. This value of the abscissa gives D_1, and the N value associated with the particular set of curves gives D_2, both for the weakest line. In calculating such curves, it is sometimes inappropriate to assume that the relative population in the multiplet levels corresponds to equilibrium at the kinetic temperature of the gas, or that the populations are in the ratio of the statistical weights (infinite temperature). In some cases values of the population ratios intermediate between these extremes must be chosen, and adjusted to get agreement with the observed relative intensities. This assumption of relative populations, plus experimental or theoretical gf values for the transitions in the multiplet, is sufficient to determine curves such as those in Fig. 4, using Eqs. (8) and (10). At small values of D_1, the ratios of intensities approach the ratios of the theoretical gf values, 5:3:1 for this oxygen multiplet. At higher optical depths the curves bend over in such a way that the intensity ratios are strongly altered, and even inverted, due to the reversing layer.

An interesting feature of these curves is the existence of a maximum at moderate optical depths when T_2 is equal to or only slightly less than T_1. This is due to the fact that I_1 cannot exceed the black body

intensity corresponding to the assumed excitation temperature, while the fraction of light transmitted by layer 2 can decrease to values arbitrarily near zero as D_2 is increased. If T_2 is sufficiently smaller than T_1, there will be no maximum, since the reversing layer cannot absorb light in the wings of the emission line. At intermediate values of T_2, the maximum in the I_2 vs D_1 curve will be followed by a minimum. All these results are consequences of the assumption that the excitation temperature is at least approximately independent of changes in discharge power, which affect only the densities of emitter and absorber, but not their ratio.

If the energy splitting in the multiplet is small compared to kT_1, the levels will be populated nearly in the ratio of their statistical weights whether or not they are strictly in thermal equilibrium. If the splitting is large, their relative population will be unknown, and values must be assumed which, in combination with a chosen N value, give results consistent with observed intensity ratios of the multiplet.

As a second example of lamp diagnosis, we have carried out this procedure with measurements of intensity ratios in the Cl I multiplet near 1350Å, emitted from a microwave discharge in 1 torr (133 Nm^{-2}) He containing 1% Cl[25]. The results are quite sensitive to values of the optical depth and to the population ratios in the lower levels of the multiplet. For example, photoelectric measurements of the intensity ratio 1364Å/1347Å of lines from the common upper level $^2P_{3/2}$ give the value 4/1, whereas the corresponding gf ratio for these lines is 1/5. The other pair of lines in this multiplet, from the upper level $^2P_{\frac{1}{2}}$, has an intensity ratio of 2.5 and the corresponding gf ratio is 2. These observations can only be explained by assuming large optical depths, and that the ratio Cl$^2P_{\frac{1}{2}}/^2P_{3/2}$ of population of the lower levels of the two transitions is much larger than the equilibrium value at any temperature which could reasonably exist in the lamp. Although the parameters characterising the lamp (optical depths, multiplet population ratios, Doppler temperature) are more numerous than the observations (two independent intensity ratios) other physical constraints on the parameters make it possible to estimate them within reasonably narrow bounds for a given lamp.

The results for Cl are however somewhat uncertain due to our lack of knowledge of isotope and hyperfine splittings in the multiplet involved. The nuclear spin splitting observed in the ground state is too small to be significant.[26] Splittings in the upper state have never been observed and are likely to be small compared to the Doppler width of 0.2 cm^{-1}.[27] If hyperfine splitting comparable to the Doppler width is present, the qualitative result that the population in the ground multiplet levels is out of equilibrium would not be affected.

V. DISCUSSION

In recent years the line absorption method has been applied both to the measurement of atom concentrations, and to the determination of f

values. The question of line shape and optical depth is of great importance in both cases. The work of Parkes, Keyser, and Kaufman[8] on f values for resonance lines of O represents the ideal case in which the light source was designed to reduce D_1 and D_2 to negligible magnitudes, thus avoiding the complications discussed in this paper. In other work aimed at the determination of f values or concentrations, the light source was not optically thin, and accounting for this considerably complicated interpretation of the results.[6,10] It has been a common practice to assume that $I_1(\nu)$, the frequency distribution of intensity from the emitting layer, has a Doppler shape, and to describe effects of optical depth in this layer by using an unnaturally large width, or "temperature" in this shape function. In Fig. 5 we compare this approximation with the correct treatment outlined in the preceding sections, using curves like those in Fig. 2. Even though the pure Doppler approximation will give a good fit to the exact curve in many cases, the "temperature" which must be used has no physical significance, and will depend strongly on the optical depth in the emitting layer. On the other hand, when optical depth in the emitting layer is treated correctly, a measured value of T_1, obtained for example by the pressure increase method[8], can be used directly.

Most of the results we have given apply to the problem of allowing for self reversal in the interpretation of line absorption measurements. Since self-reversal is undesirable from almost every point of view, it is clearly better to reduce it than to correct for it with extensive calculations. It is then appropriate to ask to what extent self-reversal can be reduced to insignificant values without greatly decreasing the total effective intensity of the lamp.[21] Here it is necessary to distinguish two different types of lamps. Let us call type A lamps those in which absorbing atoms are formed only by the discharge itself, along with the excited atoms which radiate. Absorbing atoms will then be removed by diffusion to the wall, and perhaps by chemical processes in the volume. A typical example of type A lamps is a discharge in He with a trace of H_2 emitting the Lyman α line of H. In type B lamps, on the other hand, the absorbing atoms are unreactive and are present more or less uniformly through the gas volume. A typical example here is a Kr resonance lamp. In either of these cases, it is convenient to think of a trace additive, H_2 or Kr, being added to a much larger amount of He or other carrier gas in which the discharge is maintained.

In many cases in the vacuum ultraviolet it is impractical to run the discharge directly against the window, since this may decrease its transparency, or contamination may develop from the window sealing material. If the discharge cannot be operated directly against the window, there will certainly be a reversing layer in either type of lamp, and in type B discharges the optical depth of this layer will be proportional to the distance between the discharge and the window.

If the discharge can be operated against the window, the structure of the reversing layer is determined by gradients of absorber and emitter

9

density between the uniform discharge (if it has a uniform region) and the wall or window. In constricted discharges these gradients will be large, particularly for the emitting atoms, and in general the gradient for the emitters will be steeper than that for the absorbers. This situation is equivalent to the presence of an absorbing layer. In type B lamps the gradient of absorbers will be small, and their concentration may even be higher near the wall than at the center of the discharge if there is an appreciable radical temperature gradient near the wall. In type A lamps the gradient of absorber concentration toward the wall will be largely determined by the diffusion rate and the efficiency of removal of absorbers at the wall. If this removal is inefficient, the ratio n'/n will become small toward the wall and this will constitute a reversing layer. Note that a two-layer light source (Fig. 1) can produce a self reversed line shape even if the two layers are at the same Doppler temperature, provided that n'/n in the second layer is sufficiently small and that layer 1 is not optically thin.

The preceding discussion indicates that, due to wall effects, an absorbing layer will be present in any lamp. The optical depth of this layer can be reduced arbitrarily by simply reducing to sufficiently low values the concentration of the species from which the emitter is produced (H_2, Kr). Figure 3 indicates that this will also reduce the effective output of the lamp. The lamp with maximum efficiency, that is, which puts the maximum power into layer 3, will not be optically thin, and this fact must be allowed for in interpreting the results. The absorption cross section at the center of a strong atomic line Doppler broadened at room temperature can easily be as high as 10^{-13} cm^2. In this case a pressure of 1 m torr ($\sim .1$ Nm^{-2}) of absorbing atoms (H, Kr) in a 1 cm path length gives an optical depth of 3. In such cases, careful control of the additive concentration is required to avoid a greater than optimum optical depth.

Interpretation of observations on the oxygen and chlorine multiplets in terms of the two layer model leads to several generalizations applicable to microwave discharges. These may be helpful in more refined calculations or calculations for other line multiplets. The results can be summarized as follows:

a) The reversing layer 2 is best considered as a continuation of the emitting layer 1 with the Doppler temperature T_2 only slightly less than T_1.

b) The length of layer 2 is less than layer 1 as should be typical of the type A discharge defined above.

c) The optical density of layer 2 depends not only on the physical length of this layer, but is particularly sensitive to the relative population of atoms in the ground state multiplet levels. These populations

are in general not fixed by the Doppler temperature of the layer since the system is often far from being at thermal equilibrium.

d) The discharge temperature is determined primarily by the carrier gas so that the temperature of the discharge and the ratio T_1/T_2 for one line source may apply rather well to that of a different line source.

VI.   APPENDIX

The model discussed in I assumes that there is no emission from layers 2 and 3. Since light is being absorbed in these layers, it is producing excited atoms and these can radiate[8] if they are not otherwise deactivated. In the preceding discussion we have not allowed for this radiation. It is the purpose of this appendix to do so in a very crude and qualitative way.

Taking layer 3 as an example, the problem has two parts. One is to estimate the steady state concentration of emitters as a function of depth in the layer, and the other is to estimate the total intensity radiated from the layer by these emitters. This second part is similar to the calculation made for layer 1, except that in that case the emitter concentration was assumed constant within the layer.

Up to now our treatment has described plane parallel layers, although we have had in mind a cylindrical discharge tube viewed end-on. Now we must include the effects of cylindrical geometry, particularly the escape of photons perpendicular to the tube axis through a gas that may not be optically thin. The concentration of emitters at a given cross section of the cylinder will be determined, roughly speaking, by the balance between their rate of formation by absorption of light in that volume element, and the rate loss by radiation (or diffusion) of photons radially toward the tube walls. If we take the effective diffusion constant to be[3] $D = [(2\bar{\sigma} n)^2 \tau]^{-1}$ then the mean time required to diffuse the average distance R/2 is $t = \tau \bar{D}_R^2$. Here τ is the radiative lifetime of the transition and $\bar{D}_R$ is the average (over frequency) optical depth in the radial direction. This form for the diffusion time suggests that a reasonable qualitative form for the rate constant for escape of photons would be

$$\frac{1}{t_{escape}} = [\tau(1 + \bar{D}_R^2)]^{-1} \tag{11}$$

Balancing this rate of escape (the net destruction rate for n') against the rate of formation by absorption of light gives as the estimate of the emitter concentration

$$n'(\ell) = \bar{\bar{\sigma}}(\ell)n \tau (1 + \bar{D}_R^2) \ I_2 \exp(-n \int_0^\ell \bar{\bar{\sigma}}(\ell)d\ell) \qquad (12)$$

The average optical depths or cross sections appearing here and below hide a good deal of complexity, but, with the exception of $\bar{D}_R$, they can all be defined rigorously in terms of the sorts of integrals we have previously evaluated.

When Eq. (12) is used to calculate the intensity due to fluorescence, and this is combined with $I_3^{(tr)}$, the directly transmitted intensity of I_2 through layer 3, the result for the total intensity per unit solid angle leaving layer 3 is

$$I_3 = I_3^{(tr)}\left[1 + \frac{\bar{\bar{D}}(1 + \bar{D}_R^2)}{\bar{D} - \bar{\bar{D}}} \ (1 - e^{-(\bar{D}-\bar{\bar{D}})})\right]. \qquad (13)$$

Since this result is only intended as a rough estimate, it is sufficient to say that $\bar{\bar{D}}$ is an average optical depth appropriate to light with the frequency distribution $I_2(\nu)$, while $\bar{D}$ is appropriate for emission with a pure Doppler distribution at the same temperature as the absorber, i.e., the scattered light in layer 3. If $I_2(\nu)$ is strongly broadened due to large D_1, or reversed due to large D_2, we will have $\bar{\bar{D}} \ll D_3$. We may expect on the other hand that $\bar{D} \lesssim D_3$ except for very high D_3. In Eq. (13) the term

$$\frac{1 - e^{-(\bar{D}-\bar{\bar{D}})}}{\bar{D} - \bar{\bar{D}}}$$

is unity only in the limit $\bar{\bar{D}} \to \bar{D}$ and decreases as $\bar{D} - \bar{\bar{D}}$ increases. In well designed lamps $\bar{D}_R$ will seldom be greater than 1, so the correction to $I^{(tr)}$ due to fluorescent emission will be of the order of $\bar{\bar{D}}$, perhaps reduced by a factor of two or so due to the $\bar{D} - \bar{\bar{D}}$ term. Calculations indicate that $\bar{\bar{D}}$ will be small even when D_3 is not small, for many practical lamps. When D_3 itself is small, $\bar{\bar{D}}$ is smaller still. Whenever the fluorescent emission is a small fraction of the transmitted intensity, it can be roughly estimated using Eq. (13).

In all the preceding we have been considering light intensity per unit solid angle, avoiding the unnatural constructs of parallel light and point source. We have not explicitly introduced the aperture of the

spectrometer which isolates the emission line, but in fact the geometry
of light collection is quite important when fluorescent emission is
significant.[8] If the spectrometer collects fluorescent light from a
larger volume of system than that from which it collects transmitted
light, the effects of fluorescence will be exaggerated beyond the
predictions of Eq. (13).

VII. REFERENCES

1. G. M. Lawrence, D. L. Mickey, and K. Dressler, J. Chem. Phys. 48, 1989 (1968).

2. T. Carrington, J. Chem. Phys. 31, 1243 (1959).

3. A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge Univ. Press (1934).

4. H. J. Kostkowski and A. M. Bass, J. Opt. Soc. Am. 46, 1060 (1956).

5. T. G. Kyle and J. O. Green, J. Opt. Soc. Am. 55, 895 (1965).

6. J. V. Michael and R. E. Weston, Jr., J. Chem. Phys. 45, 3632 (1966).

7. A. Walsh, in Advances in Spectroscopy 2, 1-22 (1961), edited by W. H. Thompson (Interscience).

8. D. A. Parkes, L. F. Keyser and F. Kaufman, Astrophys. J. 149, 217 (1967).

9. F. A. Morse and F. Kaufman, J. Chem. Phys. 42, 1785 (1965).

10. A. B. Prag, C. E. Fairchild, and K. C. Clark, Phys. Rev. 137A, 1358 (1965).

11. S. E. Frish and O. P. Bochkova, Vestnik Leningrad Univ. 16, Ser. Fiz. and Khim. 16, 40 (1961); Vestnik Leningrad Univ. 4, Ser. Fiz. and Khim. 1, 173 (1962) (Russian). U. S. Dept. Commerce, Office of Technical Services, Washington, D. C. 20230, AD 422 515. (English).

12. W. Braun and M. Lenzi, Dis. Faraday Soc. 44, 252 (1967).

13. H. E. Gunning and O. P. Strausz, in Advances in Photochemistry, Vol. 1, edited by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr. (Interscience, 1963).

14. H. P. Hooymayers and C. Th. J. Alkemade, J. Quant. Spectry. and Radiative Transfer 6, 501 (1966).

15. R. D. Cowan and G. H. Dieke, Rev. Mod. Phys., 20, 418 (1948).

16. W. Bleeker, Zeit. f. Physik, 52, 808 (1929).

17. S. S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities, Addison-Wesley, Reading, Mass. (1959).

18. D. G. Hummer, Mem. Roy. Astron. Soc. 70, 1 (1965).

19. H. Prugger, Optik 21, 320 (1964).

20. J. Hilsenrath, G. G. Ziegler, C. G. Messina, P. J. Walsh, and R. J. Herbold, Natl. Bur. Std. Handbook 101 (March 1966).

21. H. Okabe, J. Opt. Soc. Am. 54, 478 (1964).

22. L. J. Stief and R. J. Mataloni, Appl. Opt. 4, 1674 (1965).

23. C. W. Allen, Astrophysical Quantities, Univ. London (1963).

24. J. Vanier, Appl. Opt. 6, 167 (1967).

25. D. Davis and W. Braun, Appl. Optics 7, 2071 (1968).

26. L. Davis, Jr., B. T. Feld, C. W. Zabel, and J. R. Zacharias, Phys. Rev. 73, 525 (1948).

27. L. J. Radziemski and V. Kaufman, private communcation, to be published.

Figure 1: Three layer model for light source and absorber. T, D, and I are Doppler temperature, optical depth at center of line, and outgoing intensity.

Figure 2: "Curves of Growth" showing effect of optical depth of reversing layer on absorption. For each curve the temperature ratios are $T_1/T_2/T_3 = 1/0.5/0.39$ and $D_1 = 3$. From top to bottom, $D_2 = 0$, 3, 5, and 7.

Figure 3: Power absorbed in layer 3 as a function of D_1 for various values of the ratio D_2/D_1. For each curve $D_3 = 0.1$ and $T_1/T_2/T_3 = 1/0.5/0.39$.

Figure 4: Relative intensities of the oxygen resonance triplet $^3P_{2,1,0} - ^3S$ as a function of optical depth in the line with smallest gf. S, M, and W refer to the lines with relative gf values 5, 3, and 1. Curves are calculated, points are intensities observed[25] with addition of small amounts ($< .01\%$) of O_2 to a 2450 MHz discharge in 1 torr He. The calculations were done with the value $D_2/D_1 = 1/2$ for the line with smallest gf. The relative populations in the three levels of the ground multiplet were assumed to correspond to $T_1 = 600$ K, $T_2 = 500$ K.

Figure 5: Comparison of "curve of growth" for optically thick emitter, $D_2 = 3$ from Fig. 2, with approximation corresponding to optically thin emitter with unnaturally large Doppler temperature, T_1/T_2.
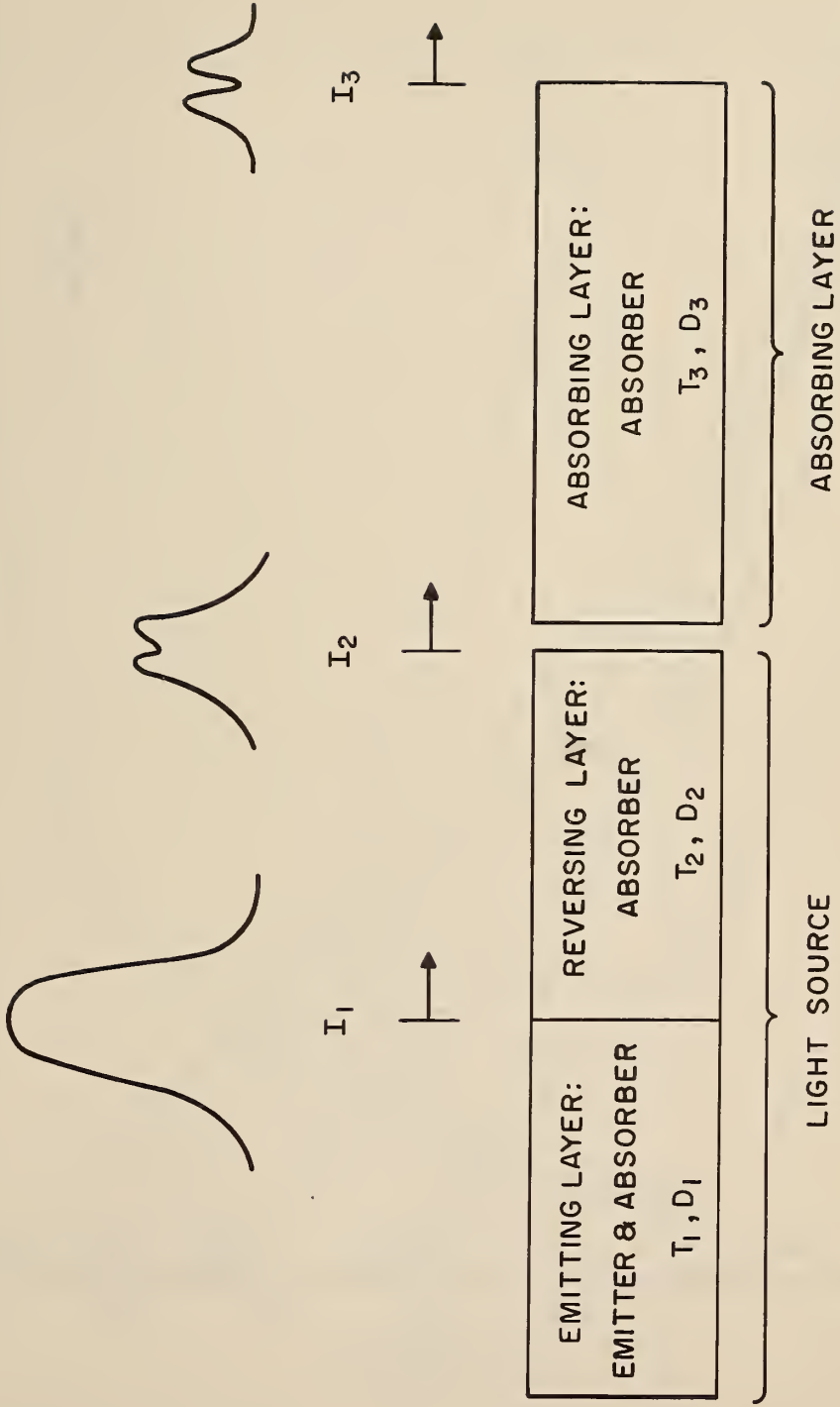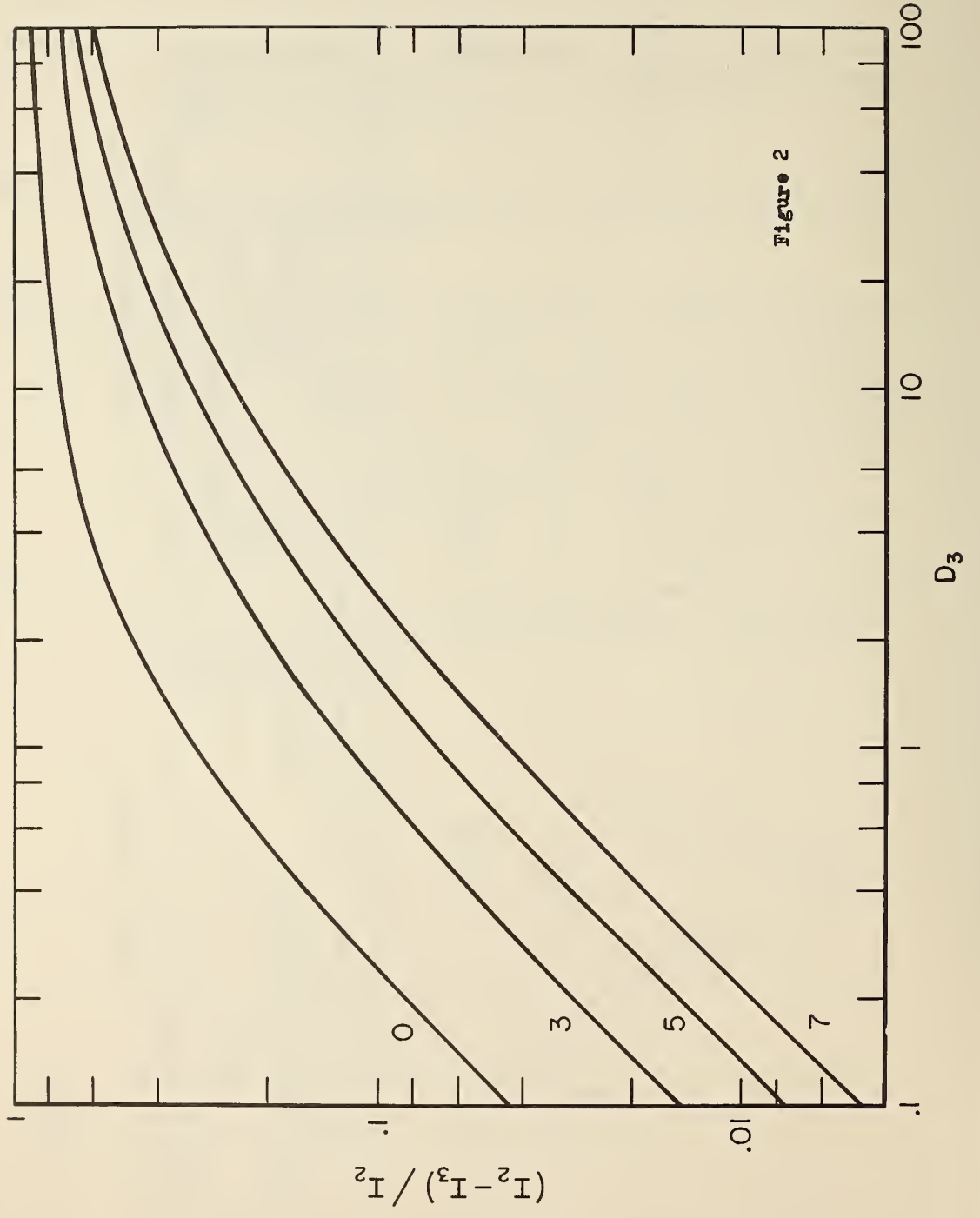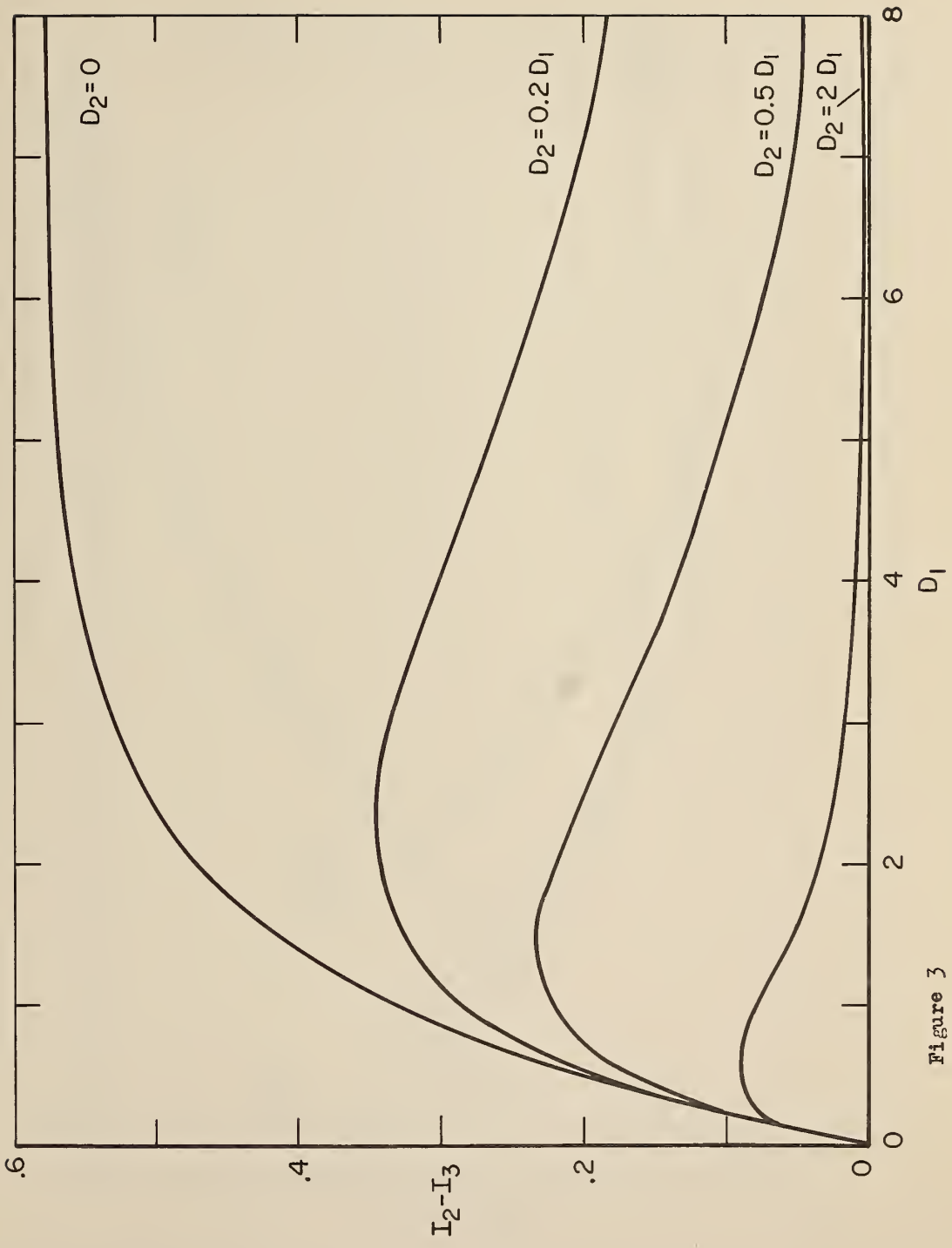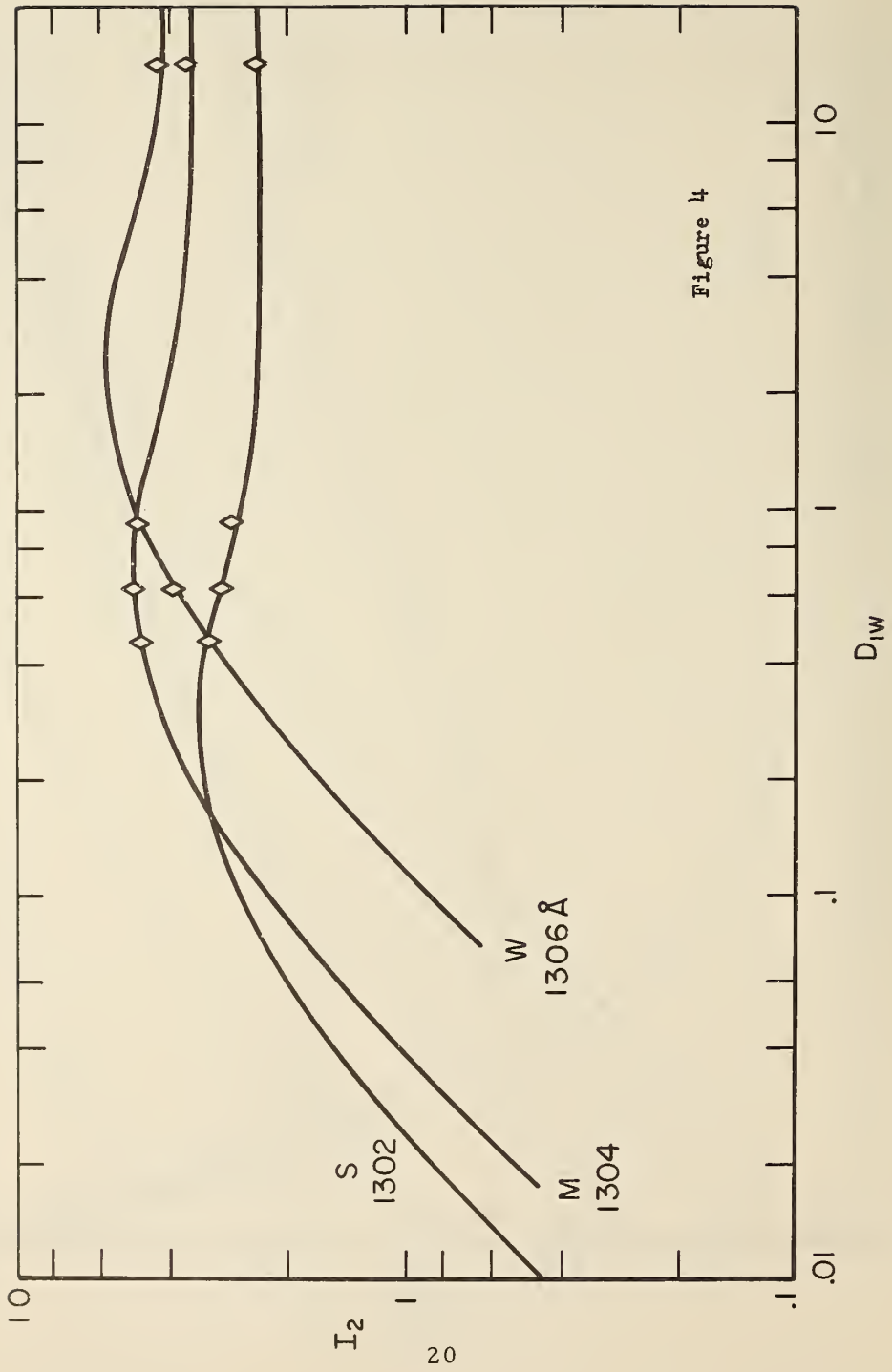
Figure 1

Figure 2

18

Figure 3

19

Figure 4

20

Figure 5

21