Self-Absorption of Spectrum Lines

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I. INTRODUCTION

WHEN light is emitted from any kind of light source, it usually has to travel from some part in the interior of the source to the outside. During this passage it is subject to absorption because there are in its path atoms or molecules of the same kind that cause the emission. The light observed outside the source is thus weakened. Different spectrum lines may be weakened to quite a different degree, and even within a single spectrum line the absorption will vary pronouncedly as a function of the wave-length. This phenomenon of absorption in the light source itself is called *self-absorption*. It may happen that the absorption at the center of the line is so much stronger than on the sides that the emerging line is darker in the center than on the sides. When this happens we speak of *self-reversal*, which is therefore only an extreme case of self-absorption.

The intensities of spectrum lines are of great importance from many points of view. They can be used to obtain transition probabilities of atoms and molecules, which are important clues for the structure of the atoms or molecules concerned. The intensity distribution within one line can be used for obtaining important data on the physical nature of the gas or vapor that emits the line. For the industrial spectrographer the relative intensities are a means of obtaining the concentration of a particular element in a mixture. In all these cases the intensities which the theoretical physicist or the industrial spectrographer requires are the intensities which would be observed without self-absorption. The effect of self-absorption, unless properly accounted for, is to falsify the results. The consequences in many cases can by no means be taken care of by small corrections. In a metal arc under ordinary operating conditions there are many lines which lose as much as 95 percent of their original intensity by self-absorption. Under more severe conditions this may even be considerably larger.

While the severe cases of self-absorption can (in most light sources) be easily detected as self-reversals, there is nothing to distinguish offhand a line which is only moderately self-absorbed from one free from self-absorption. Nevertheless, by using such lines serious mistakes can be made in the intensity ratios.

The present paper tries to present a thorough quantitative study of the mechanism of self-absorption and its effects on the intensities and line shapes of spectrum lines. It turns out that a relatively simple model is quite adequate to give account of the observed facts in such important cases as arcs and sparks, and that refinements in the theory change the results only in relatively minor details. A number of experiments have been made to test the results of the theory.

In the past, workers interested in measuring line intensities in order to use them for theoretical considerations have usually been content to eliminate the effects of self-absorption by selecting the proper experimental conditions, without bothering to study self-absorption in detail. The theoretical side of the subject has been especially neglected. A number of papers have been published which deal with self-absorption in a homogeneous light source, as exemplified by a gas discharge at reduced pressure (e.g., Ladenburg and Reiche (27),[a] Venkatesachar (52), Pokrowski (42), Burger and van Cittert (4), Minkowski (36), Ladenburg and Levy (25)).

Self-reversal cannot occur under such circumstances. We are aware of only two previous attempts to treat theoretically self-absorption in light sources in which self-reversal can occur. These papers by Bleeker (2) and Sibaiya (45), however, deal only with extreme cases and then only briefly. A treatment of self-absorption in the general case, which includes such sources as arcs and sparks in air at atmospheric pressure, is entirely lacking. Accordingly, although in the following pages the discussion is held as general as possible and references are made to previous investigations, special emphasis is placed on such non-homogeneous light sources as are typified by an arc between metal electrodes—in

particular, the direct current iron arc. The bibliography at the end of the paper gives a list of the previous investigations. References are given in the text so that the reader can find his way through them. Most of the examples, however, have been obtained from work carried out in our own laboratory.

II. FUNDAMENTAL CONSIDERATIONS

First we shall treat the case of how the light of a spectrum line emitted by atoms (or molecules[b]) at one definite place in the light source is absorbed during the passage through the light source or its immediate surroundings. The results would apply equally well to parts of a continuous spectrum but have less practical interest for that case.

Let us assume that the center of the spectrum line has the frequency ν_0 and that the intensity distribution within this line is given by the function $\rho(\nu)$. Without loss in generality we can assume that $\rho(\nu)d\nu$ is the radiation energy per unit volume of radiation in the frequency interval $d\nu$ which travels with the velocity c in the form of plane waves in a given direction which we take as the direction of the x axis.

The absorption in a given interval dx, besides being proportional to the radiation density $\rho(\nu)$, depends on the number of atoms per unit volume capable of absorbing the particular line and on the properties of the individual atoms. The latter determine the frequency dependence of the absorption. This can be expressed in the following way.

$$[1/c][d\rho(\nu)/dt] = [d\rho(\nu)/dx]$$
$$= -kP_a(\nu,x)\rho(\nu). \quad (1)$$

$P_a(\nu,x)$ expresses the shape of the absorption line. It is taken to be a normalized function:

$$\int_0^\infty P_a(\nu,x)d\nu = 1 \quad \text{for all } x. \quad (2)$$

The integral, strictly speaking, should be extended only over the width of the particular spectrum line. By extending it from zero to

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[a] Numbered references will be found at the end of the paper.

[b] Obviously, for our purpose it is immaterial whether the spectrum line is emitted by atoms or diatomic or polyatomic molecules. Therefore, wherever reference is made in this paper to atoms the statement applies equally well to molecules.

infinity we disregard for this purpose the presence of other spectrum lines, which will cause an appreciable error only when there are other lines very close to the line in question. $P(\nu,x)$ depends on x as well as on the frequency because the shape of the absorption line may, for instance, depend on the density, which, in general, is a function of x.

k is a constant which can be evaluated in terms of other significant constants in the following way. Let us consider absorption of radiant energy from a continuous spectrum with an energy distribution which is substantially constant over the width of the absorption line. The rate at which energy E of all frequencies is absorbed is

$$dE/dt = -ck \int_0^\infty P_a(\nu,x)\rho d\nu.$$

Now $-dE/dt$ is equal to the number of photons absorbed per unit volume per second multiplied by the energy per photon. In our case where ρ is a constant independent of ν, by definition of the Einstein coefficient of absorption B, this is

$$n_a(x)B\rho h\nu_0.$$

Here $n_a(x)$ is the density of atoms capable of absorbing the line—or, more exactly, the number of atoms per unit volume existing in each of the (degenerate) quantum states having energy E''; and B is the total probability of transition from all states of energy E'' to all states of energy E'. Thus

$$ck\rho = h\nu_0 Bn_a(x)\rho,$$

or from Eq. (1)

$$d\rho(\nu)/\rho(\nu) = (-h\nu_0 B/c)n_a(x)P_a(\nu,x)dx, \quad (3)$$

from which

$$\rho(\nu,r) = \rho(\nu,r_0)$$

$$\times \exp\left[(-h\nu_0 B/c)\int_{r_0}^r n_a(x)P_a(\nu,x)dx \right]. \quad (3a)$$

This is true for plane waves where, without absorption, $\rho(\nu,x)$ is independent of x. If we are dealing with spherical waves emitted from one point, $\rho(\nu,r)$ decreases as function of r according to the inverse square law. The attenuation due to absorption is superimposed on this. We can take

care of this state of affairs by replacing $\rho(\nu,r_0)$ in (3a) by $\rho_0(\nu,r)$ which represents the energy density that would be observed at a distance r from the source without absorption.

$$\rho(\nu,r) = \rho_0(\nu,r)\exp\left[(-h\nu_0 B/c)\int_{r_0}^r n_a(x)P_a(\nu,x)dx \right].$$

This expression gives the frequency distribution of energy density at a point r in terms of the density of absorbing atoms along the path between r_0 and r and the frequency distribution $\rho_0(\nu,r)$ which would exist at r if $n_a(x)$ were zero everywhere between r_0 and r. In particular, if r_0 is the location of the atom which is the source of the energy and if $P_e(\nu,r_0)$ is a normalized function giving the frequency distribution of the emitted energy, we can express the result in terms of the intensities, and then the intensity of the light at r is

$$I(\nu,r) = I_0 P_e(\nu,r_0)$$

$$\times \exp\left[(-h\nu_0 B/c)\int_{r_0}^r n_a(x)P_a(\nu,x)dx \right], \quad (4)$$

where $I_0 P_e(\nu,r_0)$ is the intensity distribution which would exist at r if there were no absorption, and I_0 is the total intensity (at r) of the spectrum line for no absorption.

Now the light radiated by a source is not emitted at a single point r_0, but is emitted by atoms which are, in general, scattered throughout the source, and the absorption will be, in general, different for the light coming from the various parts. The intensity distribution for the source as a whole is therefore found by averaging (4) over all points, r_0, in the source.

Before carrying out the averaging process, it may be of some interest to examine the effect of absorption on the frequency distribution of light coming from the single point r_0. In practically all cases it is true that

$$P_e(\nu,x) = P_a(\nu,x) = P(\nu,x)$$

(Kirchhoff's Law). For simplicity, it will also be assumed that P is independent of x and can therefore be written $P(\nu)$. Then, with the intro-

duction of a quantity

$$p = (h\nu_0 B/c)P(\nu_0) \int n_a(x)dx,$$

Eq. (4) reduces to

$$I(\nu) = I_0 P(\nu)\exp\left[-p\frac{P(\nu)}{P(\nu_0)}\right].$$ (5)

For no absorption, $p=0$ and the form of $I(\nu)$ is, of course, the same as that of $P(\nu)$. When $n_a \neq 0$, we may distinguish two cases of importance.

(1) For a given spectrum line B is a constant. The quantity p can then be regarded as a function of the total amount of absorbing vapor,

$N_a = \int n_a dx$, that the light has to traverse, and will therefore increase with the vapor density. $I(\nu)$ varies as shown in Fig. 1. (For purposes of illustration $P(\nu)$ was here taken to be a resonance distribution of the form $(\delta/\pi)/(u^2+\delta^2)$, with δ constant and $u = \nu - \nu_0$.)

Figure 1 shows the extent of the weakening for the different values of p indicated with each trace. For $p > 1$ there is a dip in the center, which means true self-reversal. We see that in the middle of the line the intensity is reduced to e^{-1} for $p = 1$. A shape such as that shown for $p = 0.5$, which has an intensity reduction of about 40 percent in the center, could hardly be dis-
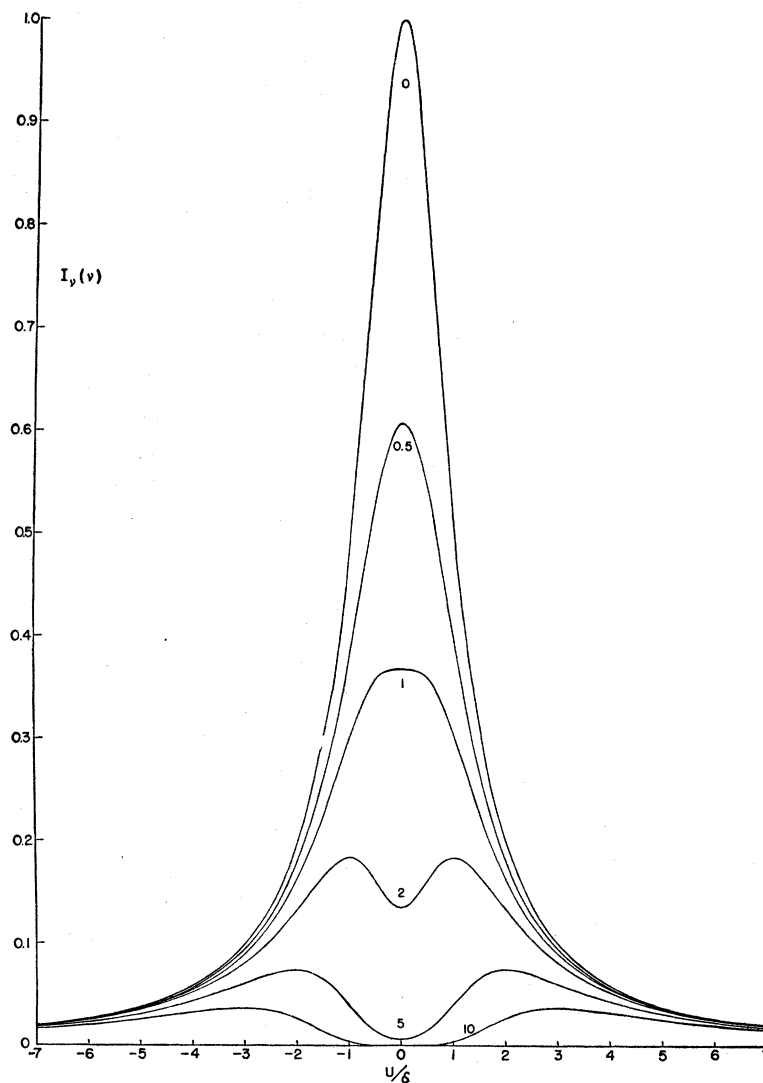

FIG. 1. Line shapes with varying degree of self-absorption as expressed by the absorption parameter p. The lines are plotted so that the unabsorbed line in each case would have the shape shown for $p=0$.
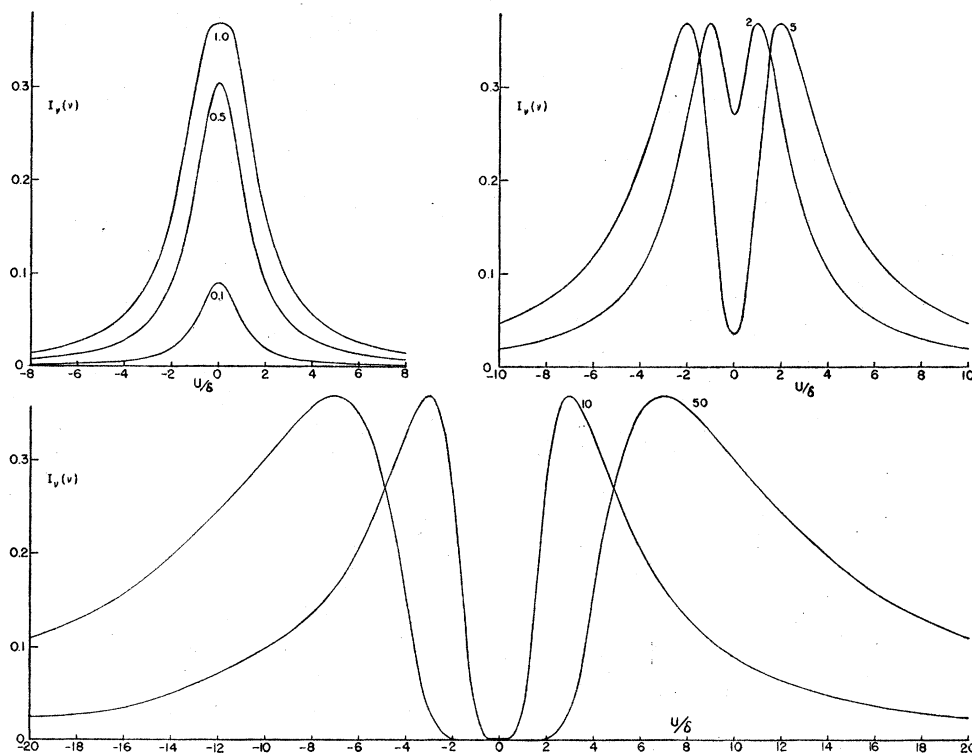
FIG. 2. Line shapes with varying degree of self-absorption plotted so that the maximum of the unab-
sorbed line is proportional to p.

tinguished from the shape of a line without
self-absorption ($p = 0$) without exact meas-
urements.

(2) Consider now different lines in the spec-
trum of a given source, all the lines, however,
having about the same value of E' and about
the same value of E'' (as would be the case, for
example, for lines produced by transitions be-
tween two multiplets in which the splitting is
fairly small). Then the number of emitting atoms
N_e in each quantum state belonging to the en-
ergy E' is the same for all the lines, and from
the definition of the Einstein coefficient A and
the relation $A \propto \nu_0^3 B$,

$$I_0 \propto h\nu_0 A N_e = \text{constant} \cdot B,$$

as N_e and ν_0 are approximately constants. Simi-
larly, N_a is the same for all the lines considered,
so that p is proportional to I_0. The $I(\nu)$ curves
then change with p or I_0 as indicated in Fig. 2.
Note that the maximum value of $I(\nu)$ is, in this
case, independent of B for $p \geq 1$. It will be shown

that this property remains essentially true even
when some of the simplifying assumptions are
dropped.

In returning to the averaging process, it must
be noted that the form of the average required
depends on the manner in which the source is
observed. Usually the entire source is not util-
ized. Rather, an image of the source is produced
on the spectrograph slit with a condensing lens,
so that the only light reaching the photographic
plate is that which passes through (or near) the
vertical central axis of the source. Thus, if the
source is approximately symmetrical about this
axis or if the angle subtended at the source by
the lens is not too great, the desired average of
Eq. (4) can be written as a one-dimensional
integral. This is the only case which will be
considered in this paper. As the variable of
integration will be taken the distance r along
the optic axis of the spectrograph, the positive
direction being that from source to slit, and the

origin being chosen such that

$$N_a = \int_0^\infty n_a(r)dr = \tfrac{1}{2}\int_{-\infty}^{+\infty} n_a(r)dr. \qquad (6)$$

We let further

$$N_e = \int_{-\infty}^{+\infty} n_e(r)dr,$$

$$\bar{n}_a(r) = [n_a(r)/N_a], \quad \bar{n}_e(r) = [n_e(r)/N_e],$$

where $n_e(r)$ is the space density of atoms in each quantum state of the energy level E', and let

$$\bar{P}_a(\nu) = \tfrac{1}{2}\int_{-\infty}^{+\infty} \bar{n}_a(x)P_a(\nu,x)dx,$$

$$p = (h\nu_0 B/c)\bar{P}_a(\nu_0)N_a. \qquad (7)$$

Then since the intensity of light emitted at a point r is proportional to $n_e(r)$, we have as a final average

$$I(\nu) = I_0\int_{-\infty}^{+\infty} \bar{n}_e(r)P_e(\nu,r)$$

$$\times \exp\left\{-\left[p/\bar{P}_a(\nu_0)\right]\int_r^\infty \bar{n}_a(x)P_a(\nu,x)dx\right\}dr. \qquad (8)$$

Even though the expression for $I(\nu)$ has been reduced to a one-dimensional integral, it still remains so complicated that except in specific cases one can learn little from it. It has already been pointed out that usually $P_e(\nu,x) = P_a(\nu,x)$. It will also be assumed in nearly all the work which follows that $P(\nu,x)$ is independent of x. This is certainly a reasonable first approximation in sources where there are no extreme variations in pressure or Doppler broadening. That this condition is well satisfied in the ordinary light source is shown by the good agreement between theory and experiment. Such extreme cases as the spectra of exploded wires (Anderson (1), Fukuda (11), King (19), Menzies (33)) or of a metallic spark under water (Hulburt (16)), fall outside the scope of the treatment given in this paper.

In addition, for some of the considerations which follow—notably the calculation of the total intensity

$$I = \int_0^\infty I(\nu)d\nu$$

—it will be necessary to know the particular form of the distribution function $P(\nu)$. It will be impossible to consider here all the forms of $P(\nu)$ which may conceivably occur; in particular, highly asymmetrical pressure or Stark effect broadening will be passed over without further comment.

It will also be assumed that $P(\nu)$ is not composite in form; i.e., that any hyperfine or other splitting either is large compared to the half-widths of the various components so that the latter are well separated (in which case $P(\nu)$ refers to only one of the components), or else that the presence of collision and other broadening completely wipes out all hyperfine structure—as is usually the case, for example, in the spectra of metallic arcs and sparks at atmospheric pressure. (In connection with hyperfine structure see Lau, Reichenheim, and Johannesson (28); Metcalfe and Venkatesachar (35); Venkatesachar (53); and Sibaiya (45).) Only two cases will be considered at length: the first being that in which $P(\nu)$ is essentially the Doppler distribution,

$$P(\nu) = \left(\frac{\ln 2}{\pi \nu^2}\right)^{\frac{1}{2}} \exp\left[-\frac{\ln 2}{\delta^2}(\nu-\nu_0)^2\right], \qquad (9)$$

where with thermal equilibrium, the half-width at half the maximum amplitude is

$$\delta = [\ln 2(2kT\nu_0^2/mc^2)]^{\frac{1}{2}},$$

and the second that in which $P(\nu)$ is the natural resonance form

$$P(\nu) = (\delta/\pi)/[(\nu-\nu_0)^2+\delta^2]. \qquad (10)$$

Both of these functions are important in the study of self-absorption. The natural half-width of a spectrum line is usually much smaller than the half-width of the Doppler function, so that the latter is of importance whenever there is little pressure or other broadening. On the other hand, resonance and collision broadening do not greatly affect the analytical form of Eq. (10) but only increase the half-width, and this type of broadening is present in some sources (e.g., arcs and sparks at atmospheric pressure) to a much greater extent than is often realized. Even when the resonance half-width is considerably smaller than the Doppler half-width, the reson-

ance distribution becomes the controlling one when the degree of self-absorption becomes moderately great, as than the important part of the line is that for $|\nu - \nu_0| \gg \delta$ (see Fig. 1) where the intensity due to the Doppler distribution is negligibly small.

III. SELF-ABSORPTION FROM A WAVE-MECHANICAL POINT OF VIEW

Equation (8), which will be the basis for all further considerations, was deduced from Eq. (3). The derivation of the latter expression through use of the statistical quantity B is a familiar one[c] and is quite simple. It regards all atoms as independent of each other. A wave-mechanical treatment of self-absorption, which takes into account the coupling between the various atoms, requires, on the other hand, a very lengthy calculation. This has been attempted elsewhere (6), and, as it produces no new useful results, only a bare outline will be given here.

One may consider first a single atom in an excited state surrounded by a thin ("one-atom" thick) spherical shell of atoms, all in the ground state. Energy radiated by the first atom may be absorbed by one of the others, and the probability of absorption can be calculated from the equations of interaction of atoms with radiation.[d] The absorbing atom may reradiate or may lose its excitation energy by collision or by radiation of light of a different frequency. One can then recalculate the energy in the radiation field by considering both the original radiating atom and the second (fluorescing) atom. The two atoms are coupled by the field so that they radiate coherently; the total field then shows a change in frequency distribution from the distribution in the field of the first atom alone, and the total energy present is less than that originally radiated because of the energy absorbed and not reradiated by the second atom. Integrating over all the possible absorbing atoms, and averaging over all orientations of the dipole moments of the various atoms give finally an expression for $d\rho(\nu)/\rho(\nu)$ which, when the dipole

moment D is eliminated by means of the relation[e] $B = 8\pi^3 |D|^2/3h^2$, is identical with Eq. (3) except that $P_a(\nu)$ is of course replaced by the natural resonance function (10). The frequency dependence can then be generalized by taking into account the Doppler effect and other factors which may result in a (real or apparent) shift in the natural frequency ν_0 of the emitting and absorbing atoms.

In these calculations it was necessary, in order to avoid mathematical complications, to assume that the distance between atoms was greater than about 5λ, which implies (for $\lambda = 3000A$) a density of atoms *in the appropriate quantum states* of less than $3 \cdot 10^{11}$ cm^{-3}. At higher densities the problem becomes complicated by the correspondingly greater coupling between atoms—i.e., the presence of resonance broadening. A quantum-mechanical treatment of such broadening in the case where no energy is lost by collision (38) shows that the resonance form of the function (10) is not changed but only that the half-width is increased. It seems probable then that even at high densities a wave-mechanical treatment of self-absorption would agree with the expression (3) obtained by much simpler means.

The presence of fluorescent and induced radiation was ignored entirely in the derivation of (8). However, the former can have only a negligible effect on the observed line shape, for the amount of fluorescent light present cannot be greater than the amount of light absorbed. Since it is radiated in all directions, only a small fraction of it enters the spectrograph slit and affects the photographic plate. Moreover, in a low density source where the rate of collisions between atoms is small, the frequency distribution of the fluorescent light is identical with that of the absorbed radiation; thus the effect of the fluorescence is only to reduce the apparent density of absorbing atoms, $n_a(r)$, without affecting the form of (8). On the other hand, in a source where the pressure is much higher, the collision rate is so great that the frequency distribution of any radiation emitted by optically excited atoms is the same as that of the radiation emitted by

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c See, for example, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Teddington, England, 1935), pp. 109 ff.

d See, for example, E. Fermi, "Quantum theory of radiation," Rev. Mod. Phys. 4, 87 (1932).

e See, for example, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Teddington, England, 1935), p. 102.

atoms excited by collisions; the effect of fluorescence is then to increase the density of emitting atoms, $n_e(r)$, again without affecting the form of Eq. (8).

The effects of induced emission on the observed line shape are more difficult to determine, but in the case of a source at atmospheric pressure collisions probably cause the frequency distribution of the induced radiation to be the same as that of light emitted spontaneously. Equation (8) would not be affected in such a case.

IV. THE GENERAL CASE OF SELF-ABSORPTION

Equation (8) can be brought into a slightly different form in order to render it more suitable for the treatment of the more specialized cases.

As before, we assume that the shapes of the absorption and emission lines are the same and independent of the place in the light source, which means that

$$P_a(\nu,x) = P_e(\nu,x) = P(\nu).$$

With

$$u = \nu - \nu_0 \tag{11}$$

and

$$P(\nu) \rightarrow P(u),$$

(8) becomes

$$I(u) = I_0 P(u) \int_{-\infty}^{+\infty} \bar{n}_e(r)$$

$$\times \exp\left[-p\frac{P(u)}{P(0)}\int_r^\infty \bar{n}_a(x)dx\right]dr. \tag{12}$$

It will be convenient to introduce the abbreviation

$$\mu(u) = p[P(u)/P(0)], \tag{13}$$

where $\mu(u)$ is the value of the exponent at $r=0$; to make the substitution

$$y = \int_r^\infty \bar{n}_a(x)dx \tag{14}$$

(which is permissible because $n_a(r)$ cannot be zero when $n_e(r)$ is not zero); and to let

$$E(y) = \bar{n}_e(r)/\bar{n}_a(r). \tag{15}$$

Then

$$I(u) = I_0 P(u) \int_0^2 E(y)e^{-\mu(u)y}dy. \tag{16}$$

y is the relative number of atoms capable of absorbing the line present per unit cross section between the point under consideration and the outside of the source. It is zero at the boundary toward the observer, one at the center, and two at the boundary away from the observer.

It is evident from this that the shape and intensity of a spectrum line depends on only three factors: (1) the distribution function $P(u)$, which represents the line shape for negligible absorption; (2) the absorption parameter p; (3) $E(y)$, which measures the relative excitation at a particular point. It can assume values from zero (when there is no excitation) to infinity (when all the atoms are excited). The function $E(y)$ therefore specifies the type of light source. Note that the line shape is not explicitly dependent on the two functions $n_e(r)$ and $n_a(r)$, nor on the functions $\bar{n}_e(r)$ and $\bar{n}_a(r)$, nor even on the ratio of the latter two, but only on the form which this ratio takes when reduced to a function of the variable y. (In geometrical terms, self-absorption is invariant under any continuous one-to-one deformation of the source in the direction of the optic axis, provided the deformation does not change the form of $P(u)$.)

Without making any assumptions regarding the particular forms of the functions $P(u)$ and $E(y)$ one can still draw some conclusions concerning the self-reversal of spectrum lines. If reversal is present, $I(u)$ will have maxima at frequencies other than that for which $P'(u) = 0$. Differentiation of (16) then gives as a condition for reversal

$$\int_0^2 \{1 - \mu y\}E(y)e^{-\mu y}dy = 0. \tag{17}$$

In the special case of a uniformly excited source ($E = $ constant), this reduces to

$$2e^{-2\mu} = 2e^{-2p[P(u)/P(0)]} = 0.$$

This expression has no solution for finite values of p. Therefore, self-reversed lines are never present in the spectrum of a source of this type.

In any common source which is *not* uniformly excited, the excitation decreases from some inner portion of the source outward; i.e., the value of $E(y)$ is smallest at $y=0$. In such a case $E(y)$ has a maximum at a value $y_0 \leqq 2$. (If E has

maxima at more than one value of y, let y_0 be the smallest of these.) Partial integration of Eq. (17) and division by exponent $-\mu y_0$ gives

$$2E(2)e^{-\mu(2-y_0)} - \int_{y_0}^{2} yE'(y)e^{-\mu(y-y_0)}dy$$

$$- \int_{0}^{y_0} yE'(y)e^{+\mu(y_0-y)}dy = 0.$$

Now, as μ is increased indefinitely, the first two terms of this expression decrease in magnitude (their sum tending to zero if $y_0<2$ or to $2E(2)$ if $y_0=2$), while the final integral is positive and increases without bound. Thus for large μ Eq. (17) is negative, while for $\mu=0$ it is obviously positive. Consequently, in any source for which $E(y)$ has a minimum at $y=0$, there is at least one real value, k, of μ which is a solution of Eq. (17); i.e., $I(u)$ has maxima at frequencies given by

$$\mu = p[P(u)/P(0)] = k. \qquad (18)$$

It will be shown in Section VII that $k \geq 1$.

It is an obvious, but not particularly important, fact that with a suitable source having more than one excitation maximum (for example, a source consisting of a high-current arc placed behind a low-current one), lines with more than the two intensity maxima characteristic of self-reversal could be obtained.

Since $P(u) \leq P(0)$, the relation (18) indicates that a given line will be reversed only when the value of p for that line is greater than k (a "constant" which, in general, is different for different lines in the same spectrum). For $p=k$, the line is just on the point of becoming reversed, and then the only intensity maximum occurs at $u=0$. The maxima obviously lie at $u=\pm\delta$ when $p=2k$. For other values of p, the maxima lie at frequencies which depend on the particular form of $P(u)$. For the Doppler and resonance distributions (9) and (10), Eq. (18) reduces, respectively, to

$$u_{max}^2/\delta^2 = (\ln p - \ln k)/\ln 2 \qquad (19)$$

and

$$u_{max}^2/\delta^2 = (p/k) - 1. \qquad (20)$$

Since the intensity maxima of a reversed spectrum line lie at frequencies satisfying Eq.

(18), then from Eqs. (16) and (7) the maximum value of $I(u)$ is

$$I_{max} = I_0(kc/h\nu_0 BN_a) \int_0^2 E(y)e^{-ky}dy.$$

Consider a set of lines all of which arise from upper levels of nearly the same energy and which likewise have lower levels of nearly equal energy (e.g., lines due to transitions between two multiplets, in an atom having fairly small multiplet splitting). Then $n_e(r)$ is the same for all these lines, as are also $n_a(r)$, N_e, N_a, $E(y)$ and, from Eq. (17), k. Since $I_0 \propto h\nu_0 AN_e$ it follows that for these lines (compare Fig. 2)

$$I_{max} \propto (AN_e/BN_a) = 8\pi h\nu_0^3 N_e/c^3 N_a. \qquad (21)$$

ν_0 does not vary greatly for the different lines, so that the maximum intensity is essentially the same for all of them. This fact can be easily verified experimentally (9).

Similarly, if one considers a single spectrum line and various sources of the same type, then N_e/N_a has the same value for all sources, and again the intensity maximum is a constant (provided, of course, the line remains reversed). Thus, for example, increasing the current through an arc will not (at least to a first approximation) produce an essentially different source, but merely increase I_0 and p proportionately to each other for each spectrum line, and the maximum intensity of any reversed line will remain constant in value (though of course the two maxima will become more widely separated with increasing p—cf. Fig. 2).

The discussion of the effect of self-absorption on line shape will be continued for a few special types of sources.

V. UNIFORMLY EXCITED SOURCES

For a source in which the excitation is constant (e.g., a flame source or discharge tube of suitable design), and under the restriction that $P_e=P_a$, the intensity distribution is found from Eq. (8) to be

$$I(u) = I_0 \frac{P(0)\bar{n}_e}{p\bar{n}_a}\{1 - e^{-2pQ(u)}\}$$

$$= I_0 \frac{P(0)}{2p}\{1 - e^{-2pQ(u)}\}, \qquad (22)$$

where

$$Q(u) = P(u)/P(0).$$

If $P(u)$ is not independent of r it must be replaced in Eq. (22) by the averages $\bar{P}(u)$ and $\bar{P}(0)$ over the path. Since $I_0 \propto h\nu_0 A N_e$, this can also be written

$$I(u) \propto (An_e/Bn_a)\{1 - e^{-2pQ(u)}\}, \qquad (23)$$

Expressions of similar form have been derived (under less general assumptions) in several papers (4, 27, 52). They show that self-reversal never occurs in sources such as those under discussion. With increasing absorption (increasing values of p) $I(u)$ tends to a maximum value

$$I(u) \propto \frac{An_e}{Bn_a}$$

$$= \frac{\text{emissivity of a very thin layer of vapor}}{\text{absorptivity of a very thin layer of vapor}},$$

which is independent of the frequency (within a given spectrum line).

This is of the same form as Eq. (21), but there is an essential difference: In the case of self-reversal, the intensity maximum is actually attained for finite values of p; in the present case, the maximum is only approached as a limit.

It should be emphasized that it is not required for the above results that $n_e(r)$ and $n_a(r)$ be constant, but only that the ratio n_e/n_a be a constant. Thus in the case of thermal excitation in a flame source, for example, these results apply provided only that the temperature of the flame be uniform throughout the region occupied by the radiating atoms, the distribution of atoms throughout this region being immaterial.

Line shapes of the form (23) with $P(u)$ a Doppler distribution have been observed by Ladenburg and Levy (25) in the spectrum of a neon discharge and by Venkatesachar (52) in the spectrum of a mercury vapor discharge.

The fact that reversed lines are sometimes observed in the spectra of flame or discharge tube sources does not necessarily contradict the theory, as special precautions must be taken to ensure uniform excitation throughout the portion of the source involved. It has been suggested by several writers that reversals which they have observed may be due to a frequency dependence

of the ratio of emissivity to absorptivity (34, 56), that is, to a difference between the two functions $P_e(u)$ and $P_a(u)$. If $P_e \neq P_a$, but both are independent of r (as would be the case in a strictly homogeneous source), then integration of Eq. (8) gives

$$I(u) = \frac{I_0 P_a(0)}{2p} \frac{P_e(u)}{P_a(u)}\{1 - e^{-2pQa(u)}\}$$

$$\propto \frac{An_e P_e(u)}{Bn_a P_a(u)}\{1 - e^{-2pQa(u)}\}.$$

Reversal is obviously possible if P_a is greater than P_e at $u = 0$ as, for example, in the case suggested by Merton (34).

VI. SOURCE WITH EMITTING AND ABSORBING ATOMS SPATIALLY SEPARATED

Of the sources in which self-reversal is possible, one of the commonest and most easily constructed is the direct current arc between metal electrodes. The iron arc is of particular importance because it serves as standard reference source in many applications of spectroscopy. Such an arc consists of a bright bluish central core surrounded by a less luminous yellow flame. The excitation in the core is relatively high and includes most of the emitting atoms; the excitation in the outer flame is much lower and probably contains a large proportion of all those atoms which are in the ground state.

As a first approximation to such a source we may consider a simplified model in which all the emitting atoms lie in the center (or about a central axis) while all the absorbing atoms lie outside this region.

The line shape is given by a relation similar to Eq. (4):

$$I(u) = I_0 P_e(u)e^{-pQa(u)}, \qquad (24)$$

where P_e and P_a can be understood to be averages of the form

$$P_e(u) = \int_{-\infty}^{+\infty} \bar{n}_e(r)P_e(u,r)dr;$$

$$P_a(u) = \int_0^{+\infty} \bar{n}_a(r)P_a(u,r)dr. \qquad (24a)$$

An expression of this form has been applied by Sibaiya (45) to self-reversed lines observed in the spectra of various hollow-cathode dis-
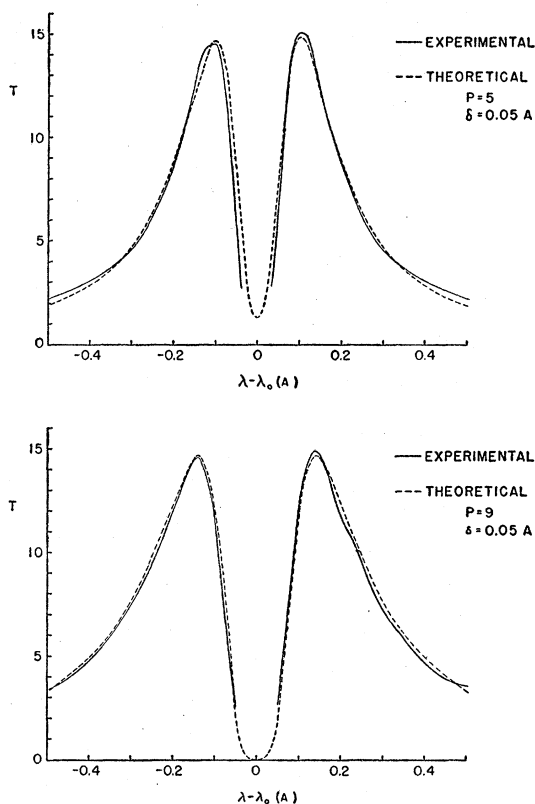
FIG. 3. Reversal of FeI lines 2966A and 3047A. Comparison of theory and experiment.

charges. It was assumed that P_e was a Doppler distribution, while P_a was of a resonance form with zero half-width. Under these assumptions spectrum lines would always be reversed, and an expression was derived for the wave-length separation of the maxima of such a line as a function of (in effect) the absorption parameter p. The reportedly good agreement with experiment was probably fortuitous, as there is no reason why P_e and P_a should be greatly different in form.

Using a resonance distribution of the form (10) for both P_e and P_a, very good agreement was obtained in measurements made by Crosswhite (9) between curves of the form (24) and the experimentally determined shapes of reversed lines in the spectrum of a high-current iron arc (wave-lengths 2966 and 3047A; lower level a^5D, ground state). (Fig. 3.) The values of p giving the best fit were 5 and 9, respectively; these are typical of lines showing fairly strong reversal. The value of δ was 0.05A. This is much greater

than the Doppler half-width (which would be 0.010A at a temperature of 5000°K), and is presumably due to collision and resonance broadening both of which preserve the natural resonance line shape. (See also Section XD.)

For the resonance distribution (10), the explicit form of the intensity distribution becomes

$$I(u) = M\frac{\delta^2}{\delta^2+u^2}e^{-p[\delta^2/(\delta^2+u^2)]} \qquad (25)$$

where M, the maximum of the unreversed line, is introduced instead of the total intensity, I_0.

$$I_0 = M\pi\delta.$$

The expression (25) for the shape of the reversed line contains the three constants M, δ, and p. Of these, M and δ determine the vertical and horizontal scales but do not affect the shape otherwise. The parameter p, on the other hand, determines the character of the curve and is therefore a direct measure for the amount of self-reversal.

The following facts are easily derived from (25) and help to evaluate self-reversal:

If $p<1$, the line has a maximum only for $u=0$, i.e., at the center of the line. This central maximum is equal to

$$I(0) = Me^{-p}; \qquad (26)$$

i.e., it is depressed by a factor e^{-p}. If $p>1$ the center is a minimum, again given by Eq. (26). There are maxima for

$$u_{max} = \pm\delta(p-1)^{\frac{1}{2}}, \qquad (27)$$

and the intensity at these side maxima is

$$I_{max} = M/ep. \qquad (28)$$

The ratio of maximum to minimum is

$$I_{max}/I(0) = e^{p-1}/p \quad p\geq1 \qquad (29)$$

independent of the width of the line. (The expressions (26), (28), and (29) hold not only for a resonance distribution, but also for any other form of the function $P(u)$.)

VII. OTHER NON-HOMOGENEOUS SOURCES

Although the source model just discussed in which the emitting and absorbing atoms were assumed to be spatially separated gives results in good agreement with experimental results obtained with arc sources, the model itself is,

of course, far from the actual state of affairs in an actual light source.

A slightly more general model, suggested by Bleeker (2), can be obtained by combining the two preceding ones; that is, by assuming the core to contain absorbing as well as emitting atoms with constant excitation throughout, the core being surrounded as before with absorbing atoms. This model would apply very well to the study of the absorption, by an unexcited vapor, of light emitted by a uniformly excited source containing the same kind of vapor, but is a poor approximation to an arc source because of the sudden change in excitation between the excited and unexcited portions.

Slightly modified, the model applies to numerous studies of absorption (not necessarily of resonance lines) by a weakly excited vapor. In one arrangement for experiments of this type, the source consists of two discharge tubes placed end to end, the light emitted by the first (strongly excited) tube passing through the second (weakly excited) tube before entering the spectrograph and being partially absorbed in the process (Meissner (32), A; Eckstein (10), Ne; Newman (40), Na; Metcalfe and Venkatesachar (35), Hg; Ladenburg and Levy (25), Ne). In the second arrangement, a single tube containing three or four electrodes is used, the vapor between the two electrodes farthest from the spectrograph being excited more strongly than that between the two nearest electrodes (Kimura and Nakamura (18), H; McLennan, Ainslee, and Cale (31), Hg; McCurdy (30), He; Nagaoka and Mishima (39), Ne; Pflüger (41), H). In either case, the absorption of spectrum lines having lower levels other than the ground level can be observed. With sufficiently high absorption the lines are also reversed (see Section IV). The line shape is given by the expression (see Eqs. (22), (23))

$$I(u) = \frac{I_{01}P(0)}{p_1}\{1 - e^{-p_1 Q(u)}\}e^{-p_2 Q(u)}$$

$$+ \frac{I_{02}P(0)}{p_2}\{1 - e^{-p_2 Q(u)}\} \propto \frac{A}{B}\left(\frac{n_e}{n_a}\right)_1$$

$$\times \{1 - e^{-p_1 Q(u)}\}e^{-p_2 Q(u)} + \frac{A}{B}\left(\frac{n_e}{n_a}\right)_2\{1 - e^{-p_2 Q(u)}\},$$

where the subscripts 1 and 2 refer, respectively, to the strongly and weakly excited portions of the source, and the values of the absorption parameters p correspond to the entire lengths of the respective portions. Unfortunately, the lack of sufficient experimental data (e.g., values of n_e/n_a) in the papers quoted makes quantitative comparison with the theoretical expressions impossible. Values of n_e/n_a have been determined by Ladenburg and Levy for the weakly excited column, but no values are given for the strongly excited source.

Measurements of the ratio n_e/n_a in excited gases have also been made by Kohn (20, 21), Ne, Kopfermann and Ladenburg (22, 24), Ne, and Carst and Ladenburg (23), H, by studying absorption from a continuous (rather than a line) spectrum. The experiments are closely related to those mentioned above in the special case $p_1 \gg p_2$ (i.e., the strongly excited column much longer than the absorbing column), as then the lines in the (strongly excited) source become very broad and flat-topped, thus providing—in effect—a continuous spectrum.

However, arrangements such as these do not approximate conditions which one may expect to find in the more usual single-unit sources, and therefore lie outside the scope of this paper.

We return now to the question of an arc or similar source in which the excitation at a given point in the source varies greatly, but gradually, with the location of the point. Since little is known about the exact form of the excitation function $E(r)$ for an arc, the best that can be done is to assume a variety of reasonable forms and then compare the resulting line shapes. It will be found that the general intensity distribution within a line depends very little on the particular assumption made and is never far from that of the model of Section VI. This justifies using the results obtained with the simplified model for comparison with actual light sources.

A set of functions in which the excitation decreases gradually from the center of the source outward and which do not introduce undue mathematical complications into the evaluation of (12) can be constructed as follows: The distribution of absorbing atoms $n_a(r)$ may assume an arbitrary form except for the physically

TABLE I. Minimum values of p for self-reversal.

n	μ_n
1	(∞)
2	1.26
3	1.13
4	1.08
5	1.05
10	1.02
∞	1.00

imposed restrictions that it must be continuous, greater than zero within the source, and such that N_a is finite so that $\bar{n}_a(r)$ is defined. It is also assumed for mathematical simplicity that the source is symmetric (i.e., that n_a is an even function of r). Let

$$\bar{n}_e(r) = \frac{n}{2}\bar{n}_a(r)\left[\int_{|r|}^{\infty}\bar{n}_a(x)dx\right]^{n-1}, \qquad (30)$$

where n is any positive integer, and the factor $n/2$ arises from the normalization condition (6).

One possible form of these functions is

$$\bar{n}_a(r) = ke^{-k|r|},$$
$$\bar{n}_e(r) = (n/2)ke^{-nk|r|}. \qquad (k>0)$$

These are not very satisfactory physically because of their form at $r=0$. A somewhat better pair of functions ($\bar{n}_a$ assumed arbitrarily, $\bar{n}_e$ obtained by graphical integration) is shown in Fig. 4 for the case $n=2$.
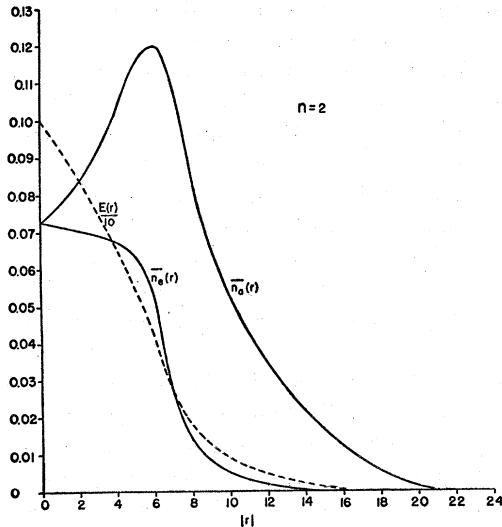

FIG. 4. Density of absorbing (n_a) and emitting (n_e) atoms and excitation function $E(r)$ in a light source with $n=2$.

In any case, (12) becomes

$$I(u) = I_0P(u)\frac{n}{2}\int_{-\infty}^{+\infty}\left\{\int_{|r|}^{\infty}\bar{n}_a(x)dx\right\}^{n-1}$$

$$\times \exp\left[-\mu\int_{r}^{\infty}\bar{n}_a(x)dx\right]\bar{n}_a(r)dr$$

$$= I_0P(u)\frac{n}{2}\left\{\int_0^1 y^{n-1}e^{-\mu y}dy + e^{-2\mu}\int_0^1 y^{n-1}e^{\mu y}dy\right\}.$$

A series of partial integrations reduces this to

$$I(u) = I_0P(u)\frac{n!}{2\mu^n}e^{-\mu}\left\{[e^{\mu}+(-1)^n e^{-\mu}]\right.$$

$$\left. -\sum_{j=0}^{n-1}\left[\frac{\mu^j}{j!}+\frac{(-1)^n(-\mu)^j}{j!}\right]\right\} \qquad (31)$$

$$= I_0P(u)e^{-\mu}\sum_{j=0}^{\infty}\frac{n!\mu^{2j}}{(2j+n)!}$$

In the special case $n=1$, the excitation is constant and Eq. (31) reduces to:

$$I(u) = \frac{I_0P(0)}{2p}\{1-e^{-2pQ(u)}\}$$

which is the same as Eq. (22) except for the (unnecessary) assumption that $P(u)$ be independent of r.

In the limit $n\rightarrow\infty$,

$$I(u) = I_0P(u)e^{-pQ(u)}, \qquad (32)$$

which is identical with Eq. (24) obtained for the simplified model. The reason for this is, of course, that with increasing n the emitting atoms are crowded into a smaller and smaller volume (about the central axis of the source) containing correspondingly fewer absorbing atoms. The special model of Section VI, therefore, is obtained as a limiting case of the more general assumptions of the present section.

The general case $n>1$ and finite gives a gradual transition between the extremes of uniform excitation and the spatially separated model of Section VI. Self-reversal is possible in all of them, as was shown in Section IV. The frequencies at which the maxima of a reversed line occur can be determined as before by differentiation of the expression for $I(u)$. The resulting

FIG. 5. Line shapes for a self-absorbed line ($p=4$) in light sources of different distribution of emitting and absorbing atoms expressed by the values of n. $n=1$ means uniform distribution, $n=\infty$ emitting and absorbing atoms completely separated.
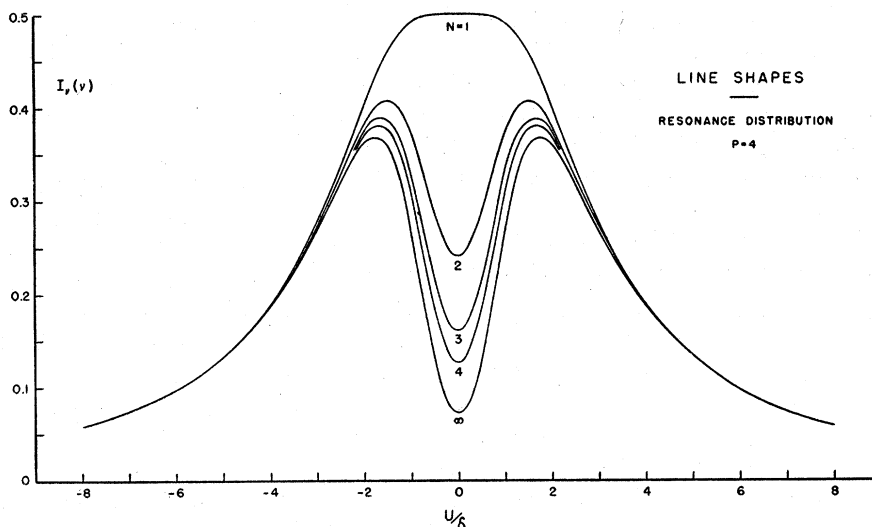
condition on u, again expressed in terms of μ according to (13), is

$$\sum_{j=0}^{\infty} \frac{n!}{(2j+n)!}[\mu-(2j+1)]\mu^{2j}=0.$$

For $n=1$, this reduces to $e^{-\mu}=e^{-pQ(u)}=0$ which has no solution for any value of u except in the limit $p\to\infty$, in which case it is satisfied by *all* values of u. For other values of n the above series converges so rapidly for the values of μ concerned that solutions are easily obtained by trial and error. The results are given in Table I. The value 1.00 for $n=\infty$ can, of course, be derived directly from Eq. (32).

Judging from the values of μ_n for $n=1$ and $n=2$, one might be inclined to think that the case $n=2$ is a very poor approximation to a uniformly excited source. This is doubtless true, and a discharge tube or flame source which is homogeneous except for a weakly excited region at its outer edges is probably best approximated by Bleeker's model. In the case of most arcs and sparks at atmospheric pressure, however, the ease with which self-reversal can be obtained indicates that the region of low excitation must be comparable in extent to that of high excitation. Such sources must be fairly well represented by the curves of Fig. 4. (Cf. Section XIB.)

FIG. 6. Comparison of the line shapes made under different assumptions about the distribution of emitting and absorbing atoms in the light source.
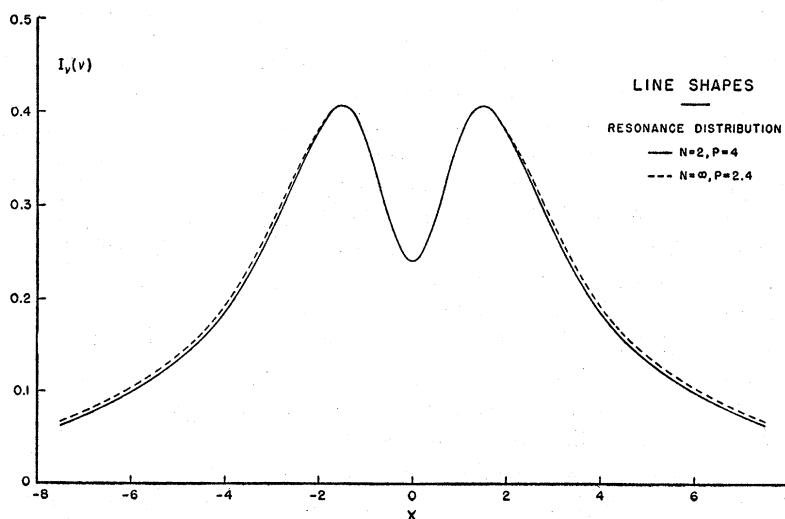
Since $P(u) \leq P(0)$, the minimum value of p for which reversal can occur is $p = \mu_n$. As shown by the table, this value is least for large n and increases more and more rapidly for smaller and smaller n—becoming infinite for $n = 1$, in which case reversal cannot occur (under the present assumption $P_e = P_a$).

The separation of the two intensity maxima of a reversed line can be found from the expression

$$pQ(u) = p[P(u)/P(0)] = \mu_n. \qquad (33)$$

This is, of course, identical with the general expression (18).

Line shapes for a resonance distribution and $p = 4$ are shown in Fig. 5 for $n = 1, 2, 3, 4$, and ∞. A closer comparison of the curves in which reversal is present is given in Fig. 6. The curve for $n = 2$ is replotted as in Fig. 5. A second curve is plotted for $n = \infty$, but with $p = 2.40$ (to give the same ratio of maximum to minimum intensity as for $n = 2$) and on different horizontal and vertical scales.

The similarity of the two curves (with $n = 2$ and $n = \infty$) is greater than one might expect. They are identical within the error of plotting at all points between the two maxima and differ by only 7 percent at points four times as far from the center of the line as the maximum (the intensity there being about one-fourth the maximum intensity). This shows how insensitive the self-reversal shapes are to the details of the distribution of emitting and absorbing atoms within the light source. (See Section XIB for further discussion.)

Doubtlessly the originally assumed expression (30) is not too close an approximation to the true distribution in any type of light source. However, the results of this section give one some idea of the effect of varying the form of the excitation function; in view of the similarity of the line shapes in the extreme cases $n = 2$ and $n = \infty$, it seems unlikely that other, more accurate expressions would lead to essentially different results. In particular, this similarity indicates that even with the crude model of Section VI the agreement between theory and experiment may be quite good. Thus one can use this simple model with considerable confidence that the theoretical results obtained will be meaningful and a good first approximation to the true state of affairs.

VIII. TOTAL LINE INTENSITIES

The shapes of self-absorbed spectral lines, discussed theoretically in the preceding pages, can be observed experimentally only with a spectrograph of sufficiently high dispersion and resolving power used with a slit which is very narrow compared to the line width. These conditions often are not realized. Furthermore, for many applications the total intensity of the line is required. The latter can be obtained most simply by opening the spectrograph slit to a width large compared with the line width. Then, at the middle of the image of a spectral line the intensity is the integrated intensity of the whole line.

Corresponding theoretical expressions will be obtained by integrating the line shape $I(u)$ over all frequencies. The variation of the total intensity

$$I = \int_{-\infty}^{+\infty} I(u)du$$

with the absorption parameter p can be conveniently presented graphically by plotting the ratio I/I_0 against p on a log-log scale. The curves thus obtained will be called reversal curves. This term will be used somewhat loosely to refer also to curves in which the ordinate is not the ratio of the total intensities I/I_0, but one of various similar ratios, such as

$$I(0)/I_0(0) \quad \text{or} \quad I_{max}/I_{0\,max}.$$

A. Resonance Distribution

1. Arbitrary Light Source

The shape of a spectrum line is given in general by Eq. (12). The total intensity is then

$$I = I_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} P(u)\bar{n}_e(r)$$

$$\times \exp\left[-pQ(u) \int_r^{\infty} \bar{n}_a(x)dx \right]drdu$$

or, interchanging the order of integration and

using the abbreviation

$$p_r = p \int_r^\infty \bar{n}_a(x) dx,$$

$$I/I_0 = \int_{-\infty}^{+\infty} \bar{n}_e(r) \int_{-\infty}^{+\infty} P(u) e^{-p_r Q(u)} du dr.$$

In the case of a resonance line shape (10),

$$\frac{I}{I_0} = \frac{1}{\pi} \int_{-\infty}^{+\infty} \bar{n}_e(r) \int_{-\infty}^{+\infty} [e^{-[p_r/(x^2+1)]}/x^2 + 1] dx dr.$$

With the substitution

$$x = \tan\theta/2, \qquad (34)$$

this reduces to

$$I/I_0 = (1/2\pi) \int_{-\infty}^{+\infty} \bar{n}_e(r) e^{-p_r/2} \int_{-\pi}^{+\pi} e^{-(p_r/2)\cos\theta} d\theta dr$$

$$= \int_{-\infty}^{+\infty} \bar{n}_e(r) e^{-p_r/2} J_0(ip_r/2) dr, \qquad (35)$$

where

$$J_n(z) = (1/2\pi i^n) \int_{-\pi}^{+\pi} e^{iz \cos\theta + in\theta} d\theta \qquad (36)$$

is the Bessel function of the first kind and of order n.[f] For small values of p, $e^{-p_r/2} J_0(ip_r/2)$ differs only slightly from unity; e.g., for $p = 0.05$, $p_r/2 \leqq 0.05$ and $e^{-p_r/2} J_0(ip_r/2)$ differs from unity by less than five percent. Then, of course, $I/I_0 \cong 1$.

For large values of p use can be made of the asymptotic relation[g]

$$J_n(z) \sim (2/\pi z)^{\frac{1}{2}} \cos[z - (n+\frac{1}{2})(\pi/2)] \qquad (37)$$

or

$$J_n(ip_r/2) \sim i^n e^{p_r/2}/(\pi p_r)^{\frac{1}{2}}.$$

For large p, p_r is too small for this expression to hold accurately, only when r is greater than some positive value R. It can be easily shown that p

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[f] See for example, G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Teddington, England, 1922), p. 177 or E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1943), p. 149.

[g] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Teddington, England, 1922), p. 199 or E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1943), pp. 137-8.

can be chosen so large that

$$\int_R^\infty \bar{n}_e(r) e^{-p_r/2} J_0(ip_r/2) dr$$

is a negligible part of Eq. (35). Thus

$$I/I_0 \sim \int_{-\infty}^R [\bar{n}_e(r)/(\pi p_r)^{\frac{1}{2}}] dr$$

$$= p^{-\frac{1}{2}} \int_{-\infty}^R \frac{\bar{n}_e(r) dr}{\left[\pi \int_r^\infty \bar{n}_a(x) dx\right]^{\frac{1}{2}}}, \qquad (38)$$

$$\log I/I_0 \sim -\frac{1}{2} \log p + \text{constant}.$$

Thus when I/I_0 is plotted against p on a log-log scale, the resulting reversal curve tends asymptotically to a slope of $-\frac{1}{2}$, and this value is independent of the distribution of atoms in the source.

2. Uniformly Excited Source

With a uniformly excited source the line shape is given by Eq. (22). Then

$$\frac{I}{I_0} = \frac{1}{2\pi p} \int_{-\infty}^{+\infty} (1 - e^{-[2p/(x^2+1)]}) dx.$$

With the substitution (34) and an integration by parts this can be reduced to

$$\frac{I}{I_0} = (e^{-p}/2\pi) \int_{-\pi}^{+\pi} (1 - e^{i\theta}) e^{-p \cos\theta} d\theta,$$

or, from Eq. (36),

$$\frac{I}{I_0} = e^{-p} \{ J_0(ip) - iJ_1(ip) \}. \qquad (39)$$

Values of $J_0(ip)$ and $-iJ_1(ip)$ are tabulated by Jahnke and Emde[h] for $0 \leqq p < 10$ and values of $e^{-p} J_0(ip)$ and $-ie^{-p} J_1(ip)$ in Watson[i] for $0 \leqq p \leqq 16$. For values of p greater than these, the asymptotic expression (37) can be used. The errors involved are, for $J_0(ip)$: less than 1.31 percent for $p > 10$ and less than 0.80 percent for

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[h] E. Jahnke and F. Emde, *Tables of Function* (Dover Publications, New York, 1943), pp. 226-229.

[i] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Teddington, England, 1922), pp. 698-713.
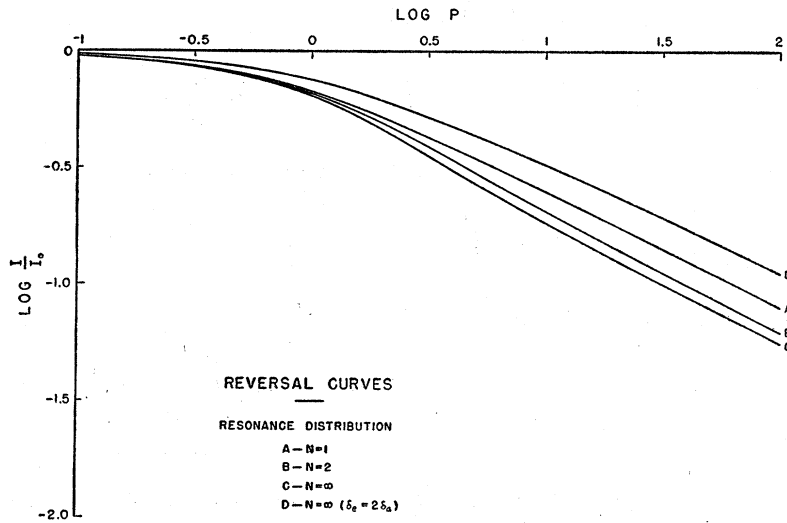
FIG. 7. Reversal curves for various distributions of atoms in the light source. Resonance line shape.

$p > 16$; for $J_1(ip)$: less than 4.04 percent and 2.45 percent for $p > 10$ and $p > 16$, respectively. The asymptotic form of (39) is

$$I/I_0 \sim (2/\pi p)^{\frac{1}{2}},$$
$$\log I/I_0 \sim -\frac{1}{2}\log p - \frac{1}{2}\log \pi/2. \tag{40}$$

This is a special case of (38).

A reversal curve drawn from (39) and (40) is shown in Fig. 7 (curve A). Like Eq. (23), these expressions are not essentially new, having been derived thirty years ago by Ladenburg and Reiche (27), they are included here for the sake of completeness.

3. Light Source with Emitting and Absorbing Atoms Spatially Separated

When the line shape is given by Eq. (24) with $P_e = P_a = 1/\pi\delta(x^2+1)$,

$$I/I_0 = e^{-p/2}J_0(ip/2) \sim 1/(\pi p)^{\frac{1}{2}},$$
$$\log I/I_0 \sim -\frac{1}{2}\log p - \frac{1}{2}\log \pi. \tag{41}$$

This expression is plotted in Fig. 7 (curve C) along with (39). A comparison of the two shows, as one might suspect, that the total energy absorbed is greater in the present case than for a uniformly excited source.

4. Other Non-Homogenous Sources

For a light source of the type (30) and in the special cases $n = 1$ and $n = \infty$, the total line intensities are given by Eqs. (39) and (41),

respectively. The only other case that will be treated is the case $n = 2$. From (31)

$$I/I_0 = \int_{-\infty}^{+\infty} P(u)\{(1 - e^{-\mu})/\mu\}^2 du$$

$$= (1/\pi p^2)\int_{-\infty}^{+\infty} \{1 - e^{-[p/(1+x^2)]}\}^2(x^2+1)dx.$$

With the substitution (34), two partial integrations, and Eq. (36) this can be reduced to

$$I/I_0 = \{2e^{-p}J_0(ip) - e^{-p/2}J_0(ip/2)\}$$

$$+\frac{4}{3}\{2e^{-p}[-iJ_1(ip)] - e^{-p/2}[-iJ_1(ip/2)]\}$$

$$+\frac{1}{3}\{2e^{-p}[-J_2(ip)] - e^{-p/2}[-J_2(ip/2)]\}, \tag{42}$$

$$I/I_0 \sim \frac{8}{3}(\sqrt{2}-1)/(\pi p)^{\frac{1}{2}} \cong 1.105/(\pi p)^{\frac{1}{2}}.$$

As was to be expected, this lies in between the value $(2/\pi p)^{\frac{1}{2}}$ for $n = 1$ and the value $1/(\pi p)^{\frac{1}{2}}$ for $n = \infty$.

The curve (42) is shown in Fig. 7B.

5. Source with Spatially Separated Emitting and Absorbing Atoms: $P_e \neq P_a$

In all the cases just discussed it has been assumed that $P(u)$ is independent of r. This is

probably true only as a first approximation since, due to the higher temperature and greater density of atoms at the center of the source, the degree of resonance and collision broadening decreases with increasing values of r. Some idea of the effect of the radial dependence of $P(u)$ on the shape of the reversal curve (and, in particular, on the asymptotic slope of the curve) can be obtained by considering the following special case.

The line shape is given by Eq. (24). Both P_e and P_a are of a resonance form, but the effective half-width for the region occupied only by emitting atoms is twice that for the region occupied only by absorbing atoms. Then with the substitution $u = \delta_a \tan\varphi$

$$\frac{I}{I_0} = \left(\int_0^{\pi/2} \frac{e^{-p\cos^2\varphi}}{1+3\cos^2\varphi} d\varphi \bigg/ \int_0^{\pi/2} \frac{d\varphi}{1+3\cos^2\varphi} \right).$$

This expression has been integrated graphically and the results plotted in Fig. 7 (curve D). The curve is similar to that for the case $P_e = P_a$ and as in that case, tends asymptotically to a slope of $-\frac{1}{2}$.

B. Doppler Distribution

1. Uniformly Excited Source

If the distribution function $P(u)$ is determined solely by the Doppler effect, then

$$P(u) = \left(\frac{\ln 2}{\pi\delta^2} \right)^{\frac{1}{2}} e^{-\ln 2(u/\delta)^2}$$

where δ is, as before, the half-width at half the maximum.

For a uniformly excited source in which $P(u)$ is independent of r, $I(u)$ is given by (22) and

$$\frac{I}{I_0} = \frac{1}{2p} \left(\frac{\ln 2}{\pi\delta^2} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} (1 - \exp[-2pe^{-(\ln 2)(u/\delta)^2}]) du$$

$$= \sum_{m=0}^{\infty} \frac{(-2p)^m}{(m+1)^{\frac{1}{2}}(m+1)!}. \qquad (43)$$

This expression has been obtained by Ladenburg (26) who gives a table of values of I/I_0 for values of p from 0.05 to 500. From these data a reversal curve has been plotted in Fig. 8 (curve A).

It has been shown by Hardy[j] that the series (43) can be represented asymptotically by the
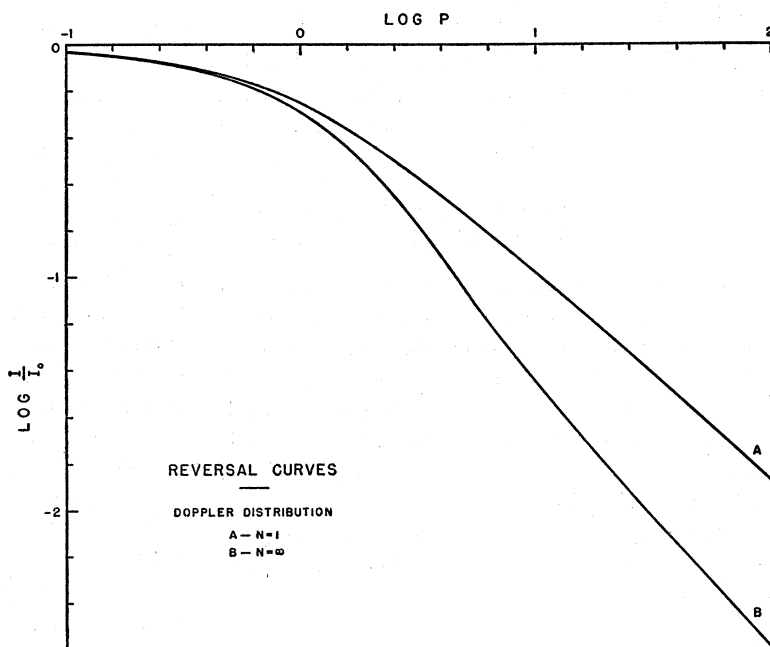

FIG. 8. Reversal curves for various distributions of atoms in the light source. Doppler shape.

[j] G. H. Hardy, Proc. London Math. Soc. 2, 428 (1905).

expression

$$I/I_0 \sim [1/(\pi)^{\frac{1}{2}}][(\ln 2p)^{\frac{1}{2}}/p]$$
$$\ln(I/I_0) \sim -\ln p + \tfrac{1}{2} \ln \ln 2p - \tfrac{1}{2} \ln \pi.$$

The asymptotic value of the slope is thus

$$\frac{d \ln(I/I_0)}{d \ln p} \sim -1 + (1/2 \ln 2p) \sim -1. \qquad (44)$$

2. Source with Spatially Separated Emitting and Absorbing Atoms

$$I/I_0 = (\ln 2/\pi \delta^2)^{\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-(\ln 2)(u^2/\delta^2)}$$

$$\times \exp[-pe^{-\ln 2(u^2/\delta^2)}]du = \sum_{m=0}^{\infty} \frac{(-p)^m}{(m+1)^{\frac{1}{2}} m!}. \qquad (45)$$

Values of I/I_0 obtained by graphical integration of (45) are plotted in Fig. 8 (curve B). According to Hardy, for large p

$$I/I_0 \sim \frac{1}{(\pi)^{\frac{1}{2}}} \frac{1}{p(\ln p)^{\frac{1}{2}}}$$

$$\ln I/I_0 \sim -\ln p - \tfrac{1}{2} \ln \ln p - \tfrac{1}{2} \ln \pi.$$

The asymptotic slope is

$$d \ln(I/I_0)/d \ln p \sim -1 - (1/2 \ln p) \sim -1. \qquad (46)$$

It is interesting to note that when the variation of p is due only to that of I_0 (through variation of the line strength B), a slope less than -1 indicates a decrease in I with an increase in I_0.

C. Comparison of Resonance and Doppler Distributions

The results derived above show that the general form of reversal curves for a resonance distribution differs greatly from that for a Doppler distribution. Strictly speaking, neither of these two types of curves can be observed experimentally, as the actual distribution $P(u)$ is always a combination of the resonance and Doppler distributions.

If the Doppler broadening is small compared with the resonance and collision broadening, the corresponding reversal curve will be very similar to the curve for a purely resonance distribution.

On the other hand, if the Doppler broadening accounts for a large part of the line width, the experimental reversal curve will resemble the theoretical curve for a strict Doppler distribution only for small and moderately large values of p. For the Doppler shift affects the distribution function $P(u)$ appreciably only at comparatively small values of u, while with a very high degree of self-absorption an increase in the value of p affects the line shape $I(u)/I_0$ only at large values of u. Thus the slope of the experimental curve will be approximately -1 for moderate values of p and will gradually increase to $-\tfrac{1}{2}$ for very large values of p.

Curves showing the transition between the case of a purely resonance line shape and that of a purely Doppler shape are given by van der Held (49). As presented in his paper, the curves represent the total energy absorbed from a continuous spectrum by layers of absorbing gas of various thicknesses. Mathematically, however, the corresponding calculations are identical with those giving I/I_0 as a function of p for a uniformly excited source.

For further details and references in connection with the mathematical aspects of the problem, see Mitchell and Zemansky (37) and Kendall (17).

IX. THE EFFECT OF SELF-ABSORPTION ON WORKING CURVES FOR SPECTRO-CHEMICAL ANALYSIS

In making a spectrographic quantitative analysis of the composition of an alloy or other substance, it is necessary to establish first a so-called working curve, in which the concentration C_A of an element A in the alloy is plotted against the intensity I_A of one of the spectral lines of A in the spectrum of the alloy produced by a suitable light source. To a first approximation, the number of atoms of A vaporized in the source is directly proportional to the concentration C_A. Since I_{0A} is proportional to the number of emitting atoms of A (and therefore proportional to the total number of atoms of A), it follows that
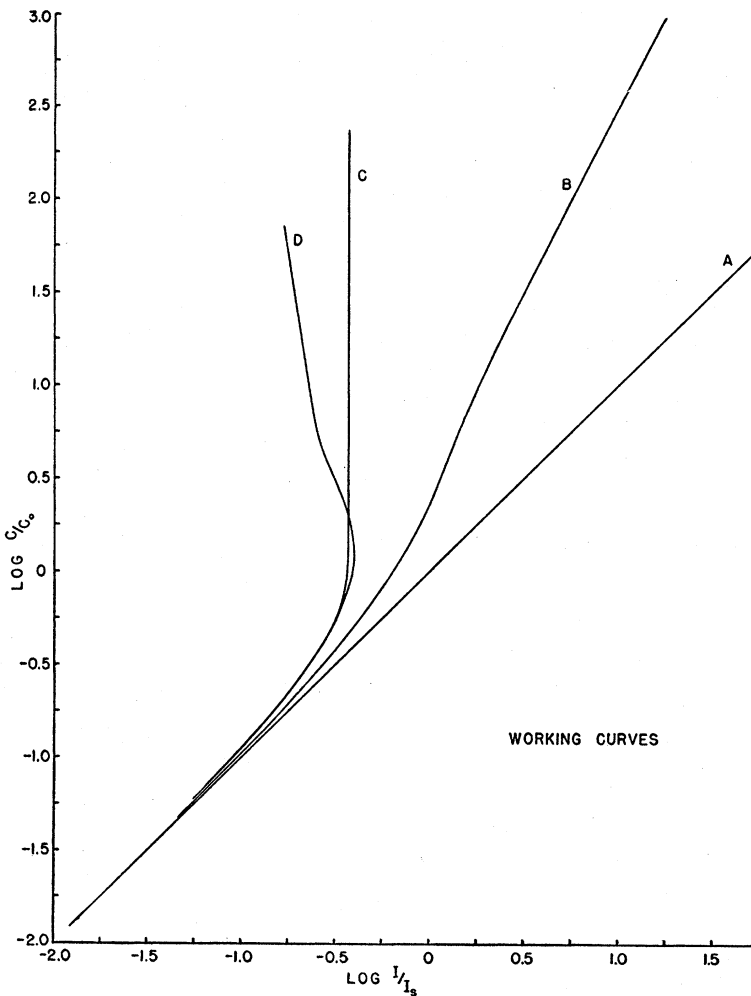
$$I_{0A} \propto C_A$$

or

$$\log I_{0A} = \log C_A + \text{constant}.$$

Thus, if there is no self-absorption present, the working curve is (when plotted on log-log paper) a straight line with unit slope.

FIG. 9. Spectrochemical working curves under various conditions of self-absorption. A: no self-absorption. B: resonance shape, total intensities measured. C: resonance shape, line maxima measured. D: Doppler shape, total intensity measured.

The effect of self-absorption is easy to determine. Assuming as before that $I_{0A} \propto C_A$, then

$$I_A \propto C_A I_A / I_{0A}$$

and, corresponding to the usual manner of drawing the working curve,

$$\log C_A = \log I_A - \log I_A / I_{0A} + \text{constant}. \quad (47)$$

The quantity $-\log I_A / I_{0A}$ was evaluated in the preceding section and was seen to be a positive quantity whose value increases with p (which is proportional to C_A, since $p \propto N_a \propto N_e$—provided the character of the source does not change). Thus the effect of self-absorption is to increase the slope of the working curve and, in general, to cause it to be curved rather than a straight line.

Some of the forms which the working curve may assume as a result of self-absorption are shown in Fig. 9. The curves are all for a source for which the simplified model of Section VI is a good approximation. The arbitrary constant in Eq. (47) was chosen so that (47) reduces to

$$\log p = \log I_A - \log \left[\frac{I_A}{I_{0A}}(p) \right].$$

Data for plotting the curves were then obtained from the results of the previous section. (Indeed, the working curve differs from a reversal curve only in the manner of plotting.) A is the ideal curve for no absorption; B and D are curves for a resonance and a Doppler distribution, respectively. The intensities plotted in curves A,

B, D are the total intensities of the lines. On the other hand, curve C represents the expression

$$\log p = \log I - \log I(u)_{\max}/I_0(u)_{\max}$$

It uses the line maxima instead of the total intensities. Such a curve would be obtained from the usual densitometer readings if a very narrow spectrograph slit were used. A comparison of B and C shows, then, the influence of slit width on the working curve. The effect of slit width is discussed further in the following section.

The actual concentration at which the effects of self-absorption become perceptible depends on the constant of proportionality between p and C_A. For any given concentration, p can be made as small as desired by using any of the following obvious means: (1) using a "weak" line, for which the transition probability B is small; (2) using a low power arc or spark (and a correspondingly longer exposure time) to reduce the number of absorbing atoms in the source; (3) avoiding whenever possible the use of resonance lines and other lines ending on low lying energy levels, as n_a is particularly large for such lines in the cooler vapor surrounding the core of the source.

X. EXPERIMENTAL

The literature on the subject of self-absorption is fairly extensive, but many of the papers (for example Royds (43), Takamine and Suga (48)) are purely descriptive of observed self-reversals, or at most are semiquantitative in nature. The available data which are adequate for a quantitative comparison with theory are very limited in extent.

For purposes of drawing such a comparison it may be noted first that for a given form of the function $P(u)$ and for a given type of light source, the various characteristics of a self-absorbed line depend only on the absorption parameter (see Eq. (7)),

$$p = (h\nu_0/c)BN_aP(0).$$

This can be written in the form

$$p = [BN_aP(0)/AN_ec](h\nu_0AN_e)$$
$$\propto [P(0)N_a/\nu_0{}^3N_e]I_0, \quad (48)$$

where the value $P(0)$ depends on the particular form of the distribution function $P(u)$.

It is evident that for application to experiments p can be given either of two meanings:

(1) For a given spectrum line, ν_0, $P(0)$, B, and A are constant so that

$$p \propto N_a,$$

or, if N_a/N_e is held constant,

$$p \propto N_e.$$

(2) For a given multiplet and a given light source, ν_0, $P(0)$, and N_a are essentially constant so that p depends on the strengths of the various lines:

$$p \propto B \propto A.$$

In either case, $p \propto I_0$, where the variation of I_0 is due either (1) to the concentration N_e of atoms in the source, or (2) to the intrinsic strength A.

From these considerations it is immediately obvious that in a light source with a mixture of elements and with given excitation characteristics, self-absorption is primarily determined by the intensity I_0 of the line. It does not matter, for example, whether a line appears relatively strong because it is an intrinsically strong line (large transition probability) with a relatively small concentration of the element, or whether the line is intrinsically weak but appears strong due to the large concentration of the element in the source. Secondly, the ratio N_a/N_e is important. This ratio, in a source where there is temperature equilibrium is, for a given temperature, a function of the wave-length and, for a given wave-length, a function of the temperature. In general, it does not depend much on the type of excitation unless the lower level is the normal level of the atom or a metastable one. Self-absorption is relatively larger for such lines. Finally, self-absorption depends on the line shape, which is expressed by $P(0)$ in (48), and it is also, with everything else equal, proportional to the third power of the wave-length.

Experimental data concerning these points will be dealt with in turn in the succeeding sections.

A. Total Intensity as a Function of N_e

Numerous investigators have studied the dependence of the observed total intensity I of a spectrum line on the total number of atoms, N,

in a light source. In most cases, the source was a Bunsen flame into which was sprayed a solution of NaCl or NaOH. The intensity of the sodium D lines was measured (with a spectrophotometer) as a function of the concentration of the salt solution and the thickness of the source. The earliest experiments were performed in 1879 by Gouy (12); a comparison of his results with theory can be found in the papers by Ladenburg and Reiche (27) and Schütz (44). More elaborate investigations have since been made by Wilson (54), (55), Locher (29), Child (5), and Bonner (3).

The results of these investigations indicate that the observed intensity I depends only on N, and not on the distribution of atoms in the flame (see Section V). This result is to be expected only in a flame producing substantially a uniform excitation (constant n_a/n_e) throughout the source, and then only if $n_e(r)$ is directly proportional to the density of sodium atoms at the point r. It follows then that $N_e \propto N$.

To a close approximation it was found that for large N, I was proportional to $N^{\frac{1}{2}}$ and therefore also to $N_e^{\frac{1}{2}}$. Thus $I/I_0 \propto N_e^{-\frac{1}{2}} \propto p^{-\frac{1}{2}}$. This is exactly the theoretical result for a resonance distribution [Eqs. (38) and (40)]. Although the Doppler half-width for sodium is much greater than the natural line breadth, the experimental curves do not have the prominent inflection point present in the theoretical curves of van der Held (49) which should apply in that case. This is probably due to the presence of sufficient collision broadening to produce a resonance distribution comparable in width to the Doppler broadening (37), (44).

Both Child and Bonner found that for very large values of N, the intensity increased somewhat less rapidly than the square root of N. No explanation for this was given, but two of the more likely possibilities are:

(1) A continuous spectrum is absorbed according to the familiar exponential law, and thus increases in intensity less rapidly than $N_e^{\frac{1}{2}}$. Thus the presence of an appreciable continuous background would decrease the slope of the $I-N$ curve.

(2) Increasing the value of N_e (and thereby the value of p) increases the apparent width of a spectral line. If too narrow a spectrometer slit is used, a larger and larger fraction of the total line intensity is lost, thus making the measured intensity increase less rapidly than the true intensity. This is discussed further in Section XC.

The effects of self-absorption on the variation of I with N_e in arc and spark sources have not been studied as thoroughly as they have for flame sources. The analytical working curve discussed in Section IX gives the intensity of a line of a given element as a function of the concentration of that element in an alloy or other mixture, but due to various factors N_e may not increase linearly with the concentration—as is shown by the fact that the working curve is not always a straight line with unit slope even in cases where self-absorption is negligible. In addition, arc and spark sources are not easily reproducible due to variations in the distribution of atoms in the source, air currents which may blow away the absorbing vapor which surrounds the core of the source, etc. For these and other reasons it is difficult to make quantitative comparisons between theory and the innumerable experimental curves found in the literature on industrial spectrochemical analysis.

B. Total Intensity as a Function of the Transition Probability A

The effect of the transition probability A on the degree of self-absorption can be best studied in the more complex atomic spectra, such as those of iron and similar elements, which contain —even in fairly limited wave-length intervals— numerous lines of widely varying intensities. To eliminate the effect of excitation on the relative intensities of spectral lines and on the degree of self-absorption, it is convenient to deal at one time only with lines having upper levels of nearly the same excitation potential. This is usually the case for the lines belonging to one multiplet. N_e is then the same for each of the lines, and since I_0 is proportional to $A N_e$ it follows that the intensity of the non-absorbed line can be used as a measure of A.

Harrison and Engwicht (13), (14) have worked with multiplets of the titanium spectrum, using relative values of I_0 obtained theoretically and checked experimentally with a source in which self-absorption was negligible. Relative values of I were determined photographically with a source in which there was great absorption, and
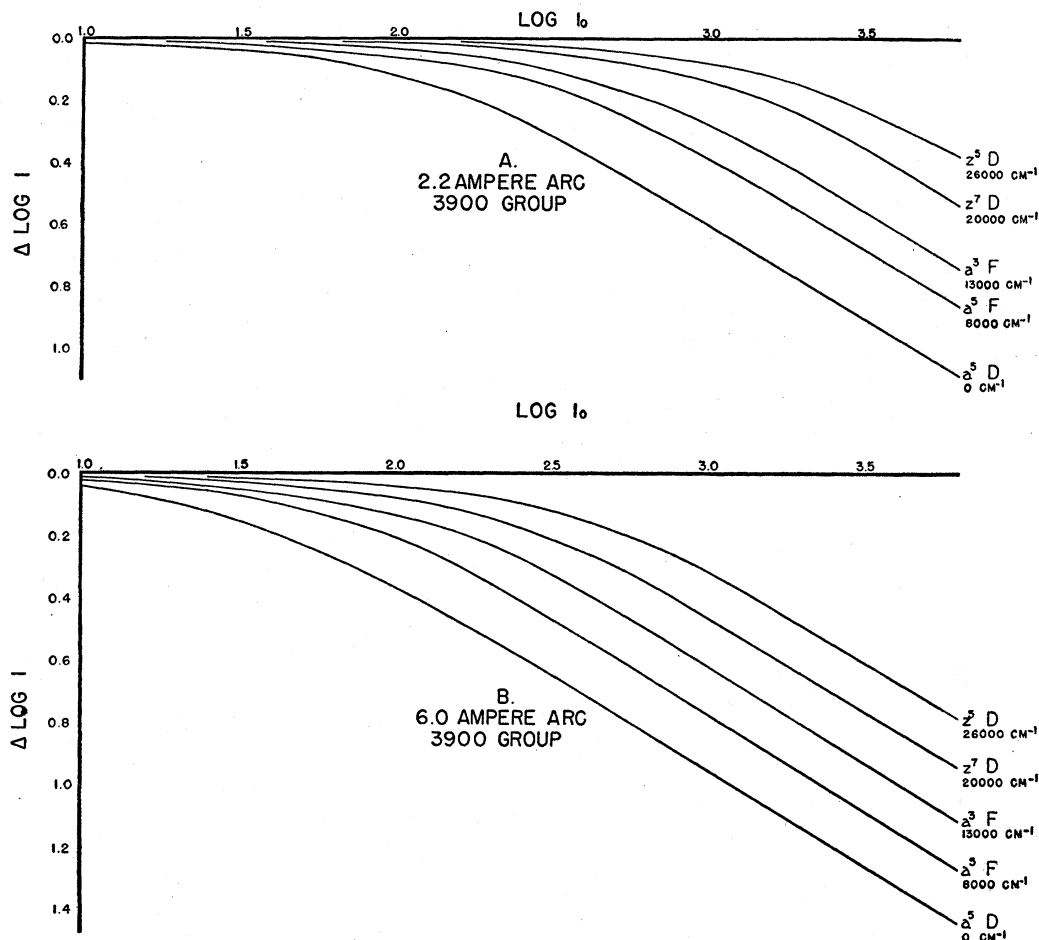
FIG. 10. Experimental reversal curves of iron lines obtained for line groups ending on different lower states (indicated at the right). The effect of a change in the arc current and the effect of the final state (indicated at the right) are shown.

curves showing I as a function of I_0 are given. Harrison attempted to fit these curves with some sort of simple theoretical expression, but with admittedly poor agreement.

Intensity measurements in numerous multiplets in the iron arc spectrum have been made by van Milaan (50), (51) for various arc currents, but primarily in order to determine the values of I_0 for each line rather than the values of I/I_0 when absorption is present.

Extensive measurements on the self-absorption of lines in various multiplets of the iron arc spectrum have been made at Johns Hopkins University (6), (7), (8), (9). The earlier experiments were made chiefly to study the self-absorption properties of various light sources.

They cannot be used for a quantitative comparison with the theory as the influence of the slit width was not fully taken into account. This is probably true also of similar results of most other observers. The influence of slit width is discussed fully in the next section, which shows that when the measurements are made properly the asymptotic slope of the reversal curve is $-\frac{1}{2}$, in agreement with the theoretical result for resonance shape.

Figure 10 gives a number of reversal curves obtained photoelectrically in the iron arc by Crosswhite (7). Each curve represents the data for a group of homogenous lines, i.e., lines with the same excitation potential lying in the same wave-length region. The final state is indicated

in each case at the right. The non-reversal intensities I_0 were determined by measuring the lines in a source that had iron only as an impurity and where the self-absorption was negligible.

The curves show that the asymptotic slope is the same for all line groups and its value is very close to $-\frac{1}{2}$. The curves show that the weakening of some lines by self-absorption is as much as by a factor 10 in an arc with a current of only 2.2 amperes. Other lines show an even greater weakening under the same conditions. The curves B show the influence of a higher current. Because of the higher temperature and therefore the higher density of iron atoms, self-absorption is greatly increased.

The curves of Fig. 10 also show the dependence of self-absorption on the value of N_a/N_e. This, as far as the evidence goes, seems to be only a function of the height of the levels above the ground level and does not depend on the nature of the level. The higher the levels, the less the self-absorption.

Finally the data show the effect of wave-length on line groups. They confirm the prediction that everything else being equal, lines of longer wave-length have greater self-reversal. The results, however, besides this explicit wave-length dependence, also contain variations of N_a/N_e with wave-length. Obviously, when the wave-length is changed, upper and lower levels cannot both be left the same.

Hemmendinger (15) worked with both titanium and iron, but did not confine himself to lines of one multiplet at a time. His work, then, deals with neither of the two special cases $p \propto N_e$ and $p \propto A$, but with the general case $p \propto N_e A$. Relative values of A were taken from the tables of f values given by King;[k] relative values of N_e were obtained by assuming N_e to vary exponentially with excitation potential according to Boltzmann's formula, and determining experimentally an effective "excitation temperature." Because of the more complicated procedure, the scatter of the experimental points in the curves given is somewhat greater than in the experi-
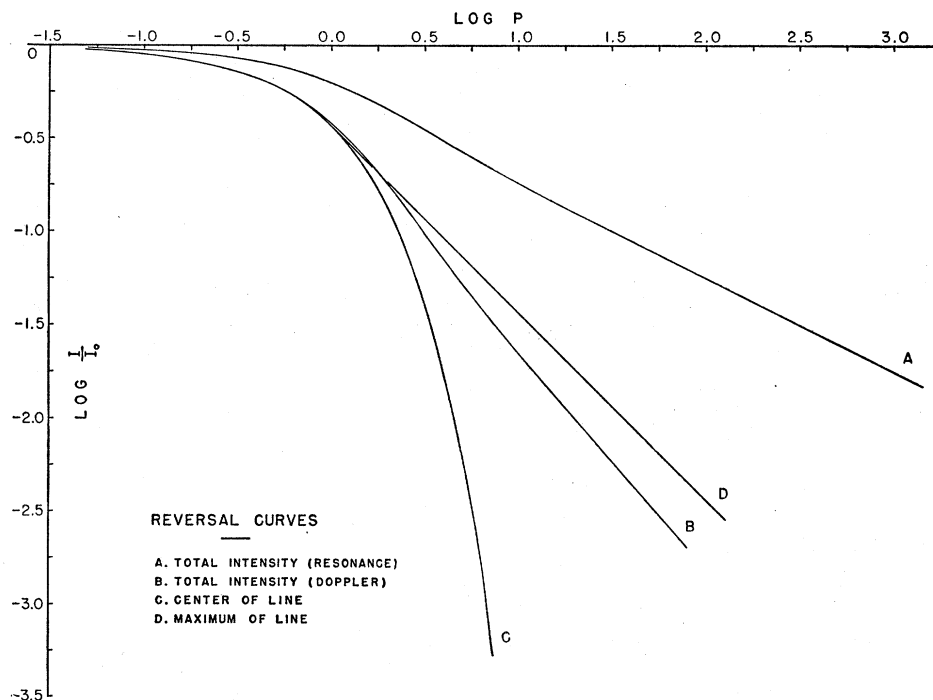

FIG. 11. Calculated reversal curves obtained under different conditions of line shape and measurement. A: resonance shape; I is total intensity. B: same for Doppler shape. C: arbitrary shape; I is intensity at center of line. D: arbitrary shape; I is intensity at line maximum.

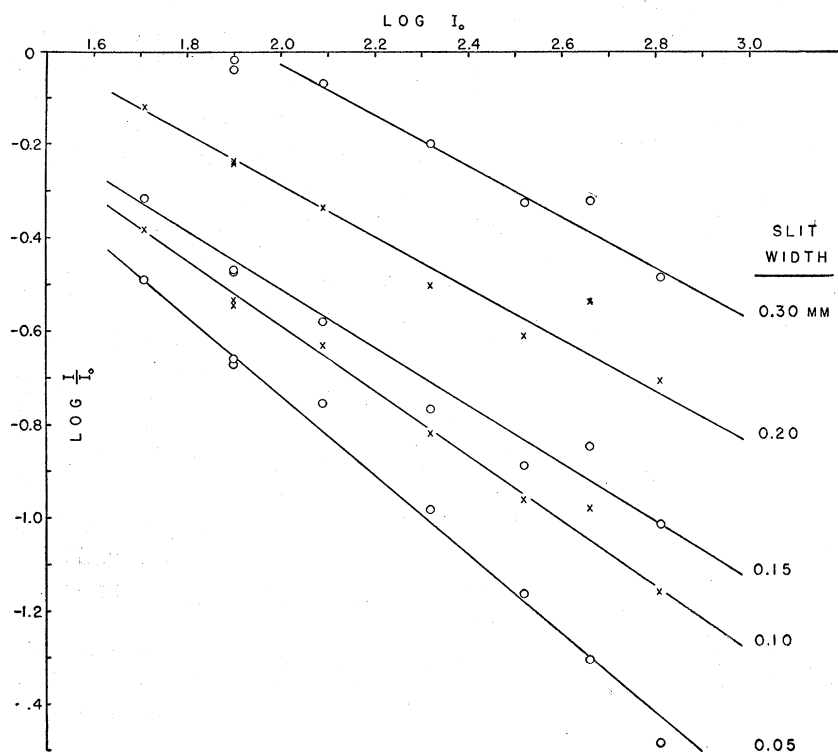[k] R. B. King and A. S. King, Astrophys. J. **87**, 24 (1938).

FIG. 12. Effect of slit width on measured slope of reversal curve.

ments of Harrison and of Crosswhite. The general shape of the curves is, however, the same in all papers.

Perhaps the most interesting of Hemmendinger's results was obtained with a 3-ampere arc between electrodes consisting of 1 percent Fe and 99 percent Ti. He found that all the titanium lines gave experimental points lying on a single curve, while the iron points fell on different curves according to the excitation potential of the corresponding lines. This he explained by suggesting that the titanium lines were only self-absorbed, while the iron lines were in addition self-reversed; i.e., that the cloud of relatively cool absorbing vapor surrounding the central core of the arc contained very little titanium. Thus in $p \propto (N_a/N_e)(N_e A)$, the ratio N_a/N_e is increased for iron by the weakly excited absorbing cloud and is increased more for the low lying levels than for the higher ones. However, a much simpler explanation is perhaps found in the fact that the width of the iron and titanium lines is very different (compare Section XE).

C. Effect of Slit Width on Observed Reversal Curves

In all intensity measurements of spectrum lines serious errors can be made if the slit width of the spectrograph does not have the proper value.

On the whole there are two limiting cases where total line intensities can be evaluated without any complications. If the slit is narrow compared with the width of the lines a true contour of the line is obtained and the total intensity is found by integrating under the line contour. This implies that the resolving power of the spectrograph is sufficient to give the actual line contour. While working with a narrow slit would undoubtedly give the best results with strongly reversed lines, the method is of less practical value becuase of the considerable labor involved.

Reliable values of the total intensity of spectrum lines are obtained easily when the slit width is large compared to the line width. In that case the intensity at the center of the line is the integrated intensity. Under ordinary cir-

cumstances, with reasonably sharp lines it is usually not difficult to fulfill this condition. With strongly self-reversed lines, however, a considerable part of the strength of the line is in its extreme wings and unless the slit is wide enough to include these, too small values for the total intensities are recorded. The more strongly the line is self-reversed, the more this discrepancy makes itself felt. This became apparent when during the earlier stages of the investigation attempts were made to obtain self-reversal curves. Instead of obtaining the slope $-\frac{1}{2}$ predicted by the theory, the slope actually found was closer to -1.

The value -1 for the asymptotic slope must be expected if the slit width is such that instead of the total integrated intensity the maximum of the line is measured. According to (21) and (23) I_{max} is constant for sufficiently large values of p, which does produce a reversal curve with a slope of -1.

We have seen previously that the reversal curves depend also on the line shape. A Doppler shape would also produce a reversal curve with a slope close to -1.

Figure 11 summarizes the shape of the reversal curve (for a source of the type discussed in Section VI) under various extreme conditions.

A. Total intensity, $\log I/I_0$ for resonance distribution

B. Total intensity, $\log I/I_0$ for Doppler distribution.

C. Center of line, $\log I(0)/I_0(0) = \log e^{-p}$

D. Line maximum, $\log I_{max}/I_{0\ max}$
$$= \begin{cases} \log e^{-p} & p \leqq 1 \\ -\log e p & p \geqq 1 \end{cases}$$

Figure 11 shows that a slope in excess of $-\frac{1}{2}$ can be attributed to various causes. An experimental investigation was therefore made in order to clear up the situation for the iron arc.

A group of homogeneous iron lines was selected for which the values of I_0 had been determined by Crosswhite in the manner indicated in Section XB. Their intensities were measured in the standard manner in an 8-ampere direct current iron arc and the reversal curves plotted. The lines were chosen so that under the conditions present in the arc they would all lie on the straight line part of the curve. This was done for slit widths varying between wide limits. A typical set of results is shown in Fig. 12. For the narrowest slit width the slope of the curve is closest to that of D of Fig. 11 with an indication of curvature which would make it closer to curve C for the line center. This is exactly what is to be
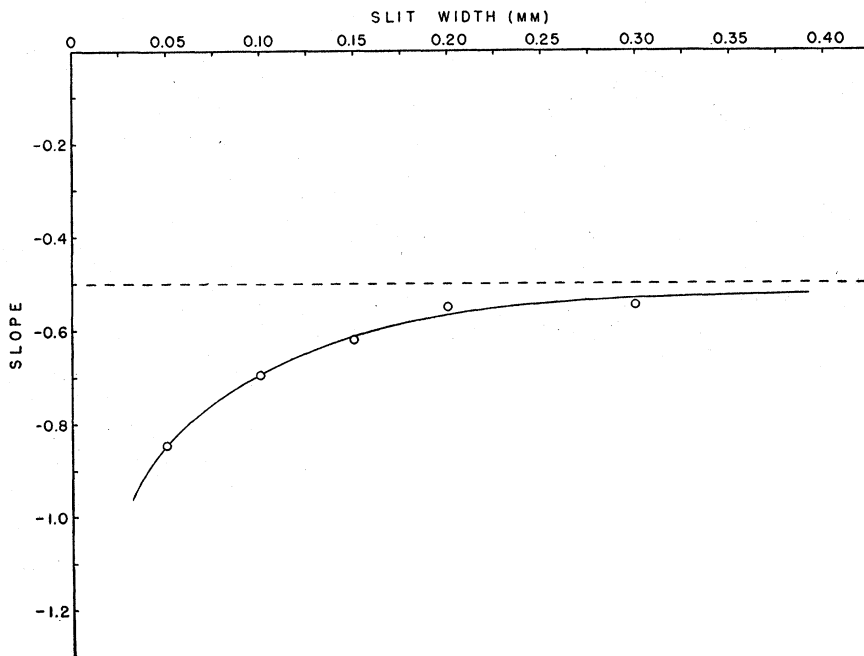

FIG. 13. Effect of slit width on slope of reversal curve. The slopes taken from Fig. 12 are plotted as function of the slit width.
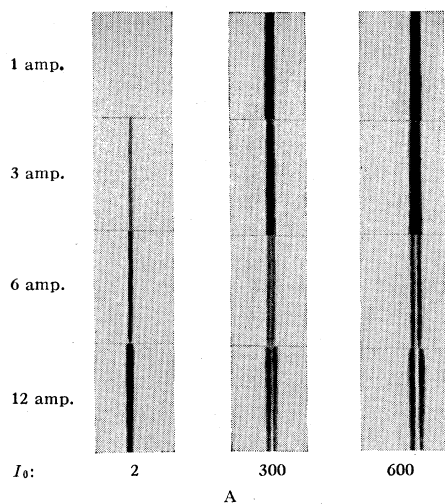
FIG. 14. Photographs of self-reversed lines. A: iron lines of different intensities at different arc currents; B: reversal in the band lines of the OH-band at 3064A. The lower figures are the unreversed intensities. All lines with $I_0 > 20$ show self-reversal in the lower half, which was taken with a large flame thickness. (The upper figures indicate the classification of the lines.)
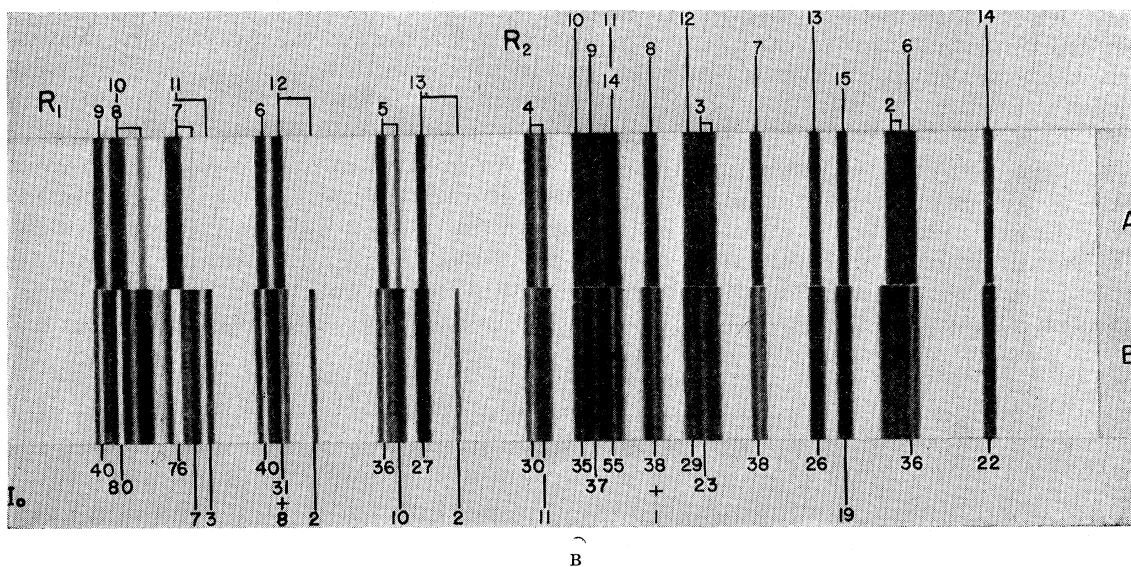
expected if the slit is considerably narrower than the line width. (By line width we mean here the total width inside of which almost all the intensity of the reversed line is contained. It may be many times the so-called half-width of the unreversed line.)

The change in slope with increasing slit width is quite evident from Fig. 12. The measured slopes are plotted as function of the slit width in Fig. 13. It shows that with increasing slit width the slope approaches the value $-\frac{1}{2}$, which is the theoretical value for resonance shape. These measurements show thus quite conclusively that the line shape in an iron arc is not

at all controlled by the Doppler effect. Further evidence for this will be found in the next two sections.

It is at first somewhat surprising that slit widths of the order of magnitude of 0.5 millimeters are required to measure correctly the integrated intensities of reversed lines. (The dispersion of the particular spectrograph was 2.5A/mm.) However, considering the fact that such a large percentage of the intensity of such lines is in the wings and that the lines are considerably widened by resonance broadening, the results are quite plausible.

The iron lines considered here are by no

means extreme cases. Figure 15 shows the microphotometer trace of the magnesium resonance line 2852A in a 25-ampere arc. Here the equivalent slit width (actual slit width times magnification of spectrograph times reciprocal dispersion of spectrograph) would have to be several hundred angstrom units in order to obtain the integrated intensity, and the actual slit width would have to be several centimeters.

Obviously, such large slit widths cannot be realized, and the intensities of such lines can only be obtained with narrow slit widths and integration of the intensity-wave-length curve.

If the slit of the spectrograph is neither very narrow nor very wide compared with the line width, some quite anomalous spurious patterns may be obtained and great care is needed with the interpretation of such patterns.

Figure 16 shows the calculated pattern of a reversed line for various slit widths. The actual shape of the line is indicated by the dotted curve. The slit width is expressed in multiples of the half-width δ of the unreversed line. We see that even for a slit as wide as 10δ the in-

tensity in the middle of the line is only about 70 percent of the integrated intensity which would be obtained for very wide slits.

As the maximum slit width that can be used is usually determined by the presence of neighboring lines, it is evident that in crowded spectra like the iron spectrum one cannot expect to get reliable intensities of heavily self-reversed lines by measuring in the usual way the maximum of the line obtained with a wide slit.

Figure 17 shows a number of experimental curves obtained with an intermediate slit width on reversed iron lines of different character.

D. Separation of the Maxima of a Reversed Line as a Function of the Transition Probability A

It is well known that the wave-length separation of the maxima of a self-reversed line is not the same for all reversed lines in a given spectrum. In wave-length tables, for example, lines tending to show "wide self-reversal" are sometimes distinguished from those showing "narrow self-reversal" by affixing "R" or "r," respectively, to the intensity value of the line. Yet,
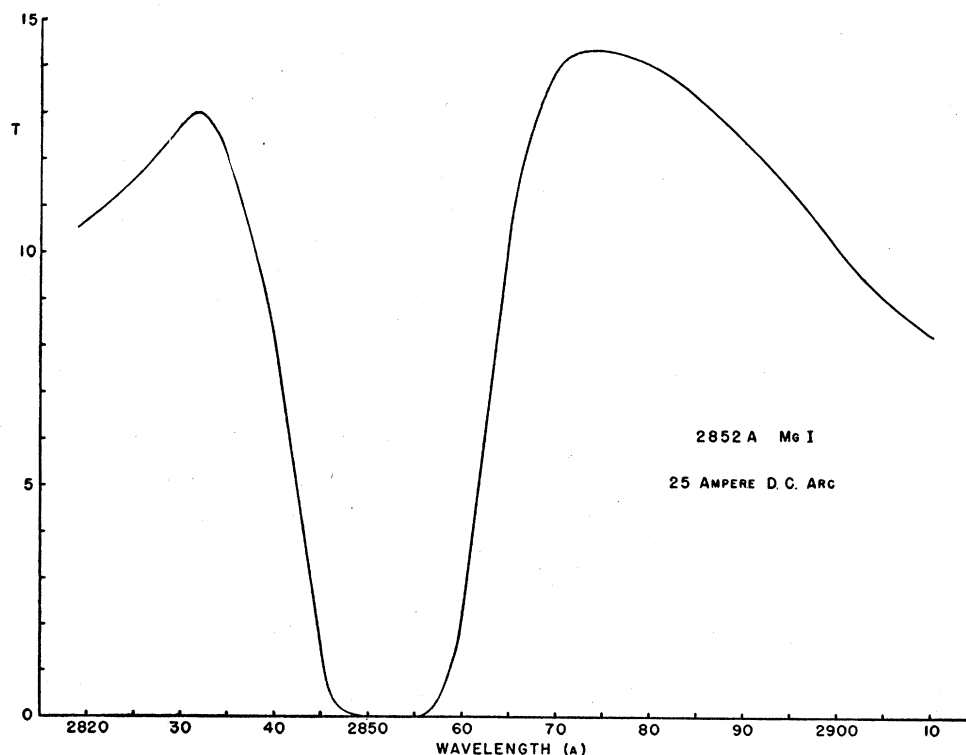

FIG. 15. Microphotometer trace of a heavily self-reversed line (MgI, 2852A in 25-ampere arc).
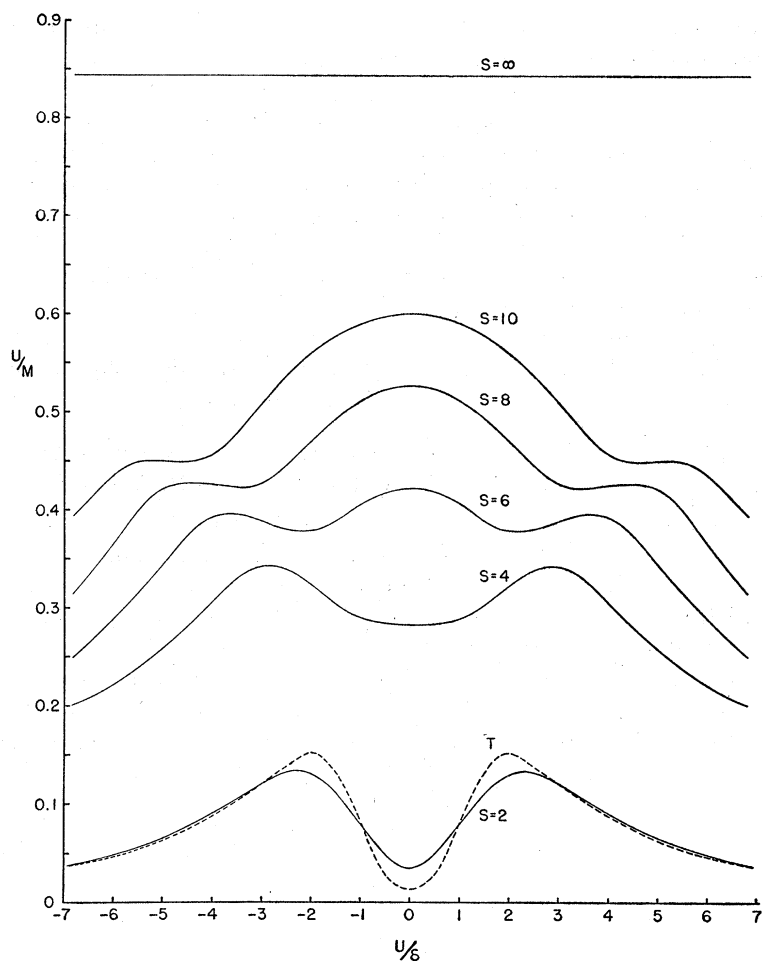
FIG. 16. Apparent shape of a reversed line $(p=5)$ as function of slit width. Dotted curve is true shape.

except for the short paper by Sibaiya (45), which deals only with an extreme case, the writers are not aware of any quantitative measurements on the subject.

Experimental data were obtained using as a source a 220-volt direct current iron arc stabilized with an iron-core inductance (as well as the usual ballast resistor) and operated at currents up to 25 amperes. The spectrum was photographed with the narrowest feasible slit in the second order of a 21-foot grating in a Paschen mounting with a resolving power of 300,000 and a dispersion of 0.6A/mm. Exposures of fifteen seconds were sufficient with Eastman Spectrum Analysis I plates, which were used because of their fine grain and high contrast. The lines used were those which had wave-lengths between 2912 and 3134A and the lower levels a^5D and a^5F. The profile of each line was traced with a

Leeds and Northrup recording microphotometer, the resulting dispersion on the chart paper being 0.065A/inch.

Measurements on the paper could easily be made to one millimeter, or about 0.003A or 0.03 cm^{-1}. The accuracy in determining the separation of the maxima of a reversed line was, however, somewhat less than this due to the broadness of the maxima, especially for the strongest (and therefore most highly reversed) lines. Furthermore, the theoretical resolving power of the grating is only about 0.01A at 3000A.

Half the separation thus determined was taken as the experimental value of u_{max}, the separation of each intensity maximum from ν_0. Relative p values for the lines used were taken from the tables of Crosswhite (9).

Typical experimental results are shown in

Figs. 18 and 19, where u^2_{max} is plotted against p (in arbitrary units) for a^5D and a^5F lines, respectively, in the spectrum of a 24-ampere arc. For the most part, the experimental points indicate a linear relationship between u^2_{max} and p. According to the general Eq. (18) and its special cases (19) and (20), this indicates a resonance rather than purely a Doppler distribution, in agreement with the conclusions of the previous section.

For the purpose of comparison, both linear curves suitable for a resonance shape and logarithmic curves suitable for a Doppler shape have been included in the figures. The latter were drawn according to the expressions

$$u^2 = 1.6 \log p - 4.2$$

and

$$u^2 = 0.5 \log p - 1.0,$$

which give as good an agreement with the experimental data as it is possible to obtain for Figs. 18 and 19, respectively. The curves obviously do not fit the experimental data, but if one assumed that they did, the indicated values of the Doppler half-widths found from (19) would be 0.7 and 0.4 cm^{-1}, respectively. These would correspond to temperatures of about

250,000 and 80,000°C—which, in addition to being unequal, are absurd values for the temperature within an iron arc.

On the other hand, the function $P(u)$ is not strictly a resonance distribution either. The corresponding theoretical expression (20) is satisfied only approximatly, as can be seen from the a^5F curve:

In the first place, this curve is not a straight line for small values of p. This might reasonably be attributed to experimental error (the values of u_{max} concerned are of the order of magnitude of the resolving power of both spectrograph and photometer), except that this would not explain the second discrepancy between theory and experiment—namely, the positive u_{max}^2-intercept obtained by extending the straight-line part of the curve. Probably both these differences are due mainly to the influence of the Doppler effect on the distribution function $P(u)$, as the positive u_{max}^2-intercept was also found in the a^5D curve when the arc current was decreased to 10 amperes. With the lower current the smaller degree of collision and resonance broadening present might well make the Doppler effect relatively more important.
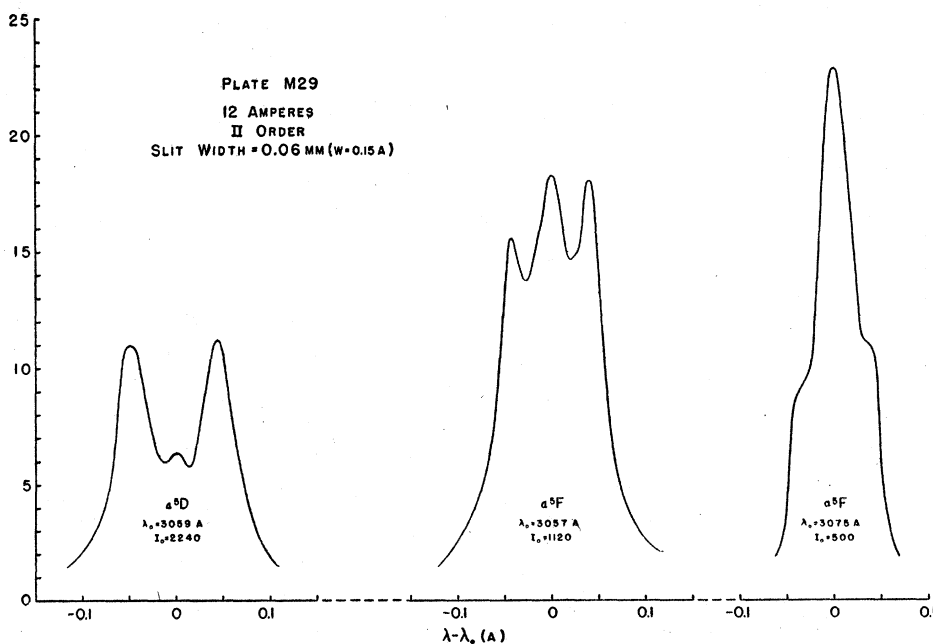
There are, of course, numerous other factors

FIG. 17. Observed line shapes of reversed lines for intermediate slit widths.

which might contribute to the deviations of the experimental curves from the theoretical curve for a resonance distribution. Among these might be mentioned variation in the function $P(u)$ throughout the source, possible differences in the half-widths δ, of the various lines, and a definite asymmetry in the observed shape of most reversed lines (that is, a difference in the intensity of the two maxima, discussed in Section XIA).

E. Line Shape and Line Width in a Metal Arc

The preceding paragraphs have shown that the quantitative behavior of self-absorption is intimately connected with the shape of the unabsorbed line in the particular light source. Shape and width of spectrum lines may vary between wide limits for different light sources and different types of lines. We shall restrict ourselves here to the metal arc in air, particularly the iron arc.

1. Natural Width

An atom completely left to itself in an excited state has a lifetime of approximately 10^{-8} sec. in that state, which corresponds to a half-width of about 4.15×10^{-5}A. The shape of the line would be the resonance shape (10), but the natural width is so small that it cannot possibly be resolved in the visible or near ultraviolet with any spectrograph.

A grating with a resolving power of 300,000, which is close to the limit of what can actually be achieved with a grating, would resolve about 0.01A at 3000A and this would also be approximately the observed width of an infinitely narrow line taken with a very narrow slit with this spectrograph. This is a width about 250 times as wide as that of the natural width, and, therefore, under ordinary conditions we have no possibility of observing directly the natural line shape, as it is hidden by the shape produced by the spectrograph. The use of interferometers or
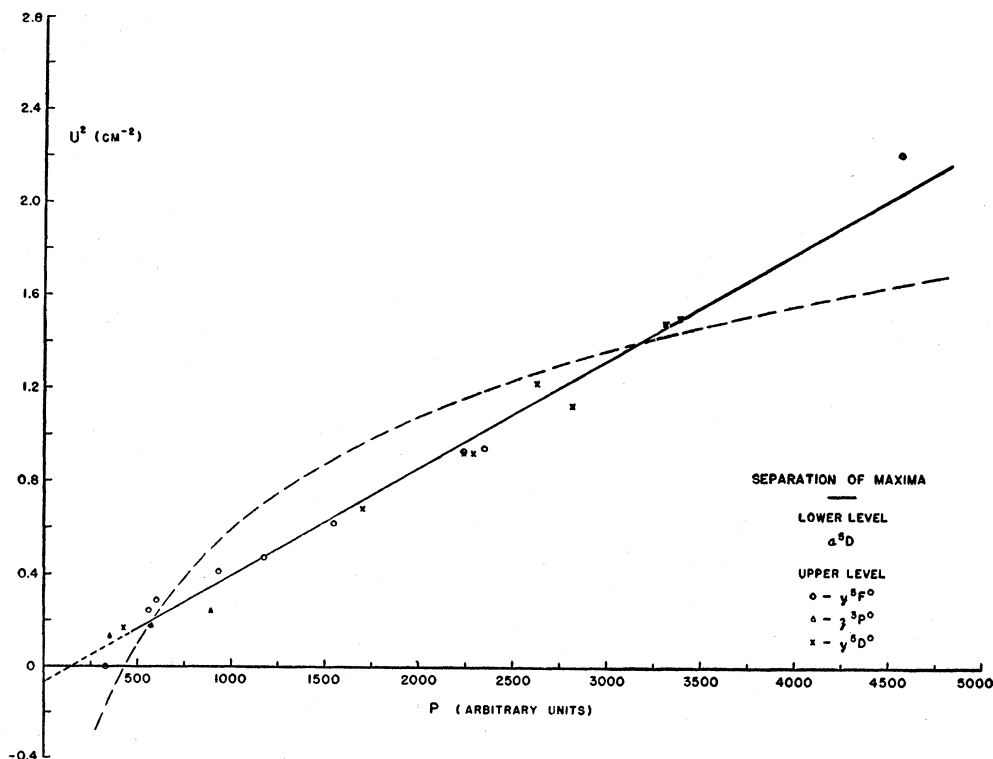

FIG. 18. Separation of maxima of self-reversed iron lines. The ordinates are plotted on a quadratic scale. The solid line is the theoretical curve for resonance shape; the broken line that for Doppler shape.
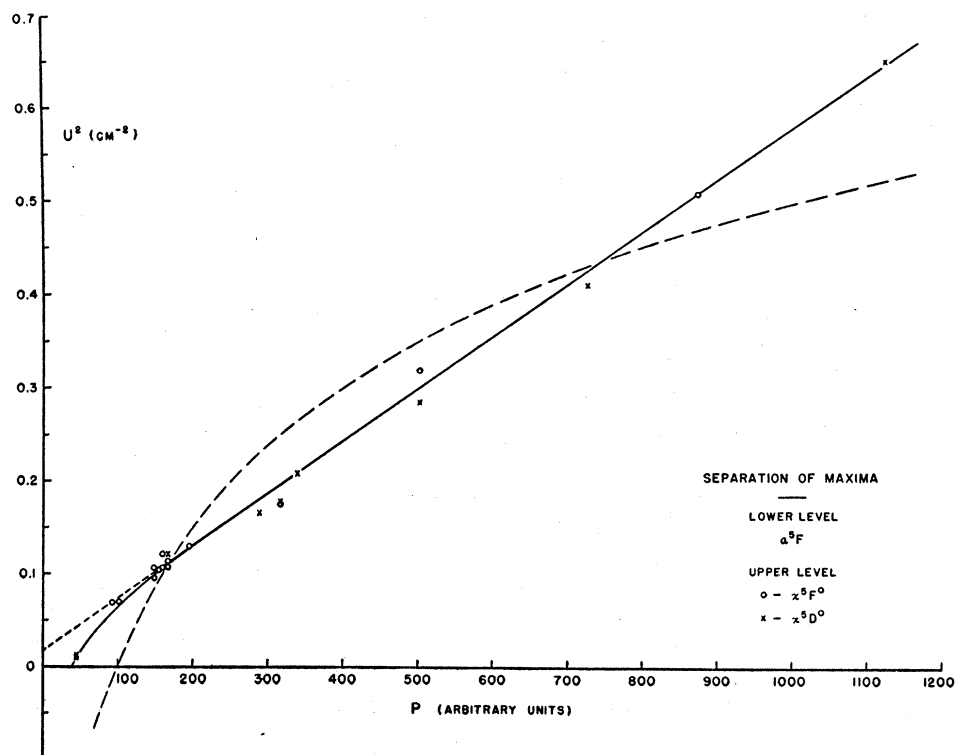
FIG. 19. Same as Fig. 18, but different group of lines.

other devices of high resolving power will not change this, as the increase in resolving power is not nearly enough.

2. Doppler Width

The half-width of a line having Doppler shape (see Eq. (9)) is, when the constants are replaced by their numerical values,

$$\Delta\lambda = 3.58 \cdot 10^{-7}\lambda(T/A)^{\frac{1}{2}},$$

where T is the absolute temperature of the emitting gas and A its atomic weight.

For the iron arc at 5000°K at a wave-length 3000A, this yields a half-width of about 0.01A, which is much larger than the natural half-width but smaller than or at best of the same order of magnitude as the instrument width of the spectrograph.

3. Actual Line Widths

The experimental results of the preceding paragraphs on the asymptotic slope of reversal curves and on the separation of the maxima of reversed lines definitely indicate that the lines in the spectrum of an arc have essentially a resonance shape. However, it is quite obvious from a direct inspection of the lines under high dispersion or from the dependence of the reversal curves on slit width, that the width of the lines must be very much larger than the natural width. The width must be determined by other factors. It can be measured directly if the spectrograph is of sufficiently high resolving power.

Such measurements were made by getting the traces of lines photographed in the 2nd, 3rd, or 4th order of a 21-ft. Wadsworth spectrograph. (Theoretical resolving powers: 150,000, 225,000 and 300,000, respectively.) In order that the width have any definite meaning, it is important that non-absorbed lines be used or that the lines be reversed to such a degree that both the central minimum and the side maxima can be measured. For unabsorbed lines the procedure is obvious, but it is not easy to know whether a line has actually suffered no absorption.

For self-reversed lines we have seen that for

TABLE II.

	δ_λ	δ_ν	Current	Order	Method
3200A group	0.022A	0.21 cm⁻¹	1.5 amp.	II	
	0.017	0.17	1.5	IV	
	0.016	0.15	1.5	IV	Direct
	0.018	0.17	1.5	IV	
	0.038	0.36	12	II	
3600A group	0.026	0.21	1.5	III	
2966A	0.05	0.40	12	II	From reversal
3047A	0.05	0.40	12	II	

the model of Section VI the distance between the side maxima is (for a resonance line shape, see Eq. (27))

$$2u_{max} = 2\delta(p-1)^{\frac{1}{2}} \qquad (49)$$

and that the intensity ratio of the side maxima to the central minimum is (Eq. (29))

$$I_{max}/I(0) = e^{p-1}/p, \qquad p \geqq 1. \qquad (50)$$

Equation (50) allows us to determine p, which then enables us to get δ from (49). In order that this procedure be applicable, p must be larger than one and not so large that Eq. (50) is impossible or difficult to measure. $p=5$ gives a ratio 11:1 which is about the limit of what can be measure easily without special precautions or special devices.

The Eqs. (49) and (50) hold exactly only in the case $n = \infty$ of Section VII (i.e., emitting and absorbing atoms spatially separated). However, for the cases $2 \leqq n < \infty$, the errors in the two equations partially cancel, so that at least the order of magnitude of δ can be calculated. For example, with a source characterized by $n=2$, it can be seen from Eq. (31) and Table I that

$$I_{max}/I(0) = (1 - e^{-\mu_2})^2/\mu_2 \div (1 - e^{-p})^2/p$$
$$= 0.407p/(1 - e^{-p})^2, \quad p \geqq 1.26 \qquad (51)$$

and

$$2u_{max} = 2\delta((p/\mu_2) - 1)^{\frac{1}{2}} = 2\delta((p/1.26) - 1)^{\frac{1}{2}}.$$

In the example of Fig. 6, the value of p calculated from Eq. (50) is 2.4, while the true value of p is 4.0. The value of δ calculated from (49) is thus 25 percent too large. For greater values of p the error is larger: if $I_{max}/I(0) = 10.9$, giving $p=5$ from (50), then the calculated value of δ is 125 percent too large.

Experimental values for the half-widths of a number of typical iron lines are given in Table II.

All measurements were made on unabsorbed lines except those on the last two, which were obtained from the self-reversal of the lines in Fig. 3. These values reveal the following facts.

1. The half-widths are much larger than the natural widths.

2. The half-widths increase with increasing current. They are considerably wider in the spark, as shown by additional measurements.

3. They are not significantly different for the different lines at the same light source conditions, although there is some difference. (The lines from low lying levels seem to be sharper.)

4. Impurity lines remain sharp, while the iron lines widen. Conversely, if iron appears as impurity in other substances, the width of the iron lines is chiefly determined by the concentration of iron atoms rather than by the total concentration of atoms. This means we have here the so-called resonance broadening.

The photometry of the lines is not easy because we are working close to the limit of the resolving power of spectrograph and densitometer. However, there seems to be little doubt about the reality of the effects.

All this shows that in the usual light sources the width of the lines is entirely controlled by the interaction of the atoms during collision and that the actual width is about 1000 times larger than the natural width.

XI. SUMMARY: SOME APPLICATIONS TO SPECTROSCOPIC PROBLEMS

It was shown in Section IV that under certain simplifying assumptions self-absorption is completely described by three quantities: the line shape for no absorption, $P(u)$; the absorption parameter, p; and the excitation function, $E(y)$. Conversely, from appropriate experimental measurements on self-absorption it should be possible to determine these quantities more or less accurately for any given spectrum line. The best methods of doing this are summarized below and possible applications to several spectroscopic problems are pointed out.

A. Experimental Determination of Line Shape

The developments of Section VIII (cf. also XB) make it possible to distinguish experimentally the true shape of spectral lines even

when the resolving power of the spectrograph is not sufficient or when there are other factors which obscure a direct measurement of the shape.

In particular, it is possible to make experimentally a decision as to whether the shape is the resonance shape (10) or the Doppler shape (9). For this purpose select a number of homogeneous lines of increasing strength for which the unreversed intensities I_0 have been determined by measuring them in a light source free from self-absorption. Then measure the total intensity I (taking care that a sufficiently wide spectrograph slit is used) in a source with strong self-absorption.

Plot $y = \log I/I_0$ as a function of $x = \log I_0$. We have seen previously that x and the reversal parameter $\log p$ differ only by an additive constant. For large enough values of I_0 we should therefore, according to (38), obtain a straight line with a slope -0.5 if the lines have resonance shapes, but, according to Eqs. (44) and (46), with a slope of approximately -0.8 to -1.2 (depending on the type of light source) if they have Doppler shape. If the slope reaches a value

of about -1.0 for moderate values of p and then increases for larger p to -0.5, the line shape consists of a combination of resonance and Doppler distributions with comparable half-widths.

With the form of $P(u)$ determined, the half-width of a reversed line can be found in the manner described in the preceding section—calculating p from the measured value of $I_{max}/I(0)$ and then determining δ from the appropriate form of Eq. (33).

1. Asymmetrical Self-Reversal

When a self-reversed spectrum line is photographed with a narrow spectrograph slit, it often proves to be asymmetrical, one of the side maxima being higher than the other. This appears in Fig. 15, but is there probably due largely to the change in plate sensitivity over the extent of the line.

When the lines are narrower this cannot be the cause for the asymmetry, which may be quite pronounced in many cases (see Fig. 20). The explanation lies in a shift or asymmetric broadening of the emission line with increasing
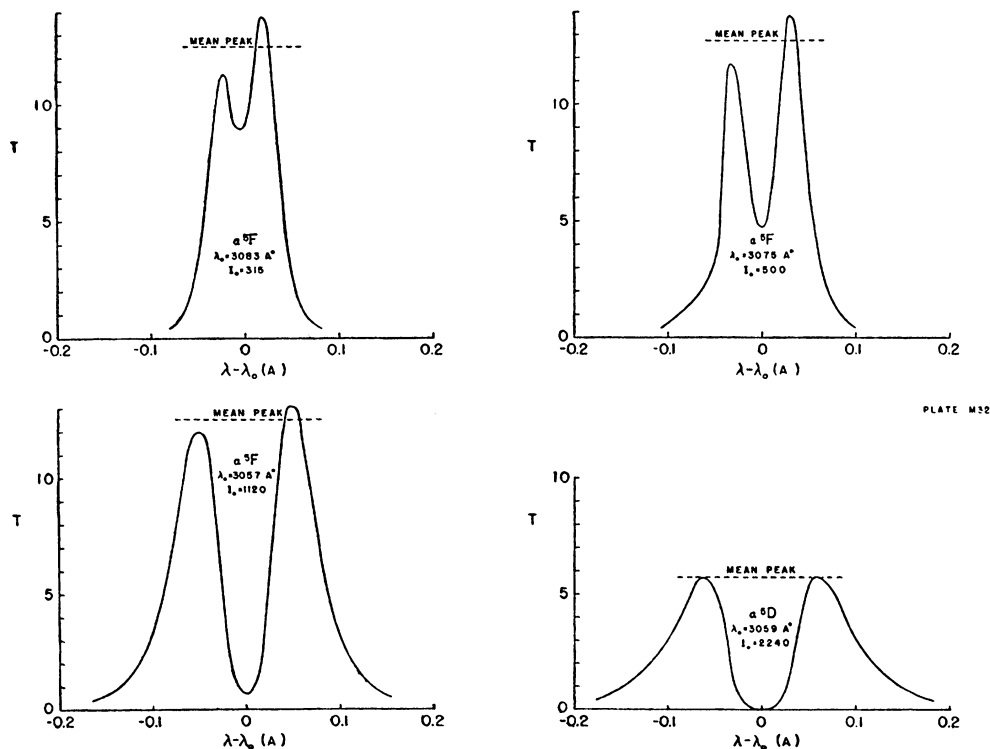

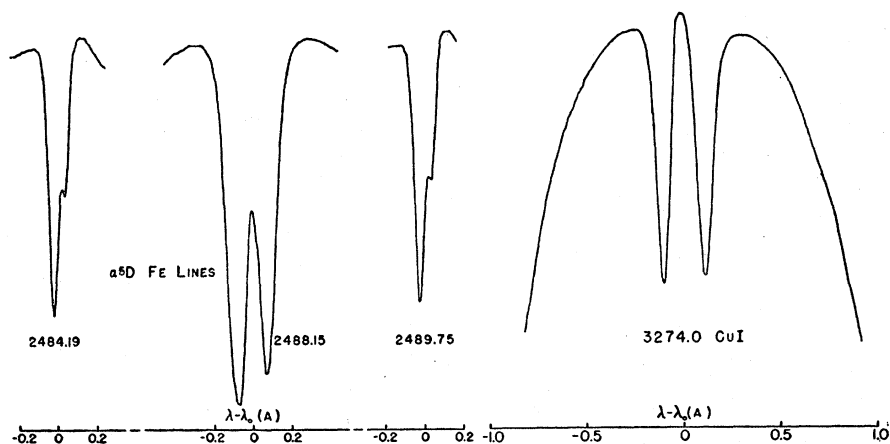Fig. 20. Self-reversed iron lines showing asymmetry.

FIG. 21. Microphotometer traces of reversed lines with the unreversed line superimposed.

pressures of the vapor, while the shift in the absorption line is slightly less.

To test this, plates were taken under the following conditions: on a heavily self-reversed line was superimposed a narrow unreversed line produced when the element in question appeared only as impurity in something else. Spectrograph and plate were not touched between the exposures. The narrow, unreversed line then appeared in the absorbed part of the self-reversed line, and by suitable choice of exposures it could be judged with great precision whether the narrow line was in the exact center of the reversed part. If the broadening of the line was perfectly symmetrical and there was no pressure shift, the narrow line would have to be in the exact center of the reversed part, otherwise shifted slightly to one side.

A number of such plates were taken for elements like Na, K, Ca, Mg, Cu, and Fe. In some cases the line was symmetrical (e.g., Ca4226), in others there was a shift. Such shifts are shown in Fig. 21, which presents the densitometer tracing of a number of lines obtained in the manner just described. In all cases where there is a shift of the unreversed line with respect to the absorption line there is also an asymmetry in the intensity of the peaks of the reversed line and vice versa, and the unreversed line is always closer to the stronger of the two peaks. The shift is toward the shorter wave-lengths in the copper line, and in the opposite direction in the iron lines. There seems thus a definite connection between the asymmetry of the peaks and a shift or asymmetric broadening of the line.

The cause for the shift is not entirely clear yet, and further experiments would be necessary to elucidate this further. It may be due to an internal Stark effect or other causes.

The pressure shift of spectral lines has been a subject of much study.[1] Because of the smallness of the shift compared to the line width, the establishment and measurement of this shift has often necessitated long series of very accurate wave-length measurements which were quite tedious.

If the lines can be obtained self-reversed, which is possible under suitable conditions for all strong and moderately strong lines, and the connection between wave-length shift and asymmetry in the secondary maxima is substantiated, the observation of these secondary maxima will be a very much simpler method for the study of this shift.

B. Excitation Conditions in Light Sources

Uniformly excited sources are easily recognizable in that a high degree of self-absorption does not result in reversal but only in flat-topped, apparently broadened spectrum lines.

Non-uniformly excited sources are even more easily recognizable by the presence of reversed lines. Very little is known, however, about the exact form of the excitation function $E(r)$ for such sources. Nor can a study of self-absorption solve this problem entirely, because the various characteristics of a reversed line are too insensi-

[1] See, for example, H. Margenau and W. W. Watson "Pressure effects on spectral lines," Rev. Mod. Phys. **8** 22–53 (1936).

tive to the type of excitation. Nonetheless, a partial answer can be obtained: it should be possible to tell how closely an arc or similar source is approximated by the simple model in which emitting and absorbing atoms are entirely separated—i.e., to determine for approximately which value of n expression (30) best describes the source. For this purpose, the experimental determination of a reversal curve or of the intensity distribution within a single reversed line is inadequate because of the small effect which the value of n has on the form of these curves (see Figs. 6 and 7).

The most promising method theoretically (though practically the one requiring the greatest resolving power) consists of the measurement of the value $I_{max}/I(0)$ for each of a set of reversed lines having known total intensities I_0. Theoretical expressions for this ratio as a function of p for the cases $n=2$ and $n=\infty$ are given by Eqs. (51) and (50), respectively. These show that in the one case, $I_{max}/I(0)$ increases approximately linearly with p, while in the second it increases almost exponentially. Consequently, it should not be difficult to distinguish between the two cases—nor even between these cases and an excitation function corresponding to $n=3$ or $n=4$.

No extensive measurements of this type have been made because insufficient resolving power and scattering of light within the photographic emulsion make accurate determination of $I(0)$ very difficult, but the two lines shown in Fig. 3 provide a case in point. The values of p calculated from (50) are 5 and 9, so that $p_2/p_1=1.8$. Corresponding values of p calculated from (51) are 27 and 810, so that $p_2/p_1=30$. Since measurements of the total intensities of the unabsorbed lines give $I_{02}/I_{01}=1.7$, it may be concluded that the source involved is very closely approximated by the case $n=\infty$ (or by the model of Section VI).

C. Wave-Length Calibration of Spectrograph Sensitivity

It has been shown (Section XE) that under favorable circumstances the absorption parameter,

$$p \propto (c^2 P(0) N_a / 8\pi h \nu_0{}^3 N_e) I_0,$$

can be determined experimentally from the shape of the reversed line. As p is proportional to I_0 (except for the factor $1/\nu_0{}^3$, which is easily taken care of), this makes it possible to determine relative intensities in cases where direct intensity measurements might be difficult—for example, when the lines cannot be obtained free from self-absorption or when they lie in entirely different spectral regions. In the latter case, the value of N_a/N_e will necessarily be different for different lines and something will have to be known about the excitation characteristics of the light source. Often the source has a definite temperature which can be determined experimentally; in such a case everything is known which is necessary for determining the relative intensities of the lines.

When the lines can be obtained under conditions of no absorption, the procedure is considerably simplified. It is then necessary only to measure the ratio of total intensities I/I_0 for each line, using first a source in which there is no self-absorption and then one in which the absorption is moderately great. Then lines having the same value of I/I_0 correspond to a single value of p, regardless of the wave-lengths of the lines (provided, of course, that they have the same shape $P(u)$ and correspond to the same excitation function $E(r)$). Correcting as before for the factors $1/\nu_0{}^3$ and N_a/N_e, relative I_0 values for the lines are readily obtained.

By determining relative intensities in this way one can obtain all the necessary data for calibrating the sensitivity of a spectrograph (plus photographic plate) as a function of the wavelength. At the present time there is often no other satisfactory way of doing this. Following this procedure, intensity values have been determined for a number of iron lines throughout the ultraviolet and visible regions (9). These lines were later measured directly by photoelectric methods (7) and reasonable agreement was found with the values obtained from self-absorption.

The method of obtaining intensities from the self-absorption properties of spectrum lines may be of some use in the extreme ultraviolet, where no other entirely satisfactory methods are available.

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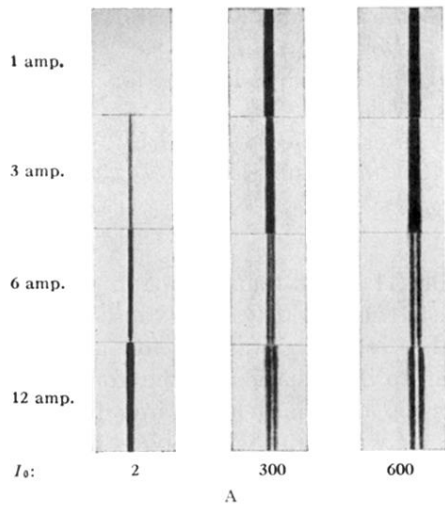(56) R. W. Wood, "Self-reversal of the red hydrogen line," Phil. Mag. **2**, 876–880 (1926).

FIG. 14. Photographs of self-reversed lines. A: iron lines of different intensities at different arc currents; B: reversal in the band lines of the OH-band at 3064A. The lower figures are the unreversed intensities. All lines with $I_0 > 20$ show self-reversal in the lower half, which was taken with a large flame thickness. (The upper figures indicate the classification of the lines.)