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Line Shape

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I. EARLY LINE BROADENING THEORY

In approaching the subject of line broadening the original work of Michelson provides an entree which utilizes the historical and phenomenological approach simultaneously. The causes of line broadening advanced in this author's early work remain as valid today as they were sixty years ago. So let us therefore utilize this work as our starting point.

A. The Causes of Line Broadening (1895)

Michelson began his consideration of line broadening effects by a summarization of the hypotheses which had been advanced previous to that time to account for these phenomena, and a verbatim restatement may be of interest here.

"1. As a consequence of Kirchhoff's law 'the ratio of brightness of two immediately contiguous portions of a discontinuous bright-line spectrum constantly decreases, if the number of luminous strata is multiplied or if the coefficient of absorption of the single stratus is increased, until the value is reached which, for the same wavelength and the same temperature, corresponds to the ratio in the continuous spectrum of a body completely opaque for a given thickness.[100]†

"2. The direct modification of the period of the vibrating atoms in consequence of presence (sic) of the neighboring molecules.

"3. The exponential diminution in amplitude of the vibrations due to communication of energy to the surrounding medium or to other causes.

"4. The change in wavelength due to the Doppler effect of the component of the velocity of the vibrating atom in the line of sight."

To these causes Michelson added:

"5. The limitation of the number of regular vibrations by more or less abrupt changes of phase amplitude or plane of vibration caused by collisions.

"6. The possible variations in the properties of the atoms within such narrow limits as to escape detection by other than spectroscopic observations."[67]

Having presented the historical list, let us use it in a phenomenological consideration of the general line broadening situation.

We consider an emitting atom which we shall proceed to remove to infinity and reduce the "temperature" to the point where, classically at least, no translational motion exists. Now from the classical picture of a vibrating electron or the simple picture of a pair of energy levels between which our radiating transition takes place, we should expect these conditions to yield a spectral line of a single frequency. We, of course, do not obtain this result, but, rather, we obtain the familiar natural line shape which is attributable to Michelson's Cause 3. We shall not specifically deal with the problem of natural line shape.

Having observed the behavior of the emitted radiation when the atom is removed from all neighbors, its translation motion reduced, let us now give the atom a certain translational velocity. As we are, of course, aware, the resulting atomic "heat" motion leads to a line broadening which Rayleigh first demonstrated as due to the Doppler effect.[73]

B. The Doppler Effect in Line Broadening

First, let us define the word "intensity" of emission (absorption) as the energy emitted (absorbed) per unit area per unit time. Then, if one makes a plot of frequency *vs* intensity for this "almost homogeneous" radiation, one obtains a distribution of intensities over a small frequency range giving rise to a spectral line of definite shape. We are desirous of eventually obtaining the intensity distribution.

We suppose our emitting molecule possessed of a velocity component ξ in the line of sight of the observer. Then if the molecule is emitting radiation of wavelength λ, the Doppler effect decrees that our observer will receive radiation of wavelength λ', such that

$$\lambda' \doteq \lambda(1-\xi/c) \tag{I.1}$$

in which expression we assume that $\xi \ll c$.

The distribution of the velocities in the line of sight is given by the Maxwellian distribution as $\exp[-\beta\xi^2]$ where

$$\beta = m/2kT. \tag{I.2}$$

In Eq. (I.2) m is the molecular mass, k is the Boltzmann constant, and T is the temperature in degrees Kelvin.

From Eq. (I.1)

$$\xi^2 = \lambda^2(\Delta\nu)^2. \tag{I.3}$$

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† References are listed at the end of this article.

In Eq. (I.3) λ may now be considered as the wavelength corresponding to the maximum intensity of the line (line center), and $\Delta\nu$ as the frequency increment between the line center and the frequency whose displacement corresponds to the line of sight velocity ξ.

Thus, if one arbitrarily equates the line center intensity to one, the Doppler effect alone produces a distribution of intensities over the spectral line which may be represented by the expression

$$I=\exp\left[-\frac{m\lambda^2(\Delta\nu)^2}{kT}\right]. \qquad (\text{I.4})$$

Let us define the quantity "half-width" which we shall designate by the symbol δ and which we shall encounter rather frequently throughout our considerations of line shape. Quite simply, this quantity is defined as the width—a frequency measurement—of the spectral line at an intensity equivalent to one-half the maximum intensity in the line. In the present case then

$$\delta=\frac{2}{\lambda}\left(\frac{kT}{m}\ln 2\right)^{\frac{1}{2}}. \qquad (\text{I.5})$$

These equations are Lord Rayleigh's solution to Michelson's Point 4 and our explanation of the results of "warming" our atom.

We next bring this emitter in from infinity so that it is surrounded by other atoms and inquire as to the effect of these neighbors on the radiation which is emitted. The answer to this inquiry is furnished by Michelson's Causes 2 and 5. Indeed these line broadening causes are quite as valid from the contemporary viewpoint as from any earlier one.

Cause 2 provides an explanation of the statistical theory which we shall consider in a good bit more detail at a later point. For the statistical considerations we shall find it necessary to proceed from a classical consideration of electron vibrational frequency disturbance to atomic energy level distortion, but the analogy is quite precise.

Cause 5 underlies what has variously been called collision broadening, impact broadening, velocity broadening, and what have you. We shall designate this phenomenon interruption broadening, the mathematics of which were originally contributed by Michelson.

C. The Application of the Fourier Analysis to Line Broadening

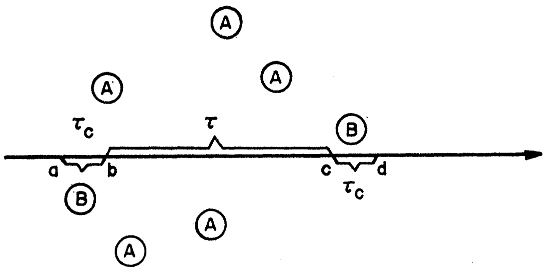

FIG. 1. A physical model for the interruption theory.

In considering the Michelson development, we shall begin by referring to Fig. 1. The circles in the figure in question represent the broadening atoms while the arrow we suppose to be the path of the emitter amongst this assemblage of broadeners. Now Michelson used a billiard ball atomic model so that a collision between the emitter and a broadener will have taken place when the separation of the emitter and broadener centers is equal to or less than their mean atomic diameter. Let us suppose that at point "c" on our emitter path such a collision has just taken place. Then Michelson supposed that this collision has the following effect.

For all practical purposes we may suppose that the classical oscillator model of the emitting atom began emitting at time minus infinity and will continue to do so until plus infinlty. The collision which occurred at "c" has the effect of rendering the radiation emitted prior to the collision completely incoherent with the radiation emitted subsequent to this time. This is the crux of the argument for it forms the basis for the Michelson broadening mechanism.

Thus, according to our theory, since a collision has just been undergone at point "b" (on Fig. 1), radiation will effectively begin at this point. If τ is now the time which elapses before the next collision, this is also the time during which radiation continues. Finally the radiation is terminated at point "c," and we are left with a wave train of finite length $c\tau$ where c is, of course, the velocity of light.

Now we may recall that the functions, $e^{i\omega t}$ form a complete orthonormal set, in terms of the members of which any function may be expanded. Further, each of these functions represents a wave train of appropriate frequency and infinite extent. Thus, if we expand our finite wave train in terms of these functions we are essentially expressing the finite wave train as a sum of an infinite number of wave trains of infinite extension. In this expansion the amounts of each train which we take are regulated by the magnitude of the vibrational amplitude. As a result of all this, we obtain

$$M(t)=\int J(\omega)e^{i\omega t}d\omega \qquad (\text{I.6a})$$

which is, of course, the familiar Fourier expansion with amplitudes given by

$$J(\omega)=\int M(t)e^{-i\omega t}dt=\text{const}\int e^{i(\omega_0-\omega)t}dt, \qquad (\text{I.6b})$$

where ω_0 is the angular frequency of the cut-off wave train.

The last integral is, quite naturally, carried out over the intercollision time τ, with the result

$$J(\nu)=\text{const}\frac{\sin[(\nu-\nu_0)\tau]}{(\nu-\nu_0)\pi}. \tag{I.7}$$

We now suppose the Fourier components which have been expressed as Eq. (1.7) to represent the observed spectral line. Intensity, from the classical viewpoint, is always associated with the square of the amplitude, so that Michelson supposed the distribution of intensities within the line to be given by

$$I=\text{const}\frac{\sin^2[(\nu-\nu_0)\tau]}{(\nu-\nu_0)^2\pi^2}. \tag{I.8}‡$$

If we now suppose the width of the spectral line to be the separation of the minima to either side of the line intensity maximum, the width is

$$\frac{1}{l}\cdot\frac{v}{c}=\frac{\pi v N\sigma^2}{c}. \tag{I.9}$$

Michelson found that Eq. (1.9) gave an order of magnitude agreement with experimental data. Somewhat better agreement was achieved by him when he took the "half-width" as given by Eq. (1.9) and added it to the half-width Eq. (1.5). As Michelson noted the problem is not herewith solved, but it will be of interest to see if ". . . such able contributions . . . recently . . . justify the prediction that a complete and satisfactory theory will be forthcoming in the near future."[67]

Finally, Point 1 is of no particular interest to us, and Point 6, although it shrewdly predicts isotopic spectra, is related to a "pseudobroadening" with which we shall not concern ourselves.

It seems particularly interesting to note the correctness of the factors which Michelson listed as causing line broadening, correctness at least from the contemporary viewpoint.

Certainly of great historical interest is the Lorentz theory of line broadening which appeared some ten years after Michelson's considerations. For our purposes, however, suffice it to say that this theory considered the mechanics of absorption in obtaining an interruption type result.[53]

II. STARK BROADENING

In a study of the line broadening problem that portion of the work done in the field subsequent to the period which we have designated "early" attains such voluminous proportion that some subdivision of the problem must be attempted. We shall divide the field into areas dependent on the phenomenon involved, at least insofar as this is practicable. Our areas of consideration will then be: (1) Stark broadening by the electric fields of the perturbing atoms. (2) Statistical broadening. (3) Interruption broadening. (4) Resonance broadening by like perturbers. (5) Molecular broadening. We shall take up these sometimes overlapping areas of consideration in the order in which we have enumerated them.

Holtsmark's Stark broadening treatment is admittedly a statistical one, but the phenomenon with which his treatment deals is sufficiently unique and, perhaps more important, the subsequent treatments of the phenomenon are sufficiently removed from anything statistical that the assignment of his work to this section seems the proper one.

In the theoretical treatment of the Stark broadening there have essentially been three general treatments each of which remains of importance within its range of applicability. The first of these is the venerable Holtsmark classical treatment of the ionic Stark broadening. The second is Spitzer's quantum treatment of the same problem. The last is the quantum treatment of Stark broadening by electronic fields. We shall consider these three theories in precisely this order.

A. The Simple Holtsmark Theory

Following Lorentz's treatment of broadening by atoms other than the emitter almost fifteen years were to elapse before another detailed study of the problem was to be carried out. This study was, of course, Holtsmark's classical consideration of the broadening by ionic fields.

As we are presently well aware, the Michelson-Lorentz theory of line broadening falls far short of explaining the various shifts which spectral lines may be made to undergo and the shapes which they may be made to assume. Now Stark[101] himself had suggested that some forms of line broadening might be due to fields of the surrounding atoms. Holtsmark[28,29] developed the idea and carried out the analytical attack which demonstrated precisely how these fields might be responsible for this broadening. To this attack we now turn our attention.

We begin by dividing the atoms which surround our emitter and cause broadening into (1) ions, (2) dipoles, or (3) quadrupoles and further specify that there will be only one type of field producer present. A certain spatial configuration of these surrounding, broadening atoms will produce a certain electric field at the emitter. Since all field producers will be of the same type, the only difference between one electric field and another will be a difference in perturber configuration. This is simply because the other factor which enters into the field strength determination, the electrical constants (ionic charge, dipole moment, quadrupole constant) are just that, constants. Now the heat motion of these perturbers will result in various electric fields at the emitter which will occur, of course, with various probabilities. If we

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‡ We shall see that the mere application of a random distribution of intercollision times to this intensity distribution yields the more familiar Interruption shape.

suppose a random spatial distribution, then the probability of a particular field strength will be a function of the spatial configuration and hence expressible as a function of the field strength itself. Finally a given field strength will be responsible for a certain Stark splitting of the emitted spectral line. Since the field strength probability is a function of the field strength, the probability of a Stark splitting appropriate to this field strength will also be a function of the field strength. This line of reasoning and the probability expression obtainable because of it are all very well, but the mechanics of the broadening remains to be particularized.

We now suppose our spectral line to be split into its Stark components by a linear Stark effect due to one of these fields of magnitude, say, F_0. We agree that the distribution of intensities in the split spectral line is given by $I(F_0,\nu)$. If our electric field were F_1, we should obtain a different intensity distribution in the split line, and so on. The spectral line which we actually consider is made up of contributions from all these possible intensity distributions, each distribution weighted by the probability of occurrence of the electric field responsible for the contribution. Then in order to obtain the intensity distribution in the Stark broadened line we must sum over all such distributions weighted by the probability of the distribution occurrence

$$Id\nu=\int_0^\infty I(F,\nu)W(F)dF, \tag{II.1}$$

where the $W(F)$ are the field strength probability functions which we shall consider later.

The probability expression of Eq. (II.1) we can calculate but the expression for the intensity in the split line $I(F,\nu)$ is something else again. The actual expression is an extremely complicated one within the limits of the outermost Stark components, but an approximation, which proves quite satisfactory, does exist. Quite simply we suppose $I(F,\nu)$ to be a constant within the limits of the outermost Stark components and zero outside these components. A rectangle of height $I(F,\nu)$ and width $2\nu_m$—wherein we suppose different F values to yield different heights and widths but the same area, $g=2\nu_m\cdot I(F,\nu)$—then results.

This rectangular assumption would appear to require a little change in our integral limits in Eq. (II.1). Let us suppose ourselves interested in a frequency ν on the final spectral line. (This must not be confused with what might be called the initial spectral line, that is, our rectangle.) Then only those rectangles will contribute to the intensity at this frequency for which $\nu_m \geqslant \nu$ while rectangles of lesser ν_m will not contribute. Thus, for a given frequency in the final spectral line, we integrate over all electric field strengths greater than the field strength producing a splitting equal to this frequency. Equation (II.1) then becomes

$$Id\nu=d\nu\int_{F'}^\infty \frac{g}{2\nu_m}W(F)dF=d\nu\int_{F'}^\infty \frac{g}{aF}W(F)dF, \tag{II.2}$$

where the relation $2\nu_m=aF$ arises from the linear Stark effect, and F' is that field for which $\nu_m=\nu$.

In evaluating Eq. (II.2) we must first evaluate $W(F)$.

B. Probability of an Electric Field Strength at the Emitter

Holtsmark[29] began with the assumption that the probability of a particular field strength F_0 is a function of F_0, and set out to determine this probability.

Let the components of the field strength at 0 due to the nth perturber be X_n, Y_n, Z_n. The components of F_0 will then be given by

$$X_0=\sum_{n=1}^{N'} X_n;\quad Y_0=\sum_{n=1}^{N'} Y_n;\quad Z_0=\sum_{n=1}^{N'} Z_n. \tag{II.3}$$

We desire the probability that X_0 lies between X_0 and X_0+dX_0, etc.

Let the position of the nth broadener be specified by the σ coordinates x_{1n}, x_{2n}, $\cdots$, $x_{\sigma n}$. Then the X_n, Y_n, Z_n are functions of these σ coordinates. It follows that the X_0, Y_0, Z_0 of Eq. (II.1) are functions of the $N'\sigma$ coordinates thus introduced. An $N'\sigma$ dimensional space is next set up, and to each point in this space there now corresponds a stipulated field strength. These points will be distributed in space according to some probability law, or what amounts to the same thing, some density function.

The probability that all $N'\sigma$ coordinates lie in the range dx_{11}, dx_{21}, $\cdots$, $dx_{\sigma N'}$ is

$$w_1\cdots w_{N'}dx_{11}dx_{12}\cdots dx_{1\sigma}dx_{21}\cdots dx_{N'\sigma}. \tag{II.4}$$

It should be noted that this coordinate distribution establishes our electric field strength within a certain small range.

We integrate Eq. (II.4) over those portions of space satisfying the requirements X_0 between X_0 and X_0+dX_0, etc. Subsequently the proper Dirichlet factors are introduced, and we obtain

$$\begin{aligned}
&W(X_0Y_0Z_0)dX_0dY_0dZ_0\\
&\quad=\frac{1}{8\pi^3}dX_0dY_0dZ_0\iiint_{-\infty}^{+\infty} d\xi d\eta d\zeta\cdot e^{i(\xi X_0+\eta Y_0+\zeta Z_0)}\\
&\quad\quad\times\frac{1}{V_{N'}}\underset{\text{all space}}{\int\cdots\int} w_1\cdots w_{N'}\\
&\quad\quad\quad\times e^{i(\xi\Sigma X_n+\eta\Sigma Y_n+\zeta\Sigma Z_n)}dx_{11}\cdots dx_{\sigma N'}.
\end{aligned} \tag{II.5}$$

The X_n, Y_n, and Z_n are functions of the $x_{1n}\cdots x_{\sigma n}$ while the X_0, Y_0, Z_0 are constants in all the integrations.

It should be stipulated now that all the broadening atoms are considered the same, that is, the Stark broadening is not treated for the case where, for atoms, more than one element acts as a broadening agent. In this event, identical electric field strength components X_n, Y_n, Z_n will be the same functions of $x_{1n}, x_{2n}, \cdots, x_{\sigma n}$. It follows from these considerations that for identical X_n, Y_n, Z_n, $w_1, w_2, \cdots, w_{N'}$ will all be equal. As a consequence the inner integral in Eq. (II.5) can be broken up into a product of N' identical integrals, each of which is integrated only over the σ coordinates of a single atom. The result is

$$W(X_0Y_0Z_0) = \frac{1}{8\pi^3}\int_{-\infty}^{+\infty}\cdots\int d\xi d\eta d\zeta e^{-i(\xi X_0+\eta Y_0+\zeta Z_0)}\mathfrak{F}^{N'} \quad \text{(II.6a)}$$

where

$$\mathfrak{F}^{N'} = \frac{1}{V^{N'}} \times\left[\int_{\text{all space}}\cdots\int e^{i(\xi X+\eta Y+\zeta Z)}\sigma dx_1 dx_2\cdots dx_\sigma\right]^{N'}. \quad \text{(II.6b)}$$

Subsequent to assuming three types of broadeners—that is to say, (1) ions, (2) dipoles, and (3) quadrupoles—Holtsmark carried out a rather lengthy calculation (which we shall not detail) for the field strength probability functions. The result for the dipole is

$$W(X_0Y_0Z_0) = \frac{1}{\pi^3}\frac{c_3}{(c_3^2+F_0^2)^2}. \quad \text{(II.7)}$$

We note that $c_3 = 4.54\mu N$ where μ is the dipole moment of a broadener.

A "Normalfeldstarke" may be defined as

$$F_n = c_3 = 4.54\mu N \quad \text{(II.8a)}$$

with β then defined as

$$\beta = F_0/F_n. \quad \text{(II.8b)}$$

Now we replace the volume element $dX_0dY_0dZ_0$ by $4\pi^2F_0^2dF_0$ and Eq. (II.7) results in

$$W(F_0)dF_0 = 4\pi F_0^2 W(X_0Y_0Z_0)dF_0 = \frac{4}{\pi}\frac{1}{(1+\beta^2)^2}\frac{F_0^2}{c_3^3}dF_0 = \frac{4}{\pi}\frac{\beta^2 d\beta}{(1+\beta^2)^2}. \quad \text{(II.9a)}$$

Figure 2 furnishes a plot of $W(F_0)$ *vs* β as given by Eq. (II.9a). After we have obtained $W(F_0)$ for the ion and the quadrupole, we can consider the significance of these plots.

In the case of the ion

$$\frac{1}{\beta^{\frac{3}{2}}} = \frac{c_2}{F_0^{\frac{3}{2}}} = \left(\frac{F_n}{F_0}\right)^{\frac{3}{2}} \Longrightarrow F_n = c_2^{\frac{2}{3}} = 2.61N^{\frac{2}{3}}\epsilon.$$

If we take as the mean separation of two of the particles $r_0(4/3)\pi r_0^3 N = 1$ where N is, as usual, the particle density, then this mean particle separation would give about the same result for a normal field strength, namely, for $F' = 2.60N^{\frac{2}{3}}\epsilon$.

The ion result is

$$W(F_0)dF_0 = W(X_0Y_0Z_0)4\pi F_0^2 dF_0 = \frac{4}{3\pi}\beta^2 d\beta[1-0.462\beta^2+0.1227\beta^4 -0.02325\beta^6+\cdots]. \quad \text{(II.9b)}$$

Equation (II.9b) converges only for small β. For large β one obtains

$$W(F_0)dF_0 = \frac{d\beta}{\beta^{\frac{5}{2}}}1.496\left[1+\frac{2.555}{\beta^{\frac{3}{2}}} +\frac{14.43}{\beta^3}+\frac{0}{\beta^{9/2}}+\cdots\right]. \quad \text{(II.9c)§}$$

The plot resulting from Holtsmark's versions of Eqs. (II.9b) and (II.9c) is given in Fig. 2.

Finally the probability of a field strength F_0 is required for the quadrupole and has been found as

$$W(F_0)dF_0 = \frac{4}{\pi}\frac{d\beta}{\beta^{7/4}}0.805\left[1-\frac{0.730}{\beta^{\frac{3}{4}}} -\frac{0.328}{\beta^{\frac{3}{2}}}+\frac{0.621}{\beta^{9/4}}-\frac{0.163}{\beta^3}+\cdots\right] \quad \text{(II.9d)}$$

for small values of β.

Again $\beta = F_0/F_n$ where $F_n = c_4^{\frac{4}{3}}$.

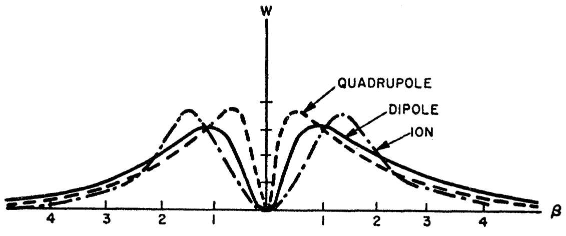

FIG. 2. The field strength probability function for the three cases. (After Holtsmark.[29])

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§ Holtsmark obtained

$$W(F_0)dF_0 = \frac{d\beta}{\pi\beta^{\frac{5}{2}}}2.350\left[1+\frac{5.106}{\beta^{\frac{3}{2}}}-\frac{7.4375}{\beta^3}+\cdots\right],$$

but a check of the work preceding is sufficient to show that this is not correct. Also see Verweiz[86] as reported by Unsold[97] which is almost correct.

For $0<\beta<1$, Holtsmark obtained

$$W(F_0)dF_0=\frac{4}{\pi}\beta^2 d\beta\frac{4}{3}[1-2.44\beta^2+11.25\beta^4-72\beta^6+\cdots]. \quad \text{(II.9e)}$$

Equations (II.9d) and (II.9e) yield the quadrupole curve in Fig. 2. Figure 2 tells us that, since the probability of zero field strength is zero, we must expect some broadening due to the Stark effect under any conditions. The maxima of the three curves give us the most probable field strengths in the three cases, and it may be noted that the slopes of these probability curves vary. The positions of the maxima indicate that the ion yields the greatest relative broadening, the dipole the intermediate, and the quadrupole the least. It should be recalled, however, that, since β depends on a different "Normalfeldstarke" F_0 in each case, these comparative considerations cannot be directly carried over to comparisons of broadened lines in the three cases.

Equations (II.9) now give the probability $W(F_0)$ for the existence at a certain time of the field F_0 due to one of three causes, which is to be utilized in Eq. (II.2).

C. Line Shape and Half-Widths According to the Early Stark Theory

When Eq. (II.9a) is substituted into Eq. (II.2), the result is

$$I d\nu=d\nu\frac{4}{\pi}\int_{\beta'}^{\infty}\frac{g}{aF_n}\frac{\beta d\beta}{(1+\beta^2)^2}=d\nu\frac{g}{2aF_n}\frac{4}{\pi}\frac{1}{(1+\beta'^2)} \quad \text{(II.10)}$$

in which $\beta'=2(\nu-\nu_0)/aF_n=2\Delta\nu/aF_n$, so that

$$I(\nu)=\frac{2g}{\pi}\frac{aF_n}{a^2F_n{}^2+4(\nu-\nu_0)^2}. \quad \text{(II.11a)}$$

The half-width of the line can be seen to be

$$\delta=aF_n=a4.54N\mu. \quad \text{(II.11b)}$$

The dependence of the line half-width on the electric dipole moment and the gas density is apparent from Eq. (II.11b). With which comment we turn our attention to the ion and the quadrupole.

Equation (II.2) may be rewritten as

$$2\nu_m=aF_n\beta \quad \text{(II.12)}$$

$$I d\nu=d\nu\frac{g}{aF_n}\int_{\beta'}^{\infty}\frac{W(\beta)d\beta}{\beta}. \quad \text{(II.13)}$$

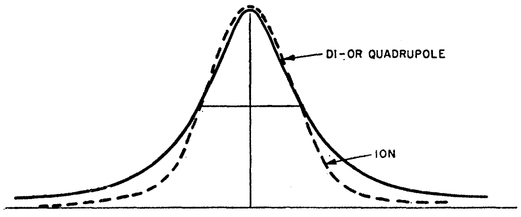

FIG. 3. Spectral line shape as predicted by the Holtsmark Stark theory. (After Holtsmark.[28])

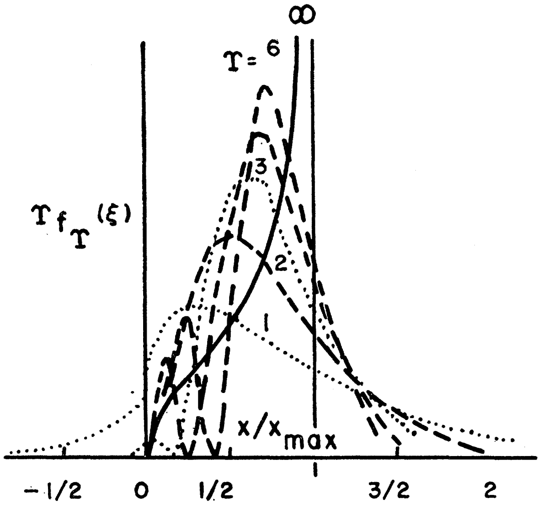

FIG. 4. The line shape according to the Spitzer theory for single encounters as a function of phase shift. (After Spitzer.[79])

Holtsmark evaluated Eq. (II.3) graphically for the cases of the ion and the quadrupole. Figure 3, represents his results for the intensity distribution for all three cases. In Fig. 3 the abscissae have been changed for the three perturbers so that the half-widths coincide, thus giving a curve shape comparison. The half-intensity β's for the ion and the quadrupole may be obtained from the curve as 1.25 and 0.67, respectively. These values of β yield the half-widths:

$$\text{Ion:} \quad \delta=1.25aF_n=3.25aN^{\frac{2}{3}} \quad \text{(II.14a)}$$

$$\text{Quadrupole:} \quad \delta=0.67aF_n=5.53aN^{\frac{4}{3}}A. \quad \text{(II.14b)}\|$$

Equations (II.14a), (II.14b), and (II.11b) show the dependence of the half-width on the electrical properties of the perturbing molecule through ϵ (charge), μ (dipole moment), or A (quadrupole constant) and also on the gas density through N.

D. The Introduction of Finite Molecular Diameters

It may be recalled that we have essentially considered the atoms involved in the theory as points, in that, when the integration was carried out over the atomic positions in space, no portions of space were excluded on the basis of previous occupancy. In 1920 Debye[13] com-

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‖ Debye[12] obtained approximate expressions for these field strengths and hence, an idea as to the behavior of the half-widths as follows: Electric charge is taken as 5×10^{-10} g$^{\frac{1}{2}}$-cm$^{\frac{3}{2}}$-sec^{-1} and the radius of the molecule as 10^{-8} cm. We assume that (a) the ion has charge 5×10^{-10} g$^{\frac{1}{2}}$-cm$^{\frac{3}{2}}$-sec^{-1}, (b) the moment of the dipole is 5×10^{-18} g$^{\frac{1}{2}}$-cm$^{5/2}$ sec^{-1} and (c) the quadrupole constant is 5×10^{-26} g$^{\frac{1}{2}}$-cm$^{7/2}$-sec^{-1}. Since the electric field has the units g$^{\frac{1}{2}}$-cm$^{\frac{3}{2}}$-sec^{-1}, and since we may assume the field to be the product of either (a), (b), or (c) and some power of N (molecules-cm^{-3}), thus yielding approximate expressions for the electric field in each of the three cases. Hence, we obtain for (a) $F=\epsilon N^{\frac{2}{3}}$, for (b) $F=\mu N$, and for (c) $F=\theta N^{4/3}$ or 4500 esu, 135 esu, and 4 esu, respectively. Multiplicative constants would yield the values obtained by Holtsmark.

mented on this "punktformig" assumption to the effect that this was responsible for the infinite value resulting for second moment of the probability distribution. This appears to be a reasonable objection, and so Holtsmark evidently considered it, for in 1924, he attacked the problem again,[30] this time with finite diameters assigned to the atoms under consideration. Gans[21] had approached the problem earlier under the assumption of finite diameters for the emitting atoms, but he had retained the point assumption for the broadening atoms. As Holtsmark noted, this would be a good assertion for the case where ions are the field producers, since we would normally expect the ions to make up only a small portion of the total number of atoms present. On the other hand, these assumptions would not appear to be valid for the dipole or quadrupole case. Gans further found a Gaussian distribution for very high field strengths, ". . . wie zu erwarten war."

In this development, Holtsmark retained the simplifying assumption which classifies the broadening atoms as ions, dipoles, or quadrupoles, that is, he again took only the first term in the series for the potential. Since these assumptions are predicated on large R (radius), it is apparent that when the gas density or pressure is high, R no longer remains large enough to justify them. How high "high" is, is, of course, a matter for discussion.¶ For these "high" densities the calculations cannot be carried out, but the field strength distribution in these cases is assumed Gaussian. Holtsmark thus limits himself to those gas densities where the first term in the potential series does give a good approximation of the electric field.

We begin with Eq. (II.5) rewritten in a slightly different form.

$$W(F_0)=\frac{2F_0}{\pi}\int_0^\infty dss\sin(F_0s)\frac{G(s)}{Q(s)}, \qquad \text{(II.15a)}$$

where

$$G(s)=\int d\sigma w e^{i\Sigma(\xi X_n+\eta Y_n+\zeta Z_n)} \qquad \text{(II.15b)}$$

$$Q(s)=\int s d\sigma \qquad \text{(II.15c)}$$

and where the integration over the angular coordinates has been carried out.

Now in the computation of $L(s)$ and $M(s)$, the finiteness of the atomic diameters is to be taken into account. In the earlier computation, it was possible to transform Eq. (II.5) into Eqs. (II.6), a product of identical integrals. This was legitimate, due to the independency of the atoms in that the motion of one atomic point is not interfered with by the other atomic points. This integral product is no longer admissible after finite diameters have been assigned the atoms, for we may not now allow the center of an atom to be separated from the center of another atom by less than this atomic diameter. We let

$$\Xi_n=e^{isF_n\cos\chi_n} \qquad \text{(II.16a)}$$

so that

$$\begin{aligned} G(s)&=\int_k d\sigma w\prod_{k-1}^{N'}\Xi_n \\ &=\int_{k_1}\Xi_1 w_1 d\sigma_1\int_{k_2}\Xi_2 w_2 d\sigma_2 \\ &\qquad\times\int\cdots\int_{k_{N'}}\Xi_{N'}w_{N'}d\sigma_{N'} \qquad \text{(II.16b)}\end{aligned}$$

where the first integral is carried over the space not occupied by the other $(N'-1)$ atoms and the 0th atom (emitter). Thus, the first integral is dependent on the coordinates of the other atoms and must be included under the integral sign of the second integral, and so on. This fact obviously does not simplify matters. The difficulty may be eliminated, however, by selecting a suitable initial distribution for atoms. This selection would appear to be justified, since our results should not depend on the arbitrary initial distribution of the atoms. As an initial distribution we group all the atoms together at a point, of arbitrary initial selection but remaining fixed during the first $N'-1$ integrations. The position of the first atom is chosen for this union. After locating the atoms in this manner, we may move atom N' about space in the process of the integration, while keeping the remaining atoms at position one. This process is carried out for $N'-1$ of the atoms. Without belaboring the details of the remainder of the calculation, let us remark that Holtsmark obtained

$$W(F_0)=\left[\frac{4}{\pi}\frac{F_0^2F'}{(F'^2+F_0^2)}\right]e^{a'/3}\left\{1+b\frac{3F'^2-F_0^2}{F'^2+F_0^2}\right\} \qquad \text{(II.17)}$$

where $F'=4.54N\mu$.

The factor in brackets in Eq. (II.17) is identical to Eq. (II.9a) the probability for the case of point atoms, while the remaining factors essentially correct it for finite diameters. Gans had already obtained the corrective factor $e^{a'/3}$ which, it may be noted, is independent of field strength, and thus does not take into account any field strength changes. As a consequence, this factor will not influence the broadening. We should remember that Eq. (II.17) breaks down for very large field strengths, and the Gaussian probability function must be utilized. Equation (II.17) may be written as

$$W(\eta)=\frac{4}{\pi}\frac{\eta^2}{(\eta^2+1)^2}e^{a'/3}\left\{1+b\frac{3-\eta^2}{1+\eta^2}\right\}, \qquad \text{(II.18)}$$

¶ In a somewhat similar consideration, Spitzer (see infra, this Chapter) takes as a limit a pressure such that $R=10r_e$ where r_e is the radius of the Bohr orbit.

where

$$\eta = F_0/F'.$$

A simple calculation shows the maximum of the probability curve to fall at $\eta = 1-b$, while this maximum is at $\eta = 1$ for the dipole on the uncorrected curve. The resulting line width is changed by the same percentile amount.

E. Dipole Line Shape from Refined Stark Broadening Theory

Although Holtsmark did not work out the line shape for this corrected case, let us make the short calculation necessary to obtain an idea of this shape. We shall utilize Eq. (II.13) and assume that for $\eta' \leqslant \eta \leqslant \eta''$. Equation (II.18) yields the correct form of $W(\eta)$ while for $\eta'' \leqslant \eta \leqslant \infty$ $\mathrm{Erf}(\eta)$ yields the correct $W(\eta)$. We are assuming η'' very large. Equation (II.13) becomes

$$I(\nu)d\nu = d\nu e^{a'/3} \frac{4}{\pi} \frac{g}{aF_n} \int_{\eta'}^{\eta''} \frac{\eta}{(1+\eta^2)^2} \left\{ 1 + b \frac{3-\eta^2}{(1+\eta^2)} \right\} d\eta$$

$$+ d\nu \frac{4}{\pi} \frac{g}{aF_n} \int_{\eta''}^{\infty} \mathrm{Erf}(\eta) d\eta$$

$$= \frac{4}{\pi} \frac{g}{aF_n} \frac{e^{a'/3}}{4} \frac{(2+5b)+(2+4b)\eta'^2}{(1+\eta'^2)^2} + O(\eta''). \quad \text{(II.19)}$$

The spectral line given by Eq. (II.19), if we neglect the $O(\eta'')$ term, will still be symmetrical about the line center. For small b, and b has been assumed small, the curve shape as given by Eq. (II.19) is very nearly identical with the shape given by Eq. (II.10). A good approximation for values of b up to 0.0020 is

$$I(\nu) = \frac{4}{\pi} \frac{g}{2aF_n} e^{a'/3} \frac{1+2b}{(1+\eta'^2)} = \frac{2g}{\pi} e^{a'/3} \frac{(1+2b)aF_n}{a^2F_n{}^2 + 4(\nu-\nu_0)^2}$$

$$= \frac{g}{\pi} e^{a'/3} \frac{(1+2b)(\delta/2)}{(\nu-\nu_0)^2 + (\delta/2)^2}. \quad \text{(II.20)}$$

Holtsmark calculated b for four monatomic and four diatomic gases on the basis of Debye's work[13] and obtained values of $b < 0.0020$ in all but one instance.

F. The Line Shift

We might now, with Holtsmark, consider another form of broadening which may arise. Suppose the line is not split to give a band for the field strength F as was assumed in deriving Eqs. (II.10) and (II.20), but that it is simply displaced by a frequency $\Delta\nu$. Now for a linear Stark effect the right (or left) side of the $W(F_0)$ curve is the intensity distribution curve for the broadened spectral line, since the probabilities for a shift of the line by an amount corresponding to this field strength, and, hence, the relative intensities at those frequencies. If γ is the line shift per unit field strength, we may read the shifts of the line intensity maxima directly from Fig. 4 as

$$\Delta\nu = 1.5\gamma F_n \text{ Ion} \quad \text{(II.21a)}$$

$$\Delta\nu = 1.0\gamma F_n \text{ Dipole} \quad \text{(II.21b)}$$

$$\Delta\nu = 0.65\gamma F_n \text{ Quadrupole.} \quad \text{(II.21c)}$$

Thus, this type consideration gives an asymmetrical spectral line whose maximum intensity has undergone a frequency shift. Qualitative examples of this shift and asymmetry had been given by Takamine and Kokubu[82] for certain He lines and for many metal lines by Takamine.[81]

The Holtsmark Stark broadening theory has its region of applicability although, it is not, of course, the complete answer to the problem. Some conclusions as to applicability were drawn by Holtsmark as a result of his comparison of theory with experiment.

Two possibilities arose from these comparisons. (1) The Stark effect, if it is a factor, is not the only factor which contributes to the broadening of a spectral line. With this statement there can be little disagreement. (2) Simultaneous broadening by both ions and dipoles or quadrupoles occurs and the fields produced may be inhomogeneous ones.

A further comment in definition of this inhomogeneity may be in order. Let us consider, say, an alkali atom in which we may only be concerned with the spectrum-producing valence electron. For our purposes here we can deal either with a Bohr orbit for this electron or those regions of space where $\bar{\psi}\psi d\sigma$ is relatively high for the electron. Then in order that the fields producing Stark broadening be homogeneous for this case, these fields must be essentially constant over the region of the orbit or of high $\bar{\psi}\psi d\sigma$.

We have restricted our gas to low pressure in order that the results may be valid, and another restriction has been inferred but not actually stipulated. If a given field F at time t is to broaden a line into one of the rectangles which have been assumed for the various values of F, the F must be a constant for a time interval sufficient to allow the atom to emit under conditions which will produce this rectangle. The field at the emitter varies due to the motion of the atomic broadeners, and this means that an upper limit, which depends on the lifetime of the upper of the two quantum states involved in the emission, must be placed on these atomic velocities, and hence, the gas temperature.

These considerations also demonstrate the necessity for forbidding the application of this theory to the fields of neighboring electrons.

G. The Adiabatic Quantum Broadening Problem

We first remark that Epstein[16] has shown that, when the problem of the Stark effect in hydrogen is considered in parabolic coordinates, one obtains

$$E^{(1)}=\frac{3\hbar^2F}{2\mu\epsilon}n(k_2-k_1)=\frac{q}{r^2} \qquad \text{(II.22a)}$$

for the linear Stark effect, and

$$E^{(2)}=-\frac{F^2}{16\mu^2}\left(\frac{\hbar}{\epsilon}\right)^6 \times n^4[17n^2-3(k_2-k_1)-9m^2+19] \qquad \text{(II.22b)}$$

for the quadratic Stark effect.

Spitzer began with three simplifying assumptions: "(1) the matrix elements of the interaction potential between states of different total quantum number may be neglected, and . . . the other matrix elements may be computed on the assumption that the atom is in a homogeneous field of strength $Z\epsilon^2/r\cdots$. (2) Each collision . . . may be assumed isolated from all others. (3) The mass of the colliding particles may be taken infinitely large."[79]

Assumption (1) supposes a homogeneous field F over the "boundaries" of the atom, or, say, over the electron orbit. If a field is imposed from "outside" there can be little objection to this. Now, however, we are supposing our field to be produced by an ion, and, if the separation of the hydrogen and the ion r is not large compared to the average distance of the electron from the hydrogen nucleus $\langle r_e\rangle$, this approximation surely breaks down. Thus, some lower limit R must be set on r, and Spitzer chooses this limit as $R>10\langle r_e\rangle$. Now $\langle r_e\rangle$ may have as its maximum value $3na_0^2/2\cdots a_0$ is the radius of the first Bohr orbit—so that $R>8.0\times10^{-8}\ n^2$ where n is the total quantum number. The exchange integrals as well as quadratic Stark effects will be small for these distances as we may show by Eqs. (II.22).

$$\frac{\Delta\nu_1}{\Delta\nu_2}=\frac{E^{(1)}}{E^{(2)}}=\frac{24n(k_1-k_2)R^2}{n^4[17n^2-3(k_2-k_1)^2+9m^2+19]a^2}.$$

When k_2-k_1 is set equal to $n/2$ and m and 19 are neglected, the result is

$$\frac{\Delta\nu_1}{\Delta\nu_2}\doteq\frac{3R^2}{4a^2n^4}=\frac{27}{16}\left(\frac{R}{\langle r_e\rangle}\right)^2>150.$$

This is the binary assumption which, together with the third assumption, will become familiar ones. It is certainly obvious that the treatment of a two particle interaction is far simpler than the treatment of a three or more particle interaction. In addition, it is rather apparent that at the lower pressures the approximation should be a reasonable one by virtue of the following. The highest probability is that the separation of a single one of the surrounding molecules from the emitter is sufficiently small to insure that its interaction overshadows that of the remaining broadeners. It might be said that, although Assumption (3) is reasonable for heavy particles, this will certainly not be true where the ions are electrons.

In considering the broadening problem we suppose the change in the potential as adiabatic so that the quantum state of the system will remain unchanged during a collision. Let us digress for just a moment on the subject of adiabatic processes, since we shall encounter them continuously in our further consideration of line broadening theories.

An adiabatic process may be considered as one in which the entropy of the system—or the degree of disorder thereof—remains unchanged. Now if the probability that an atom is in state X has the value unity before and after the occurrence of some phenomenon which affects the atom "system," the degree of disorder of this system remains unchanged and hence, the occurrence of the phenomenon constitutes an adiabatic process. On the other hand, if the probability for state X is unity at the initiation of the process and changes by virtue of the occurrence of this process to 0.6 for state X, 0.3 for state Y, and 0.1 for state Z, the degree of system disorder has changed, and in consequence, a nonadiabatic process has occurred.

In the present adiabatic case, a two state atom with an upper state A and a lower state B is considered where E_A and E_B, respectively, are the energy of the two states.

Since the electric field is assumed directed along the z axis of the emitting hydrogen atom, and since this electric field is radial from the perturber to the emitter—this, of course, would only be strictly correct for the one perturber assumed—the coordinate system will rotate with the passage of the ion so that the z axis is always directed toward the ion. Adiabaticity requires that this rotation occur for the following reason. The quantum number m specifies the projection of the angular momentum on the electric field of the ion. In order that m remain constant as required by the adiabatic hypothesis the atom must rotate with the changing direction of the ionic field.

We now define $\mathcal{H}$ as the atom-field Hamiltonian, ψ_A as the eigenfunction for the upper state (no photons in the field), and ψ_{b_i} the function for the lower state (a photon of frequency ν_i in the field).

The Schroedinger equations,

$$\mathcal{H}\psi_a^{(0)}=E_A(t)\psi_a(t) \qquad \text{(II.23a)}$$

$$\mathcal{H}\psi_{b_i}^{(0)}=[E_B(t)+h\nu_i]\psi_{b_i}(t) \qquad \text{(II.23b)}$$

result.

In Eqs. (II.23) t is a parameter, and $E_A(t)$ and $E_B(t)$ are the atomic level energies *as perturbed by the linear Stark effect* of the ionic field.

The state growth equations are

$$i\hbar\dot{a}=E_A(t)+a(t)+\sum_i\mathcal{H}_{ab_i}b_i(t) \qquad \text{(II.24a)}$$

$$i\hbar\dot{b}_i=\{E_B(t)+h\nu_i\}b_i(t)+\mathcal{H}_{b_ia}a(t). \qquad \text{(II.24b)}$$

As usual we suppose $a(0)=1$ and $b_i(0)=0$ to obtain the solutions

$$a(t)=e^{-\frac{1}{2}\gamma t}\exp\left\{-\frac{i}{\hbar}\int_0^t E_A(t')dt'\right\} \tag{II.25a}$$

$$b_i(t)=-\frac{i\mathcal{H}_{b_ia}}{\hbar}\exp\left\{-2\pi i\nu_i t-\frac{i}{\hbar}\int_0^t E_B(t')dt'\right\}$$
$$\cdot\int_0^t e^{-\frac{1}{2}\gamma t'}dt'\exp\left\{2\pi i\nu_i t'+\frac{i}{\hbar}\right.$$
$$\left.\times\int_0^{t'}[E_B(t'')-E_A(t'')]dt''\right\}. \tag{II.26b}$$

By time $t=\infty$ the emitter will certainly be in the ground state, and a photon of frequency ν will be in the field. The intensity distribution in the spectral line is surely given by $|b_{i(\nu)}(\infty)|^2$, since this will represent the probabilities for the appearance of these various frequencies. If we call $I'(\nu)$ the intensity of the frequency ν there results

$$I'(\nu)=\frac{(\mathcal{H}_{b_ia})^2}{\hbar^2}\left|\int_0^\infty e^{-\frac{1}{2}\gamma t'}dt'\exp\left\{2\pi i\nu_i t'+\frac{i}{\hbar}\right.\right.$$
$$\left.\left.\times\int_0^t[E_B(t'')-E_A(t'')]dt''\right\}\right|^2. \tag{II.26}$$

A few algebraic manipulations lead to

$$I(x)=\frac{\gamma}{2\pi x^2}\left\{1+\frac{W(\Upsilon,\xi)}{\gamma}\Upsilon^2 f_\Upsilon^2(\xi)\right\}, \tag{II.27a}$$

where

$$f_\Upsilon(\xi)=\int_{-\infty}^{+\infty}\frac{\exp[i(\xi u-\Upsilon\tan^{-1}u)]}{1+u^2}du \tag{II.27b}$$

and

$$\xi=\frac{xR}{v};\quad u=\frac{vt''}{R};\quad t'=t''+t_0;\quad \Upsilon=\frac{q_A-q_B}{\hbar Rv} \tag{II.27c}$$

where q has been defined by Eq. (II.22a). $W(\Upsilon,\xi)=v/R$ is the number of collisions per second.

From Eq. (II.27a) it is possible to show that for ξ small (v large or the density small and hence ρ large) the interruption distribution (which we consider in Chapter IV) holds. It is also possible to demonstrate the applicability of the statistical distribution (which we consider in Chapter III) for ξ large (v small or the density large). Finally, Eq. (II.27a) may be integrated, if rather laboriously—an operation which we shall not detail.

Figure 4 gives the results of Spitzer's calculations for several values of Υ. $x_{\max}$ is nothing more than $(q_A-q_B)/\hbar R^2$. The limiting value for $\Upsilon=\infty$ corresponds, of course, to zero velocity according to Eq. (II.27c). Thus, this value of Υ should yield the line shape as given by the statistical theory.

These then are the Spitzer results for the Stark broadening of a line due to the adiabatic collision of the emitter with a broadener of a particular velocity and distance of closest approach. A detailed consideration of the nonadiabatic case for the first Lyman lines of hydrogen showed that the breakdown of the adiabatic hypothesis (for this particular case) necessitated the replacement of Υ by σ where now $\sigma^2=1+\Upsilon^2$. We might remark that there is no particular reason to expect the same replacement for any other situation since the problem applies solely to these first Lyman lines.

The problem which remains consists of the averaging of Eq. (II.27a) over the requisite distributions of the optical collision diameter (distance of closest approach) and the velocity.[80] Together with the sum over the various type broadeners these operations result in

$$I(x)=\frac{\gamma}{2\pi x^2}\left\{1+\frac{1}{\gamma}\sum_m\int_0^\infty dv\right.$$
$$\left.\times\int_0^s W(\rho,v)\Upsilon^2 f_\sigma^{\,2}(\xi)d\rho\right\}. \tag{II.28}$$

$W(\rho,v)$ is the collision frequency for collisions of diameter ρ and velocity v. The introduction of a Maxwellian velocity distribution and a random collision diameter distribution leads to an integral whose evaluation requires approximations and graphical evaluations which we shall not detail. Equation (II.28) may be rewritten without much difficulty, however, as

$$I(x)=\frac{\gamma}{2\pi x^2}\left\{1+\frac{4}{\gamma}\left(\frac{\pi}{x}\right)^{\frac{1}{2}}\right.$$
$$\left.\times\sum_m\frac{N_m(q_{A_m}-q_{B_m})^{\frac{3}{2}}}{\hbar^{\frac{3}{2}}}(\gamma_1)^{\frac{1}{2}}H_m(x)\right\} \tag{II.29a}$$

where

$$H_m(x)=\int_0^\infty e^{-u}du\int_0^{\gamma_1/\gamma_2\sqrt{u}}f_\sigma^{\,2}(\xi)\frac{d\xi}{\xi} \tag{II.29b}$$

$$\gamma_1=\frac{(q_{A_m}-q_{B_m})l_m x}{\hbar};\quad \gamma_2=\frac{(q_{A_m}-q_{B_m})(l_m)^{\frac{1}{2}}}{\hbar s};$$

$$l_m=\frac{1}{2kT}\frac{M_Bm_H}{M_B+m_H} \tag{II.29c}$$

and N_m is the broadener density in the collision class m.

The Holtsmark β of our classical Stark considerations may be obtained by the transformation

$$W(\beta)d\beta=I(x)dx\Longleftrightarrow\beta^2W(\beta)$$
$$=\frac{3}{\pi^{\frac{3}{2}}}\sum_m\frac{\gamma_2H_m(x)N_m}{N} \tag{II.30a}$$

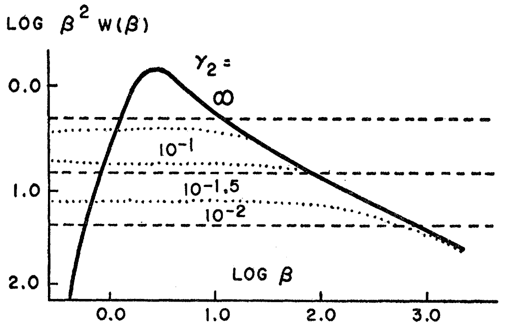

FIG. 5. The line shape for a single H line component. The solid line is the Holtsmark result. The dashed lines arise from the simple interruption theory. (After Spitzer.[80])

where

$$\beta = \frac{xs^2\hbar}{q_A - q_B}. \tag{II.30b}$$

These results through Fig. 5 afford a convenient method of comparing this theory with the interruption and statistical theories as well as demonstrating the predictions of the theory itself.

The horizontal lines in the figure represent the interruption result—the oft-called Weisskopf result—for several values of γ_2. Inner agreement is actually obtained only for $\gamma_2 = 0.047$. This is a demonstration of the error involved in the failure of the simple interruption theory to include the effect of distant collisions and nonadiabaticity. We mention this fact with no special emphasis, since we shall go into a much more detailed consideration of these facets of the interruption theory in Chapter 4.

One other rather obvious point seems worthy of mention in connection with Fig. 5. Equation (II.29c) tells us that γ_2 is directly proportional to the density, since it is inversely proportional to the mean molecular separation. The result is that as the density increases the theory tends toward the statistical theory, and conversely, as the pressure decreases, the theory tends toward the interruption theory. This may be seen directly from Fig. 5. These are facts which we shall encounter on several subsequent occasions, but this seems a particularly simple way to demonstrate these facts about the two types of theories. One more item of interest may be garnered from a perusal of the figure in question. The parameter γ_2 in addition to being density dependent, is inversely velocity dependent through l_m [see Eq. (II.29c)]. Firstly then, it is rather obvious that we tend toward the statistical theory with decreasing velocity—this too we shall later divine from different considerations.

In toto the quantum Stark theory is restricted by the approximations: (1) linear Stark effect; (2) binary collisions; (3) broadeners of infinite mass. These restrictions tend in general to restrict the applicability to low pressures such that $R > r_e$ and ionic (as opposed to electronic) broadeners.

Spitzer's and Holtsmark's work on ionic broadening still appears to leave the field of electronic Stark broadening rather neglected so that for this area of consideration we must turn our attention to recent work of Kivel, Bloom, and Margenau,[40a] and Meyerott and Margenau.[66a]

H. The Broadening Effect of Electrons

Perhaps the prime reason for the inability of the theories which we have thus far considered to deal with the broadening of spectral lines by electrons is their implicit assumption of a classical path. When an expression for the perturbation due to the broadening particle depends primarily on an emitter-broadener separation, then a classical path assumption has surely been made. Now the Heisenberg uncertainty principle tells us that such an assumption constitutes an extremely poor approximation when the particles involved are electrons, so we must look to a completely quantum treatment of this type broadening.

The familiar time dependent form of the Schroedinger equation

$$\left(\mathcal{H} - i\hbar\frac{\partial}{\partial t}\right)\psi = 0 \tag{II.31}$$

we suppose satisfied by the expansion

$$\Psi = \sum_n \sum_\Lambda{}^n a_{n\Lambda}(t)\psi_n(\mathbf{r})\varphi_\Lambda{}^n(\mathbf{R}) \times \exp[-i(\mathcal{E}_\Lambda{}^n + E_n)t/\hbar]. \tag{II.32}$$

The Hamiltonian appearing in Eq. (II.31) may be written out as

$$\mathcal{H} = \mathcal{H}_a(\mathbf{r}) + \mathcal{H}_e(\mathbf{R}) + \mathcal{H}'(\mathbf{r},\mathbf{R}) + \mathcal{H}''(\mathbf{r}) \tag{II.33}$$

where $\mathcal{H}_a(\mathbf{r})$ is the Hamiltonian of the isolated atom; $\mathcal{H}_e(\mathbf{R})$ is the Hamiltonian of the electron in the field of this atom; $\mathcal{H}'(\mathbf{r},\mathbf{R})$ the Hamiltonian of the atom-electron interaction; and $\mathcal{H}''(\mathbf{r})$ the Hamiltonian of the atom-field interaction. The eigenfunctions of the expansion Eq. (II.32) are given by

$$\left(\mathcal{H}_a + \int \bar{\varphi}_\Lambda{}''\mathcal{H}'\varphi_\Lambda{}''d\mathbf{R}\right)\psi_n{}^\Lambda = E_n{}^\Lambda\psi_n{}^\Lambda \tag{II.34a}$$

and

$$\left(\mathcal{H}_e + \int \bar{\psi}_n{}^\Lambda\mathcal{H}'\psi_n{}^\Lambda d\mathbf{r}\right)\varphi_\Lambda{}^n = \mathcal{E}_\Lambda{}^n\varphi_n{}^\Lambda. \tag{II.34b}$$

The substitution of Eq. (II.31) into Eq. (II.32) results in the state growth equation

$$\begin{aligned} i\hbar a_{mM} &\exp[-i(\mathcal{E}_M{}^m + E_m)t/\hbar] \\ &= \sum_n \sum_\Lambda{}^n a_{n\Lambda}\mathcal{H}_{mn}{}'' \int \bar{\varphi}_M{}^m\varphi_\Lambda{}^n d\mathbf{R} \\ &\quad \times \exp[-i(\mathcal{E}_\Lambda{}^n + E_n)t/\hbar] \\ &\quad + \sum_{n\neq m} \sum_\Lambda{}^n a_{n\Lambda} \int \bar{\varphi}_M{}^m\mathcal{H}_{mn}{}'\varphi_\Lambda{}^n d\mathbf{R} \\ &\quad \times \exp[-i(\mathcal{E}_\Lambda{}^n + E_n)t/\hbar] \end{aligned} \tag{II.35}$$

wherein we must recall that the electron eigenfunctions are not orthonormal.

The second term on the right of Eq. (II.35) represents what Kivel, Bloom, and Margenau (KBM hereafter) have called the "polarization effect." For the two states of our atom degenerate or nearly so this term is actually a polarization term. For such not the case the combination of these states through this term represents a quenching effect. We shall consider this in a little more detail at a later point, but let us now turn our attention to the subject of this section which is representable by the first term on the right side of Eq. (II.35).

The first term represents what these authors have dubbed "universal broadening," or, perhaps more concisely, it represents the interaction effect responsible for this phenomenon. The effect was termed universal since it will always be present by virtue of requiring no change in the atomic state. It represents a radiating atomic transition during which a change in the interacting electron energy takes place.

In our sketchy treatment of the mathematics of the situation we shall begin by neglecting the $\mathcal{H}_{nm}'$ in Eq. (II.35). We thus consider a two state atom whose transition simply takes place in the field of a broadening electron. The coefficient a_Λ we take to be associated with the upper of the two states wherein no photon is in the radiation field. The coefficient b_{rM} refers to the lower of the two atomic states in conjunction with which a photon of frequency ω_r is in the field. Further $\hbar\Omega_{\Lambda' M}=\mathcal{E}_{\Lambda'}{}^1-\mathcal{E}_M{}^0$ and $\omega_r=\omega_{\text{atom}}-\omega$. Next we shall accept the exponential decay quality of a_Λ, the proof of which may be found in Kivel, Bloom, and Margenau. At any rate, one may then obtain for the line intensity distribution

$$I_U(\omega)=\Upsilon_r\sum_M|b_{rM}(\infty)|^2$$

$$=\Upsilon_r|\mathcal{H}'/\hbar|^2\frac{\sum_M\left|\int\bar{\varphi}_M{}^0\varphi_n{}^1d\mathbf{R}\right|^2}{\gamma^2+(\omega+\Omega_{\Lambda M})^2}. \qquad \text{(II.36)}$$

The introduction of the time development matrix representation for $a(t)$ and $b(t)$ and a goodly bit of additional manipulation of an algebraic nature leads to

$$I_U=\frac{\Upsilon|J/\hbar|^2}{\gamma^2+\omega^2}\left\{1+\frac{R}{\gamma^2+\omega^2}\right\} \qquad \text{(II.37a)}$$

where

$$R=\sum_\Lambda\Upsilon_{\Lambda\Lambda}{}^0\sum_M R_{\Lambda M};$$

$$\text{(II.37b)}$$

$$R_{\Lambda M}=\frac{A_{\Lambda M}}{\gamma^2+(\omega-\Omega_{\Lambda M})^2}+\frac{B_{\Lambda M}}{\gamma^2+(\omega+\Omega_{\Lambda M})^2}$$

and

$$\gamma\equiv\pi\Upsilon|J/\hbar|^2. \qquad \text{(II.37c)}$$

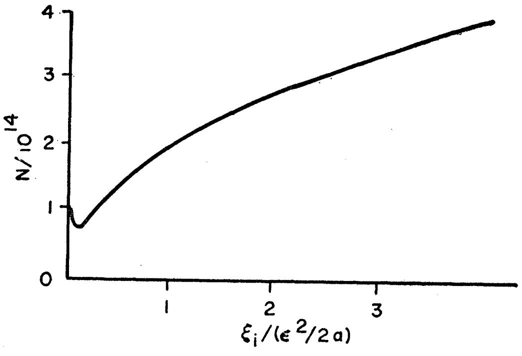

FIG. 6. Electron density *versus* energy. In the region below the curve the universal broadening effect is negligible compared to the natural line width. (Kivel, Bloom, and Margenau.[40a])

In Eq. (II.37b) the first term in $R_{\Lambda M}$ arises for the situation in which energy is not conserved during the radiation process. The resonance condition,

$$\Omega_{\Lambda M}=\omega$$

we suppose to exist. Then, when $\omega_r>\omega_a$ the radiation has received more energy than the atom gave up. It hasn't received this additional energy from the electron, however, since the electron too has gained energy. The effect, resulting from this nonconservative phenomenon, these authors point out, will be small. The second term in the expression for $R_{\Lambda M}$ represents energy transfer which adds up in such a way that conservation can be claimed. This may be demonstrated as was the first case.

The remainder of our consideration of this treatment will be just sufficient so that the terms with which we shall be presented will be defined with a degree of clarity. To begin with the electron-field interaction may be written as

$$\mathcal{H}_{nn}'=-\frac{\epsilon^2}{|\mathbf{R}|}+\epsilon^2\int\frac{|\psi_n(\mathbf{r})|^2}{|\mathbf{R}-\mathbf{r}|}dr.$$

We may surely write the unperturbed electron functions as plane waves

$$u_\Lambda=\frac{1}{\sqrt{V}}\exp(i\mathbf{k}_\Lambda\cdot\mathbf{R})$$

where now $\mathbf{k}_\Lambda$ is the electron momentum vector. At the same time we define a momentum transfer vector $\mathbf{K}=\mathbf{k}_M-\mathbf{k}_\Lambda$ which enters our considerations through the electron eigenfunction products arising in the matrix elements. Also

$$\frac{1}{V}\int e^{i\mathbf{K}\cdot\mathbf{R}}\mathcal{H}_{nn}'dR=(\mathcal{H}_{mn}')_{\Lambda M}=\frac{1}{V}\frac{4\pi\epsilon^2}{K^2}[G_{nn}-1].$$

One finally obtains for the universal broadening line shape

$$I_U=\frac{\Upsilon_r|\mathcal{H}'/\hbar|^2(\gamma+\gamma_U)/\gamma}{\omega^2+(\gamma+\gamma_U)^2}. \qquad \text{(II.38)}$$

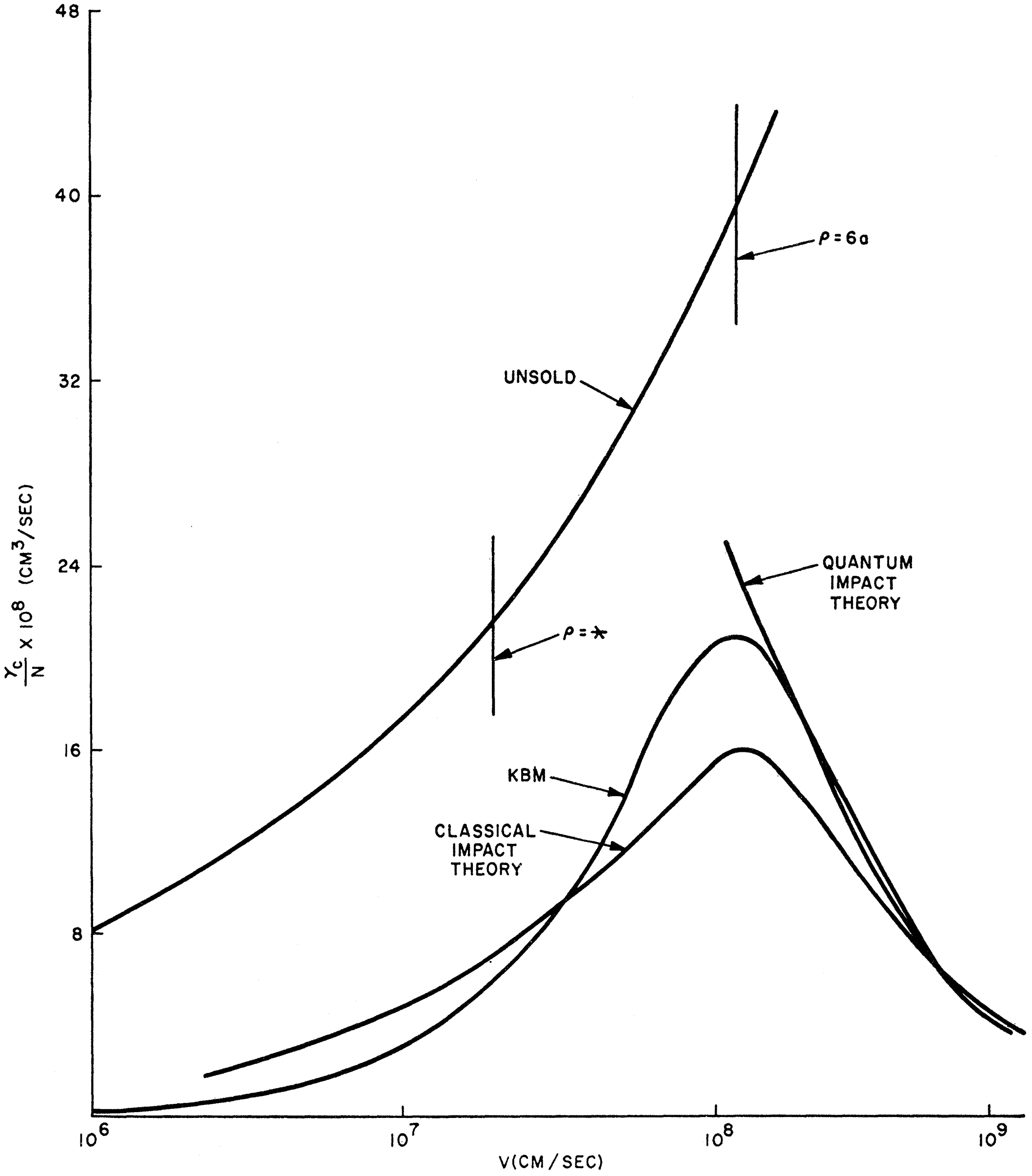

FIG. 7. The collision frequency as a function of velocity according to various of the electron broadening theories. (After Meyerott and Margenau.[66a])

The line width of this distribution is given by

$$\delta = 2\gamma_U = 2fS_U\gamma, \qquad \text{(II.39)}$$

where we now must needs define the additional terms:

$$f = 2nv_A\sigma_A/\gamma \Longrightarrow \sigma_A = \pi(\hbar/mv_A)^2.$$

In Fig. 6 is given a representation of the region of applicability of this theory. The curve represents a value of one tenth for the ratio γ_U/γ, that is, the ratio between the universal and the natural widths. Below the curve it does not hold due to certain approximations which were made in the expansions for the time development matrices for $a(t)$ and $b(t)$. As we get farther above the curve (very high densities) a statistical type (static) theory may be used.

As Meyerott and Margenau have pointed out, S_U may be approximately written as

$$S_U = 4.3(1 - e^{-4.1x}). \qquad \text{(II.40)}$$

The collision frequency ($\nu_c = \gamma_U$) obtainable through Eq. (II.39) from Eq. (II.40) is plotted in Fig. 7. Also indicated in this figure are collision frequencies as obtainable from certain other theories of electron broadening. First let us consider the Unsold result.

We suppose the frequency perturbation due to the atomic charge distribution at $\mathbf{r}$ to be

$$\Delta\omega=\frac{\epsilon}{\hbar}U(\mathbf{r}).$$

Then the Weisskopf form of the interruption theory (we shall consider this in detail in Chapter IV) yields

$$\gamma_c=Nv\pi\rho_0^2 \tag{II.41}$$

where ρ_0 is the minimum transit distance for perturbations effective in broadening.

The classical result which has been obtained by Lindholm—and which we shall also consider in Chapter IV—is

$$\gamma_c=Nv\int_0^\infty 4\pi\rho d\rho \sin^2\frac{\eta}{2} \tag{II.42}$$

and the phase shifts may be calculated from

$$\eta=\frac{2}{v}f(\rho)=\frac{2}{v}\int_0^\infty \{U_{2p}[(\rho^2+x^2)^{\frac{1}{2}}]-U_{1s}[(\rho^2+x^2)^{\frac{1}{2}}]\}dx$$

wherein we remark that particular atomic states have been specified. The potentials are those of the atomic distribution—averaged over angles—that act on the broadening electron specifically

$$U_{2p}(r)=\frac{\epsilon}{a}\left[\frac{1}{r}+\frac{3}{4}+\frac{r}{4}+\frac{r^2}{24}\right]e^{-r}$$

$$U_{1s}(r)=\frac{\epsilon}{a}\left[\frac{1}{r}+1\right]e^{-2r}.$$

The quantum form of the Lindholm result,

$$\gamma_c=Nv\sum_l \sigma_l[1-\cos(\eta_l-\eta_l')], \tag{II.43}$$

also appears in Fig. 7. Meyerott and Margenau have used the calculations of Swan and Massey and Moiseiwitsch in addition to their own for the phase shift evaluations in this equation.

The comparisons between the universal broadening effect of KBM and these other theories should be rather apparent from the figure in question.

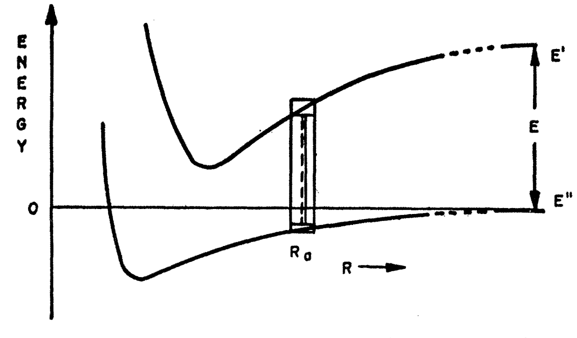

FIG. 8. Potential curves going with two different electronic states for consideration in connection with the statistical theory.

Let us now conclude our study of Stark broadening by an inclusion of the second term in Eq. (II.35).

As we have remarked, this term results in what these authors have called "polarization broadening." The line shape is of the same form, and when both the polarization and universal effects are included, one obtains

$$I(\omega)\propto\frac{1}{(\omega-\omega_0)^2+(\gamma+\gamma_U+\gamma_P)^2}$$

where, as for the universal effect,

$$\gamma=2Nv\sigma S_P$$

$$S_P\equiv\int_0^{x+}\frac{|G_{nm}|^2}{x^2}dx \tag{II 44a}$$

$$G_{nm}=\int e^{i\mathbf{K}\cdot\mathbf{r}}\bar{\psi}_n(r)\psi_m(r)dr. \tag{II.44b}$$

KBM have given a comparison of the universal, polarization, and ionic Stark broadening effects for the Lyman α line which we reproduce:

Universal broadening:	$\gamma_U/\gamma=$	0.13
Polarization by reorientation ($2p0\rightarrow 2p\pm 1$):	$\gamma_{P1}/\gamma=$	0.027
Quenching ($2p0\rightarrow 1s0$):	γ_Q/γ	0.0013
Polarization by induction ($2p0\rightarrow 2s0$):	$\gamma_{P2}/\gamma=$	2.7
Ionic stark broadening:	$\gamma_{\text{Stark}}/\gamma\doteq$	80.

As concerns γ_{P1}, γ_{P2}, γ_Q we note that they all arise from the second term in Eq. (II.35). The only difference is the specific off-diagonal matrix element which is involved. Depending on what this element is, one can physically qualify the phenomenon involved as "polarization by induction," "polarization by reorientation," or "quenching." For example, if we reorient the dipole from $m=0$ to $m=1$, we obtain the "polarization by reorientation" effect.

III. STATISTICAL BROADENING

A. A First Approach

Any consideration of statistical broadening may perhaps best begin with some mention of the Franck-Condon[9,18] principle, for if we are to point to any one concept as fundamental to this type broadening, then it is to this principle that we must apply ourselves. As one might suppose, the Franck-Condon principle was first enunciated by Franck and enlarged and clarified by Condon. Having startled the reader with this opening statement, let us consider the principle itself.

In doing so we consider the potential curves of Fig. 8. Although the principle in question was first advanced in connection with the constituent atoms in a diatomic molecule, our considerations will relate to two free atoms. The potential curves of the figure we suppose give the energy, as a function of atomic separation, for two atomic states. In the form in which we shall utilize it, this principle hypothesizes that the atomic transition takes place vertically on the figure, that is, it supposes the interatomic separation R to remain unchanged during this transition.

Jablonski[33] first utilized this principle in advancing a qualitative explanation of spectral line broadening. Now during an electronic transition we suppose (as a consequence of the Franck-Condon principle) that (1) the separation and (2) the relative velocity of the interacting emitter and broadener remain unchanged. Let us again consider Fig. 8 in detailing the fashion in which such a pair of assumptions may be expected to lead to line broadening.

First of all, the level separation at infinite interatomic distance corresponds to the frequency of the emitted radiation in the absence of any broadening perturbations. Next let us suppose the transition to take place when the atomic separation is R_a. Under these conditions the level energy separation will be different from the unperturbed separation, and radiation of a different frequency will be emitted. From this it follows (and we are supposing binary collisions for conceptual clarity) that the line intensity maximum will be shifted to the frequency corresponding to the most probable atomic separation. Around this maximum will then be distributed other frequencies—corresponding to other separations—with the intensity (probability) of these frequencies corresponding to the probabilities for the various separations requisite for the frequencies. As we shall later see detailed the type of spectral line will depend on the type of interaction curve.

This process has been described by Oldenberg[71,72] and Minkowski[69] as one in which the difference between the "natural frequency" of the atom and the frequency observed is made up from the relative velocity of the two particles involved. To our two potential curves—which, we remark, must be different in order that any but one frequency be emitted as a function of separation—there will correspond two different kinetic curves. Now, although the relative velocity will remain constant during the transition, it will change (in that it will be governed by a new kinetic curve) subsequent to the collision. In this fashion one can create a picture of this radiation-kinetic energy exchange.

B. Statistical Theory

In a series of papers on the subject Margenau[55–58,62] has developed the statistical theory from the qualitative explanation of the last section to the sophisticated, contemporary theory.[62] In his earlier studies of the subject, he devoted himself largely to the specific treatment of the van der Waals broadening, primarily, it would seem, because he felt this was the explanation of the broadening by foreign gas atoms possessed of no permanent poles. From our present apparent vantage point, the Holtsmark theory appears to be simply an explanation of Stark broadening which we may neatly categorize and apply at the proper time. At the time it was written, however, it was meant to be a little more than this. It was advanced in order—at least so the author tells us in the original article—to supplant the earlier Michelson-Lorentz theory which had been found wanting in general applications. It was found wanting, as we might suppose, since it requires the possession of a permanent pole on the part of the broadener. Margenau essentially advanced the van der Waals force as a broadening agent quite applicable to such situations and, at the same time, created the theory which was to provide the framework within which this broadening agent could be utilized. Some time later, however, he set forth the development of the generalized theory which we shall detail and from which the earlier work may be obtained.

The broadening we attribute to some sort of forces which act between the two atoms. Now these forces give rise to potential curves of the type which we have discussed in the preceding section. Let us further suppose that the differential energy level distortion due to these forces is given $U=\sum_i U_i$ where U_i is the interaction between the emitter and the ith broadener. The assumption of such additivity of potentials, of course, supposes that there are no interactions between broadeners, an assumption corresponding to the assumption of point broadeners in the simple Holtsmark Stark theory. The mathematics of the statistical theory is now devoted to answering the following question: What is the chance that a configuration of broadeners exists such that a displacement of the spectral line corresponding to U results? This "chance" is, of course, precisely the intensity of the displaced frequency in the broadened line.

In detailing the mathematics of the situation, we must begin by determining an expression for the potential. Firstly, we suppose this potential to depend on some inverse power of the emitter-broadener separation since van der Waals, dipole-dipole, and many other interactions of a type which we shall wish to investigate are dependent on such a separation. Primarily in order that the potential may change sign—this is not to say that this does not describe the physical situation—we also introduce a spin interaction $u(\xi)$ such that $u(\xi)$ disappears in the mean. If the assumption as to $u(\xi)$ is incorrect, it will lead only to incorrect numerical factors. All of which leads us to the following choice for the potential:

$$U_i = a r_i^{-j} u(\xi_i) \tag{III.1}$$

where

$$u(\xi_i) = \begin{matrix} -1 & \text{for} & \xi_i \leqslant 0 \\ +1 & \text{for} & \xi_i > 0 \end{matrix}; \quad -1 \leqslant \xi_i \leqslant 1. \tag{III.2}$$

We suppose the volume occupied by the entire gas to be $(4/3)\pi R^3$. The distribution of broadeners may be taken as random** so that the probability that the emitter-broadener separation be r is

$$\frac{dV}{V}=\frac{r^2 \sin\vartheta d\vartheta d\varphi dr}{(4/3)\pi R^3}\Longleftrightarrow p(r)dr=\frac{3}{R^3}r^2dr \qquad \text{(III.3a)}$$

and of a spin ξ

$$p(\xi)d\xi=\frac{dl}{l}=\tfrac{1}{2}d\xi. \qquad \text{(III.3b)}$$

The probability that the spectral frequency radiated by the emitter differs in energy from the unperturbed frequency by an amount between U and $U+dU$ is

$$I(U)dU=\prod_i \frac{3}{2R^3}\int\int_U r_i^2dr_id\xi_i. \qquad \text{(III.4)}$$

The integration in Eq. (III.4) is to be carried out over those portions of space which yield the perturbation in question. This integration may be extended to one over all space by an application of the proper Dirichlet factor

$$\begin{aligned}I(U)dU=&\frac{\zeta}{2R^3}\int\int r_1\cdots r_n dr_1\cdots dr_n d\xi_1\cdots d\xi_n\\ &\cdot\frac{1}{\pi}\int\frac{\sin[(\frac{1}{2}dU)s]}{s}e^{i\Upsilon s}ds\\ \doteq&\frac{3}{4\pi R^3}dU\int\int\int_{\text{all space}} r_1\cdots r_n e^{i\Upsilon s}dr_1\cdots\\ &\times dr_n d\xi_1\cdots d\xi_n ds\end{aligned} \qquad \text{(III.5a)}$$

where

$$\Upsilon=\sum_i U_i-U. \qquad \text{(III.5b)}$$

Now we have supposed there to be no interactions between broadeners so that the n product integrals here are identical, and we may rewrite Eq. (III.5a) as

$$W_n(U)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-isU}A_n(s)ds \qquad \text{(III.6a)}$$

where

$$A_n(s)=\left\{\int p(\xi)d\xi\int p(r)dr \exp[isar^{-j}u(\xi)]\right\}^n. \qquad \text{(III.6b)}$$

Using no subterfuge whatever, we may rewrite Eq. (III.6b) as

$$A_n(s)=[1-3B(s)/2R^3] \qquad \text{(III.7a)}$$

where

$$B(s)=\int_{-1}^{+1}d\xi\int_0^R\{1-\exp[isar^{-j}u(\xi)]\}r^2dr. \qquad \text{(III.7b)}$$

Equation (III.7a) may surely be expanded according to the binomial theorem. In the result we allow R to approach infinity which converts our binomial expansion into the infinite MacLaurin series for

$$A(s)=\exp[-2\pi NB(s)] \qquad \text{(III.7c)}$$

so that our Eq. (III.6a) becomes

$$W(U)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\exp[-isU-2\pi NB(s)]ds. \qquad \text{(III.8)}$$

Next, Eq. (III.7b) may be integrated over ξ so that

$$B(s)=2\int_0^{+\infty}(1-\cos sv)r^2dr \qquad \text{(III.9a)}$$

where

$$v=ar^{-j}. \qquad \text{(III.9b)}$$

If we let

$$sv=\mathfrak{F}, \qquad \text{(III.9c)}$$

B may be written as

$$B=\tfrac{2}{3}(a|s|)^{3/j}\int_0^\infty \mathfrak{F}^{-3/j}\sin\mathfrak{F}d\mathfrak{F} \qquad \text{(III.10)}$$

where integration by parts has been utilized and l'Hospital's rule applied. This application of l'Hospital's rule results in the restriction of j such that $j>\frac{3}{2}$. This is actually no restriction on the theory, since none of our interaction laws will require a value of less than $\frac{3}{2}$.

For convenience, let

$$(4/3)a^{3/j}\int_0^\infty \mathfrak{F}^{-3/j}\sin\mathfrak{F}d\mathfrak{F}=g_j \qquad \text{(III.11a)}$$

so that

$$2\pi B(s)=g_j|s|^{3/j}. \qquad \text{(III.11b)}$$

Our probability $W(U)$ is a real affair, and the utilization of this reality and Eq. (III.11b) in Eq. (III.8) yields

$$W(U)=\frac{1}{\pi}\int_0^\infty \exp[-Ng_js^{3/j}]\cos(sU)ds \qquad \text{(III.12)}$$

since the integrand is an even function.

By evaluating Eq. (III.12) for the case $U=0$ (no shift)

$$W(0)=\frac{j}{3\pi}\Gamma\left(\frac{j}{3}\right)\frac{1}{(Ng_j)^{j/3}}. \qquad \text{(III.13)}$$

Margenau demonstrated the interesting result that the line center intensity decreases as $N^{-j/3}$.

If we define a function I_j as,

$$I_j(x)=\int_0^\infty \exp\left[-\left(\frac{u}{x}\right)^{3/j}\right]\cos udu \qquad \text{(III.14a)}$$

** A Maxwell-Boltzmann distribution was found by Margenau to have little effect.

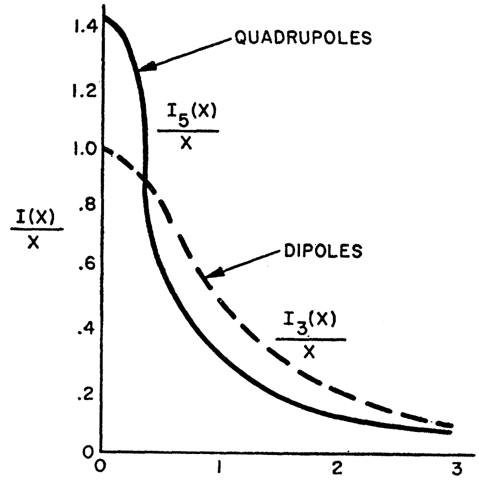

FIG. 9. Dipole and quadrupole line shapes according to the statistical theory. (After Margenau.[62])

then Eq. (III.12) may quite readily be written as

$$W(U)=\frac{1}{\pi|U|}I_j\left(\frac{U}{U_0}\right) \qquad \text{(III.14b)}$$

where

$$U_0=(Ng_j)^{j/3}. \qquad \text{(III.14c)}$$

All of which leads us to the departure point of special cases, and, with Margenau, we shall consider three, namely, broadening by (1) permanent dipoles, (2) quadrupoles, and (3) forces which do not change sign.

In the dipole case we have $j=3$ so that from Eqs. (III.14c), (III.11), and (III.14a)

$$U_0=\tfrac{2}{3}\pi^2Na;\quad I_3(x)=\frac{x}{1+x^2}$$

so that Eq. (III.14b) becomes

$$W(U)=\frac{U_0}{\pi(U^2+U_0^2)} \qquad \text{(III.15a)}$$

or, when we recall that $U=\hbar(\omega_0-\omega)$

$$W(\omega)=\frac{U_0/\hbar^2\pi}{(\omega_0-\omega)^2+(U_0/\hbar)^2}. \qquad \text{(III.15b)}$$

This is of some interest, since it is the Michelson-Lorentz or dispersion form of the line shape.

A consideration of Eq. (III.11a) and Eq. (III.14a) should suffice to justify the statement that numerical calculations or series expansions are requisite for the evaluation of the integrals in these equations for other values of j. Margenau has carried out this numerical evaluation for the quadrupole case, $j=5$, and the resulting curve $I_5(x)/x$ is compared to the one for the dipole case in Fig. 9.

As our third example we consider the van der Waals force as the broadening agent. In this instance we take the same sign so that the spin interaction factor in the potential energy expression is simply equated to unity. As we have remarked the statistical theory was originally developed by Margenau in conjunction with a consideration of these van der Waals forces.

Under these conditions we obtain in place of Eq. (III.10)

$$\begin{aligned}B(s)&=2\int_0^\infty(1-e^{isv})r^2dr\\&=-i\tfrac{2}{3}(a|s|)^{3/j}\int_0^\infty\mathfrak{F}^{-3/j}\exp(i\mathfrak{F})d\mathfrak{F}\\&=\tfrac{1}{2}|s|^{3/j}g=\frac{1}{2\pi}|s|^{3/j}(g'+ig'')\end{aligned} \qquad \text{(III.16)}$$

corresponding to which one obtains

$$W(U)=\frac{1}{\pi}\int_0^\infty\exp(-Ng's^{3/j})\times\cos(sU+g''s^{3/j}N)ds \qquad \text{(III.17)}$$

for forces which do not change sign. For the van der Waals interaction $m=6$, and Eq. (III.17) may be evaluated utilizing the g' and g'' values obtainable from Eq. (III.16) with the result

$$\begin{aligned}I(\Delta\nu)&=\frac{1}{\pi}\int_0^\infty\exp[-\tfrac{2}{3}\pi N(2\pi as)^{\frac{1}{2}}]\times\cos[s(\Delta\nu)-\tfrac{2}{3}\pi N(2nas)^{\frac{1}{2}}]ds\\&=\frac{2\pi\sqrt{a}}{(\nu-\nu_0)^{\frac{3}{2}}}N\exp\left[-\frac{4}{9}\frac{\pi^3aN^2}{(\nu-\nu_0)}\right]\end{aligned} \qquad \text{(III.18)}$$

which is precisely the result Margenau had originally obtained for this special case. The half-width of this distribution is

$$\delta=0.82\pi^3aN^2 \qquad \text{(III.19a)}$$

and the line shift

$$\Delta\nu_{\max}=(\tfrac{2}{3}\pi)^3aN^2. \qquad \text{(III.19b)}$$

We have compared the van der Waals distribution predicted by the theory with an observed line in Fig. 10. Although the good agreement in the red wing is ap-

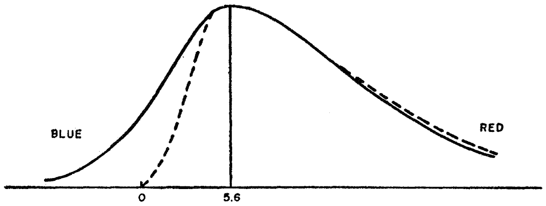

FIG. 10. A comparison of the theoretical prediction of the statistical theory for the van der Waals forces with an experimental result. (After Margenau.[56])

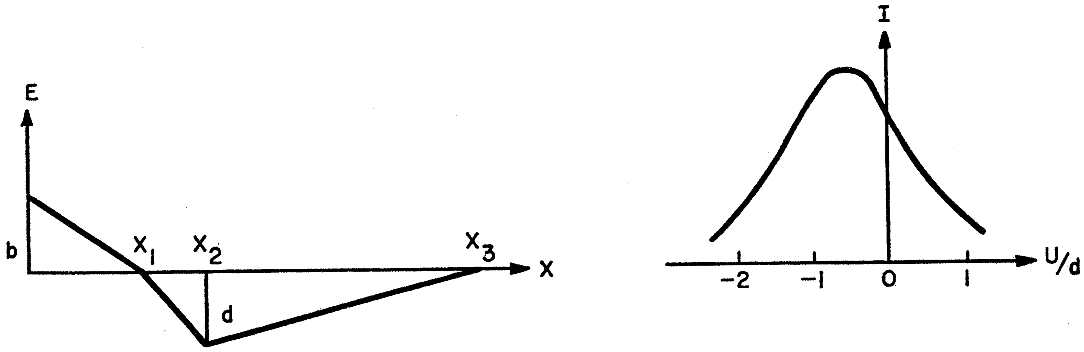

FIG. 11. An example of Margenau's application of the integrable block and triangle function to the statistical theory. (After Margenau.[57])

parent, we note the poor agreement between theory and experiment in the blue wing. Albeit other limits (such as the low velocity approximation) are imposed on the theory, one reason for the discrepancies appears worthy of mention at this point. Were the theory itself completely free of limiting assumptions, the precise potential curve for a given broadening situation would have to be known in order that a precise agreement between the theoretical results and the observations could be obtained. In general (although one could probably say in all cases) the potential curve due to the interaction between emitter and surrounding broadeners is known with but little accuracy. Thus, an approximate curve must be used which may be a reasonable assumption but which cannot be expected to detail the behavior of the potential energy and from which we can hardly expect to obtain completely correct broadening answers. Along this line, Margenau had, in one of his early studies of the situation, considered a block and triangle approximation to the interaction potential curves and then numerically integrated the results of inserting these approximations into the line shape integrals. As an interesting example of the method we give a few of his results in Fig. 11. Particularly in the study of forces by means of line shapes does it appear that this technique might have some interesting possibilities.

C. The Jablonski Theory

Jablonski felt that a wave mechanical theory of line broadening should be developed and that this development might well follow the line of attack utilized by certain authors in their treatment of molecular rotation-vibration spectra. To this end Jablonski's paper of 1937[34] and those which followed[35–38] were devoted.††

We begin, with Jablonski, by assuming that our absorber (emitter) and the N' foreign gas atoms, whose perturbing influence shall be responsible for the broadening of the spectral line, go to make up a very large, $(N'+1)$-atomic molecule.

In treating the molecule Jablonski applied the technique which had originally been developed in connection with molecular electronic-vibration theory, that is to say, he supposed the $(N'+1)$-atomic molecular eigenfunction to be a product of one electronic and N' two atomic eigenfunctions each of these latter is concerned with the interaction between the emitter and one of its perturbers. Since such is the case, the probability for the shift in the emitted radiation frequency will be partially dependent on the matrix element whose evaluation is possible through a utilization of these eigenfunctions. The calculation inferred is one familiar from inelastic scattering theory.

We now suppose that we know the probability distributions $P_1(x_1)$, $P_2(x_2)$, $\cdots$, $P_N(x_{N'})$ of the quantities $x_1, x_2, \cdots, x_{N'}$. Then the problem with which Jablonski was faced was the determination of the probability distribution of

$$X=\sum_{i=1}^{N'} x_i$$

which by the judicious utilization of an inductive proof he was able to show was

$$\int_{\Delta X} P(X)dX=\int_{\Delta X}\left[\delta(X)e^{-\zeta N'}+\sum_{m=1}^{N'}\binom{N'}{m}\right.$$
$$\left.\times W^{(m)}(X)e^{-\zeta(N'-m)}\right]dX. \quad \text{(III.20)}$$

Let us make the connection between Eq. (III.20) and the development somewhat more apparent. To begin with we shall wish that $x_i=E_i'-E_i$, that is, this variable refers to the translational energy separation between two levels à propos to the two particle system consisting of the emitter and the ith broadener. $\int_{\Delta X} P(X)dX$ gives the probability for the small indicated range of the variable for the translational energy of the $N'+1$ particles comprising the emitting-broadening system. As to the terms within the right-hand integral the first term represents the probability for no translational energy change in the system; the first

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†† One of these articles[36] was not available to the author. The material contained in this article, however, is covered by subsequent papers which were consulted.

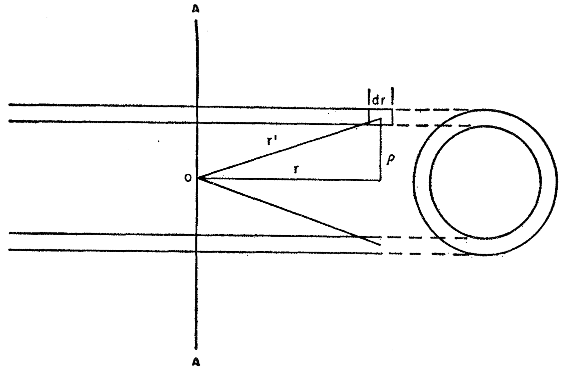

FIG. 12. A physical model for the calculation of the optical collision diameter probability.

term within the sum (the second term on the right of the equation) gives the probability of a binary collision, that is, of a collision between the emitter and one broadener; the second term within the sum gives the probability for an emitter-two-broadener collision, and so on. The probability distribution in question then allocates the requisite relative importance to the various types of collisions and may certainly be of some interest under certain broadening situations, although it has not been utilized in any problems. What we now do is effectively ignore our result, Eq. (III.20), and again suppose binary collisions. Thus, we content ourselves with an interest in $W^{(1)}(X)$.

Now the probability that the emitter-broadener system in a state $n'l$ shall undergo a transition to a state $n''l$ is given by

$$W^{(1)}(X)=W^{(1)}(E_{n'}-E_{n''})$$

$$=\sum_{l=0}^{l_{\max}} Q(l)\frac{\mathfrak{D}_{n'n''}{}^2}{\sum_{n'=1}^{\infty}\mathfrak{D}_{n'n''}{}^2}\frac{dn'}{dE_{n'}}$$

$$=\int_0^{l_{\max}} Q(l)\frac{\mathfrak{D}_{n'n''}{}^2}{S}\frac{dn'}{dE_{n'}}dl$$

$$=\int_0^{l_{\max}} Q(l)A_{n'n''}{}^2\frac{dn'}{dE_{n'}}dl \qquad \text{(III.21)}$$

wherein we have utilized the relations $S=\mathfrak{M}_0{}^2$, $\mathfrak{D}_{n'n''}\doteq\mathfrak{M}_0A_{n'n''}$, and $\mathfrak{D}_{n'n''}$ is the matrix element for the electronic transition. $Q(l)$ is the probability of occurrence of a certain l and $dn'/dE_{n'}$ the density of levels in the upper state. In the case of emission we replace $dn'/dE_{n'}$ by $dn''/dE_{n''}$.

We consider probability $Q(l)$ of a particular l value. Firstly, let us make an appeal to correspondences (on the assumption of high l values) in order to equate the classical and quantum angular momenta:

$$(2mE_l)^{\frac{1}{2}}\rho=[l(l+1)]^{\frac{1}{2}}\hbar\Longleftrightarrow Q(l)dl\doteq Q'(\rho)d\rho \qquad \text{(III.22)}$$

where, as usual, ρ is the distance of closest approach of broadener to emitter.

We turn our attention to Fig. 12 for an evaluation of $Q(\rho)$.

In the figure, one half the atoms may be considered as moving toward (or across) the plane A–A from the left, while the remainder proceed toward the plane from the right. The probability under a random probability assumption, that a collision of optical collision diameter between ρ and $\rho+d\rho$ occurs is thus the volume of the tube shell of thickness $d\rho$ divided by the total volume available to the broadeners. We suppose the assemblage to be confined to a sphere of radius R. In consequence

$$Q'(\rho)d\rho=\frac{\int_0^{r_{\max}}2\pi\rho d\rho dr}{(4/3)\pi R^3}=\frac{3}{R^3}r_{\max}\rho d\rho$$

from which when we suppose

$$Q'(\rho)d\rho=\frac{3}{2R^2}d(\rho^2)\Longleftrightarrow Q'(\rho)d\rho$$

$$=\frac{3\hbar^2}{4R^2mE}(2l+1)dl. \qquad \text{(III.23)}$$

Next the evaluation of $A_{n'n''}$ leads, for Eq. (III.21), to the result

$$W^{(1)}(X)=\frac{3r_c{}^2}{R^3\left|\frac{dX}{dr}\right|_{r=r_c}}\left(1-\frac{U''(r_c)}{E_{n''}}\right)^{\frac{1}{2}}$$

$$\times\left[1-\left(1-\frac{l_1(l_1+1)}{l_t(l_t+1)}\right)^{\frac{1}{2}}\right]+\zeta(X,l_t). \qquad \text{(III.24)}$$

The asymptotic form $(l=l_t)$ of $W^{(1)}(X)$ is

$$W^{(1)}(X)=\frac{3r_c{}^2(1-U''(r_c)/E_{n''})^{\frac{1}{2}}}{R^3\left|\frac{dX}{dr}\right|_{r=r_c}} \qquad \text{(III.25)}$$

and a corresponding form results for the emission line.

Although it is from Eq. (III.25) that we shall obtain the line shape, let us remark the implications of a complete calculation.

It has been tacitly assumed that there is one interaction curve for the upper electronic state and one for the lower. This is not generally the case for there may well be several interaction curves for each electronic state, and for single encounters we would then have various $W_i{}^{(1)}(X)$ (see Eq. (III.20) for the various pairs of curves. Our $W^{(1)}(X)$ would then have the form

$$W^{(1)}=\sum a_iW_i{}^{(1)}(X). \qquad \text{(III.26)}$$

It should also be apparent that since each $A_{n'n''}$ would be different for each $W_i^{(1)}(X)$, each $A_{n'n''}$ would have to comprise a separate calculation for each $W_i^{(1)}(X)$. When one considers that we have here discussed only single encounters, the complexity of the accurate computation for multiple collisions appears rather staggering. In general, we do not know one such pair of curves with any accuracy, however, so we shall content ourselves with having mentioned the general case.

In Eq. (III.25) we now suppose the potential function to depend only on some inverse power of the collision partner separation—$\Delta\omega=(1/\hbar)X=K/r_c^{\eta}$—so that this equation becomes

$$I(\omega)=\frac{4\pi NK^{3/\eta}}{\eta(\Delta\omega)^{\eta+3/\eta}}\left(1+\frac{2a''\Delta\omega}{3KkT}\right)^{\frac{1}{2}}. \qquad \text{(III.27)}$$

Equation (III.27) corresponds to the statistical result after an approximate fashion in the wings of the line, the second circumstance restricting the theory to this region.

The fact that the Jablonski theory simply leads via another route to the Margenau statistical results renders its practical value somewhat limited. However, the worth of the theory appears to lie in the quantum treatment involved, and, perhaps, some additional results may be drawn from the theory itself by a slightly different use of the approximations or the replacement of certain of them. Foley used certain approximations to show that his form of the Lorentz result could be obtained from the Jablonski theory. This led to a mild controversy, but the flaw in the theory which we have just considered lies not so much in the fact that a judicious utilization of approximations results in someone else's theory—this is usually the case—but in the necessity for the approximations which must be used to obtain any results whatever, for these are the limiting features.

IV. INTERRUPTION BROADENING

A. The Interruption Theory for Zero Collision Time

Now we have remarked in Chapter III that the Holtsmark Stark broadening theory was originally advanced partly due to the belief on Holtsmark's part that the Lorentz—and consequently the Michelson—theories could not be expected to withstand the advent of the quantum theory. Beginning with Lenz's appeal to correspondences in 1924,[46] however, a large number of authors have devoted themselves to demonstrating the incorrectness of such a viewpoint, quite often in no uncertain terms. We shall give one short consideration of quantum classical equivalence a bit later, but now we consider the early work of Lenz only in order to extract from it his major contribution to the development of the interruption theory.

We have seen the fashion in which Michelson's utilization of the Fourier transform results in Eq. (I.8) for the spectral line shape. Let us also remark the Lorentz utilization of a random distribution of electronic vibrational coordinate and time derivative thereof. Now our further interruption considerations will consist to a large extent in developing the Michelson conception of line broadening. First in this development then is the Lenz procedure of averaging Eq. (I.8) over the Lorentz distribution of τ. If we let the I of Eq. (I.8) be given by I' and consider τ as the mean intercollision time, there then results

$$I(\nu)=\int_0^\infty I'(\nu)e^{-\tau'/\tau}d\tau' = \text{const}\frac{(1/2\pi\tau)}{(\nu-\nu_0)^2+(1/2\pi\tau)^2} \qquad \text{(IV.1)}$$

wherein the exponential function defines the Lorentz distribution.

This rather familiar line shape equation has as its half-width

$$\delta=\frac{1}{\pi\tau}=\frac{1}{\pi}\frac{\langle v\rangle}{l}=\langle v\rangle N\rho^2 \qquad \text{(IV.2)}$$

wherein $\langle v\rangle$ is the relative velocity. The symbol l refers to the mean free path. In defining the symbol ρ we shall find the next refinement in the theory arising quite naturally and almost unbidden.

In the Michelson consideration we recall that ρ is simply the atomic diameter since the atom was considered a billiard ball sort of thing whose diameter occurs specifically in the expression for the free path. This is admittedly a more strained physical interpretation than the one subsequently given by Weisskopf.[92,93]

Now surely we can expect, say, the van der Waals forces between an emitter and a broadener to exert some influence on the broadening of a spectral line before the two collision partners are separated by an atomic diameter, and we must suppose ourselves capable of defining this latter quantity. Weisskopf suggested that we define ρ as the "optical collision diameter," a quantity which defines an atomic collision for purposes of line broadening and which we now proceed to consider in some detail.

We begin by considering the quantity ω_0 in Eq. (I.6b). This quantity, of course, represents the angular vibrational frequency of the spectrum producing valence electron. In the Michelson treatment it was a constant, since nothing was present which could change it until the sudden bang of the billiard ball collision. With the Weisskopf assumption of action at a distance through some sort of interaction force, however, this situation is changed. As a result of this force ω_0 will begin to change with time (this temporal coordinate is introduced by the heat motion of the emitter) as soon as the emitter is within the range of these forces. Now if these forces are, say, a function of emitter broadener separation—which we generally consider them—of the form $\Delta(r)$ then

$$\omega_0=\omega_0'+\int_0^t \Delta(r)dt'=\omega_0'+\eta \qquad \text{(IV.3)}$$

wherein ω_0' is the vibrational frequency of the photoelectron in the absence of any perturbing forces while the remaining term is the change in the phase of this vibration due to perturbing influence of the collision partners. Perhaps redundantly, let us note that for conceptual clarity we are considering binary collisions. All of which means that the phase of the emitted radiation will change with the approach of the emitter. And at this point we introduce the crux of the Weisskopf argument: A collision has been undergone by the emitter when the phase of the emitted radiation, η, has changed by unity. This is an admittedly arbitrary collision definition, but one which has proven quite satisfactory for certain physical situations and, further, one which forms one of the bases for the simple form of the interruption theory.

Having defined an optical collision we now simply consider the ω_0 of Eq. (I.6b) again a constant between two such collisions in order to obtain once more Eqs. (IV.1) and (IV.2) for the line shape and half-width. The optical collision diameter which we shall now evaluate from our definition of an optical collision has been changed by this new collision definition. As an example, let us determine the optical collision diameter for use in Eq. (IV.2) for the case of van der Waals forces. For this case $\Delta(r)=C/r^6$ in Eq. (IV.3). If we now let $x=\langle v\rangle t/\rho$, we may then write

$$\eta=\int_{-\infty}^{+\infty}\frac{Cdt}{(\langle v\rangle^2t^2+\rho^2)^3}=\frac{C}{\rho^5\langle v\rangle}\int_{-\infty}^{+\infty}\frac{dx}{(x^2+1)^3}$$
$$=\frac{C}{\rho^5\langle v\rangle}\left(\frac{3\pi}{8}\right)\sim 1$$

and wherein we see that from our definition of a collision, the closest approach occurs at $t=0$, from which

$$\rho=\left(\frac{3\pi C}{8\langle v\rangle}\right)^{1/5}$$

and we remark that C is in angular frequency units, ω.

In this section then we have discussed the Lenz-Weisskopf modifications of the Michelson theory which resulted in what may be called the simple form of the interruption theory. This simple theory certainly has its areas of application which may roughly be described as low pressures and frequencies near line center. Now the reasons for such restrictions to the theory may be rendered quite physically plausible by a reference to Fig. 1.

In our ruminations of Chapter I we considered points "b" and "c" as positions at which billiard ball collisions occurred. Now we simply consider these locations as defining the optical collisions of this section. The remainder of our earlier description of the figure is precisely the same. Now then, it is apparent that such a physical picture of the optical collision process is possessed of the following flaws: (1) It neglects the effects of distant collisions. In this connection let us consider the "A" broadeners. They will actually have some effect on the resulting spectral line, but, since they are too far removed from the emitter path to cause phase shifts as great as unity, their presence is neglected by the theory. (2) The effect of close collisions is also neglected. At point "c" the emitter is at such a distance from the "B" broadener that the phase has changed by unity. As a result we declare a collision to have occurred and cut off the wave train. Thus, we neglect the effect of greater phase changes. This second neglect is essentially the same as neglecting the time of collision. A further consideration of the physical situation suffices to demonstrate that (1) limits our application of the theory to relatively low pressures while (2) restricts the application in the line wing. This second restriction arises since surely we may expect the large frequency perturbations of the line wing to arise as a result of phase shifts greater than unity. Although, as we have remarked, there is a definite region of applicability of this theory, there are refinements which result in theories of more comprehensive application. The first and perhaps most obvious of these is the inclusion of the time of collision. Such an inclusion was first attempted by Lenz[47] in an effort to obtain an interruption theory which would allow for the shifts and asymmetries often observed in spectral lines and totally unprovided for in this simple theory. He did, indeed, achieve his end, but, unfortunately at the expense of applicability, for his result was even more restricted than those which we have already considered. Lindholm[50] showed that these shifts and asymmetries may be obtained from the interruption theory without considering the time of collision. Actually, he eliminated approximation (1) rather than approximation (2) as we shall see.

B. The Inclusion of Various Phase Shifts

Let us begin by rewriting Eq. (I.6b) with the help of Eq. (IV.3) as

$$J(\omega)=\int_{-\infty}^{+\infty} e^{i2\pi(\nu-\nu_0)t+i\eta(t)}dt$$

from which we may obtain for the spectral line shape:

$$I(\nu)=|J(\omega)|^2$$
$$=\iint_{-\infty}^{+\infty} e^{i2\pi(\nu-\nu_0)(t''-t')+i[\eta(t'')-\eta(t')]}dt'dt''$$
$$=\int_{-\infty}^{+\infty} e^{i2\pi(\nu-\nu_0)t}dt\int_{-\infty}^{+\infty} e^{i[\eta(t+t')-\eta(t')]}dt'. \qquad \text{(IV.4)}$$

We now consider the integral over dt' in Eq. (IV.4). It was Lenz who developed the ingenious method of evaluation which we shall presently detail: Lindholm later utilized it, and Foley[17] appears to have named it. At any rate the Lenz idea may be described as follows.

If we suppose a random distribution in time, then the integral in t' has the look of a time average, specifically, the time average of the exponential. Now let us recall Boltzmann's ergodic hypothesis. A consideration of this hypothesis in connection with the average in question suffices to demonstrate the equality of this time average and a statistical average of the exponential. Quite simply then we evaluate this integral by determining the statistical average of the exponential. We will surely agree it legitimate to equate the average to $\exp[-A(t)+iB(t)]$. Since $I(\nu)$ and $\eta(t)$ are real, we require $A(-t)=A(t)$ and $B(-t)=-B(t)$ so that

$$I(\nu)=\int_0^\infty e^{-A(t)}\cos[2\pi(\nu-\nu_0)t+B(t)]dt. \qquad \text{(IV.5)}$$

Next it is assumed that but three different phase changes occur on collision.‡‡ These we shall designate as η_a, η_b, η_c. This in turn would mean that three different "differential collision cross sections," σ_i occur.

The total cross section is $\sigma=\sigma_a+\sigma_b+\sigma_c$, and the mean time between collisions is τ. The probability that n collisions of type a corresponding to a phase shift η_a (a collisions), m b collisions, and l c collisions will occur in time t is

$$\left(\frac{\sigma_a}{\sigma}\right)^n\left(\frac{\sigma_b}{\sigma}\right)^m\left(\frac{\sigma_c}{\sigma}\right)^l\frac{1}{n!m!l!}\left(\frac{t}{\tau}\right)^{n+m+l}e^{-t/\tau}. \qquad \text{(IV.6)}$$

Further, our exponential may be evaluated as

$$\eta(t+t')-\eta(t')=\sum_k[\eta_k(t+t')-\eta_k(t')]$$
$$=n\eta_a+m\eta_b+l\eta_c. \qquad \text{(IV.7)}$$

In this case then the mean value of $e^{i[\eta(t+t')-\eta(t')]}$ which Lindholm assumed equal to the second integral in Eq. (IV.4) is given by

$$\langle e^{i[\eta(t+t')-\eta(t')]}\rangle$$
$$=\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\sum_{l=0}^{\infty}\left(\frac{\sigma_a}{\sigma}\right)^n\left(\frac{\sigma_b}{\sigma}\right)^m\left(\frac{\sigma_c}{\sigma}\right)^l$$
$$\times\frac{1}{n!m!l!}\left(\frac{t}{\tau}\right)^{n+m+l}e^{-t/\tau}\{e^{i[n\eta_a+m\eta_b+l\eta_c]}\}. \qquad \text{(IV.8)}$$

Since

$$\sum_{n=0}^{\infty}\left(\frac{\sigma_a t e^{i\eta_a}}{\sigma\tau}\right)\frac{1}{n!}=\exp\left[\frac{\sigma_a t}{\sigma\tau}e^{i\eta_a}\right], \text{ etc.}$$

Equation (IV.8) becomes

$$\langle e^{i[\eta(t+t')-\eta(t')]}\rangle$$
$$=\exp\left\{\frac{t}{\tau\sigma}[\sigma_a e^{i\eta_a}+\sigma_b e^{i\eta_b}+\sigma_c e^{i\eta_c}]\right\}. \qquad \text{(IV.9)}$$

Utilizing Eq. (IV.9) in Eq. (IV.4) we obtain

$$I(\nu)=\Re\int e^{2\pi i(\nu-\nu_0)}$$
$$\times\exp\left\{\frac{t}{\tau\sigma}[\sum_i\sigma_i(\cos\eta_i+i\sin\eta_i)-\sigma]\right\}dt$$
$$=\int\exp\left\{-\frac{t}{\tau\sigma}\sum_i[\sigma-\sigma_i\cos\eta_i]\right\}$$
$$\times\cos\left[\frac{t}{\tau\sigma}\sum_i\sigma_i\sin\eta_i+2\pi(\nu-\nu_0)\right]dt \qquad \text{(IV.10)}$$

where we have taken the real part of $\exp(i\sin\eta_i)$ since the intensity is a real quantity. Thus, from Eqs. (IV.5) and (IV.10) there results

$$A=t\sum_i\frac{\sigma_i}{\sigma\tau}[\sigma-\sigma_i\cos\eta_i]=\alpha t \qquad \text{(IV.11a)}$$

$$B=t\sum_i\frac{\sigma_i}{\sigma\tau}\sin\eta_i=\beta t, \qquad \text{(IV.11b)}$$

and Eq. (IV.5) becomes

$$I(\nu)=\int_0^\infty e^{-\alpha t}\cos\{[2\pi(\nu-\nu_0)+\beta]t\}dt$$
$$=\frac{\text{const}}{\left[(\nu-\nu_0)+\dfrac{\beta}{2\pi}\right]^2+\left[\dfrac{\alpha}{2\pi}\right]^2}. \qquad \text{(IV.12)}$$

In obtaining Eq. (IV.12) the collision time has been neglected in that we simply took the various phase changes as having occurred, thus neglecting the effects of close collisions. Equation (IV.12) of course, yields no line asymmetry. This we shall obtain on consideration of close collisions.

It might also be noted that we restricted ourselves to three phase changes η_a, η_b, and η_c, in setting up Eq. (IV.8), but there is no reason to restrict Eqs. (IV.11) for the shift and half-width in this manner.

In Sec. A of this chapter we have remarked the fashion in which the simple interruption theory ignores the effects of (1) distant and (2) close collisions. In the developement which we have just considered the effect of this ignoration of distant collisions has been demonstrated. In other words we have demonstrated the

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‡‡ As we shall see, we could initially assume some other number and later extend the number of allowed phase changes as desired.

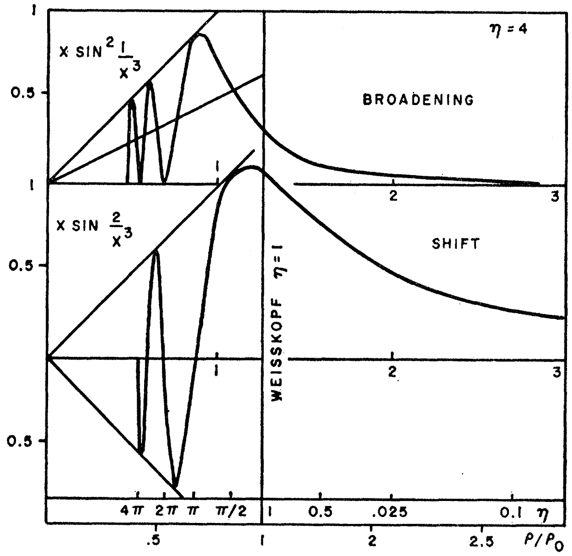

FIG. 13. An illustration of the reason for the failure of the simple interruption theory to yield a line shift. (After Lindholm[99] and Unsold.[97])

fashion in which consideration of these distant collisions leads to a line shift. This fact is further borne out by a study of Fig. 13.

The vertical line in about the center of the figure is the Weisskopf collision diameter. Now the area under the upper curve is related to the integral in Eq. (IV.11a) and is hence a measure of the broadening. In like manner the area under the lower curve is a measure of the shift. The simple theory only considers those areas to the left of the abscissa specifying the Weisskopf collision diameter. It thus becomes quite apparent that with the adoption of this diameter we obtain almost all the broadening effects (insofar as this theory is concerned) while we obtain almost none of the shift effects. In addition these curves serve to illustrate the relative importance of near and distant collisions in broadening and shift.

C. The Effect of Close Collisions

Next Lindholm[51] considered the problem with the collision time included, thus essentially including the effects of both near and distant collisions.

Although our consideration of this more general interruption treatment shall be quite sketchy, we particularly want to emphasize Lindholm's manner of including the time of collision (close collisions) within the framework of his earlier theory.

Let the collision time be t_i, and the phase change per unit of time during the collision be k_i. Then the total phase change in collision will be $\eta_i = k_i t_i$. Let us consider Fig. 14. The coordinates x and y measure time back from t' and t'' respectively as shown. The five arrows below the temporal axis represent five different collisions whose duration is represented by the respective arrow lengths. Only those collisions which occur at least partly during $t''-t'$ are to be included.

It can be seen directly from our definitions that these collisions will contribute to $e^{i[\eta(t'')-\eta(t')]}$ the factor

$$e^{inxiki\varphi(t_i-x)} \tag{IV.13a}$$

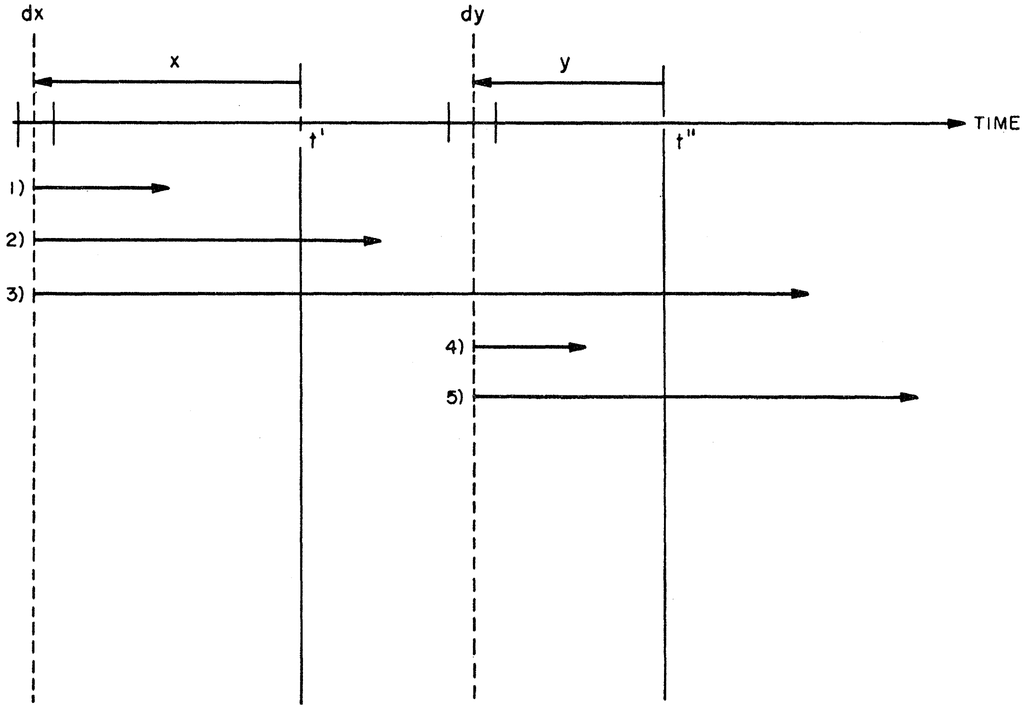

FIG. 14. The Lindholm method of classifying collisions as to duration. (After Lindholm.[51])

where

$$\begin{aligned} \varphi(t_i-x)&=0 && \text{for} \quad t_i-x<0 \\ \varphi(t_i-x)&=t_i-x && \text{for} \quad 0<t_i-x<t''-t' \qquad \text{(IV.13b)} \\ \varphi(t_i-x)&=t && \text{for} \quad t''-t'<t_i-x. \end{aligned}$$

Equation (IV.13b) is merely a restatement of our restriction of the collision such that at least a portion of it occurs within $t''-t'$, and the method of including close collisions has been demonstrated.

In analogy to Eq. (IV.8) one obtains for the present case

$$\begin{aligned} &\langle e^{i[\eta(t'')-\eta(t')]}\rangle \\ &= \sum_{nx(1)1=0}^{\infty} \cdots \sum_{nx(1)i=0}^{\infty} \sum_{nx(2)i=0}^{\infty} \cdots \sum_{ny(j)i=0}^{\infty} \prod_{i} \prod_{dx(l)} \prod_{dy(j)} \\ &\times \frac{1}{n_{x(l)i}!e^{dx(l)/\tau}} \left(\frac{\sigma_i}{\sigma} \frac{dx(l)}{\tau}\right)^{nx(l)i} \\ &\cdot \frac{1}{n_{y(j)i}e^{dy(i)/\tau}} \left(\frac{\sigma_i}{\sigma} \frac{dy(j)}{\tau}\right)^{ny(j)i} \\ &\times e^{i[nx(l)ik_i\varphi(t_i-x)+ny(j)ik_i\psi(t_i-y)]}. \qquad \text{(IV.14)} \end{aligned}$$

In Eq. (IV.14) the $x(l)$ represent the possible dx time intervals during which included collisions may originate. The $y(j)$ represent the possible dy time intervals during which included collisions may originate. Thus, $n_{x(l)1}$ is the number of collisions of the type one originating with some probability during the $dx(l)$ time interval.

Equation (IV.14) in conjunction with Eqs. (IV.4) and (IV.5) may be evaluated for the van der Waals case. For high pressures the result is

$$I(\nu)=I_0=c_1N\langle v\rangle^{6/5}(\Delta\nu)^{-\frac{3}{2}}\exp(-N^2c_2/\Delta\nu). \qquad \text{(IV.15)}$$

A consideration of Eq. (IV.15) shows that Lindholm's line shape has reduced to Margenau's statistical shape for the case of high pressure. If we let the phase shift $\mathfrak{H}=16/3\pi=1.7$ instead of the 0.75 which Lenz had used, we obtain exact agreement between the exponentials in the Margenau statistical theory Eq. (IV.15). Since the statistical theory had yielded such excellent agreement with experiment at high pressure Lindholm chose $16/3\pi$ as the value for $\mathfrak{H}$ on the basis of this resulting agreement. Lindholm justified his disagreement as follows.

First, let us recall that the time duration of the collision is essentially $2\mathfrak{H}$ and consider Fig. 15. Curve (a) in this figure is the actual curve for the phase integral $2\pi b\int dt/(\langle v\rangle^2t^2+\rho^2)^3$. Curve (b) is Lenz's approximate curve where $\mathfrak{H}=0.75$, and curve (c) is the Lindholm curve where $\mathfrak{H}=1.7$. Lindholm felt that the larger $\mathfrak{H}$ value is more justified in that it includes the slow frequency shifts at either end of the true curve (a).

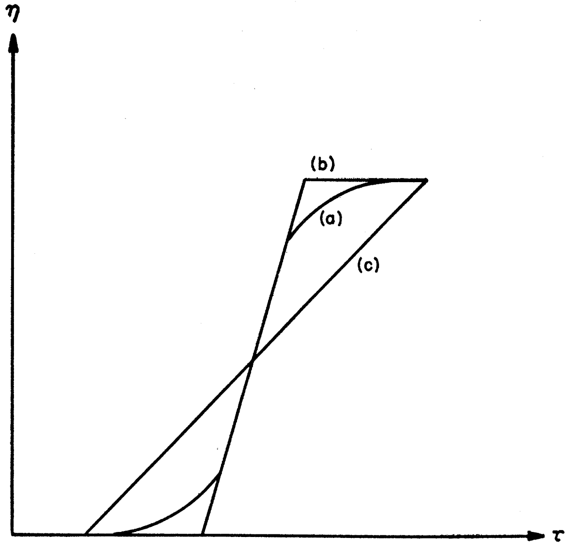

FIG. 15. The Lenz and Lindholm approximations to the phase shift function. (After Lindholm.[51])

The low pressure solution for van der Waals forces yielded

$$\begin{aligned} I_\nu&=I_0+I_\infty \\ &=0.795\frac{1-(k+0.577l)\dfrac{0.227}{0.795}-0.165l}{(0.795l)^2+(0.577l+k)^2}, \qquad \text{(IV.16)} \end{aligned}$$

where the definitions of l and k may be inferred from Eqs. (IV.17). The line shift and half-width are given by

$$\Delta\nu_0=\frac{0.577}{\dfrac{2\pi\mathfrak{H}}{\langle v\rangle}\left[\dfrac{3\pi^2b}{8\langle v\rangle}\right]^{1/5}}=\frac{0.577l}{c}=0.97N\langle v\rangle^{3/5}b^{2/5} \qquad \text{(IV.17a)}$$

$$\tfrac{1}{2}\delta=\frac{0.795l}{c}=2.68N\langle v\rangle^{3/5}b^{2/5} \qquad \text{(IV.17b)}$$

which is essentially the Lenz result.

Having considered the Lenz and Margenau limiting cases, let us turn our attention to the behavior of the van der Waals result in the wings of the line.

For this case, Lindholm was able to use an approximate numerical evaluation to obtain the following two equations for the red and violet wings of the line, respectively,

$$\begin{aligned} I(\nu)=&\frac{0.741l}{(-k)^{3/2}}+\frac{0.254l}{(-k)^{7/3}} \\ &-\frac{0.129l^3}{(-k)^{5/2}}+\frac{0.532l^2}{(-k)^{17/6}}-\cdots \qquad \text{(IV.18a)} \end{aligned}$$

$$I(\nu)=\frac{0.507l}{k^{7/3}}-\frac{0.614l^2}{k^{17/6}}+\frac{0.320l^3}{k^{10/3}}-\cdots. \qquad \text{(IV.18b)}$$

If the first term in Eq. (IV.18a) is taken as the expression for the intensity in the red wing, agreement with the expressions of Kuhn[42] and Margenau is, of course, obtained. The earlier verification of Kuhn's expression for the intensity distribution in the red wing in the case of Na broadened by A as obtained by Kuhn[43] provide experimental justification for the Lindholm result.

Let us assume that the first term in Eq. (IV.18b) is sufficient to describe the intensity distribution in the violet wing. When a comparison of this expression with the measurements of Minkowski[70] for the violet wing of the Na D_2 line broadened by A is made, really excellent agreement is obtained. It might be mentioned here that, although the $(\Delta\nu)^{-\frac{3}{2}}$ dependence had been previously obtained for the red wing, the $(\Delta\nu)^{-7/3}$ dependence had certainly not been previously obtained for the violet wing. Minkowski had attempted to use a $(\Delta\nu)^{-2}$ dependence without the success which attended Lindholm's utilization of $(\Delta\nu)^{-7/3}$.

Kleman and Lindholm[41] experimentally investigated the broadening of Na lines by A and obtained excellent agreement in shift, half-width, and line contour with this theory.

The interruption theories to which we have so far devoted our attention may reasonably be classified as classical ones based on the Michelson application of the Fourier analysis to the problem. We shall show rather shortly that a quantum consideration also may lead to the mathematics of the Fourier analysis. Before doing so however, let us consider the interesting and important matters of distributions and detailed balancing which were studied by Van Vleck and Weisskopf and by Van Vleck and Margenau, respectively.

D. A Maxwell Distribution of Dipole Moments

Van Vleck and Weisskopf[88] were of the opinion that a revision of Lorentz' development, such that an agreement between this work and that of Debye be obtained was required. In essence this revision consisted in substituting for the random Lorentz distribution of x and $\dot{x}$ after a collision the Maxwell-Boltzmann distribution, and let us detail this.

The Lorentz solution to the equation of motion for the vibrating photoelectron is

$$x=\Re\left\{\frac{\epsilon a e^{i\omega t}}{m(\omega_0{}^2-\omega^2)}\left[1-\frac{1+(\omega/\omega_0)}{2\tau[-i(\omega_0-\omega)+1/\tau]}-\frac{1-(\omega/\omega_0)}{2\tau[i(\omega+\omega_0)+1/\tau]}\right]\right\} \quad \text{(IV.19a)}$$

$$=\Re\{ae^{i\omega t}(x'-ix'')\}. \quad \text{(IV.19b)}$$

In order to write down the desired result from Eq. (IV.19b), it is necessary to disgress for a moment.

We begin by considering a molecule of electric dipole moment $\boldsymbol{\mu}$ which makes an angle ϑ with an external electric field a $\cos\omega t$. In this case now, we assume that after collision a Maxwell-Boltzmann distribution governs the dipole orientation (and hence, the orientation of x). If the last collision occurred at time t_0, the energy due to the dipole-field interaction is $\boldsymbol{\mu}\cdot\mathbf{a}$. Then we may obtain the mean polarization

$$\langle\mathfrak{M}\rangle=\frac{\mu\int_0^\pi \cos\vartheta\exp[\mu a\cos\vartheta\cos(\omega t_0)/kT]\sin\vartheta d\vartheta}{\int_0^\pi \exp[\mu a\cos(\omega t_0)/kT]\sin\vartheta d\vartheta}$$

$$\doteq\frac{\mu^2 a\cos(\omega t_0)\int_0^\pi\cos^2\vartheta\sin\vartheta d\vartheta}{kT_0\int_0^\pi\sin\vartheta d\vartheta}$$

$$=\frac{\mu^2 a}{3kT}\Re\{e^{i\omega_0 t}\} \quad \text{(IV.20)}$$

when we have expanded the exponential in a MacLaurin series and only retained the term containing a. The polarization per cubic centimeter may be obtained by averaging Eq. (IV.20) over the Lorentz distribution a $\exp(-t/\tau)$. The result is

$$P=\frac{Na\mu^2}{3kT}\Re\left\{\frac{e^{i\omega t}}{1+i\omega\tau}\right\}=a\Re\{(b_1-ib_2)e^{i\omega t}\}. \quad \text{(IV.21)}$$

The work done on the molecule by the radiation field will surely be given by the average value of **a** $\cos\omega t(dp/dt)$. Finally, if we divide this work by the energy flow in the field, $ca^2/8\pi$, we should determine the energy taken out of the field by the molecule, or, simply, the absorption coefficient.

Now

$$a\cos(\omega t)\frac{dp}{dt}=F\cos\omega t\left[\frac{Na\mu^2}{3kT}\frac{\omega^2\tau\cos(\omega t)}{1+\omega^2\tau^2}\right]$$

$$=\frac{Na\mu^2}{3kT}\frac{\omega^2\tau\cos(\omega t)}{1+\omega^2\tau^2} \quad \text{(IV.22a)}$$

and the average value is

$$\left\langle F\cos(\omega t)\frac{dp}{dt}\right\rangle=\frac{Na^2\mu^2}{6kT}\frac{\omega^2\tau}{1+\omega^2\tau^2}. \quad \text{(IV.22b)}$$

As a consequence we obtain the Debye result

$$\mathfrak{H}=\frac{\omega}{c}\frac{4\pi N\mu^2}{3kT}\frac{\omega\tau}{1+\omega^2\tau^2} \quad \text{(IV.23)}$$

for the absorption coefficient.

Now we note that the same result could have been obtained if we had set

$$\mathfrak{H}=\frac{4\pi b_2\omega}{c} \tag{IV.24}$$

from Eq. (IV.21). This tells us then that, from Eq. (IV.19b),

$$\mathfrak{H}=\frac{4\pi N\omega\epsilon x''}{c}=\frac{2\pi N\epsilon^2}{mc}\left(\frac{\omega}{\omega_0}\right)\times\left[\frac{1/\tau}{(\omega-\omega_0)^2+(1/\tau)^2}-\frac{1/\tau}{(\omega+\omega_0)^2+(1/\tau)^2}\right]. \tag{IV.25}$$

From the Lorentz theory we obtained Eq. (IV.25), the quantum analog of which is obtained by replacing $1/m$ by $(4/3)\pi/\hbar\nu_{ij}|\mathbf{x}_{ij}|^2$. Next we introduce a Maxwell-Boltzmann distribution over the energy states and sum over these states with the result

$$\mathfrak{H}=\left(\frac{4\pi\nu N\epsilon^2}{3\hbar c}\right)\frac{\sum_j\sum_i|\mathbf{x}_{ij}|^2f(\nu_{ij},\nu)e^{-E_j/kT}}{\sum_j e^{-E_j/kT}} \tag{IV.26a}$$

where the "shape factor" is given by

$$f(\nu_{ij},\nu)=\frac{1}{\pi}\left[\frac{(\delta/2)}{(\nu_{ij}-\nu)^2+(\delta/2)^2}-\frac{(\delta/2)}{(\nu_{ij}+\nu)^2+(\delta/2)^2}\right] \tag{IV.26b}$$

$$\delta=\frac{1}{\pi\tau}. \tag{IV.26c}$$

Let us now write

$$\begin{aligned}\sum_j\sum_i|\mathbf{x}_{ij}|^2f(\nu_{ij},\nu)e^{-E_j/kT}&=\sum\sum_{j\neq i}[|\mathbf{x}_{ij}|^2f(\nu_{ij},\nu)e^{-E_j/kT}+|\mathbf{x}_{ji}|^2f(\nu_{ji},\nu)e^{-E_i/kT}]\\&=\sum_i\sum_j|\mathbf{x}_{ij}|^2f(\nu_{ij},\nu)\frac{h\nu_{ij}}{2kT}e^{-E_j/kT}\end{aligned}$$

since

$$\nu_{ji}=-\nu_{ij};\quad f(\nu_{ij},\nu)=-f(\nu_{ji},\nu);\quad |\mathbf{x}_{ij}|=|\mathbf{x}_{ji}|$$

and

$$(e^{-y}-e^{-x-y})\doteq\tfrac{1}{2}x(e^{-y}+e^{-x-y})\quad\text{for}\quad x\ll 1$$

so that Eq. (IV.19a) becomes:

$$\mathfrak{H}=\left(\frac{4\pi\nu N\epsilon^2}{6\hbar c}\right)\frac{h}{2kT}\frac{\sum_j\sum_i|\mathbf{x}_{ij}|^2\nu_{ij}f(\nu_{ij},\nu)e^{-E_j/kT}}{\sum_j e^{-E_j/kT}}. \tag{IV.27}$$

Now if Eqs. (IV.25) and (IV.27) were truly equivalent, as it would appear they should be, the latter would be expected to reduce to the former for $\nu_{ij}=0$. It is rather apparent that zero instead of such a reduction results. Van Vleck and Weisskopf remedied this discrepancy by using a Maxwell-Boltzmann distribution for x and $\dot{x}$ in the equations of motion for the vibrating photoelectron. Lorentz had used a random distribution of x and $\dot{x}$ in these equations.

A solution under these conditions yields, in place of Eq. (IV.19),

$$\langle x\rangle=\mathcal{R}\left[\frac{\epsilon Fe^{i\omega t}}{m(\omega_0^2-\omega^2)}\left\{1-\frac{(\omega_0+\omega)(\omega/\omega_0^2\tau)}{2[1/\tau-i(\omega_0-\omega)]}+\frac{(\omega_0-\omega)(\omega/\omega_0^2\tau)}{2[1/\tau+i(\omega_0+\omega)]}\right\}\right]. \tag{IV.28}$$

In analogy to the method of obtaining Eq. (IV.25) we may then obtain

$$\mathfrak{H}=\frac{2\pi N\epsilon^2}{mc}\left(\frac{\omega}{\omega_0}\right)^2\times\left[\frac{1/\tau}{(\omega-\omega_0)^2+(1/\tau)^2}+\frac{1/\tau}{(\omega+\omega_0)^2+(1/\tau)^2}\right] \tag{IV.29}$$

of quantum equivalent

$$\mathfrak{H}=\left(\frac{4\pi\nu N\epsilon^2}{6\hbar c}\right)\frac{h}{kT}\frac{\sum_j\sum_i|\mathbf{x}_{ij}|^2\nu_{ij}f(\nu_{ij},\nu)e^{-E_j/kT}}{\sum_j e^{-E_j/kT}} \tag{IV.30a}$$

where

$$f(\nu_{ij},\nu)=\frac{1}{\pi}\frac{\nu}{\nu_{ij}}\left[\frac{\Delta\nu}{(\nu_{ij}-\nu)^2+(\Delta\nu)^2}+\frac{\Delta\nu}{(\nu_{ij}+\nu)^2+(\Delta\nu)^2}\right]. \tag{IV.30b}$$

Utilizing Eqs. (IV.30), we do indeed obtain Eq. (IV.23) for the case of zero resonant frequency, $\nu_{ij}=0$, and $\epsilon^2\sum|\mathbf{x}_{ij}|^2=\mu^2$ which at least is of import in resolving the paradox in the low-frequency region. Equation (IV.29) on the other hand, offers little change in the visible region, the $(\omega/\omega_0)^2$ factor yielding slightly more line asymmetry.

E. Detailed Balancing

The studies of Van Vleck and Margenau[87] did not serve to actually change the shape of the proposed absorption line, but they did finally show that the shapes of the spectral lines are the same in emission as in absorption, a point of no mean import. At any rate, since we accept the thesis that the integrated absorption and emission balance each other in a Rayleigh-Jeans radiation field, detailed balance of emission and absorption results from this equivalence of absorption and emission line shapes. That is, a given frequency interval absorbs as much as it emits. The balance was obtained by a hitherto untried technique, that is, the summing of the work done on the oscillator by the electric field at collision as well as during the intercollision intervals. This yielded the same frequency by frequency power as that emitted between two collisions.

If our oscillator motion is described by $x(t) = x_0 \cos(\omega_0 t+\varphi)$ we may quite readily write down the Fourier analysis of $x(t)$. We may then integrate the expression for $x(\omega)$ and average $|x(\omega)|^2$ over a random distribution of φ to obtain a result which, when averaged over a random distribution of intercollision times, yields§§

$$|x(\omega)|^2=\frac{x_0^2}{4\pi}\left[\frac{1}{a^2+(\omega_0-\omega)^2}+\frac{1}{a^2+(\omega_0+\omega)^2}\right] \tag{IV.31}$$

where now $a=1/\tau$.

A point charge which is oscillating in one dimension radiates power of amount

$$\frac{2}{3}\frac{\epsilon^2}{c^3}\ddot{x}^2.$$

from the equation for simple harmonic motion $\ddot{x}=-\omega^2x$. In addition, normalization of the Fourier components requires

$$\int_{-\infty}^{+\infty}[x(t)]^2dt=\int_{-\infty}^{+\infty}|x(\omega)|^2d\omega=2\int_{0}^{\infty}|x(\omega)|^2d\omega$$

so that

$$\ddot{x}^2=-\omega^4|x(t)|^2=-\omega^4|x(\omega)|^2.$$

We thus obtain for the power emitted by the oscillator in the frequency interval between ω and $\omega+d\omega$

$$P_E'(\omega)d\omega=\frac{2\epsilon^2}{3c^3}2\omega^4|x(\omega)|^2d\omega. \tag{IV.32a}$$

This must be modified to include the intervals between all collisions over a long period t, however, since the Fourier analysis has only been carried out over one such period. As a result, Eq. (IV.32a) becomes

$$P_E(\omega)d\omega=\frac{atP_E'(\omega)d\omega}{t}=\frac{2}{3}\frac{\epsilon^2}{c^3}2\omega^4|x(\omega)|^2a\,d\omega. \tag{IV.32b}$$

Substitution of Eq. (IV.31) into Eq. (IV.32b) then yields

$$P_E(\omega)=\frac{\epsilon^2x_0^2}{3\pi c^3}\omega^4\left[\frac{a}{a^2+(\omega_0-\omega)^2}+\frac{a}{a^2+(\omega_0+\omega)^2}\right]. \tag{IV.33}$$

Now in order to obtain detailed balancing, we must needs show that $P_A(\omega)$, the power absorbed at the frequency ω, corresponds to this.

If the velocity proportional viscous drag force $g\dot{x}$ is dropped from the electronic equation of motion, the Van Vleck-Margenau equation is obtained as

$$\ddot{x}+\omega_0^2x=\frac{\epsilon F}{m}\cos(\omega t+\varphi)$$

a solution to which is sought under the Lorentz boundary conditions, $x=\dot{x}=0$.

The solution in question leads to the following result for the work done—per unit time—by the field on the electron *between* collisions:

$$\frac{W}{t}=\frac{\epsilon^2F^2}{4m}\left[\frac{a}{a^2+(\omega-\omega_0)^2}+\frac{a}{a^2+(\omega+\omega_0)^2}\right]. \tag{IV.34}$$

The work done—per unit of time—by the field *at* collision may be obtained as

$$\frac{\epsilon^2F^2a}{4m\omega}\left[\frac{\omega-\omega_0}{a^2+(\omega-\omega_0)^2}-\frac{\omega+\omega_0}{a^2+(\omega+\omega_0)^2}\right] \tag{IV.35}$$

which, when added to Eq. (IV.34), yields

$$P_A(\omega)=\frac{W}{t}=\frac{\epsilon^2F^2\omega}{4m\omega_0}\times\left[\frac{a}{a^2+(\omega-\omega_0)^2}-\frac{a}{a^2+(\omega+\omega_0)^2}\right]. \tag{IV.36}$$

A consideration of Eqs. (IV.33) and (IV.36) is sufficient to show that detailed balance has not been obtained if for no other reason than that the shape factors as given by the brackets in the two equations differ. Van Vleck and Margenau overcame this difficulty by passing from the Lorentz to the Van Vleck-Weisskopf boundary conditions on x and $\dot{x}$ at collision. This has the effect of adding the term

$$\frac{\epsilon^2Fa}{4m\omega^2}\left[\frac{\omega^2-\omega\omega_0}{a^2+(\omega-\omega_0)^2}+\frac{\omega^2+\omega\omega_0}{a^2+(\omega+\omega_0)^2}\right] \tag{IV.37}$$

to Eq. (IV.37) to arrive at the power absorbed from the light wave as a function of frequency.

If we let $\Upsilon(\omega)d\omega$ be the energy density in the field for the frequency interval ω to $\omega+d\omega$, we may replace F^2 in

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§§ In evaluating the Fourier integral we have taken the limits 0 and ϑ where ϑ is the time between two collisions, thus integrating $x_0\cos(\omega t+\varphi)$ over the time between two collisions to obtain $x(\omega)$.

Eqs. (IV.36) and (IV.37) by

$$F^2 = \frac{4}{3}\frac{m\omega^2\omega_0^2}{\pi c^3}x_0^2 \tag{IV.38}$$

in the sum of Eqs. (IV.36) and (IV.37) to obtain

$$P_A(\omega) = \frac{\epsilon^2 x_0^2}{3\pi c^3}\omega^4\left[\frac{a}{a^2+(\omega_0-\omega)^2}+\frac{a}{a^2+(\omega_0+\omega)^2}\right]. \tag{IV.39}$$

A comparison of Eqs. (IV.33) and (IV.39) shows that a detailed balance condition between absorption and emission has indeed been obtained by considering, in absorption, the work done by the field (a) *between* collisions and (b) *at* collisions and by including the Maxwell-Boltzmann boundary conditions.

We have remarked that the boundary conditions especially are an approximation. In an actual atomic system, of course, finite collision times would have to be considered. In addition, the Planck radiation law would more logically replace the Rayleigh-Jeans law. In the limit of low frequency, however, the former reduces to the latter, so that, as in the case of the earlier Van Vleck-Weisskopf considerations, the results are particularly applicable to the microwave region.

F. The Correlation Function Treatment

At the beginning of the present chapter we remarked on the various methods which have been utilized to demonstrate the quantum justification of the use of the Fourier analysis in line broadening. We shall now give an extremely simple demonstration of such a justification by using the state growth equations for transitions accompanied by the emission of radiation.

Let us suppose that the natural width of the spectral line is small compared to the interruption width so that we may neglect the radiation damping constant, γ in Eq. (II.24). Then this equation may be approximately written down as

$$b_i(t) = -i\,\text{const}\int_0^t dt' \times\exp\left\{\frac{i}{\hbar}\int_0^{t'}[E_B(t'')-E_A(t'')]dt''+\omega_i t\right\}. \tag{IV.40}$$

We have previously considered the argument which results in the relation between state growth coefficient and line intensity distribution:

$$I(\omega) = |b_\omega(\infty)|^2 = \int_0^\infty dt'\int_0^\infty dt'' \times\exp\left[-i\int_{t''}^{t'}P(t)dt+i\omega(t'-t'')\right] \tag{IV.41}$$

where now $P(t)$ is the angular frequency separation of the perturbed energy levels.

We will agree that Eq. (IV.41) is a form of the Fourier integral which we have previously encountered, for example, Eq. (IV.4). Having obtained this Fourier integral after a quantum fashion, we should now feel justified, as did Foley,[17] in proceeding with the treatment of what this latter author was pleased to dub the "correlation function."

In connection with the evaluation of Eq. (IV.4) we mentioned the replacement of the second integral by the statistical average. The principal behind such a procedure had, as we have remarked, been set forth by Lenz. The exponential factor [which we now designate as $\varphi(t_0)$] was named by Foley. The remainder of the work which has been done on the interruption theory has consisted of the attempts of Foley[17] and Anderson[2] to evaluate this correlation function, a term which appears to have been given a favorable reception. Let us sketch Foley's evaluation and turn to that of Anderson which does seem a bit more general of application.

We write:

$$\varphi(t_0) = \langle y(t_0)\rangle = \int_0^\infty dt''\exp\left[i\int_{t''}^{t''+t_0}P(t)dt\right] = \left\langle\exp\left[i\int_0^{t_0}P(t)dt\right]\right\rangle. \tag{IV.42}$$

Much after the Lindholm fashion we may replace the integral within the exponent by a sum over phase shifts:

$$\sum_{i=1}^n \eta_i = \int P(t)dt$$

which we now average over the distribution of phase shifts, $p(\eta)$:

$$\int dt''\exp[-i\sum_{i=1}^n \eta_i] = \prod_{i=1}^n\int_{-\infty}^{+\infty}d\eta\, p(\eta)(\cos\eta - i\sin\eta) = (A-iB)^n. \tag{IV.43}$$

Finally this result is averaged over the standard distribution of intercollision times,

$$\varphi(t_0) = \sum_{n=0}^\infty \frac{e^{-\vartheta/\tau}}{n!}\left(\frac{\vartheta}{\tau}\right)^n (A-iB)^n = \exp\left[\frac{A-iB}{\tau}\vartheta - \frac{\vartheta}{\tau}\right] \tag{IV.44}$$

which, when substituted into Eq. (IV.41), results in

$$I(\omega) = \frac{(1-A)/\pi\tau}{[(1-A)/\tau]^2+[B/\tau-\omega]^2}. \tag{IV.45}$$

The line shift and half-width for this intensity distribution are then

$$\Delta = B/\tau \tag{IV.46a}$$

$$\delta = \frac{2(1-A)}{\tau}. \tag{IV.46b}$$

Equation (IV.43) provides the means for the requisite evaluation of the coefficients A and B, a somewhat lengthy procedure which we shall not detail. With which we turn our attention to Anderson's work on the subject.

Margenau[58] had early (1935) demonstrated that the Fourier integral will reduce to the Margenau statistical distribution for sufficiently low velocities. Now Anderson, armed with the Lenz method of evaluation, has carried this procedure a step further. He has (1) obtained the statistical distribution for high pressures and for the line wing, (2) obtained the simple interruption result for low pressures and near line center, and (3) numerically evaluated the intermediate cases.

We begin by supposing that the perturbations arising due to the various members of our gaseous assembly are additive so that

$$\Delta\omega = \sum_{i=1}^{n} \Delta\omega(R_i). \tag{IV.47}$$

This means that Eq. (IV.42) assumes the form

$$\varphi(t_0) = \left\langle \exp\left[i \int_0^{t_0} \nu(t)dt \right] \right\rangle = \left\langle \prod_{i=1}^{n} \exp\left[i \int_0^{t_0} \nu(R_i)dt \right] \right\rangle = \left\langle \exp\left[i \int_0^{t_0} \nu(R)dt \right] \right\rangle^n. \tag{IV.48}$$

Now let us remark in connection with this equation that the replacement of the average of the product by the product of n identical averages is predicated on (1) the identical nature of all broadeners and (2) the absence (assumed) of interactions between these broadeners. No justification appears required for

$$R^2 = (x_0 + \langle v \rangle t)^2 + \rho^2.$$

This means, however, that the averaging process will now be one over x_0 and ρ

$$\begin{aligned} \varphi(t_0) &= \frac{1}{V^n} \left\{ \int_0^\infty 2\pi\rho d\rho \int_{-\infty}^{+\infty} dx_0 \exp\left[i \int_0^{t_0} \nu(R)dt \right] \right\}^n \\ &= \left[1 - \frac{2\pi N}{n} \int_0^\infty \rho d\rho \int_{-\infty}^{+\infty} dx_0 \times \left(1 - \exp\left[i \int \nu(R)dt \right] \right) \right]^n \\ &= \exp[-NV'(t_0)] \end{aligned} \tag{IV.49a}$$

since

$$\lim_{n\to\infty} \left[1 - \frac{A}{n} \right]^n = \exp[-A]$$

and where

$$V'(t_0) = 2\pi \int_0^\infty \rho d\rho \int_{-\infty}^{+\infty} dx_0 \times \left\{ 1 - \exp\left[i \int_0^{t_0} \nu([(x_0 + \langle v \rangle t)^2 + \rho^2]^{\frac{1}{2}})dt \right] \right\} \tag{IV.49b}$$

with $V = n/N$.

Now in order to obtain the low velocity statistical limit, one simply lets $\langle v \rangle = 0$ with the desired result. A comparison with Eq. (III.8) serves to demonstrate this quite nicely.

For the simple interruption theory limit we suppose the reverse situation to prevail, namely, $\langle v \rangle$ large compared to x_0, thus justifying ignoring this latter coordinate in the exponential. It would seem intuitively apparent that the range of integration $-\langle v \rangle \tau$ to $+\langle v \rangle \tau$ would make the greatest contribution to the integral in x_0. Such a limitation on the range of integration of x_0 leads to

$$\varphi = \langle v \rangle \tau \int_0^\infty \rho d\rho \left(1 - \exp\left[i \int_{-\infty}^{+\infty} \nu([\rho^2 + \langle v \rangle^2 t^2]^{\frac{1}{2}})dt \right] \right) = (\sigma_r + \sigma_i)\langle v \rangle \tau = \sigma \langle v \rangle \tau \tag{IV.50a}$$

from which one obtains [through Eq. (IV.58)] for the intensity distribution

$$I(\omega) = \frac{N\langle v \rangle \sigma_r}{(\omega - \omega_0 - N\langle v \rangle \sigma_i)^2 + (N\langle v \rangle \sigma_r)^2}. \tag{IV.50b}$$

This should suffice to demonstrate the fashion in which the theory reduces in the two limiting cases. For the intermediate values numerical calculation is required. It is understood that Anderson has carried out such calculations, but the results have not as yet been published.

V. RESONANCE BROADENING

A. The Qualitative Basis of Self-Broadening

In our specific studies of the last three chapters the broadening phenomena considered have resulted from the presence of other atoms. Although different interatomic forces have been utilized as agents for this broadening, no direct consideration has been given to the relation between the emitter and the broadener, that is, no consideration has been given to whether the broadeners are of the same or of a different species than the emitter. In this chapter we propose to devote ourselves to that unique set of phenomena which occur when the broadeners are the same type atoms as the emitter, as opposed to the various broadenings which may occur when the broadeners are of a different type from the emitter.

In 1915 Rayleigh[74] appears to have first raised the question as to the possible difference in broadening effects in the presence of like atoms as broadeners and in the presence of foreign gas atoms. When foreign and self-broadening were subsequently studied as distinct phenomena, it was early recognized that the magnitude of the latter was much greater than that of the former. We may rather easily present a qualitative picture of these self broadening (a term which we shall subsequently replace by resonance broadening) effects either from the classical or quantum viewpoint. Since such is the case, let us begin with the classical explanation of the phenomenon.

In the classical sense, the similar atoms of a radiating gas are made up of a collection of like oscillators of the same natural frequency. Because of the sameness of this natural frequency, a strong coupling of these oscillators may be expected to occur in the usual classical manner given some basic, say electrostatic, coupling force. This in turn will cause a spread of the coupled oscillator frequencies about the natural frequency of a single oscillator.

From a quantum-mechanical sense, the same strong broadening can be inferred. Let us hypothesize a two-atom system in which the level degeneracy arising from the sameness of the atoms results in an energy perturbation dependent on the inverse cube of the atomic separation. We recall that under the same interaction force two unlike atoms give rise to an inverse sixth power dependence on the atomic separation. Thus, obviously greater broadening will result from the presence of like molecules. We shall later discuss the reduction in state lifetime for the case of resonance broadening which results in a broadening of the spectral line, but the state degeneracy which we have mentioned above we shall allow to suffice as an introductory consideration.

B. The Coupled Oscillator Theory

The first attack on the problem of resonance broadening was made by Holtsmark[31] in 1925. This author considered the problem from a classical point of view which depicted the atoms of the absorbing, self-broadening gas as classical oscillators.

Now we suppose a coupling force, dependent on the electric dipole moment of the atoms, to be present. Let us begin by considering two of these classical oscillators each consisting primarily of a "quasi-elastically bound" electron. If x_1 is the vibrational coordinate of the first oscillator and x_2 that of the second, and these two coordinates are coupled through the potential term $k_3x_1x_2$, then the frequencies of the coupled system are surely

$$\omega^2=\tfrac{1}{2}\left(\omega_1^2+\omega_2^2\pm\left[(\omega_1^2-\omega_2^2)+4\left(\frac{k_3}{m}\right)^2\right]^{\frac{1}{2}}\right). \qquad \text{(V.1)}$$

If the two atoms are unlike then $|\omega_1^2-\omega_2^2|\gg k_3/m$ and we obtain

$$\omega^2-\omega_{1,2}^2=\pm\frac{k_3^2}{m^2(\omega_1^2-\omega_2^2)} \qquad \text{(V.2)}$$

whereas, in the case $\omega_1=\omega_2=\omega_0$ (like atoms), we obtain

$$\omega^2-\omega_0^2=\pm\frac{k_3}{m}. \qquad \text{(V.3)}$$

A consideration of Eqs. (V.2) and (V.3) serves to illustrate the much larger frequency shift accompanying the coupling of like oscillators since k_3 is always small. This essentially forms the basis for Holtsmark's considerations. Let us first determine k_3, and then proceed with the problem.

We have assumed our coupling force to arise from the electric dipole moments of the oscillators, and we may write the dipole potential as

$$U=\mathfrak{F}_i\cdot\boldsymbol{\mu}_k=\frac{\epsilon^2}{r^3}[1-3\cos^2\gamma_{ik}]x_ix_k, \qquad \text{(V.4)}$$

where $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_k$ are the dipole moments of the ith and kth atom.

γ_{ik} is now the angle between either $\boldsymbol{\mu}_i$ or $\boldsymbol{\mu}_k$ and $\mathbf{r}$. We further have supposed $\boldsymbol{\mu}_i\|\boldsymbol{\mu}_k$.

Then the force on atom i due to the field produced by atom k is, since $\mathfrak{F}=-\nabla U$

$$\mathfrak{F}=\frac{\epsilon^2u_{ik}x_k}{r_{ik}^3}=ma_{ik}x_k \qquad \text{(V.5a)}$$

with

$$u_{ik}=(1-3\cos^2\gamma_{ik}). \qquad \text{(V.5b)}$$

Now if we consider a system of n atoms instead of our original two-atom system we may obtain

$$\ddot{x}_i+\omega_0^2x_i+\sum_k a_{ik}x_k=0 \qquad \begin{matrix} k\lessgtr i \\ i=1,2,\cdots,n. \end{matrix} \qquad \text{(V.6)}$$

From Eq. (V.6) we evolve the secular determinant for the problem

$$\begin{vmatrix} \Lambda & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & \Lambda & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{32} & \Lambda & \cdots & a_{3n} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ a_{n1} & a_{n2} & a_{n3} & \cdots & \Lambda \end{vmatrix}=0 \qquad \text{(V.7)}$$

where the abbreviation $\Lambda=\omega^2-\omega_0^2$ has been utilized.

Now it is rather obvious that it would be somewhat difficult at best to obtain the roots of the determinant of Eq. (V.7) for the general case, in fact, it presently appears impossible. We can, however, determine the mean and the root-mean-square spread of the roots of this equation after a fashion which we shall not detail. After Holtsmark had done precisely this, he proceeded to make an assumption which does not appear too well justified in the light of subsequent—and one might add previous—knowledge of resonance broadening. Quite simply he supposed the spectral line to be of a Gaussian shape. In the extreme wings of the line this appears to be a reasonable supposition, and we might recall that earlier Holtsmark had been required to assume such a shape in the wings of the electric field strength distribution in connection with the Stark broadening. The connection between the two situations is certainly obscure, however, and subsequent studies of resonance broadening seem to confirm the fact that the Gaussian distribution is not the proper one. At any rate, such an assumption leads to

$$I(\omega')=\frac{1}{[2\pi\langle\omega'^2\rangle]^{\frac{1}{2}}}\exp(-\omega'^2/\langle\omega'^2\rangle) \tag{V.8a}$$

of half-width

$$\delta=2\omega'=2.36[\langle\omega'^2\rangle]^{\frac{1}{2}}=103.5\times10^7\frac{\sqrt{N}}{\rho^{\frac{3}{2}}}\frac{1}{2\omega_0} \tag{V.8b}$$

in which $\langle\ \rangle$ indicates the mean value of the quantity enclosed.

The feature in the half-width equation which appears most striking—although perhaps not most pleasingly so—is the dependence on the root of the density. Other theories as well as available experimental evidence appear to be unanimous in their refutation of any such dependence claim. A consideration of the half-width equation will probably indicate to the reader, however, that ρ offers a bonnet out of which we might possibly produce a different pressure dependence. Schutz-Mensing[66] has produced just such a dependence in what seems a very straightforward manner.

We take the separation of the emitter and the ith broadener as ρ_i, and proceed to average over the ρ_i. Schutz-Mensing obtained a value $0.55N^{-\frac{1}{3}}$ for $\langle\rho\rangle$. It is obvious that such a value for ρ in Eq. (V.8b) results in a linear density dependence for the half-width. For the root mean square spread of the energies—resulting from the roots of the determinant—this author obtained

$$[\langle\omega'^2\rangle]^{\frac{1}{2}}=\left[\frac{24\pi}{15}\right]^{\frac{1}{2}}\frac{1}{\omega_0}\left(\frac{\epsilon^2}{m}\right)N. \tag{V.9}$$

C. The Statistical Resonance for Binary Encounters

Let us assume that one member of our two like particle system will proceed from a state of energy E_1 to the ground state of energy E_0 with accompanying radiation. Then familiar degenerate perturbation theory yields, as the energy of this interaction

$$E_1^{(1)}=h(\Delta\nu)=\begin{cases}-\dfrac{2}{3}\dfrac{\epsilon^2}{r^3}|r_{12}|^2 & \text{for}\quad m=0\\[2ex] +\dfrac{1}{3}\dfrac{\epsilon^2}{r^3}|r_{12}|^2 & \text{for}\quad m=\pm1\end{cases} \tag{V.10a}$$

where, as usual, m is the magnetic quantum number, and where

$$|r_{12}|^2=\frac{3h}{8\pi^2m\nu_0}f_{12}; \tag{V.10b}$$

all of which leads to

$$\Delta\nu=\begin{cases}-\dfrac{\epsilon^2}{r^3}\dfrac{2}{8\pi^2m\nu_0}f_{12} & \text{for}\quad m=0\\[2ex] +\dfrac{\epsilon^2}{r^3}\dfrac{1}{8\pi^2m\nu_0}f_{12} & \text{for}\quad m=\pm1.\end{cases} \tag{V.11}$$

From Eqs. (V.3) and (V.4) the classical result,

$$\begin{aligned}\Delta\nu&=\pm\frac{\epsilon^2}{r^3}\frac{(1-3\cos^2\gamma_{ik})}{4\pi^2m(\nu+\nu_0)}\\ &\doteq\pm\frac{\epsilon^2}{r^3}\frac{(1-3\cos^2\gamma_{ik})}{8\pi^2m\nu_0},\end{aligned} \tag{V.12}$$

may be written down for comparison.

Equation (V.11) may be rewritten as

$$E_1^{(1)}=h\nu'=\gamma\left(\frac{\epsilon^2hf_{12}}{8\pi^2m\nu_0}\right)\frac{1}{r^3} \tag{V.13}$$

where γ is the statistical weight factor associated with m. After the fashion of Margenau and Watson, let us equate γ to unity. We consider this an averaging process over the possible atomic orientations. The result is

$$U=E_1^{(1)}=ar^{-m}=\left(\frac{\epsilon^2hf_{12}}{8\pi^2m\nu_0}\right)r^{-3} \tag{V.14a}$$

so that

$$a=\frac{\epsilon^2hf_{12}}{8\pi^2m\nu_0}. \tag{V.14b}$$

From Eq. (III.15) the half-width of the resonance broadened spectral line is

$$\delta=\frac{2U_0}{h}=\frac{4}{3}\pi^2Na,$$

so that

$$\delta=\frac{\epsilon^2f_{12}}{6m\nu_0}N. \tag{V.15}$$

Equation (V.15) was originally obtained by Margenau and Watson[95] in a slightly different manner.

D. The Simple Interruption Result

As we recall the simple interruption theory prognosticates the same spectral line form regardless of the interaction forces which give rise to the broadening under consideration. Thus, Eqs. (IV.1) and (IV.2) for the line shape and half-width remain unchanged by virtue of the resonance forces. Now this is, of course, not the case for the optical collision diameter ρ for it will be given by Eq. (IV.3). Let us specificize.

The resonance interaction may be expressed in the form

$$\Delta(r)=K/r^3$$

which means that the phase change is

$$\eta=\int_{-\infty}^{+\infty}\frac{Kdt}{[(\langle v\rangle^2t^2+\rho^2)^3]^{\frac{1}{2}}}=\frac{K}{\langle v\rangle\rho^2}\int_{-\infty}^{+\infty}\frac{dx}{[(x^2+1)^3]^{\frac{1}{2}}}$$
$$=\frac{2K}{\langle v\rangle\rho^2}=1. \qquad \text{(V.16)}$$

From Eq. (V.16) we obtain

$$\rho=\left[\frac{2K}{\langle v\rangle}\right]^{\frac{1}{2}} \qquad \text{(V.17)}$$

which is here expressed in angular frequency units ω. Now Eq. (V.13) tells us that

$$K=\epsilon^2/2m\omega_0. \qquad \text{(V.18)}$$

The substitution of Eqs. (V.17) and (V.18) yields the optical collision diameter from which we may obtain the half-width as

$$\delta=2\pi\frac{\epsilon^2}{m\omega_0}f_{nm}N. \qquad \text{(V.19)}$$

E. Qualitative Consideration of the Energy Transfer Theory

Some four years after the publication of Weisskopf's theory Furssow and Wlassow[19] entered the field with what did amount to a new conceptual approach. Their entry was marked by the intriguing statement that the Weisskopf theory—and the Lenz theory in passing—was completely incorrect.[‖‖] It would appear reasonable for us to briefly consider the reasons which they advance for this conclusion.

For greatest accuracy of consideration let us quote the Furssow and Wlassow statement verbatim before attempting to consider their reasoning.

"To be sure Weisskopf's considerations of the collisions between the like atoms is not entirely correct. Weisskopf without foundation applies the correct concept of the mechanism of the collision damping in the case of non-extinguishing atoms of different types to the case of like atoms. As is known the broadening of the lines through collisions result not only when the wave train emitted by the atom is propagated after the collision (extinguishing gases) but also at the time when at the collision a change of the vibration phase of the excited atoms sets in (non-extinguishing gases). In order to compute the phase shift during the collision one must take the *change of frequency* $\Delta\omega$[¶¶] of the emitting atom which occurs through the interaction with foreign atoms *and integrate over the collision time*.[¶¶] If one makes this integral equal to one then the magnitude of the optical collision diameter can be evaluated. The collisions of the like atoms Weisskopf takes instead of arbitrarily the difference between the frequency of one of the normal vibrations of a system of two dipole linked like linear oscillators and the frequency of the isolated atom. It is clear that this computation is based on a misunderstanding. $\Delta\omega$ is in terms of its nature the change of the frequency of the emitting atom, the light of which is analyzed according to Fourier. That however which Weisskopf substitutes instead of it has nothing at all to do with the matter because of the degeneracy . . . the concept that in the collision of two like atoms one of which is excited and the other of which is unexcited the vibration phase of the excited atom is changed does not at all correspond to reality."[19]

It might be remarked first that the $\Delta\omega$ which they believe to have been improperly chosen seems to be the very one whose choice they advocate for the following reason ". . . *take the change of the frequency* $\Delta\omega$ . . . and *integrate over the collision time*."[19] Now it is true that integration is not extended over these limits in Eq. (V.16), but let us recall that these limits are a good approximation which is predicated on the reasonable assumption that no appreciable contribution to the integral arises outside the proper limits. If they base their argument on the "degeneracy"—they do not define this degeneracy but we can assume that it is that degeneracy arising from the indistinguishability of the atoms of our ensemble—then the question of which approach is more nearly correct has to be answered a little more conclusively than has been done to date. Surely though the simple interruption theory has not been so devastated by the above quoted argument that it cannot be considered as remainlng a reasonable approximation on proper application.

The Furssow and Wlassow theory really has its basis in a conception advanced by Kallmann and London[41] in 1929 to the effect that like atoms may simply exchange energy between each other without accompanying radiation. Even a cursory consideration of this conception gives an inkling of an application to the theory of self-broadening. We may examine it from either a quantum or a classical viewpoint.

First the classical viewpoint. To begin with we consider our atoms as classical oscillators, and again we have the dipole interaction between two like oscillators, one of which is excited and the other of which is unexcited. As a result of this interaction the amplitude of oscillation of the excited atom decreases while that of

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[‖‖] Houston took mild exception to this statement to the effect that ". . . the criticism of Weisskopf's work contained in this paper does not appear to be justified . . ."[32] but did not reply to the Furssow and Wlassow criticism specifically.

[¶¶] Italics added.

the unexcited atom increases, that is, an energy transfer occurs. This is effectively the same as damping the oscillations of the excited atom, and, as in the case of the Lorentz damping will result in a broadening of the spectral line. Let us now consider qualitatively the quantum-mechanical explanation of this effect.

Energy is assumed to be transferred as a result again of the dipole interaction from an excited to an unexcited atom of the same kind. Whatever the lifetime of the excited state would be under conditions of no transfer this lifetime will be greatly shortened by a high probability of transfer before radiation. Now we may recall that one form of the Heisenberg uncertainty principle states that $\Delta E \Delta t > h$. Thus, if, as is the case in the ground state, the state lifetime is infinite, the ground state will be infinitely well defined or virtually infinitely narrow. As soon as we consider a state with a finite lifetime, however, the situation changes. A certain lifetime Δt will give us a certain indefiniteness ΔE in the state energy, or a certain level width. This level width in turn will mean that a spectral line arising from the combination of this level with another will be broadened as a consequence. If we decrease our state lifetime by this energy transfer, quantum mechanics decrees that we indirectly broaden our spectral line by widening the energy level.

These then are the classical and quantum forms of the theory as advanced by Furssow and Wlassow. It now remains only to rewrite our qualitative conjectures after a quantitative fashion. Let us do so rather briefly.

F. The Classical Energy Transfer (Low Pressure)

To begin with it is of course necessary to make a few simple assumptions regarding our system. In this consideration we are assuming our atom to be a classical harmonic oscillator. Now we shall consider that the electronic transition which gives rise to our broadened spectral line proceeds to the ground state. We will assume that only one valence electron is responsible for the spectral line under consideration. Finally let us suppose that the excited atom, of which our system contains one for our purposes here, moves in the neighborhood of the remainder of the unexcited atoms. The excited atom we then consider as moving rectilinearly with velocity v. We might possibly bring up the same type of objection to the utilization of a linear velocity here as was brought up by Jablonski in objection to Weisskopf's utilization of a linear velocity in a central force problem. However this is probably minor at this stage.***

In considering our interaction which leads to the self-broadening of the line, we shall assume this interaction to take place between our emitter and one of the unexcited broadening atoms. The interaction in question we presume to be due to the electric dipole. Lagrange's equations may then be solved by a method of successive approximations to obtain

$$
\begin{aligned}
x_1^{(1)} &= \frac{3A}{2\omega_0}\int^t \Lambda \cos\alpha \cos\gamma dt \sin\omega_0 t \\
y_1^{(1)} &= \frac{3A}{2\omega_0}\int^t \Lambda \cos\beta \cos\gamma dt \sin\omega_0 t \\
z_1^{(1)} &= -\frac{A}{2\omega_0}\int^t \Lambda(1-3\cos^2\gamma) dt \sin\omega_0 t \\
x_2^{(1)} &= y_2^{(1)} = 0; \quad z_2^{(1)} = A\cos\omega_0 t.
\end{aligned}
\qquad \text{(V.20)}
$$

Equations (V.20) are quite enlightening in that they serve to show the manner in which the energy is transferred from the initially excited atom to the initially unexcited one during the course of an optical collision.

Let us assume that the optical collision, which serves to transfer energy from the excited to the unexcited atom, lasts a time interval τ_0. If this is the case, and if we assume the collision to begin at time $t=0$, then the collision must be initiated at a distance $-v\tau_0/2$ from ρ.

Then after a collision of duration τ_0, the amplitude, for example, of $x_1^{(1)}$ we may obtain from Eq. (V.20)

$$X_1^{(1)} = \frac{3A}{2\omega_0}\int_0^{\tau_0} \Lambda \cos\alpha \cos\gamma dt. \qquad \text{(V.21)}$$

It is apparent that $\alpha\beta\gamma$ are time dependent through the heat motion of the atoms. We may express these quantities as functions of time and integrate to obtain

$$X_1^{(1)} = \frac{\epsilon^2}{m\omega_0}\frac{A}{\rho^2 v}(2\cos\alpha_2\cos\gamma_2+\cos\alpha_1\cos\gamma_1), \text{ etc.} \qquad \text{(V.22)}$$

We are now desirous of obtaining the amount of energy which is transferred during the collision from the initially excited atom to the initially unexcited one. In the present case the energy E which has been transferred to the initially unexcited atom will be given by the sum of the squares of the amplitude components as given by Eq. (V.22) multiplied by $\frac{1}{2}m\omega_0^2$. We then obtain for the transferred energy

$$\mathcal{E} = \frac{\epsilon^4}{m^2\omega_0^2}\frac{1}{\rho^4 v^2}\sin^2\gamma_1 E \qquad \text{(V.23)}$$

where E, the initial energy of the excited molecule is, of course, $\frac{1}{2}\omega_0^2 A^2$.

Equation (V.23) is predicated on the first approximate solutions as given by Eq. (V.20). The validity of these Eqs. (V.20) is assumed only for large transit distances. Furssow and Wlassow defined the minimum distance of closest approach—transit distance—as that distance at which the transferred energy is equal to the energy at time zero of the initially excited oscillator,

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*** Most authors appear to consider it minor at any stage, although this is not conclusive.

that is, $\mathcal{E}=E$. Thus if ρ_0 is taken as the minimum transit distance Eq. (V.23) leads us to the following criteria for large distances

$$1/\rho_0^2 v = m\omega_0/\epsilon^2. \qquad \text{(V.24)}$$

In order to determine the total energy which our initially excited atom will lose in the course of time, it will be necessary to ascertain the total loss of energy to all the atoms in the neighborhood. In passing through a layer of thickness Δs lying perpendicular to the direction of motion of the excited atom to those atoms a distance ρ_0 or more away the emitter will lose energy of amount

$$dE = -2\pi N\Delta s \int_{\rho_0}^{\infty} \mathcal{E}\rho d\rho = -\pi N\Delta s \frac{\epsilon^4}{m^2\omega_0^2} \sin^2\gamma_1 \frac{1}{\rho_0^2 v^2} E$$

$$= -\pi N \frac{\epsilon^2}{m\omega_0} \sin^2\gamma_1 E dt \qquad \text{(V.25)}$$

from Eq. (V.24) and $\Delta s = vdt$. From Eq. (V.25)

$$E = E_0 e^{-\gamma t} \qquad \text{(V.26a)}$$

where

$$\gamma = \frac{2\pi}{3}\frac{N\epsilon^2}{m\omega_0}. \qquad \text{(V.26b)}$$

From this knowledge of the attenuation of the initially excited atom's energy we would like to determine the line broadening.

The electric vector of the radiation field will be of the form:

$$\mathbf{F} = \mathbf{F}_0 e^{-\gamma t/2} e^{i\nu_0 t}.$$

In the usual manner the electric vector may be expanded in a Fourier integral from which may be obtained

$$I(\nu) = |F(\nu)|^2 \propto \text{const} \frac{(\gamma/2)}{(\nu-\nu_0)^2 + (\gamma/2)^2} \qquad \text{(V.27)}$$

the half-width of the emitted spectral line is found to be

$$\delta_R' = \frac{2\pi}{3}\frac{\epsilon^2}{m\omega_0} N. \qquad \text{(V.28)}$$

It is then apparent that the effect of this energy transfer at large transit distances is a damping of the atomic oscillations resulting in a broadening of the spectral line whose half-width is given by Eq. (V.28).

For the close approaches they simply took the half-width as given by the simple interruption theory:

$$\delta_I = 2\pi\rho_0^2 N\langle v\rangle = 2\pi \frac{\epsilon^2}{m\omega_0} N. \qquad \text{(V.29)}$$

The total half-width is then

$$\delta = (\delta_R' + \delta_I') f = \frac{8\pi}{3}\frac{\epsilon^2}{m\omega_0} N f. \qquad \text{(V.30)}$$

The manner in which the dipole interaction between two like atoms causes a transfer of the oscillatory energy from the initially excited atoms to the remaining initially unexcited atoms has been shown. This energy transfer then acts as a damping force on the oscillatory motion of the atom and, as a result, the emitted radiation is broadened into a spectral line of finite width. We shall see that a quantum consideration under certain specific assumptions leads to the same results.

G. Quantum Treatment of Low-Pressure Self-Broadening

We have sketched qualitatively the quantum-mechanical theory of resonance broadening by energy transfer, and our first task in a quantitative consideration will be to ascertain the time change of eigenfunctions —probability amplitudes—of the excited atom due to this energy transfer.

Again the system is initially taken as two like atoms one of which is excited and one of which is unexcited. The motion of the atom will be considered classically as is normally done in problems of this kind with quite reasonable justification. The potential of interaction between the two atoms is still the dipole potential. The symbols such as ρ, α_1, etc. which were utilized in the classical consideration will again appear with the same connotation.

Familiar procedures of degenerate perturbation theory may be used in obtaining the state growth coefficients.

$$a_1 = a; \quad a_2 = a_3 = 0$$

$$b_1 = \frac{a}{i\hbar}\int_0^{\tau_0} U_{n00;\, m10}^{m10;\, n00} dt, \text{ etc.} \qquad \text{(V.31)}$$

The a_i refer to the states of the initially excited while the b_i refer to those of the initially unexcited atom. In finding a matrix element of U we carry the angle functions as constants—it may be recalled that these angle functions depend on the heat motion of the atoms. Finally then Eq. (V.31) becomes

$$b_1 = \frac{a}{i\hbar}\epsilon^2 (n00|z|m10)^2 \int_0^{\tau_0} \frac{(1-3\cos^2\gamma)}{R^3} dt, \text{ etc.} \qquad \text{(V.32)}$$

Again, as in the classical case, we allow τ_0 (the collision time) to approach infinity and integrate Eq. (V.32).

It is apparent that the probability for excitation of the initially unexcited atom is

$$|b_1|^2 + |b_2|^2 + |b_3|^2 = a^2 \frac{4\epsilon^4}{\hbar^2\rho^4 v^2} \sin^2\gamma_1 (n00|z|m10)^4. \qquad \text{(V.33)}$$

To find a_1, still under the assumption $a_2 = a_3 = 0$:

$$|a_1|^2 + |b_1|^2 + |b_2|^2 + |b_3|^2 + |c_1|^2 = |a|^2 + |c|^2 \qquad \text{(V.34)}$$

and, if we suppose $|c_1|^2=|c|^2$, the change in $|a|^2$ may be determined from Eq. (V.34) as

$$\Delta|a|^2=|a_1|^2-|a|^2=-(|b_1|^2+|b_2|^2+|b_3|^2)$$

$$=-|a|^2\frac{\epsilon^4}{m^2\omega_{nm}^2}f_{nm}^2\frac{1}{\rho^4v^2}\sin^2\gamma_1 \tag{V.35}$$

where

$$f_{nm}=(2m\omega_{nm}/\hbar)(n00|z|m10)^2,$$

the oscillator strength of the *mn* transition.

We earlier set the condition $\mathcal{E}=E$ for determining ρ_0. Similarly, we now establish the criteria for ρ_0 as $\Delta|a|^2=|a|^2$. From Eq. (V.35) ρ_0 may then be defined as

$$\rho_0=\left[\frac{\epsilon^2}{m\omega_{nm}}f_{nm}\frac{1}{v}\right]^{\frac{1}{2}}. \tag{V.36}$$

If there are N atoms per unit of volume of our gas then surely $2\pi\rho d\rho vN$ of them appear per unit of time lying a distance between ρ and $\rho+d\rho$ from the emitter. Furssow and Wlassow asserted this to mean that the total change of the probability per unit of time is the result of averaging over ρ:

$$\frac{d}{dt}|a|^2=-\pi|a|^2\frac{\epsilon^2}{m\omega_{nm}}f_{nm}N\sin^2\gamma_1. \tag{V.37}$$

If Eq. (V.37) is averaged over γ, and the resulting equation solved for $|a|^2$, the quantum-mechanical analog of Eq. (V.26a) is obtained:

$$|a|^2=|a_0|^2e^{-\gamma t} \tag{V.38}$$

where

$$\gamma=\frac{2\pi}{3}\frac{\epsilon^2}{m\omega_{nm}}f_{nm}N.$$

Thus the state lifetime has been decreased by the energy exchange as predicted, and this decrease is dependent on the gas density.

If we simply consider the atom-field interaction, then the state growth equations are given by

$$i\hbar\dot{a}_{m00\cdots0_s0\cdots}(t)$$

$$=\mathcal{H}^{n00\cdots1_s0\cdots}_{m00\cdots0_s0\cdots}a_{n00\cdots}(t)e^{i(\omega_{nm}-\omega_s)t} \tag{V.39}$$

of solution

$$a_{n00\cdots1_s0\cdots}(t)$$

$$=\mathcal{H}^{n00\cdots1_s0\cdots}_{m00\cdots0_s0\cdots}\frac{e^{i(\omega_s-\omega_{nm})t-\gamma t/2}-1}{-h[\omega_s-\omega_{nm}+i(\gamma/2)]} \tag{V.40}$$

and we may recall that

$$I(\omega)=\text{const}\,|a_{n00\cdots1_s0\cdots}(\infty)|^2$$

$$=\frac{\text{const}}{(\omega-\omega_{nm})^2+(\gamma/2)^2}. \tag{V.41}$$

From Eq. (V.41) it is apparent that our half-width is given by the following:

$$\delta_k=\gamma=\frac{2\pi}{3}\frac{\epsilon^2}{m\omega_{nm}}f_{nm}N. \tag{V.42}$$

It can be seen that Eq. (V.42) yields the same results for the half-width as Eq. (V.28) which latter equation was found for the case of distant collisions.

For the case of near collisions let us utilize the Heisenberg uncertainty principle in the form

$$\Delta E\Delta t=\hbar$$

where we shall now assume ΔE to be the width of the state and Δt to be the mean lifetime of the state.

Let us suppose that the life of a state is terminated by a collision so that $\Delta t=\tau$ where τ is the mean time between collisions. This means that the width of the state will now be

$$\Delta E=\frac{\hbar}{\Delta t}=\frac{\hbar}{\tau}=2\hbar\pi\frac{\epsilon^2}{m\omega_0}f_{nm}N$$

or

$$\delta_I=\Delta\omega=\frac{\Delta E}{\hbar}=2\pi\frac{\epsilon^2}{m\omega_0}f_{nm}N. \tag{V.43}$$

Finally we obtain for the half-width

$$\delta=\delta_k+\delta_I=\frac{8\pi}{3}\frac{\epsilon^2}{m\omega_0}f_{nm}N \tag{V.44}$$

which is the same as the classical result given by Eq. (V.30).

In the main Furssow and Wlassow considered their results to hold only in the case of low gas densities. We may question the Furssow-Wlassow procedure in which they work out the broadening effect of one like atom and then simply extend these results to the case of N similar atoms. Because of the procedure Furssow and Wlassow felt that their results were only applicable to low gas densities. In a later paper[20] on the subject they investigated the self-broadening of a spectral line in the case of high gas densities. They found it necessary to use a slightly different although comparable method of approach to which we now turn our attention.

H. High-Pressure Quantum Resonance Broadening

The previous theory was really predicated on a collision between two particles. Now if, as in the Schulz and Rompe experiments, we take $\omega_0=1.02\times10^{16}$ sec^{-1}, $f=1.3$, $T=6000°$, we will obtain a ρ of approximately 5.35×10^{-7}. Then with the pressure used by Schulz and Rompe $N=2.57\times10^{19}$ cm^{-3}. This means that in the "sphere of action" we shall have $(4/3)\pi\rho^3N=17$ molecules. Thus, the approximation of a two-particle collision is hardly reasonable.

A modification of the first theory is certainly called for, on the basis of these considerations.

Let us begin by supposing the gas density sufficiently high that we can expect a large number n of atoms within the "sphere of action." If we allow this system of $n+1$ atoms to possess two levels, the resonance level and the ground state, methods of degenerate perturbation theory lead to the state growth equations:

$$i\hbar\dot{a}=\sum_{k=1}^{n}(a|U|b_k)b_k \tag{V.45a}$$

$$i\hbar\dot{b}_k=(b_k|U|a)a+\sum_{k'}(b_k|U|b_{k'})b_{k'}. \tag{V.45b}$$

Again under the initial conditions stipulating that atom 0 is initially excited we obtain $a(t)=a(0)=1$ and $b(0)=0$. Subsequent to the time $t=0$ we can expect the transfer of energy from the initially excited to the unexcited atom to proceed as governed by the matrix element $(a|U|b_k)$. In addition Eq. (V.45) tells us that there will be a secondary transfer of energy among the initially unexcited atoms as governed by the matrix element $(b_k|U|b_{k'})$. We now introduce the approximation that the secondary energy transfer process as governed by $(b_k|U|b_{k'})$ can be disregarded and suppose U to be time independent. This latter is nothing more nor less than saying that the thermal motion of the atom is so small as to be considered negligible during the energy transfer process. As we shall see, at high pressure for the resonance level this is a reasonable approximation. We now substitute for $\dot{b}_k$ from the thus modified Eq. (V.45b) into a differentiated Eq. (V.45a). This yields

$$-\hbar^2\ddot{a}=a\sum_{k=1}^{n}(a|U|b_k)^2. \tag{V.46}$$

If we now ignore the angular dependence of the dipole interaction there results

$$\ddot{a}+p^2a=0 \tag{V.47a}$$

$$p^2=\sum_{k=1}^{n}\frac{\alpha}{R_k{}^6};\quad \alpha=\frac{\epsilon^4f^2}{4m^2\omega_0{}^2}. \tag{V.47b}$$

A solution of Eq. (V.47a) which satisfies the initial condition $a(0)=1$ is

$$a=\cos pt. \tag{V.48}$$

A collision has occurred when $a=0$ so that

$$\tau_0=\pi/2p. \tag{V.49}$$

We assume the step function

$$\begin{aligned} a&=1 \quad \text{for} \quad 0\leqslant t\leqslant \tau_0\\ a&=0 \quad \text{for} \quad 0<t>\tau_0 \end{aligned} \tag{V.50}$$

for a so that the Fourier integral for a is

$$\begin{aligned} a&=\int_{-\infty}^{+\infty}g(\omega)e^{i\omega t}d\omega\\ g(\omega)&=\frac{1}{2\pi}\,\frac{1-e^{-i\omega\tau}}{i\omega}. \end{aligned} \tag{V.51}$$

We average the absolute square of this expression over all collision times in order to obtain the intensity distribution in the level:

$$I(\omega)=\int_0^{\infty}|g(\omega)|^2w(\tau_0)d\tau_0. \tag{V.52}$$

Let us utilize the expression

$$\nu=\frac{\pi^2}{4\tau_0{}^2}=p^2 \tag{V.53}$$

for a change in variable in Eq. (V.52) as follows:

$$w(\tau_0)d\tau_0=\frac{\pi w(\pi/2\sqrt{\nu})}{4\sqrt{\nu^3}}d\nu=-I'(\nu)d\nu. \tag{V.54}$$

In order to find $I'(\nu)d\nu$ we suppose a random distribution of spatial coordinates to exist. Let us establish a configuration space of $3n$ dimensions whose volume is $\mathfrak{U}=V^n$ where V is the volume of our gas. Now if we temporarily disregard the interatomic forces, we can expect equal probability for the occupation of any portion of this space. This means that the followlng relation will hold:

$$I'(\nu)d\nu=\frac{\Delta\mathfrak{U}}{\mathfrak{U}}, \tag{V.55}$$

where $\Delta\mathfrak{U}$ represents that portion of configuration space for which our ν lies between ν and $\nu+d\nu$. This value of ν will, of course, depend on the distribution of the R_k in Eq. (V.47b). Thus

$$\Delta\mathfrak{U}=(4\pi)^n\int\cdots\int R_1{}^2R_2{}^2\cdots R_n{}^2dR_1dR_2\cdots dR_n. \tag{V.56}$$

The analogy to Margenau's equation (III.4) is apparent. Our solution then is given by Eq. (III.18) as

$$I'(\nu)=\tfrac{2}{3}\pi N\sqrt{\alpha}\,\frac{\exp\left(-\dfrac{4\pi^3\alpha N^2}{9\nu}\right)}{\sqrt{\nu^3}}. \tag{V.57}$$

We may now transform back to our variable τ_0 by utilizing Eq. (V.54). We obtain

$$w(\tau_0)=\frac{2\gamma}{\sqrt{\pi}}\exp(-\gamma^2\tau_0{}^2) \tag{V.58}$$

$$\gamma=(4/3)N(\pi\alpha)^{\frac{1}{2}}=\tfrac{2}{3}\sqrt{\pi}\frac{f\epsilon^2}{m\omega_0}N. \tag{V.59}$$

Equations (V.49) and (V.58) may now be substituted into Eq. (V.52) and the results integrated to obtain

$$I(\omega)=\frac{1}{2\pi^2}\frac{1-\exp[-(\omega/2\gamma)^2]}{\omega^2} \tag{V.60}$$

as the distribution of energies in the resonance level. For the breadth we obtain

$$\delta=2.54\gamma=3\frac{f\epsilon^2}{m\omega_0}N. \tag{V.61}$$

In order to find the spectral line width, it would appear reasonable to assume that we must needs have a knowledge of not only the resonance level width but also the width of the level from which the radiating transition originates.[†††] The phrase "from which" leads us to the next consideration.

Furssow and Wlassow felt that these results should only be applied to transitions proceeding from upper levels to the resonance level, that is, these results should not be applied, to the transition from the resonance level to the ground state. A short consideration renders this assertion plausible.

Let us suppose that the initially excited atom undergoes a transition from the resonance level to the ground state with the accompanying emission of radiation. This emitted radiation may be absorbed by one of the unexcited atoms where absorption would not be possible were this radiation the result of a transition to some level above the ground state. This process, which should not be confused with the transfer of energy without accompanying radiation has certainly not been considered in the theory, and, since it can be expected to have some effect on the line broadening, this theory cannot be expected to hold in such cases.

The justification for the assumption of fixed atoms, that is, $d/dt(a|U|b_k)=0$ which led to Eq. (V.46) appears worthy of note here. Let us consider the Rompe and Schulz case.[75] The pressure is 80 atmospheres and $T=2800°$. The experimental width was found to be $\delta=7\times10^{12}$ sec^{-1} so that the mean life of the resonance level is $\tau_0=1/\delta=1.4\times10^{-13}$ sec. The mean relative velocity is $\langle v\rangle=1.3\times10^5$ cm/sec, which leads us to the conclusion that during the mean level life we may expect our atoms to move a distance $\langle v\rangle\tau_0=1.8\times10^{-8}$ cm, or the order of their own diameter. Thus, the approximation appears a reasonable one.

Furssow and Wlassow's high pressure theory yields results in reasonable agreement with those of Schulz and Rompe.

I. Comparison of Some Experimental Results

Three of the equations for the half-width which we have obtained are

Weisskopf: $$\delta=\frac{\epsilon^2}{m\omega_0}f_{nm}N$$

Margenau and Watson: $$\delta=\frac{\pi}{3}\frac{\epsilon^2}{m\omega_0}f_{nm}N$$

Furssow and Wlassow: $$\delta=\frac{4}{3}\frac{\epsilon^2}{m\omega_0}f_{nm}N.$$

These three equations have been compared with the experimental results, for rubidium by Chen,[77] for sodium by Watanabe,[89] and for caesium by Gregory.[23]

Other than demonstrating the fact that none of the theories propounded in explanation of the resonance broadening phenomenon is precisely correct these experimental results indicated that the combined resonance and, say, van der Waals forces should be investigated. Such an investigation might provide the explanation of the observed line shape variations with radiating transition as well as with pressure.

VI. MOLECULAR BROADENING

A. Early Studies of Polyatomic Molecular Broadening

In beginning our considerations of the last chapter we remarked that those studies which had gone before had not distinguished between broadeners of a type different from the emitter and broadeners of the same type as the emitter. In this same vein we might now remark that, for all practical purposes, we have not differentiated between atoms and polyatomic molecules, for the broadening phenomena to which we have so far devoted some little attention are equally as applicable to the latter as to the former. It is really by the appearance of rotation and vibration spectra that we may differentiate between the polyatomic and monatomic molecule so that by such a statement we mean that these previous broadening considerations are properly applicable to this type spectra as well as to electronic spectra. It was originally felt by such authors as Kussmann[44] and Lasareff[45] and Grasse[22] that these theories were not only applicable but also sufficient. The intimation that some different approach to the broadening of rotation-vibration lines was in order appears to have arisen first in the work of Herzberg and Spinks.[27] These investigators found a decrease of the line width with higher values of the rotational quantum number J in the near infrared spectra of HCN. This would surely indicate that rotation-vibration spectra should be treated differently than electronic spectra, but this clear indication was rather clouded when the work of Cornell and Watson[11] and Herzberg, Spinks, and Watson[27] failed to verify this variation with J. The hint had been given however, and it was certainly apparent that the possibility of J width dependence and other unique molecular phenomena should be theoretically investigated.

[†††] The complexity of computing the width of a higher level may be inferred from the preceding work.

B. The Directional Effect and Rotational Resonance

In studying broadening phenomena one usually looks first to the molecular or atomic interaction to which we can attribute responsibility for the broadening in question. In molecular broadening an interaction which plays quite a major role is the directional effect, a special case of which is the rotational resonance effect, to which we now turn our attention.

Let us specify the dipole moments of two rotators by μ_1 and μ_2 and their separation by R. In this case then, the dipole-dipole interaction leads to the interaction energy

$$\langle E^{(2)}\rangle=-\frac{2}{3}\frac{\mu_1^2\mu_2^2}{R^6}\frac{1}{(2J_1+1)(2J_2+1)}\times\left\{\left[\frac{2A_1}{J_2+1}+\frac{2A_2}{J_1+1}\right]^{-1}+\left[\frac{2A_1}{J_2}-\frac{2A_2}{J_1+1}\right]^{-1}-\left[\frac{2A_1}{J_2+1}-\frac{2A_2}{J_1}\right]^{-1}+\left[\frac{2A_1}{J_2}+\frac{2A_2}{J_1}\right]^{-1}\right\} \quad \text{(VI.1)}$$

where the J_i refer to the lower state, and $A_i=\hbar^2/2I_i$.

If the two molecules are identical so that $A_1=A_2$ and $\mu_1=\mu_2$ Eq. (VI.1) becomes

$$\langle E^{(2)}\rangle=-\frac{2}{3}\frac{\mu^4 I}{\hbar^2R^6}\times\frac{J_1(J_1+1)+J_2(J_2+1)}{(J_1+J_2)(J_1+J_2+2)(J_1-J_2-1)(J_1-J_2+1)}. \quad \text{(VI.2)}$$

A special case arises when the broadener is in the ground state, a case for which we shall find specific use:

$$\langle E^{(2)}\rangle=-\frac{2}{3}\frac{\mu_1^2}{R^6}\frac{1}{2J_2''+1}\left\{\Sigma'|(00|\epsilon r|J_1'M_1')|^2\times\left(\frac{J_2''+1}{E_{J_1'}-E_0-2(J_2''+1)A}+\frac{J_2''}{E_{J_1'}-E_0+2J_2''A}\right)\right\}. \quad \text{(VI.3)}$$

In passing, let us note a corresponding expression for the dipole-dipole interaction of two symmetric top molecules possessed of dipoles as given by Carroll[7]:

$$\langle E^{(2)}\rangle=-\frac{2}{3}\frac{\mu^4}{R^6}\frac{I_A}{\hbar^2}\left\{\frac{(J_1+1)^2-K_1^2}{(J_1+1)(2J_1+1)}\left[\frac{(J_2+1)^2-K_2^2}{(J_2+1)(2J_2+1)(J_1+J_2+2)}+\frac{K_2^2}{J_2(J_2+1)(J_1+1)}+\frac{J_2^2-K_2^2}{J_2(2J_2+1)(J_1-J_2+1)}\right]+\frac{K_1^2K_2^2}{J_1(J_1+1)J_2^2(J_2+1)^2}+\frac{J_1^2-K_1^2}{J_1(2J_1+1)}\left[\frac{(J_2+1)^2-K_2^2}{(J_2+1)(2J_2+1)(J_2-J_1+1)}-\frac{K_2^2}{J_1J_2(J_2+1)}-\frac{J_2^2-K_2^2}{J_2(2J_2+1)(J_1+J_2)}\right]\right\}. \quad \text{(VI.4)}$$

A consideration of Eq. (VI.2) tells us that a rotational resonance condition sets in for identical rotators for $|J_1-J_2|=1$. Further, Eq. (VI.2) indicates that for dissimilar dipoles an accidental rotational resonance condition comes about when $J_2A_2=(J_1+1)A_1$ or $(J_2+1)A_2=J_1A_1$. For these cases a first-order perturbation energy exists and must be evaluated.

The method of evaluation which is applicable here is the variational perturbation treatment. In carrying out this treatment one obtains a determinant of the form, say, Eq. (V.7) whose order is, of course, dependent on the J values involved. This means that no solution for the general case (any J value, as, for example, is given by Eq. (VI.1)) is obtainable since no such general solution to the determinant is available. The root-mean-square value of the first-order energy perturbation is the same for all determinants, however, and it may be obtained as

$$\langle[\epsilon^{(1)}]^2\rangle^{\frac{1}{2}}=\left(\frac{2}{3}\right)^{\frac{1}{2}}\frac{J+1}{[(2J+1)(2J+3)]^{\frac{1}{2}}}\frac{\mu^2}{R^3}. \quad \text{(VI.5)}$$

As an example of the specific calculation, if we let $J_1=0$, $J_2=1$, the perturbation amounts to

$$E^{(1)}=\pm\frac{1}{3}\frac{\mu^2}{R^3},\quad \pm\frac{2}{3}\frac{\mu^2}{R^3}. \quad \text{(VI.6)}$$

A further consideration of Eq. (VI.2) suffices to show that $J_1=J_2=0$ also leads to a rotational resonance condition, but this case corresponds to the precise solution:

$$E^{(1)}=\frac{\hbar^2}{I}\left[1-\left(1+\frac{2\mu^4I^2}{3\hbar^4R^6}\right)^{\frac{1}{2}}\right]. \quad \text{(VI.7)}$$

Equation (VI.7) tells us the first order interaction energy for two like dipole linear rotators for the case $J_1=J_2=0$. For large R, the radical in this equation may be expanded with the result

$$E^{(1)}\doteq-\frac{\mu^4I}{3\hbar^2R^6} \quad \text{(VI.8a)}$$

and for small R Eq. (VI.7) becomes

$$E^{(1)} \doteq -\left(\frac{2}{3}\right)^{\frac{1}{2}} \frac{\mu^2}{R^3}. \qquad \text{(VI.8b)}$$

Let us now sketch a resonance development of London in just enough detail so that the results which we shall later utilize will be somewhat intelligible. This author used what we might call an order-of-magnitude technique to arrive at the secular determinant

$$|U_{\Upsilon_i\Upsilon_j} + (E_{\Upsilon_i}{}^{(0)} - E_{\Upsilon_k}{}^{(0)} - E_k{}^{(1)})\delta_{\Upsilon_i\Upsilon_j}| = 0. \qquad \text{(VI.9)}$$

We shall be able to define the new symbols $E_{\Upsilon_i}{}^{(0)}$ and $E_{\Upsilon_k}{}^{(0)}$ after another step in the development.

London considered only the eigenfunction $\psi_{J_1}{}^{M_1}\psi_{J_2}{}^{M_2}$ and the thirteen eigenfunctions with which this eigenfunction may combine, as always, under the influence of U, thus rendering his treatment an approximate one.

Under these restrictions then, we shall utilize the eigenfunctions:

$$\begin{aligned}
&u_0 = \psi_{J_1}{}^{M_1}\psi_{J_2}{}^{M_2} \\
&\left.\begin{aligned}
u_1 &= \psi_{J_1+1}{}^{M_1}\psi_{J_2+1}{}^{M_2} \\
u_2 &= \psi_{J_1+1}{}^{M_1+1}\psi_{J_2+1}{}^{M_2-1} \\
u_3 &= \psi_{J_1+1}{}^{M_1-1}\psi_{J_2+1}{}^{M_2+1}
\end{aligned}\right\}\Upsilon_1 \\
&\left.\begin{aligned}
u_4 &= \psi_{J_1-1}{}^{M_1}\psi_{J_2-1}{}^{M_2} \\
u_5 &= \psi_{J_1-1}{}^{M_1+1}\psi_{J_2-1}{}^{M_2-1} \\
u_6 &= \psi_{J_1-1}{}^{M_1-1}\psi_{J_2-1}{}^{M_2+1}
\end{aligned}\right\}\Upsilon_4 \\
&\left.\begin{aligned}
u_7 &= \psi_{J_1+1}{}^{M_1}\psi_{J_2-1}{}^{M_2} \\
u_8 &= \psi_{J_1+1}{}^{M_1+1}\psi_{J_2-1}{}^{M_2-1} \\
u_9 &= \psi_{J_1+1}{}^{M_1-1}\psi_{J_2-1}{}^{M_2+1}
\end{aligned}\right\}\Upsilon_7 \\
&\left.\begin{aligned}
u_{10} &= \psi_{J_1-1}{}^{M_1}\psi_{J_2+1}{}^{M_2} \\
u_{11} &= \psi_{J_1-1}{}^{M_1+1}\psi_{J_2+1}{}^{M_2-1} \\
u_{12} &= \psi_{J_1-1}{}^{M_1-1}\psi_{J_2+1}{}^{M_2+1}
\end{aligned}\right\}\Upsilon_{10}
\end{aligned} \qquad \text{(VI.10)}$$

from which we may define $E_{\Upsilon_i}{}^{(0)}$ and $E_{\Upsilon_k}{}^{(0)}$.

$E_{\Upsilon_k}{}^{(0)}$ is in all cases the zeroth-order energies going with u_0. $E_{\Upsilon_i}{}^{(0)}$ are the zeroth-order energies going with $u_1, u_2, \cdots, u_{12}$. We may note that the energies associated with u_1, u_2, u_3 are the same as are those associated with u_4, u_5, u_6 and so forth. Thus

$$E_1 = E_{\Upsilon_1}{}^{(0)} - E_{\Upsilon_0}{}^{(0)} = (J_1 + J_2 + 2)\frac{\hbar^2}{I}, \text{ etc.} \qquad \text{(VI.11)}$$

A secular determinant results. In addition, we let $U_{0i} = U_i$ and from this secular determinant, the equation

$$R^6E^{(1)} = \frac{a_1^2}{E^{(1)} - E_1} + \frac{a_2^2}{E^{(1)} - E_2} + \frac{a_3^2}{E^{(1)} - E_3} + \frac{a_4^2}{E^{(1)} - E_4} \qquad \text{(VI.12)}$$

follows, where

$$\frac{a_i^2}{R^6} = U_{3i}{}^2 + U_{3i-1}{}^2 + U_{3i-2}{}^2. \qquad \text{(VI.13)}$$

For the resonance case ($J_1 > 0$, $J_2 > 0$, $J_1 = J_2 + 1$) Eq. (VI.12) becomes

$$R^6E^{(1)} = \frac{a_1^2}{E^{(1)} - E_1} + \frac{a_2^2}{E^{(1)} - E_2} + \frac{a_3^2}{E^{(1)} - E_3} + \frac{a_4^2}{E^{(1)}}. \qquad \text{(VI.14a)}$$

For large R and $|E^{(1)}| \ll |E_i|$:

$$R^6(E^{(1)})^2 + \left(\frac{a_1^2}{E_1} + \frac{a_2^2}{E_2} + \frac{a_3^2}{E_3}\right)E^{(1)} - a_4^2 = 0 \qquad \text{(VI.14b)}$$

whose solution is

$$E^{(1)} \doteq -\tfrac{1}{2}\left(\frac{a_1^2}{E_1} + \frac{a_2^2}{E_2} + \frac{a_3^2}{E_3}\right)\frac{1}{R^6} \pm \frac{a_4}{R^3}. \qquad \text{(VI.15)}$$

Equation (VI.15) gives the first-order perturbation energy for the rotational resonance case. We note the comparison with Eq. (VI.6).

C. Broadening by Molecules with No Permanent Poles

Margenau[59] initiated the first attack on the theory of molecular broadening in 1936. He chose to investigate the case of broadening by foreign gases which possess no permanent poles since Watson and Hull[91] had previously obtained experimental data on this case. These authors had investigated the broadening of AlH by H_2 and concluded that all rotation-vibration lines associated with a particular electronic transition would be broadened by the same amount.

From Eq. (VI.3) we may obtain the perturbation on the energy of the absorber averaged over all orientations of the absorber as

$$\langle E^{(2)}\rangle = -\frac{2}{3R^6}\sum_{\Lambda\mathfrak{H}}{}' \frac{|(\epsilon r)_{0\Lambda}|^2 |(U)_{k\mathfrak{H}}|^2}{E_\Lambda - E_0 + E_{\mathfrak{H}} - E_k}, \qquad \text{(VI.16)}$$

where $\mathfrak{H}$ and Λ refer to absorber and broadener, respectively.

We have stipulated that E_0 is the lowest energy of the perturber. This means that $E_\Lambda - E_0$ will always be positive. In addition we have not allowed this perturber a permanent dipole moment. This means that no pure rotational transitions, which amount to the lowest energy transitions, are possible. Thus the vibrational transitions are the lowest energy allowed.

On the other hand, $E(\mathfrak{H}) - E_k$ may be positive or negative. Consequently $\langle E^{(2)}\rangle$ may be greater than or less than zero so that the spectral line may exhibit either a violet or a red asymmetry.

Now where we simply have dealt with a set of relatively widely spaced electronic levels in our monatomic considerations, we now also deal with the closely spaced superposed rotation-vibration levels. When we are considering the visible and ultraviolet portion of the spectrum we may, as an approximation, consider only the electronic contributions to $E(\mathfrak{H})-E_k$—they surely constitute the largest ones—and merely let the rotation-vibration levels superposed upon them amount to degeneracies accounted for by a summation in Eq. (VI.20). It follows that the result will closely correspond to that for monatomic molecules.

In order to consider the possible effect of molecular rotation let us approximate our absorber by a rigid rotator of dipole moment μ. Now I is usually of the order of 10^{-40}, and, with h of the order of 10^{-27} we see that A will be small compared to $E_\Lambda - E_0$ when the perturber has no permanent dipole. When A is neglected Eq. (VI.3) becomes

$$\langle E^{(2)}\rangle = -\frac{2}{3}\frac{\mu^2}{R^6}\sum_{\Lambda}{}' \frac{|(\epsilon r)_{0\Lambda}|^2}{E_\Lambda - E_0} = -\frac{\alpha\mu^2}{R^6}. \quad \text{(VI.17)}$$

If the dipole moment $\mu \doteq 10^{-18}$, the perturbation given by Eq. (VI.17) is about 1/20 of that for the electronic case. Now let us write Eq. (VI.3) as

$$\langle E_J{}^{(2)}\rangle = -\frac{\alpha\mu^2}{R^6}\left[1 + \frac{2A}{(E_\Lambda - E_0)} + \frac{4(J^2+J+1)A^2}{(E_\Lambda - E_0)^2} + \cdots\right]. \quad \text{(VI.18)}$$

It is apparent from Eq. (VI.22) that the portion of $\langle E_J{}^{(2)}\rangle$ which depends on J is very small due to the appearance of A^2 in the numerator and $(E_\Lambda - E_0)^2$ in the denominator involved.

Margenau carried out his considerations of the effect of molecular vibrations in an analogous manner. In this case we obtain

$$\langle E_v{}^{(2)}\rangle = 3\frac{\epsilon^2 E_v}{m\omega^2 R^6}\alpha. \quad \text{(VI.19)}$$

On the basis of these investigations, we may conclude that within the limits of experimental error all rotation-vibration lines associated with the same electronic transition should show broadening and shift of about the same degree when the broadening agent is a nonpolar molecule. In addition these lines should be affected by foreign perturbers almost in the manner of the corresponding monatomic lines under similar circumstances.

As Watson[90] has noted "dispersion forces"—the type considered—also appear to predominate in the self-broadening of nonpolar molecular lines. Were the normal resonance forces between like monatomic molecules present, we would not normally expect this to be the case, but the closely spaced rotational levels of the polyatomic molecule render this predominance reasonable. As we have noted, the rotational levels specified by, say, just J are comparatively closely spaced energywise. As a consequence a Maxwell-Boltzmann temperature distribution of molecules over these levels will not lead to the preferential population of the monatomic case, and they will be more equally divided among many levels. On the other hand, the allowed J change in transition is generally limited to ±1 or 0 so that the probability of energy exchange with the resultant degeneracy is severely restricted. In toto, then, this resonance effect would not appear to be primarily responsible for self-broadening, and we may safely look to these dispersion forces as broadening agents for nonpolar molecules. This conclusion had been verified for the case of methane by Childs,[8] Dennison and Ingram,[14] and Vedder and Mecke,[85] for atmospheric pressure and above, and for the case of acetylene by Hedfield and Mecke,[24] Herzberg and Spinks,[25] Lochte-Holtgreven and Eastwood,[52] and McKellar and Bradley[65] for atmospheric pressure.

We have broadened molecular lines by nonpolar molecules, and it would appear a logical next step to broaden these lines by polar molecules.

D. Qualitative Explanations of Broadening by Dipole Molecules

It is to the directional effect of Sec. B that we may look for an explanation of the relatively large, J-dependent broadening effects due to dipole broadeners.

To begin with we must hypothesize unpolarizable (rigid) dipoles, and we recall from Sec. B that (1) the intermolecular forces are relatively weak except when the near resonance condition, $|J_1 - J_2| < 2$ or 3, set in and (2) the lowest rotational state is most strongly influenced by other molecules in the lowest of neighboring states.

The lower state J_1'' we take as other than the lowest rotational state so that we can concern ourselves with (1). As has been mentioned, the rotational levels lie sufficiently close together so that a thermal distribution over them may be expected. Suppose J_1'' to designate a level near the maximum of this thermal distribution. Then a much greater number of perturbers can be expected to fulfill the condition $|J_1'' - J_2''| < 2$ or 3 than would be the case were the J_1'' level to be found toward the wings of this thermal distribution. Since the upper level will also enter into the line broadening one cannot say more as yet than that those most intense lines arising from J levels near the maximum of the thermal distribution should be broadened more than the remainder of the lines of the band.

In regard to (2) this indicates that a greater broadening of the line arising from the lowest rotational level is to be expected, but only under certain conditions. At normal temperatures, the thermal distribution should not populate levels lying near $J_1''=0$ very highly so that the effect may not be very pronounced. As the temperature is lowered, however, these low level populations will increase and we should expect to see an increase in the broadening of the line with $J_1''=0$ over neighboring spectral lines. It might be noted also that due to "greater flexibility downward" a violet asymmetry in this line may be expected.

We now devote ourselves to Margenau and Warren's more quantitative consideration of the broadening effected by dipole interactions.

E. Statistical Broadening by Symmetrical Top Dipole Molecules

For our two interacting molecules we choose two identical symmetrical rotators each possessed of a permanent electric dipole moment μ oriented along the molecular figure axis. The interaction potential between the two rotators is again given by Eq. (VI.1) where now $\mu_1=\mu_2=\mu$. The eigenfunctions for this system are the familiar product functions for sufficient separation R. U is not dependent on the Eulerian angle χ so that $K_1''=K_1'$ and $K_2''=K_2'$ under the aegis of U, and the matrix of U is diagonal in K_1 and K_2 as a consequence.

After a reasonable amount of mathematical manipulation one obtains

$$\begin{aligned}(M_1''M_2''|U|M_1'M_2')\\ =\frac{\mu^2}{R^3}\frac{K_1K_2}{J_1(J_1+1)J_2(J_2+1)}\\ \times\{-2M_1''M_2''\delta(M_1'M_1'')\delta(M_2'M_2'')\\ \pm\tfrac{1}{2}[(J_1-M_1''+1)(J_1+M_1'')(J_2-M_2'')\\ \times(J_2+M_2''+1)]^{\frac{1}{2}}\delta(M_1',M_1''-1)\delta(M_2',M_2''+1)\\ \pm\tfrac{1}{2}[(J_1+M_1''-1)(J_1-M_1'')(J_2-M_2''+1)\\ \times(J_2+M_2'')]^{\frac{1}{2}}\delta(M_1',M_1''+1)\\ \times\delta(M_2',M_2''-1)\}. \quad \text{(VI.20)}\end{aligned}$$

From Eq. (VI.20) it is apparent that the first-order perturbation energy does not disappear. The secular determinant breaks into blocks, with identical blocks symmetrical about the secondary diagonal. Thus every root of this determinant will be a double root so that general equation describing the level splitting due to this interaction is not to be found, but an idea as to the maximum splitting may be obtained, and the example of a special case may be presented.

We may write down from Eq. (VI.20) the double root which lies at either end of the principal diagonal and where $J_1=M_1$ and $J_2=M_2$.

$$E^{(1)}=-\frac{2\mu^2}{R^3}\frac{K_1K_2}{(J_1+1)(J_2+1)}. \quad \text{(VI.21)}$$

Figure 16 illustrates the level splitting with the rotator separation R and the magnetic quantum number M for the special case $J_1=K_1=2$, $J_2'=K_2'=1$ for the upper state and $J_1=K_1=1$, $J_2''=K_2''=1$ for the lower state.

Let us finally remark that since $K=0$ for a spherical top rotator, the matrix elements of U in Eq. (VI.20) would all be zero so that the effect considered would not take place.

Insofar as second-order effects are concerned, we certainly are aware that they will depend on the inverse sixth power of the molecular separation. In addition Margenau and Warren felt that for finding those regions in which the first order perturbations predominate, London's second-order results for diatomic molecules should be sufficient. Under these assumptions a limiting range of about 7A for the predominance of the forces which we have considered was imposed by these authors.

The root-mean-square energy perturbation may be obtained as

$$\langle[E^{(1)}]^2\rangle^{\frac{1}{2}}=\left(\frac{2}{3}\right)^{\frac{1}{2}}\frac{\mu^2}{R^3}\frac{K_1K_2}{[J_1(J_1+1)J_2(J_2+1)]^{\frac{1}{2}}}. \quad \text{(VI.22)}$$

Now surely a reasonable approximation to the half-width arising from these considerations may be expected if we equate a to

$$\left(\frac{2}{3}\right)^{\frac{1}{2}}\mu^2\frac{|K_1K_2|}{[J_1(J_1+1)J_2(J_2+1)]^{\frac{1}{2}}}$$

in order to obtain the half-width

$$\delta=\frac{4}{3}\pi^2\frac{Na}{h}=2\left(\frac{2}{3}\right)^{\frac{3}{2}}\frac{\pi^2\mu^2|K_1K_2|N}{h[J_1(J_1+1)J_2(J_2+1)]^{\frac{1}{2}}} \quad \text{(VI.23)}$$

for the statistical result.

It is true, of course, that we have here found the level width while we are really desirous of the spectral line width. The level here $(J_1K_1J_2K_2)$ would have to be

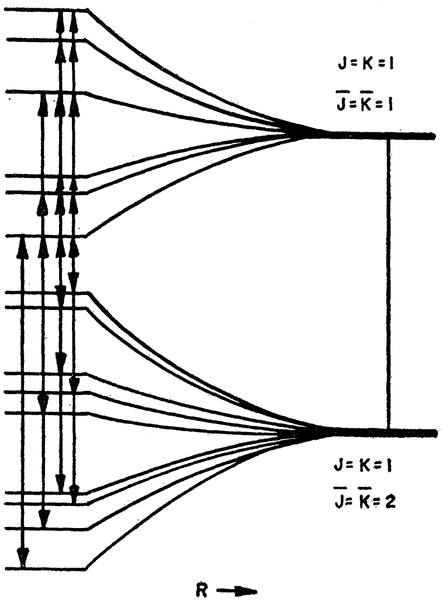

FIG. 16. The Rotational levels of the symmetric top rotator are split due to the dipole interaction. (After Margenau and Warren.[63])

considered in conjunction with another possible level $(J_1 \pm 1, 0; K_1 \pm 1, 0; J_2 K_2)$. One may perhaps consider the K_1 and J_1 appearing in Eq. (VI.23) as the mean of the quantum numbers for the two states.

We might conclude by noting that the effect as given by Eq. (VI.23) is around 20 times as weak as the self-broadening effect in monatomic resonance lines.

The results of this theory were born out order of magnitude wise by Cornell's results.[10]

F. Broadening by the Linear Dipole Molecule HCN

The first attempt at a rigorous theoretical interpretation of the self-broadening of the absorption lines of a linear dipole molecule was carried out by Lindholm,[48] for the HCN molecule. In essence Lindholm used the energy perturbations due to the directional and resonance effects within the framework of the simple interruption theory to determine the broadening of the HCN lines in a manner which we now consider.

According to the simple interruption theory the half-width of the lines for a heterogeneous gas containing N_1, molecules with optical collision diameters ρ_1, N_2 with diameters ρ_2, etc.

$$\delta = \langle v \rangle \sum_i N_i \rho_i^2 \qquad \text{(VI.24)}$$

if all molecules are of the same mass, thus allowing a common $\langle v \rangle$.‡‡‡ Let us consider the necessity for introducing Eq. (VI.24).

From Lindholm's experimental results, it is quite apparent that a marked dependence on J is present in the line width. In the interruption theory, this can only come about through some variation in N and ρ with J_1 (the absorber J value) and J_2 (the perturber J value). Thus, we hypothesize a dependence of ρ on J_1 and J_2 which a little consideration immediately bears out. To begin with a frequency perturbation $\Delta\nu = b/R^6$ (which is brought about by the directional effect $|J_1 - J_2| \neq 1$) or $\Delta\nu = B/R^3$ (due to the resonance effect $|J_1 - J_2| = 1$) leads to the optical collision diameter

$$\rho = \left(\frac{3\pi^2}{4} \frac{b}{\langle v \rangle}\right)^{1/5} \qquad \text{(VI.25a)}$$

or

$$\rho = \left(\frac{4\pi B}{\langle v \rangle}\right)^{\frac{1}{2}}, \qquad \text{(VI.25b)}$$

respectively.

This then is at least a part of the general manner in which ρ may depend on J_1 and J_2, and let us now specificize this into usefulness. Lindholm dealt only with the P branches $(\Delta J = -1)$ of the two HCN bands which he considered. Insofar as the vibrational quantum numbers involved are concerned $v_1'' = v_2'' = 0$. We now let

$$\Delta = J_2'' - J_1'' \qquad \text{(VI.26a)}$$

so that

$$J_2'' - J_1' = J_2'' - (J_1'' - 1) = \Delta + 1 \qquad \text{(VI.26b)}$$

for the upper state since we consider only the P branch. Δ is now a convenient parameter for the determination of the type effect to be considered, and leads to three cases.

Case (1): Resonance effect in ground state and directional in upper $(\Delta = \pm 1)$.

Frequency perturbation:

$$\Delta\nu = \frac{b}{R^6} \pm \frac{B}{R^3} \qquad \text{(VI.27a)}$$

$$\int 2\pi\Delta\nu dt = \left|\frac{3\pi^2 b}{4\langle v \rangle} \frac{1}{\rho^5} \pm \frac{4\pi B}{\langle v \rangle} \frac{1}{\rho^2}\right| = 1. \qquad \text{(VI.27b)}$$

Case (2): Directional in ground and resonance in upper $(\Delta = 0, -2)$.

Same as Case (1).

Case (3): Directional effect in both states (all other Δ).

Frequency perturbation:

$$\Delta\nu = b/R^6 \qquad \text{(VI.28a)}$$

$$\rho = \left[\frac{3\pi^2}{4} \frac{b}{\langle v \rangle}\right]^{1/5}. \qquad \text{(VI.28b)}$$

In cases (1) and (2) ρ may be found as roots of Eq. (VI.27b), in particular there will be roots ρ_+ for the repulsive case (positive sign) and ρ_- for the attractive case (negative sign). In all cases of multiple roots ρ the highest valued root will be taken as significant. Further we shall suppose there to be equal amounts of resonance repulsion and attraction so that for ρ^2 from Eq. (VI.27b) we shall write $\rho_+^2 + \rho_-^2/2$. Now the ρ values furnished by the three possible sets of physical conditions may be substituted into Eq. (VI.24) with the result

$$\delta = 2.2(\langle v \rangle)^{3/5} \sum_i b_i^{3/5} N_i + \langle v \rangle \sum_j N_j \frac{\rho_{+j}^2 + \rho_{-j}^2}{2}. \qquad \text{(VI.29)}$$

Let us first consider the directional effect contributions. Lindholm approximated Eq. (VI.2) for this case by the expression

$$E_{J_1 J_2}{}^{(2)} = \frac{1}{R^6} \frac{\mu^4 I}{3\hbar^2(\Delta^2 - 1)} \qquad \text{(VI.30)}$$

which he noted is asymptotic for large J, exact for $J_1 = J_2$, 86% of the correct value for $J_1 = 1$, $J_2 = 3$, and 92% of the correct value for $J_1 = 2$, $J_2 = 4$.

We obtain b for Eq. (VI.29) from Eq. (VI.30) as

$$b = \frac{R^6}{h}\left[E_{J_1' J_2'}{}^{(2)} - E_{J_1'' J_2''}{}^{(2)}\right]$$

$$= \frac{4\pi^2 \mu^4 I}{3h^3}\left[\frac{1}{(\Delta+1)^2 - 1} - \frac{1}{\Delta^2 - 1}\right] \qquad \text{(VI.31)}$$

according to Eqs. (VI.26).

---

‡‡‡ Lindholm defines $\langle v \rangle$ as the mean relative velocity.

In order to find N_i a Maxwell-Boltzmann distribution of the molecules over the rotational levels is assumed and the first term in Eq. (VI.29) now becomes

$$\delta_D = 2.2(\langle v \rangle)^{3/5}\left(\frac{4\mu^4\pi^2 I}{3h^3}\right)^{2/5}$$

$$\times \frac{N}{\sum_{J_2=0}^{\infty} w_{J_2}} \sum_{J_2=0}^{\infty} w_{J_2}\left[\frac{1}{(\Delta+1)^2-1} - \frac{1}{\Delta^2-1}\right]^{2/5}, \quad \text{(VI.32)}$$

where the prime on the summation sign decrees the dropping of those J_2 values for which $\Delta = \pm 1, 0, -2$ (resonance effect).

Lindholm found it necessary to use the first twenty or thirty terms in the sum.

We first consider the case of both molecules in the ground state with $\Delta = \pm 1$. For the vibrational quantum numbers, the same Eq. (VI.19) is valid as it stands. London has evaluated a_1, a_2, and a_3 and Lindholm evaluated a_4 so that Eq. (VI.15) becomes

$$E^{(1)} = -\frac{\pi^2\mu^4 I}{6h^2}\frac{1}{R^6} \pm \frac{\mu^2}{2.52}\frac{1}{R^3}. \quad \text{(VI.33)}$$

Equation (VI.33) then gives the *first-order* interaction energy for this resonance condition, in the lower state (Case 1). Equations (VI.27) must now be solved for ρ. In Eq. (VI.27b) B is simply given by the coefficient of R^{-3} in Eq. (VI.33), but b presents a slightly different case. Since in the upper state, we have the directional effect taking place, b_{upper} will be given by the coefficient of R^{-6} in Eq. (VI.30). On the other hand, the resonance effect of the lower state furnishes b_{lower} which is the coefficient of the R^{-6} term in Eq. (VI.33). Finally

$$b = b_{\text{upper}} - b_{\text{lower}}. \quad \text{(VI.34)}$$

The values of B and b thus obtained may now be used in Eq. (VI.27b) to yield ρ values which when properly utilized in Eq. (VI.29) yield

$$\delta_R = \langle v \rangle \frac{N}{\sum_{J'=0}^{\infty} w_{J'}}$$

$$\times[w_{J+1}7.71\times10^{-14} + w_{J-1}5.95\times10^{-14}]. \quad \text{(VI.35)}$$

Finally Case (2) remains to be investigated, and we introduce a vibrating rotator whose moments of inertia are dependent on the vibrational state. In correspondence with the u_0 of Eq. (VI.14) let us take

$$u_0' = \psi_{J+1}{}^{M_1}\psi_v(1)\psi_J{}^{M_2}\psi_{v'}(2)$$

and now there will be twenty-four additional eigenfunctions of this form which may combine with this one —we assume that v is the ground vibrational state and v' some resonating upper vibrational state. Corresponding to each of London's matrix elements $U_i = U_{0i}$ there are now two matrix elements. As an example, to U_1 there correspond

$$U_{01} = U_1' = \int \psi_{J+1}{}^{M_1}\psi_v(1)$$

$$\times \psi_J{}^{M_2} U \psi_{J+2}{}^{M_1}\psi_v(1)\psi_{J+1}{}^{M_2}\psi_{v'}(2)d\sigma \quad \text{(VI.36a)}$$

$$U_1'' = \int \psi_{J+1}{}^{M_1}\psi_v(1)\psi_J{}^{M_2}\psi_{v'}(2)$$

$$\times U\psi_{J+2}{}^{M_1}\psi_{v'}(1)\psi_{J+1}{}^{M_2}\psi_{v'}(2)d\sigma. \quad \text{(VI.36b)}$$

Let us look at Eqs. (VI.36) rather carefully since some important physical phenomena are inferred by them. The rotational resonance condition $|J_1 - J_2| = 1$ is fulfilled by all four two-molecule eigenfunctions. In Eq. (VI.36a) the individual vibrational quantum numbers remain the same for both system state functions appearing in the matrix element. Equation (VI.36b) presents a different case, however. In this matrix element, the vibrational quantum number for molecule one changes from v to v' under the aegis of U while the vibrational quantum number for molecule two changes from v' to v. Thus, one or more quanta of vibrational energy are exchanged in this process, and resonance in the sense of Chapter V sets in. It seems important to clearly differentiate between this exchange type resonance and the rotational type of Eq. (VI.2). Perhaps this type differentiation is not too satisfactory for $|J_1 - J_2| = 1$ also implies an exchange in that the two molecules may exchange one quantum of rotational energy between themselves. The semantics of the situation should hardly trouble us, however, if we have a clear picture of the physical phenomena involved. In order to determine one of the reasons for neglecting exchange resonance, the portions of Eqs. (VI.36) pertaining to vibration may be written as

$$U_{v1}' = \int \psi_v(1)\mu_1\psi_v(1)d\sigma \int \psi_{v'}(2)\mu_2\psi_{v'}(2)d\sigma = \mu^2 \quad \text{(VI.37a)}$$

$$U_{v1}'' = \int \psi_v(1)\mu_1\psi_{v'}(1)d\sigma \int \psi_v(2)\mu_2\psi_{v'}(2)d\sigma. \quad \text{(VI.37b)}$$

Equation (VI.37a) tells us that $U_i' = U_i$, London's matrix elements. Equation (VI.37b) is proportional to the intensity of the rotation-vibration band involved. For the bands which Lindholm considered, the intensity is very low which means that Eq. (VI.37b) will be small. This in turn will cause Eq. (VI.36b) to be small which allows us to neglect the exchange resonance. Another consideration leads to the weakness of exchange resonance. The dispersion f value enters this resonance broadening as we have seen in Chapter V. In this case, we divide the dispersion f value for a monatomic

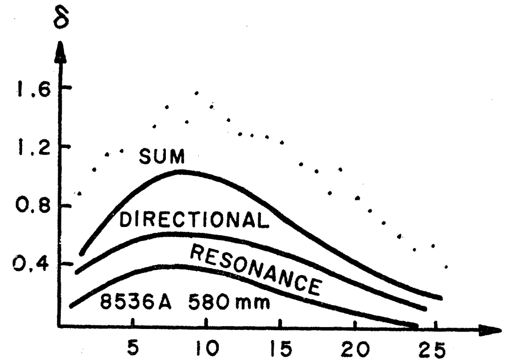

FIG. 17.

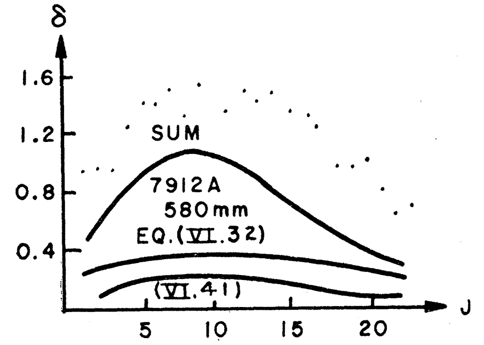

FIG. 18.

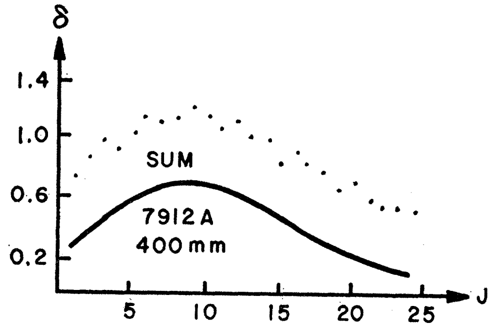

FIG. 19.

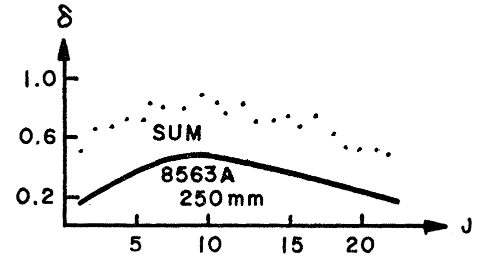

FIG. 20.

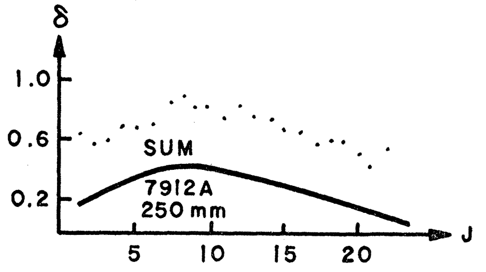

FIG. 21.

FIGS. 17–21. Comparisons of various of Lindholm's theoretical results for the HCN molecule with experimental results. (After Lindholm.[48])

transition among myriads of rotation-vibration levels. The net result of all this is a further decrease in the exchange resonance effect which we now proceed to neglect. This means that we are again only concerned with the twelve matrix elements of Eq. (VI.36a).

A calculation similar to the one leading to Eq. (VI.14) results in

$$R^6E^{(1)}=-\left(\frac{a_1^2}{E_1'}+\frac{a_2^2}{E_2'}+\frac{a_3^2}{E_3'}\right)+\frac{a_4^2}{E^{(1)}-E_4'}, \qquad \text{(VI.38)}$$

where a_i is again given by Eq. (VI.13). This equation is of solution

$$E^{(1)}=\tfrac{1}{2}\left\{E_4-\frac{\pi^2\mu^4I}{3h^2R^6}\pm\left[E_4^2+\frac{2E_4\pi^2\mu^4I}{3h^2R^6}+\frac{4\mu^4}{6R^6}\right]^{\frac{1}{2}}\right\} \qquad \text{(VI.39)}$$

in which the term in R^{-12} under the radical has been dropped.

The second term within the curly braces in Eq. (VI.39) gives us b_{upper}. b_{lower} is again obtained from Eq. (VI.30), from which

$$\frac{3\pi^2b}{4}=\frac{3\pi^2}{4}(b_{\text{upper}}-b_{\text{lower}})=-\frac{7}{8}\frac{\pi^4\mu^4I}{h^3}. \qquad \text{(VI.40)}$$

It is again necessary to solve Eq. (VI.27b) for ρ.

In his first paper on the subject Lindholm concluded that B contributed little to the optical collision diameter so that he neglected the resonance contribution in this case. This small contribution would indicate that a sharp resonance is required for effect. This sharpness is reduced by the variation of the rotational constant for the two states since this variation will in turn cause a variation in the rotational level separations for the two vibrational states.

Lindholm then obtained the Case (2) contribution as the additional directional effect contribution

$$\delta = \langle v\rangle \frac{N}{\sum_{J'=0}^{\infty} w_{J'}} [w_J 4.78\times 10^{-14} + w_{J-2} 3.43\times 10^{-14}] \quad \text{(VI.41)}$$

with the w_J defined as before.

The total half-width is now the sum of Eqs. (VI.32), (VI.39), and (VI.35). Figure 17 gives the individual directional and resonance effect contributions as well as the sum of the total directional effect plus the resonance effect. Figure 18 gives the individual directional effect contributions as well as the sum of the total directional and resonance effects. Figures 19, 20, and 21 simply give the total predicted widths in comparison with Lindholm's observed widths.

In a later paper Lindholm[49] concluded that his approximation, Eq. (VI.41), was not sufficient and that Eq. (VI.27b) in conjunction with Eq. (VI.39) and (VI.40) should be utilized for a numerical calculation of ρ for each J value. This has the effect of raising the plot of Eq. (VI.41) in Fig. 17 0.06 cm^{-1} for $J=2$, 0.12 cm^{-1} for $J=5$, 0.11 cm^{-1} for $J=10$, 0.05 cm^{-1} for $J=16$, and 0.02 cm^{-1} for $J=20$.

Lindholm also carried out an investigation similar to that of HCN for the HCl molecule. Although his results are rather impressive, the general method of their obtention is precisely the same. Thus, since we have rather thoroughly investigated this method, we shall content ourselves with having mentioned the HCl investigation.

G. An Application of Symmetric Top Dipole Broadening. Ammonia

The development of microwave spectroscopic techniques in recent years has naturally led to a quickened interest on the part of many investigators in pure rotational spectra and the line broadening particular to these spectra. In this and the next several sections we shall consider some of the theories which have been advanced in recent years aimed directly at microwave broadening effects or at microwave and infrared effects.

Bleaney and Penrose[5] have furnished the microwave field with some excellent results on the widths of the ammonia inversion lines. Some of the results of their experiments are contained in Fig. 22. Bleaney[3] used an interruption type approach to this broadening under the assumption that the disturbing ammonia molecule causes a certain perturbation of the absorbing ammonia molecule due to the field of its dipole. A collision is declared as having occurred at a certain separation or interaction energy, and, under an application of the simple interruption theory, Bleaney determines the half-widths as proportional to 3 $[K^2/(J^2+J)]^{\frac{1}{2}}$. Although a cursorily satisfactory agreement between theory and experiment was thus obtained, Margenau[60] has made a telling point which casts more than a little doubt on the meaningfulness of this agreement.

In order that this interruption approach succeed in explaining the broadening, it was found necessary that an interaction energy (corresponding to a minimum collision-defining separation) of around twice the inversion doublet level separation be used. In suggesting this, the theory implies that the molecule could go right on absorbing when the perturbation is larger than the unperturbed level separation, even resulting in a negative frequency. This appears a bit difficult to accept.

Margenau thus decided to use the interaction between two symmetric dipole rotators in conjunction with his statistical theory to account for this broadening. His results were in good agreement with those of experiment, but, equally important, they were based on tenable theoretical assumptions.

In carrying out the requisite calculation Margenau did not use any of his previous results but worked the entire problem through to obtain an answer which we shall obtain by multiplying Eq. (VI.23)—which should be applicable—by the square root of π. We do not repeat the Margenau development since it is a repetition of the obtention of the statistical theory and the root-mean-square energy perturbation. The result is

$$\delta = 2\left(\frac{2\pi}{3}\right)^{\frac{3}{2}} \frac{\mu^2}{h} N \frac{K_1K_2}{[J_1(J_1+1)J_2(J_2+1)]^{\frac{1}{2}}}. \quad \text{(VI.42)}$$

Finally the average value of the involved combination of perturber quantum numbers over a Maxwell-Boltzmann distribution is taken

$$\langle K_2J_2(J_2+1)\rangle = \frac{\sum_{J_2K_2} [K_2(J_2^2+J_2)]g(J_2K_2)e^{-E(J_2K_2)/kT}}{\sum_{J_2K_2} g(J_2K_2)e^{-E(J_2K_2)/kT}}. \quad \text{(VI.43)}$$

In Eq. (VI.43) the $E(J_2K_2)$, are the symmetric rotator energies. The $g(J_2K_2)$ are the statistical weights

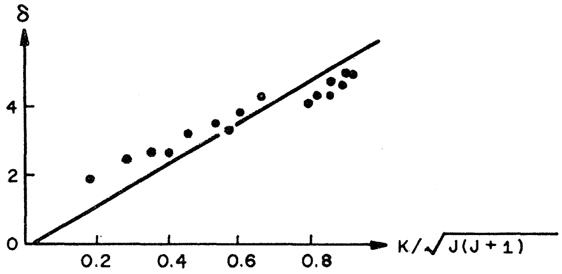

FIG. 22. The line width of the NH$_3$ inversion line as a function of rotational quantum number. (After Margenau.[60])

of the levels. Smith[78] has carried out the calculation indicated by Eq. (VI.43) to obtain 0.54 for $T=20°\text{C}$. For ammonia $\mu=1.44\times10^{-18}$ esu. On this basis Margenau obtained the result

$$\frac{\delta}{p}=1.13\times10^{-3}\times\frac{K_1}{[J_1(J_1+1)]^{\frac{1}{2}}}\ \text{cm}^{-1}\ (\text{mm Hg})^{-1}\ @\ 20°\text{C}, \qquad (\text{VI}.44)$$

and the straight line in Fig. 22 yields the results of applying this equation.

This then is Margenau's low pressure (and the theory has not here developed for any but low pressures) result for ammonia inversion lines, and its success for this case is manifestly apparent from Fig. 22. Some of the modifications which higher pressures invoke will become apparent in Margenau's more refined treatment of interactions between potential hill molecules which we consider next.

H. Interactions between Linear Vibrators with Mirror Potentials

The shift to the red with increase of pressure of the NH_3 inversion line, which had recently been observed,[4,78] provoked the Margenau investigation[61] of the phenomenon which we shall now consider. First let us note that in applying the term "linear" to NH_3 (or other mirror potential molecules) we simply wish to imply that the mirror potential of the molecule is a function only of the separation of the N atom from the H plane.

Now two interacting molecules of this type are to be considered. Margenau has carried out a variational perturbation calculation which details the effects of such an interaction. The treatment need not be given, but the results, which are rather informative, can be gleaned by a consideration of Fig. 23. On this figure the two frequencies, into which our inversion frequency has split by virtue of the interaction, are given by Δ_{I} and Δ_{II}. The probabilities—which correspond to the intensities—associated with these two frequencies also appear on the figure and are indicated as w_{I} and w_{II}. These four results of the Margenau calculation are plotted as functions of the inversion doublet separation. The parameter Λ is proportional to R^{-3}. From this figure then we may gather that the binary interaction between two such mirror potential molecules splits the inversion line into two components, the most intense of which is shifted by the greatest amount.

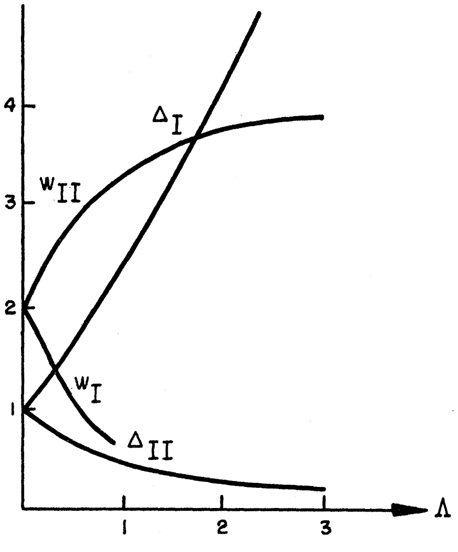

FIG. 23. The splitting and shifts of the NH_3 inversion line due to the binary interaction. Intensities are indicated. (After Margenau.[61])

The interaction between three molecules with mirror potentials was next considered by Margenau using a variational perturbation technique, and we have indicated the results in Fig. 24. The inversion line has been split into four components of which we have indicated only three since the fourth is of such low intensity as to be not reasonable of display. We might remark that the dominant intensity (frequency-wise) is more strongly so than was the case for the two molecule interaction and becomes dominant more rapidly with Λ. Further, the frequency shifts much more rapidly with Λ than does the dominant frequency in the binary encounter. The trend with higher orders of interaction appears to be apparent then and, we might add, in the proper direction. Thus, this study would indicate that as the pressure increases we may no longer accept the binary approximation as a reasonable one. Let us now consider the low pressure case further.

Under the assumption that the resonance frequency could be approximated by the mean frequency, as given by $h\langle\nu\rangle=w_{\text{I}}\Delta_{\text{I}}+w_{\text{II}}\Delta_{\text{II}}$ and that Margenau obtained for the shifted frequency

$$\langle\nu\rangle\doteq\nu_0(1-\Lambda^2). \qquad (\text{VI}.45)$$

Since

$$\Lambda=\frac{2\mu^2}{(E_1-E_2)R^3}\doteq\frac{2\mu^2N}{E_1-E_2}\doteq0.6p$$

where p is the ammonia pressure in atmospheres, $E_1-E_2\doteq0.8$ cm^{-1} $\mu=1.44\times10^{-18}$ and the temperature is taken as 0°C, Eq. (VI.45) becomes

$$\langle\nu\rangle\doteq\nu_0(1-0.36p^2). \qquad (\text{VI}.46)$$

This can only be expected to hold at low pressures since (a) it has been obtained under the assumption of a binary collision or a two particle interaction and (2) the factor Λ has been assumed as small. The "dominant" frequency may also be written approximately for low pressures from the binary theory as

$$\nu_{\text{II}}=\nu_0(1-0.6p) \qquad (\text{VI}.47)$$

and this may be compared with the experimental results.

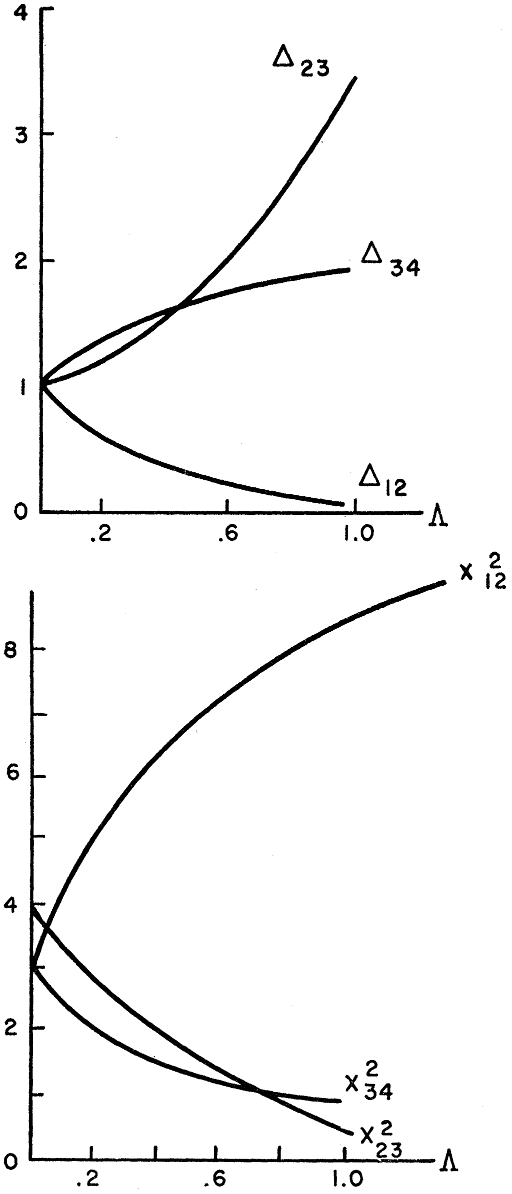

FIG. 24. The splittings of the NH_3 inversion line due to the three particle interaction. (After Margenau.[61])

I. Anderson's Line Broadening Theory

We have made some mention of the adiabatic collision approximation in our considerations of Chapters II and IV, and some additional comments on this subject appear to be necessary here. Let us suppose we are simply considering nondegenerate states which are distorted after some fashion by the collision interaction between broadener and emitter. Now in the optical region of the spectrum the separation of the energy levels of the emitter is so great that it is highly unlikely that this collision interaction will so distort the levels—energy-wise—as to effectively put the atom into another state. As we progress out into the infrared and thence to the microwave the situation changes, however, since the levels between which the contemplated transitions take place move closer and closer together. It follows quite readily that a distortion of these levels may be sufficient to bring about a change of state of the emitter. When the collision causes such a change then we have, of course, experienced a nonadiabatic collision. As a result of all this we can see that, although the adiabatic collision assumption may be a reasonable one in the visible region, it becomes less and less so as we progress into the microwave region. This theory of Anderson's[1] to which we now propose to devote some little consideration, treats nonadiabatic collisions, since it was written for application to the long wavelength transitions of the microwave and infrared regions.

We begin by making the assumption of a classical path. For all save electrons this is a reasonable approximation. We then arrive at the equation for the intensity:

$$I(\omega)=\text{const}\,\omega^4 Tr\left\|\Upsilon_0\int_{-\infty}^{+\infty} dt e^{i\omega t}\mu_z(t) \times\int_{-\infty}^{+\infty} dt' e^{-i\omega t'}\mu_z(t')\right\| \quad \text{(VI.48)}$$

which has a somewhat familiar appearance. In essence a quantum mechanical solution of this equation for the line shape, line width, and line shift under certain rather standard interruption assumptions constitute the residue of the theory.

First the matter of obtaining Eq. (VI.48) must be considered, and we shall simply accept the replacement of the classical Fourier expansion for the dipole moment by an operator and the quantum averaging of the result over a density matrix.

Letting $\|\mu(t)\|=\|U^{-1}\mu_0 U\|$, we then perform a few familiar matrix operations which transform Eq. (VI.48) into the correlation function form:

$$I(\omega)=\omega^4\,\text{const}\sum_{de}\int_{-\infty}^{+\infty} dt'' \times\exp[i(\omega-\omega_{de})t'']\varphi_{de}(t'') \quad \text{(VI.49a)}$$

$$\varphi_{de}(t'')=\int_{-\infty}^{+\infty} dt\sum_{abc}\exp[-i(\omega_{bc}+\omega_{de})t] \times(a|\Upsilon(t)|b)(b|\mu_0|c) \cdot(c|\mathfrak{F}^{-1}(t'')|d)(d|\mu_0|e)(e|\mathfrak{F}(t'')|a). \quad \text{(VI.49b)}$$

The assumption to be made is that the time between collisions is much greater than the time of collision. This assumption when applied to a consideration of the matrix elements of $\|U_0^{-1}H_1U_0\|$ leads one to the conclusion that these matrix elements and hence Eq. (VI.62b) disappear unless

$$\omega_{bc}+\omega_{de}=0. \quad \text{(VI.50)}$$

We specify the density matrix by a typical matrix element as

$$(n|\Upsilon_B|m)\delta_{nm}g_n\exp(-E_n/kT)/\sum_n g_n\exp(-E_n/kT). \qquad \text{(VI.51)}$$

We now suppose that different types (this means collisions of different optical collision diameter and direction) of collisions are designated by different values of σ. The probability that a collision will occur during the time interval dt'' and lie in the type range $d\sigma$ is given

$$p(d\sigma \text{ in } dt'')=Nvd\sigma dt''. \qquad \text{(VI.52)}$$

Next $d\varphi(t'')$ is averaged over these collisions as

$$d\varphi(t'')=dt''Nv\int d\sigma[\varphi(t''+dt'')-\varphi(t'')] \qquad \text{(VI.53)}$$

and $\varphi(t''+dt'')$ and $\varphi(t'')$ may be obtained by utilizing an isotropic collision assumption.

The solution of this equation is

$$G(t'')=e^{-Nv\sigma t''} \qquad \text{(VI.54a)}$$

where

$$\sigma=\sigma_r+i\sigma_i. \qquad \text{(VI.54b)}$$

In order to obtain the intensity distribution in the broadened spectral line we substitute Eqs. (VI.54a) in Eqs. (VI.49):

$$I(\omega)=\sum_{J_iJ_f}\frac{(J_i|\Upsilon|J_i)}{g_{J_i}}\sum_{M_iM_f}|(J_iM_i|\mu_z|J_fM_f)|^2 \times\frac{Nv\sigma_r}{(\omega-\omega_{fi}+Nv\sigma_i)^2+(Nv\sigma_r)^2}. \qquad \text{(VI.55)}$$

From Eq. (VI.55) we may obtain the line half-width and shift as

$$\delta=\frac{Nv}{\pi}\sigma_r \qquad \text{(VI.56a)}$$

$$D=\frac{Nv}{2\pi}\sigma_i. \qquad \text{(VI.56b)}$$

It would appear that were σ in a form which was amenable to calculation the problem would be essentially solved, and indeed this remains the major step to the solution. Now

$$\sigma=\sum_{J_2}(J_2|\Upsilon|J_2)\sigma_{J_2} \qquad \text{(VI.57a)}$$

and we may write σ_{J_2} as

$$\sigma_{J_2}=\int_0^\infty 2\pi\rho d\rho S(\rho), \qquad \text{(VI.57b)}$$

where $S(\rho)$ is a trace which is being averaged over all possible optical collision diameters ρ.

In evaluating Eqs. (VI.57) the assumption of a minimum distance of approach—what we might refer to as a cut-off distance—is introduced. Finally, one obtains

$$S=S_1+S_2\cdots \qquad \text{(VI.58a)}$$

$$S_1(\rho)=i\left[\sum_{M_iM_2}\frac{(J_iM_iJ_2M_2|P|J_iM_iJ_2M_2)}{(2J_i+1)(2J_2+1)}-\sum_{M_fM_2}\times\frac{(J_fM_fJ_2M_2|P|J_fM_fJ_2M_2)}{(2J_f+1)(2J_2+1)}\right] \qquad \text{(VI.58b)}$$

$$S_2(\rho)_{\text{outer}}=\tfrac{1}{2}\left[\sum_{M_iM_2}\frac{(J_iM_iJ_2M_2|P^2|J_iM_iJ_2M_2)}{(2J_i+1)(2J_2+1)}+\sum_{M_fM_2}\times\frac{(J_fM_fJ_2M_2|P^2|J_fM_fJ_2M_2)}{(2J_f+1)(2J_2+1)}\right] \qquad \text{(VI.58c)}$$

$$S_2(\rho)_{\text{middle}}=\sum_{\substack{M_iM_i'M_f\\ M_f'M_2M_2'\\ M}}\sum_{J_2'}\times\frac{(J_f1M_fM|J_f1J_2M_2)(J_f1M_f'M|J_f1J_iM_i')}{(2J_i+1)(2J_2+1)}\times(J_fM_fJ_2M_2|P|J_fM_f'J_2'M_2')\cdot(J_iM_i'J_2'M_2'|P|J_iM_iJ_2M_2), \qquad \text{(VI.58d)}$$

where

$$\|P\|=\frac{1}{\hbar}\int_{-\infty}^{+\infty}\|U_0\|^{-1}\|H_c\|\|U_0\|dt \qquad \text{(VI.58e)}$$

so that

$$S_2(\rho)=S_2(\rho)_{\text{outer}}+S_2(\rho)_{\text{middle}}. \qquad \text{(VI.59)}$$

Let us notice that $S_1(\rho)$ contributes only toward line shift while the $S_2(\rho)$ contributes only to line breadth, not that these facts should prove startling.

As has been the case with the varied and sundry theories which we have considered, the theory breaks down for small values of ρ. This transpires in the following manner. H_c depends—for the dipole-dipole interaction which is the only one which Anderson considered§§§—on r^{-3} in first order and r^{-6} in second order. This means that for sufficiently small r, P will become as large as you like. The expansion of S in terms of P, Eq. (VI.58a), is only valid, however, for small P. Thus does the theory, through S, break down for small ρ. Anderson treats this in a manner which we may now detail.

To begin with we assume that for very small values of ρ the collisions are so strong that they terminate the radiation by causing the molecule to proceed to some different nondegenerate state or when the molecule remains in the same state they result in an arbitrary phase shift that averages to zero. In either case then

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§§§ Tsao and Curnutte[84] have also considered dipole-quadrupole and quadrupole-quadrupole interaction within the framework of the Anderson theory.

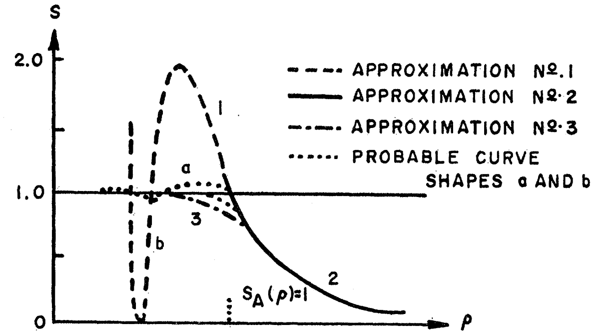

FIG. 25. Anderson's approximation to $S(\rho)$. The probable actual shapes of the curve are also given. (After Anderson.[1])

$S(\rho)$ contains only the first term, unity so that while $S_2(\rho)$ is given by Eq. (VI.76) values of ρ greater than ρ_1 where $S_2(\rho_1)=1$, it is simply given by one for lesser values of ρ.

Anderson also tried two other approximations for $S(\rho)$, namely

$$S_{\#1}(\rho)=1-\cos(-2S_2(\rho))^{\frac{1}{2}}$$

and

$$S_{\#3}(\rho)=1-\exp(-2S_2(\rho)).$$

These three possibilities for S_2 are illustrated in Fig. 25 and we might note here that Anderson found the best agreement with experiment to arise from $S_{\#2}$.

Several applications of this theory have been made, in general with a good measure of success. In some of these application was made of the dipole-dipole interaction which Anderson considered while in others the dipole-quadrupole and quadrupole-quadrupole interactions, which Tsao and Curnutte have studied, was applied. Our approximations here have mainly concerned themselves with (1) the classical path, (2) collision duration very short compared to intercollision time, (3) binary collisions. Approximation (2) is perhaps the least justifiable of the three except at quite low pressures. From our earlier considerations, it is apparent that as the pressures increase, this short collision time approximation becomes a very poor one. Quite recently Tamita[83] has produced a theory which includes the nonadiabatic considerations of Anderson and to them adds a consideration of finite collision time. In general he finds that the Anderson theory is applicable to the line center or low pressure which is what one would expect from our studies of Chapter IV. This latter theory is also primarily concerned with the region of the microwave.

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