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Theory of Pressure Effects of Foreign Gases on Spectral Lines

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The chief aim of the considerations presented is to contribute to the understanding of the effects of high pressures of foreign gases upon the shape and the position of a spectral line. A formal distinction is made between statistical and impact distributions, and the former is calculated in closed form for an interaction law of the type $\Delta\nu=-\alpha/r^6$. The distribution (Eq. (7a)) is a special case of Pearson's curves. Next the relation between the statistical and the true distribution is examined from a fundamental point of view which illuminates the character of the approximations made in the various theories of pressure broadening. Finally, by the use of a simplified procedure, approximative expressions are developed for the entire intensity distribution within the line, probably valid for pressures around 20 atmos. An expression (Eq. (18)) capable of graphical integration, is given which represents the true distribution for lower pressures. The theoretical results are compared with experimental data. Some concrete conclusions: the shift of the maximum is nearly proportional to the pressure of the perturbing gas at low pressure, proportional to its square at high pressures. The transition occurs at a pressure for which the impact half-width $\approx$ the shift of the statistical maximum. (About 20 atmos. for $K-N_2$, 50 atmos. for $Hg-N_2$.) At pressures up to ≈ 20 atmos. the impact width determines the shift of the intensity maximum, the latter being at low pressures far greater than the shift of the statistical maximum. Half-widths are also proportional to approximately the first power of the pressure at low, to the second power at high pressures. At pressures up to ≈ 10 atmos., the half-width is about twice the shift of the maximum. The shift is a function of the temperature as well as the pressure.

THE interesting features of a spectral line broadened by pressure of foreign gases are its width, the shift of its frequency maximum, and its peculiar asymmetry. It is not difficult to explain all these facts in descriptive physical terms, attributing each to a separate characteristic phenomenon. Thus it is customary to ascribe the cause of the increased width in some way to the lack of phase coherence, produced by the perturbing atoms, of the waves emitted or absorbed; the frequency shift is linked to the fact that the average energy of the levels between which a transition occurs is changed as a consequence of perturbations; the asymmetries, finally, are regarded as due to the different and in general irregular statistical weights of the various transitions of slightly different frequencies.

Theories dealing with the problem at hand are not entirely in harmony because they emphasize different aspects of it. The oldest and simplest theory is that of Lorentz, which explains, with considerable success, the width of the line on the assumption that impacts suddenly interrupt the radiation process. Weisskopf[1] has adapted this theory to the problem of continuous collisions, obtaining essentially the result of Lorentz but on physically more plausible grounds. We shall later return to it. For the present it suffices to state that, since random interruptions necessarily produce symmetrical spreading of frequencies, this method is inadequate for handling shifts and asymmetries while dealing correctly with line widths.

The present writer has attacked the problem from much the opposite standpoint.[2] Neglecting entirely the width of the line which results from the incoherence of the phases, a statistical theory was developed in which the intensity of any frequency between ν and $\nu+d\nu$ within the spectral line is considered proportional to the time interval during which the optically active atom is capable of emitting a frequency of this range. On this basis one obtains spectral distribution curves[3] which resemble closely the experimental ones observed at very high pressures, while correspondence at low pressures fails completely. The reason for this will later be clear. Moreover, the statistical theory in question yields correctly and very simply the mean frequency, $\bar{\nu}$, of the broadened line. This mean frequency is strictly proportional to the relative density of the perturbing gas. Experimentally, however, it is not the mean frequency but the maximum frequency which is measured. Yet in discussing agreement with observation, $\bar{\nu}$ has

[1] V. Weisskopf, Zeits. f. Physik **75**, 287 (1932); Physik. Zeits. **34**, 1 (1933).

[2] H. Margenau, Phys. Rev. **40**, 387 (1932).

[3] H. Margenau, Phys. Rev. **43**, 129 (1933).

been compared with the experimental $\nu_{\max.}$ because, since the exact distribution of frequencies was not known, $\bar{\nu}$ and $\nu_{\max.}$ were expected to behave similarly. This procedure, however, is fundamentally wrong, as the correct calculation of the statistical distribution will show. Curiously, however, for low pressures the expectation happens to be nearly right.—The considerations of Kulp[4] are essentially identical with those just outlined.—Any statistical theory of pressure broadening misses the important part of the line width at low pressures, as was already found, but not clearly understood, in reference 2. In a sense, it may be said to be complementary to Weisskopf's theory. Only at high pressures does the width of the statistical distribution agree with the observed line width.

A complete theory which comprises both aspects, the statistical distribution as well as that resulting from incoherence of phases, must be based upon a Fourier analysis of the varying electric moment of the radiating atom, as was emphasized by Weisskopf[1] and by Lenz.[5] The last author has treated the problem starting with this theoretically rigorous procedure. His results are notable inasmuch as they are impeccable in the range for which they hold, but, due to unavoidable analytical approximations this range is unfortunately small. Lenz claims validity for his results only up to pressures of 1 atmosphere. Furthermore, the calculatory details of his method are so unperspicuous that it is impossible to estimate the error which his treatment entails at higher pressures, where the characteristic features of the line can be more easily observed experimentally. The results of the method to be presented in this paper agree substantially with those of Lenz within the limits of validity of the latter.

Recently, Kuhn[6] has made a number of observations exhibiting some of the defects of the statistical theory of broadening sketched above. In particular he finds, on the basis of interesting plausibility arguments, that the intensity maximum should vary as the square of the pressure. His work also involves the suggestion that to each point of the statistical distribution curve should be assigned an intrinsic diffuseness. This can be done, however, only if the statistical distribution is known. The results to be obtained presently confirm, in part, Kuhn's expectations, though with quantitative modifications. They will also show how the fact that the maximum of the statistical distribution varies as the square of the relative density falls in line very naturally with observations on the shift of the intensity maximum.

For the sake of definiteness we shall continue to use the term statistical distribution (German *Häufigkeitsverteilung*) in the sense previously outlined, and refer to the spreading of frequencies due to incoherence of phases (Weisskopf's *Stossverbreiterung*) as impact broadening. Strictly speaking, the two effects cannot be separated either physically or mathematically, yet we shall treat them in this paper formally as distinct. The first step will be to obtain and discuss an approximation to the statistical distribution of frequencies in closed form (§1), the next to exhibit the relation between the statistical and the true distribution (§2). It will then be necessary to modify the former distribution by incorporating the effect of impact broadening (§3) and finally to compare the results with experiments. (§4).

§1. The Statistical Distribution

For the forces causing the displacement of energy levels as a result of interactions with foreign perturbers we may refer to London's[7] papers. His theory is applied in detail to the present problem in reference 2, where the numerical magnitude of these forces is also roughly computed. If a stationary perturber (foreign atom or molecule) is a distance r from the optically active atom, the frequency which the latter emits or absorbs differs from the normal frequency by an amount

$$\Delta\nu = -\alpha/r^6 + R, \tag{1}$$

where α is a constant and R a series of even inverse powers of r beginning with r^{-8}. At reasonably large distances, in most cases probably for $r > 10^{-7}$ cm, R may be neglected against

[4] M. Kulp, Zeits. f. Physik **79**, 495 (1932).
[5] W. Lenz, Zeits. f. Physik **80**, 423 (1933).
[6] H. Kuhn, Proc. Roy. Soc. **A18**, 987 (1934).
[7] F. London, Zeits. f. Physik **63**, 245 (1930); Zeits. f. physik. Chemie **B11**, 222 (1930).

α/r^6. Closer in there follows a range in which R becomes appreciable, and for still smaller distances of separation $\Delta\nu$ increases in general. In the analytical work in this section we shall ignore R. The error introduced thereby is considerable for higher pressures and requires discussion; as a preliminary guide we recall that at a pressure of 1 atmos. the mean distance between atoms is 3.3×10^{-7} cm. The choice of a modified law $\Delta\nu=-\alpha'/r^p$ to begin with would be of doubtful utility, for it would falsify the entire distribution curve, while the procedure here adopted will produce the maximum at the correct place, even for moderately high pressures ($\sim$10 atmos.), introducing errors for greater frequencies only. Also, the choice here made permits the evaluation of the distribution in closed form. It should be remarked that, as long as Eq. (1) holds, the contributions to $\Delta\nu$ of the different perturbers are additive. The density of emitting or absorbing atoms is taken to be very small.

Let us assume uniform distribution of the perturbers in phase space, and measure all frequencies from the position of the line at zero pressure. Then, if the statistical distribution is denoted by $I'(\nu)$ and r_i is the distance of the ith perturber from the emitting atom, the total number of perturbers being n, and the volume V,

$$I'(\nu)d\nu=(4\pi/V)^n\int\cdots\int_{d\nu}r_1^2r_2^2\cdots r_n^2dr_1\cdots dr_n. \quad (2)$$

The integration here extends over the range of r's in which

$$\nu-\frac{d\nu}{2}<-\sum_i\frac{\alpha}{r_i^6}<\nu+\frac{d\nu}{2}. \quad (3)$$

By inserting a Dirichlet factor which has the value 1 in the range (3) and vanishes outside we can transform (2) to read

$$I'(\nu)d\nu=\frac{1}{\pi}\left(\frac{4\pi}{V}\right)^n\int\cdots\int r_1^2r_2^2\cdots r_n^2dr_1\cdots dr_n\int_{-\infty}^{\infty}d\rho\frac{\sin\left(\frac{1}{2}\rho d\nu\right)}{\rho}e^{-i\nu\rho+i\alpha\rho\Sigma(1/r_j^6)}, \quad (4)$$

where now the r-integrations may be taken over all accessible configuration space. In this expression we have changed the sign of α, which is equivalent to measuring ν in the direction of decreasing frequencies. All shifts will thus conveniently appear with a positive sign although they are really negative. In (3) we shall now assume that $d\nu\rightarrow0$ which simplifies the sine-factor; we then split off the integration over the r's and write $e^{i\alpha\rho/r^6}$ in the form $1-(1-e^{i\alpha\rho/r^6})$, obtaining

$$I'(\nu)=\frac{1}{2\pi}\left(\frac{4\pi}{V}\right)^n\int_{-\infty}^{\infty}d\rho e^{-i\nu\rho}\left\{\int[1-(1-e^{i\alpha\rho/r^6})]r^2dr\right\}^n. \quad (5)$$

Consider now the term in { }. The integration is to be carried from some smallest distance of approach r_1, to the maximum distance of separation d, which may be related to the total volume by: $4\pi d^3/3=V$. But in integrating r^2dr we are permitted without appreciable error to use 0 as the lower limit, and in integrating the remainder we may replace the upper limit by ∞ because of the behavior of the integrand. If we integrate from 0, as we shall do, we are committing an error whose effect we must later investigate. With this understanding,

$$\int[1-(1-e^{i\alpha\rho/r^6})]r^2dr=\frac{V}{4\pi}\left(1-\frac{4\pi V'}{V}\right),$$

where we have used the abbreviation

$$V'=\int_0^\infty(1-e^{i\alpha\rho/r^6})r^2dr.$$

In raising this quantity to the nth power we allow the volume of the gas to increase indefinitely while maintaining $n_1=n/V$ constant. Then

$$\lim_{n\rightarrow\infty}(1-4\pi n_1V'/n)^n=e^{-4\pi n_1V'},$$

and (5) takes the form[8]

$$I'(\nu)=(1/2\pi)\int_{-\infty}^{\infty}d\rho e^{-i\nu\rho}e^{-4\pi n_1V'(\rho)}. \quad (6)$$

We now proceed to evaluate V'. After substitution of x for $\alpha\rho/r^6$ and one partial integration

[8] I am indebted to Professor Lars Onsager for showing me a mathematically more elegant way of obtaining this equation. The presentation here chosen is less abstract.

this becomes

$$V'(\rho)=\frac{(\alpha\rho)^{\frac{1}{2}}}{3}\int_0^\infty\left(\frac{\sin x}{x^{\frac{1}{2}}}-i\frac{\cos x}{x^{\frac{1}{2}}}\right)dx$$

$$=\frac{(2\pi\alpha\rho)^{\frac{1}{2}}}{6}(1-i).$$

When this is substituted into (6) there results an expression which is easily evaluated. The most convenient procedure is to change the integrand in (6) to real form by writing

$$\int_{-\infty}^{\infty}=\int_{-\infty}^{0}+\int_0^\infty,$$

and then taking for the variable of integration in the first integral $-\rho$ instead of ρ. The limits will then be 0 and ∞ for both integrals and the integrands if added, become real. The result is

$$I'(\nu)=\frac{1}{\pi}\int_0^\infty \exp\left[-\frac{2\pi}{3}n_1(2\pi\alpha\rho)^{\frac{1}{2}}\right]$$

$$\cos\left(\nu\rho-\frac{2\pi}{3}n_1(2\pi\alpha\rho)^{\frac{1}{2}}\right)d\rho.$$

This integral is known; it is of the form

$$\int_0^\infty e^{-px}\cos(x^2-px)xdx \quad \text{with} \quad x=(\nu\rho)^{\frac{1}{2}}$$

and reduces to the function

$$I'(\nu)=\tfrac{2}{3}\pi\alpha^{\frac{1}{2}}n_1\nu^{-\frac{3}{2}}\exp\left(-(4/9)\pi^3\alpha n_1^2/\nu\right). \quad (7)$$

Henceforth we shall use the abbreviation $\lambda=\frac{2}{3}\pi\alpha^{\frac{1}{2}}n_1$, so that (7) becomes

$$I'(\nu)=\lambda\nu^{-\frac{3}{2}}e^{-\pi\lambda^2/\nu}. \quad (7a)$$

This distribution is plotted in Fig. 1, where ν is measured in units $\pi\lambda^2$.

The maximum of (7) comes at

$$\nu_{\max.}=\tfrac{2}{3}\pi\lambda^2=(\tfrac{2}{3}\pi)^3\alpha n_1^2. \quad (8)$$

It varies with the square of the relative density of perturbers as was predicted by Kuhn[6] (only his numerical coefficient is in error by a factor ~ 1.35). His conclusion that for large ν the distribution should behave essentially like $\nu^{-\frac{3}{2}}$, based on the supposition of single impacts, is also verified by (7). The exponential factor in this expression represents the effect of the cooperation of several perturbers in producing the

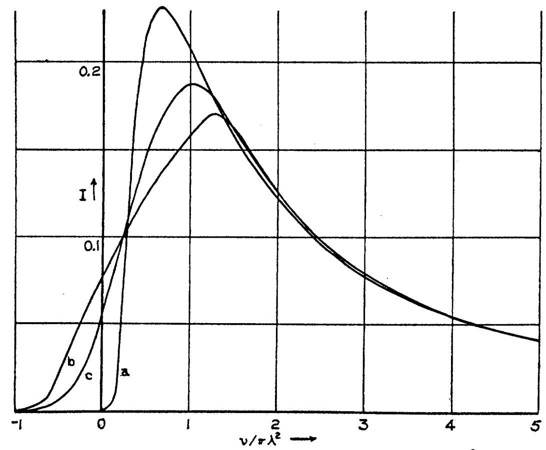

FIG. 1. (a) Statistical distribution $I'(\nu)$; (b) Eq. (21), with $\omega=2\pi\lambda^2$; (c) Eq. (23), with $\omega=2\pi\lambda^2$. Abscissae are in units $\pi\lambda^2$; the area under each curve is unity.

intensity at a given frequency. The half-width of (7) is given by $1.85\pi\lambda^2$ and is therefore also proportional to n_1^2.

Before we consider to what extent the statistical distribution now derived can be expected to be reproduced in experiments, let us investigate it more critically. The law used for the energy interaction (Eq. (1)) with the neglect of R is certainly too simple. To use round numbers which indicate the order of magnitude of the various effects, $\Delta\nu$ will fall first more rapidly than assumed as we pass from 10A inward, then less rapidly, and at smaller distances it will rise. Indeed, from about 5A inward no encounters are possible. Also, at such close distance, additivity of the perturbing effects ceases to be valid. One may therefore expect that those portions of the distribution curve (7) which correspond to single impacts at distances between about 5 and 10A are incorrect. But here the curve can sometimes be modified very simply by considering the effects of single impacts alone, although we feel that the use of a law of the form $\Delta\nu=\alpha' r^{-p}$ will be inadequate for that purpose.

If, in the region of single impacts, that is, for frequencies which cause the exponential factor in (7) to be nearly 1, $\nu=f(r)$ where $f(r)$ may contain several parameters, then the intensity at frequency ν is given by

$$I(\nu)d\nu=\text{const.}\int_{d\nu}r^2dr, \quad \text{whence}$$

$$I(\nu)=[\varphi(\nu)]^2 d\varphi/d\nu. \quad (9)$$

Here $\varphi(\nu)$ is written for the solution $r=\varphi(\nu)$ of $\nu=f(r)$. In some cases, (9) is given directly by experiment, and $f(r)$ can then be determined empirically.

Next, we must estimate the consequences of carrying the integration in all the way into the origin. Physically this means that we are including in (7) the contribution of very large frequencies at distances of approach inferior to the collision diameter, which in reality do not occur. It is clear that they will modify the tail of the distribution law which, in (7), is too long. As a result of their inclusion, the first moment of (7) does not exist, whereas the true statistical distribution has a mean (which is equal to $n_1\Delta\bar{\nu}$, $\Delta\bar{\nu}$ being the space average, calculated for a single perturber, over the true $\Delta\nu$ in place of (1); $\Delta\bar{\nu}$ as given by (1) diverges).

An upper limit for the error thus introduced may be found as follows: If we wish to cut off the integration at the lower limit r_1 we must replace V' in (6) by the function

$$\int_0^\infty(1-e^{i\alpha\rho/r^6})r^2dr+\int_0^\infty(e^{i\alpha\rho/r^6}-e^{i\rho F(r)})r^2dr,$$

where $F(r)=\alpha r^{-6}$ for $r>r_1$, but vanishes if $r<r_1$. The first integral is the old V'. Now the second integrand in this expression cannot be greater, in absolute value, than 2, hence the entire second integral has an absolute value $\leqq 2r_1^3/3$. If this is added to V' in (6) $I'(\nu)$ is multiplied by $e^{\pm(8\pi/3)n_1r_1^3}$. The exponent here is twice the number of perturbers contained, on the average, in the excluded volume. Hence, if we take r_1 to be $\sim$5A, the error in (7) cannot be greater than a few percent even for the largest frequencies considered at pressures about 1 atmos. For higher pressures, this upper limit of error grows very rapidly and is not a good index for the approximation involved.

To estimate the actual error we rely on physical considerations. We know that the true statistical distribution must give practically zero intensities for $\nu>\nu_1=\alpha/r_1^6$. The ratio $\nu_1/\nu_{\max.}$ is independent of α, the strength of interaction; it is about 10^4 for relative density unity, 10 for relative density 30 (again taking $r_1\sim$5A). In the latter case, Eq. (7) predicts an intensity about 1/10 maximum at ν_1; hence at smaller frequencies we can say that the error due to the present cause is smaller than 10 percent of the maximum. The position of the maximum, however, should not be very strongly in error even at relative densities 30.

Some caution is also necessary in applying single-impact considerations to the tail of the distribution curve. Even at $\nu=10\nu_{\max.}$ the error in neglecting the exponential factor in (7) amounts to more than 10 percent. It will be seen, however, (cf. §3), that for pressures of a few atmospheres the maximum of $I'(\nu)$ has practically nothing to do with the maximum of the experimental distribution.

It may be of theoretical interest to remark that the frequency at which the area under the curve $I'(\nu)$ is divided into two equal parts lies at $4.34\pi\lambda^2$. Statisticians will observe that $I'(\nu)$ represents a certain type of Pearson's distribution function. In a previous paper[3] an attempt was made to evaluate this function graphically, but it was not obtained in closed form. The constants in this section are so chosen that $\int_0^\infty I(\nu)d\nu=1$, and I' must be regarded as zero for $\nu<0$, although analytically it assumes complex values in that range.

§2. Relation Between Statistical and True Distribution

When an atom emits or absorbs light of constant amplitude but varying frequency $\nu(t)$, the intensity distribution in the spectral line is accurately given by the Fourier analysis of its electric moment $e^{2\pi i\int_0^t\nu(\tau)d\tau}$; that is, if $I(\nu')$ is the intensity associated with a fixed frequency ν' and $J(\nu')$ the corresponding amplitude,

$$I(\nu')=|J(\nu')|^2,$$

where

$$J(\nu')=\int dt\exp\{-2\pi i\nu' t\}\exp\{2\pi i\int_0^t\nu(\tau)d\tau\}.$$

Hence

$$I(\nu')=\int\int dt_1dt_2\exp\{2\pi i[\int_0^{t_1}\nu(\tau)d\tau-\int_0^{t_2}\nu(\tau)d\tau+\nu'(t_2-t_1)]\}.\quad(10)$$

The two integrations for which no limits are stated extend over the entire time during which the process of radiation occurs, and this interval may be taken to be infinite since we are not at present interested in natural line widths. After substitution of the variable x for (t_2-t_1) (10) takes the form

$$I(\nu')=\int dt\int dx \exp\{2\pi i[\nu' x-\int_0^x \nu(\tau)d\tau]\}. \quad (11)$$

Up to this point the analysis is straightforward, but from here on approximative methods must be adopted in the solution of any concrete problem. Two main procedures have been employed.

The first is based on a Taylor expansion of the varying phase:

$$\int_0^x \nu(\tau)d\tau=\nu_{x=0}\cdot x+\dot{\nu}\frac{x^2}{2}+\cdots$$

$$=\nu(t)x+\dot{\nu}(t)\frac{x^2}{2}+\cdots. \quad (12)$$

If here all terms but the first are disregarded and the result is substituted in (11), the integral over x in this expression becomes a δ-function which is 0 whenever $\nu(t)\neq\nu'$. The element dt is the time during which the frequency is $\nu(t)$, and is proportional to the statistical weight $I'(\nu)$ which was calculated in §1 for the problem of broadening by foreign gases. Hence to this approximation (11) simply reduces to

$$I(\nu')=\int I'(\nu)d\nu\delta(\nu-\nu')=I'(\nu').$$

This observation shows clearly in what sense the statistical distribution is in error: the second integral in (11) is not really a δ-function but has a finite width. The true distribution can be obtained from the statistical one by "diffusing" each ordinate of $I'(\nu)$ in the proper manner.

The second procedure referred to is the method of impact broadening due to Lorentz and Weisskopf.[1] Its meaning can also be most clearly understood in view of Eq. (11), for it amounts to an evaluation of this equation by substituting a δ-function for dt and by using a distribution of finite width for the factor of dt. In detail, one puts $dt=\delta(\nu-\nu'')d\nu$, and with respect to the remainder of (11) one makes the simple assumption that $\nu(\tau)=\nu$, a constant in time within the interval $-T\leqq\tau\leqq T$ and zero outside. The frequency distribution is then that of an interrupted wave train of duration $2T$, i.e.,

$$I(\nu')=\int\delta(\nu-\nu'')d\nu\int_{-T}^{T}e^{2\pi i(\nu'-\nu)x}dx$$

$$=\sin[2\pi(\nu'-\nu'')T]/\pi(\nu'-\nu'').$$

If this last result is averaged over all emission times $2T$ with the correct weight factor, the familiar "dispersion" curve (cf. reference 1) is obtained. Weisskopf's treatment differs from that of Lorentz by its method of computing the mean time of uninterrupted emission (or absorption).

In the next section we shall make an attempt at combining the two procedures now outlined, using for dt the statistical distribution, and some suitable diffusing function for the remainder. The success of the impact theories would recommend the use of a dispersion curve for this purpose. But in choosing a diffusing function we must, unfortunately, be guided by considerations as to what functions allow the analysis to be carried through. Some idea of the true nature of this function may be obtained, however, by reverting to Eq. (12).

Suppose we retain the first two terms of the expansion. Since in the case of a single perturbation $\dot{\nu}$ is proportional to the speed with which the molecules move, the second term is inappreciable at sufficiently low temperatures. The statistical distribution, as is well known, must therefore agree with the true one at very low temperatures.—On introducing (12) in (11) the integration over x leads to

$$\int_{-\infty}^{\infty}e^{2\pi i(\nu'-\nu)x-\pi i\dot{\nu}x^2}dx=\left(\frac{1}{2\dot{\nu}}\right)^{\frac{1}{2}}(1-i)e^{i\pi(\nu'-\nu)^2/\dot{\nu}}. \quad (13)$$

$\dot{\nu}$ is the time rate at which the frequency varies as the result of the combined action of all perturbers; it cannot in general be calculated by considering single impacts alone. It will depend on ν as well as on the pressure of the perturbing gas and on its temperature. For the present let us assume it to vary so slowly with ν that the width of (13) can be computed by treating it as constant. The real part of (13) is

$$\left(\frac{1}{2|\dot{\nu}|}\right)^{\frac{1}{2}}\left[\cos\frac{\pi(\nu'-\nu)^2}{|\dot{\nu}|}+\sin\frac{\pi(\nu'-\nu)^2}{|\dot{\nu}|}\right]. \quad (14)$$

The imaginary part is of no interest since it disappears in the next integration in (11). The

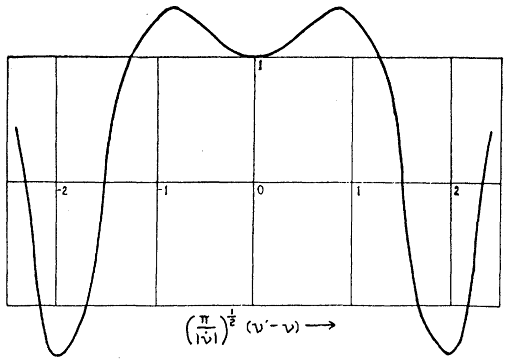

FIG. 2. Graph of the function (14).

function (14) is plotted in Fig. 2, where the unit $(|\dot{\nu}|/\pi)^{\frac{1}{2}}$ is employed in measuring $\nu'-\nu$. Its width ω is given by $(\pi/|\dot{\nu}|)^{\frac{1}{2}}\omega \approx 2$, hence

$$\omega \approx 2(|\dot{\nu}|/\pi)^{\frac{1}{2}}. \tag{15}$$

A crude estimate of the factors upon which this width depends can be obtained by calculating an average of the quantity $|\dot{\nu}|^{\frac{1}{2}}$ over all perturbers. The ith perturber will contribute

$$[|(d\nu_i/dr_i)v_i \cos(r_i v_i)|]^{\frac{1}{2}}.$$

Upon averaging over velocities and directions of motion of the foreign atoms this becomes $c(\bar{v})^{\frac{1}{2}}|d\nu_i/dr_i|^{\frac{1}{2}}$. c is some numerical constant which we do not care to determine. We now take the origin of all frequencies at the unperturbed position of the spectral line so that ν is identical with the $\Delta\nu$ of Eq. (1). The term under the radical will then be $6\alpha/r_i^7$. In summing over all perturbers we use the method of statistical mechanics:

$$\sum_i |d\nu_i/dr_i|^{\frac{1}{2}} = 4\pi n_1 \int (6\alpha/r^7)^{\frac{1}{2}} r^2 dr,$$

beginning the integration with some suitable smallest value r_1. Collecting these results we find for the average in question

$$\text{Ave } |\dot{\nu}|^{\frac{1}{2}} = Cn_1(\alpha\bar{v})^{\frac{1}{2}}, \tag{16}$$

where C, a constant, has the dimension $L^{-\frac{1}{2}}$. This expression depends but little on the choice of r_1.

It is of interest to compare this impact width with that calculated by Weisskopf. According to his theory

$$\omega = \text{const. } \bar{v}n_1\rho^2,$$

where $\rho = \text{const. } (\alpha/\bar{v})^{1/5}$. Thus

$$\omega = \text{const. } n_1\alpha^{2/5}\bar{v}^{3/5}. \tag{17}$$

The difference in the exponents of α and $\bar{v}$ in (16) and (17) is unimportant, for both expressions are only approximately true. The superiority of Weisskopf's treatment lies in its greater simplicity and in the opportunity which it offers for evaluating the constant. The point to be noticed is that ω varies linearly with the relative density of the perturbing gas. In making use of these results later we can take the constant in question from experiment.

§3. Modification of the Statistical Theory by Inclusion of Impact Broadening

In the present section we shall calculate (11), but with the use of a highly simplified distribution function representing the effect of impact broadening. The half-width of the function will be given by (16) or (17). The form of the diffusing function suggested both by experiment and theory would be of the dispersion type:[9]

$$w(x) = (\omega/2\pi)/(x^2 + \tfrac{1}{4}\omega^2),$$

so that the modified distribution becomes:

$$I(\nu) = \int_{-\infty}^{\infty} w(x-\nu)I'(x)dx \tag{18a}$$

$$= \frac{\omega}{2\pi}\int_{-\infty}^{\infty} \frac{I'(x)dx}{(x-\nu)^2+\omega^2/4}, \tag{18}$$

I' being given by (7) for a large range of pressures. (18) could be computed graphically and should agree well with the observed intensity distributions. In this procedure, ω can be taken either from (17) or from the experimental half-width of the line at small pressures; it should be allowed to increase slowly with ν across the line since large perturbations are accompanied by larger values of $|\dot{\nu}|^{\frac{1}{2}}$ (cf. Eq. (15)). The value of $I(\nu)$ for two limiting cases can be determined at once. If $-\nu \gg \omega \gg \pi\lambda^2$, that is, for the extreme blue wing of the spectral line, $I(\nu)$ varies nearly as $1/\nu^2$, i.e., it behaves like the dispersion curve.

[9] The constants are so chosen that ω represents the half-width and $w(x)$ is normalized to 1.

On the other hand, if $\nu \gg \omega$, (18) takes on the features of $I'(\nu)$. At the extreme red side of the line the true distribution should therefore approach the statistical one.

We shall not attempt to calculate (18); for some general features of the true distribution can probably be recognized by using simpler trial functions for $w(x)$. Let us first make the assumption that the impact breadth diffuses all frequencies within a range ω in a uniform manner, allowing ω for the present to be a function of ν. This assumption is likely to be better than the second one whose consequences we will investigate, namely that $w(x)$ is a triangle function which confers much greater weight upon the center than upon the "wings" of the impact distribution. Before proceeding with the work we write down some transformations of certain integrals which occur, and which the reader can readily verify.

$$\int_a^b I'(x)dx = \lambda \int_a^b x^{-\frac{3}{2}} e^{-\pi\lambda^2/x} dx = \phi((\pi\lambda^2/a)^{\frac{1}{2}}) - \phi((\pi\lambda^2/b)^{\frac{1}{2}}). \quad (19)$$

ϕ is Gauss' integral

$$\phi(x) = 2/\pi^{\frac{1}{2}} \int_0^x e^{-y^2} dy;$$

we recall that $\phi(\infty) = 1$. Finally,

$$\int_a^b x I'(x)dx = 2\lambda \{ b^{\frac{1}{2}} e^{-\pi\lambda^2/b} - a^{\frac{1}{2}} e^{-\pi\lambda^2/a} + \pi\lambda[\phi(\pi\lambda^2/b)^{\frac{1}{2}} - \phi(\pi\lambda^2/a)^{\frac{1}{2}}] \}. \quad (20)$$

1. Uniform diffusion

In accordance with the first assumption, $w(x)$ will be taken to be the constant $1/\omega$ in the range $-\omega/2 \leqq x \leqq \omega/2$, thus ensuring correct normalization. Then

$$I(\nu) = \int_{-\infty}^{\infty} w(x-\nu) I'(x) dx = \frac{1}{\omega} \int_{\nu-\omega/2}^{\nu+\omega/2} I'(x) dx.$$

Here it must be remembered that $I'(x)$ is zero for negative x. Hence, in view of (19),

$$I(\nu) = \frac{1}{\omega}\left[\phi\left(\frac{\pi\lambda^2}{\nu-\omega/2}\right)^{\frac{1}{2}} - \phi\left(\frac{\pi\lambda^2}{\nu+\omega/2}\right)^{\frac{1}{2}} \right]. \quad (21)$$

If the argument of ϕ becomes imaginary, ϕ is to be replaced by 1. In Fig. 1 is shown a graph of this function for $\omega = 2\pi\lambda^2$, the same for all values of ν. The maximum is, of course, less steep and is shifted with respect to that of $I'(\nu)$. There is now an appreciable intensity at negative ν-values.

The position of the maximum of $I(\nu)$ is in general easily obtained by differentiating (21) with respect to ν, treating ω as a function of ν. An interesting and sufficiently significant result is obtained, however, if again we take ω to be constant. The maximum, occurring at ν_0, is then given by

$$I'(\nu_0 + \omega/2) = I'(\nu_0 - \omega/2), \quad (22)$$

as is directly seen from the equation preceding (21). According to (22) ν_0 can be determined by the simple graphical procedure of finding where the $I'(\nu)$ curve has a horizontal width ω. The mean of the two abscissae defining this width is ν_0.

Now suppose that $\omega \gg \pi\lambda^2$, which is the case up to pressures of several atmospheres, as will be shown in the next section. Then, since $I'(\nu)$ rises very rapidly at $\nu = 0$, the point bounding the range of width ω on the left lies practically at $\nu = 0$, the limit on the right is about ω, and $\nu_0 \sim \omega/2$. This is true regardless of the precise behavior of $I'(\nu)$ for large ν. We see that ν_0 in this case bears very little relation to the maximum of $I'(\nu)$. Moreover, since ω varies linearly with n_1, ν also does. At low pressures the shift of the observed maximum is thus entirely occasioned by the increasing impact width of the line. If this explanation is correct the shift should roughly correspond to one-half of the half-width, as will be shown to be the case empirically.

In case $\omega \ll \pi\lambda^2$, which prevails for high pressures because λ^2 increases with n_1^2, ν_0 coincides with the maximum of I', and hence varies with n_1^2. The region in which the linear law gradually changes into the square law is given by $\omega \approx \pi\lambda^2$.

The actual shape of the line cannot be expected to be rendered accurately at all by (21) for the former case $\omega \gg \pi\lambda^2$. For the reverse condition, lack of agreement of (21) with observation, if found, should be attributed mainly to the faults of I' previously discussed.

2. Diffusion by a triangle function

To see the effect of the particular diffusing function chosen upon the distribution of intensities it seemed well to try one other choice:

$$w(x)\begin{cases} 0 & \text{if} \quad x<-\omega/2 \\ (4/\omega^2)(x+\omega/2) & \text{if} \quad -\omega/2\leqq x<0 \\ (4/\omega^2)(\omega/2-x) & \text{if} \quad 0\leqq x<\omega/2 \\ 0 & \text{if} \quad x>\omega/2 \end{cases}$$

w represents an isosceles triangle with base ω and area 1. If this is substituted in (18a) with x everywhere replaced by $(x-\nu)$, the result is

$$I(\nu)=\frac{4}{\omega^2}\int_{\nu-\omega/2}^{\nu}\left(\frac{\omega}{2}-\nu+x\right)I'(x)dx +\frac{4}{\omega^2}\int_{\nu}^{\nu+\omega/2}\left(\frac{\omega}{2}+\nu-x\right)I'(x)dx.$$

The integrals can be evaluated by the use of (19) and (20), yielding finally

$$I(\nu)=\frac{4\pi\lambda^2}{\omega^2}\left[2G\left(\frac{\pi\lambda^2}{\nu}\right)^{\frac{1}{2}}-G\left(\frac{\pi\lambda^2}{\nu+\frac{\omega}{2}}\right)^{\frac{1}{2}}-G\left(\frac{\pi\lambda^2}{\nu-\frac{\omega}{2}}\right)^{\frac{1}{2}}\right]\cdot \quad (23)$$

The function G is defined as follows:

$$G(x)=\frac{\phi(x)}{x^2}+2\phi(x)+(2/\pi^{\frac{1}{2}})e^{-x^2}/x.$$

The procedure must be modified somewhat when $\nu<\omega/2$, for then the arguments of some of the G's become imaginary. Closer inspection shows that when this happens the corresponding $G(x)$ is to be replaced by $(2+1/x^2)$. We shall not reproduce here the details of the calculation.

Eq. (23) is also plotted in Fig. 1, again assuming ω to be independent of ν. As before, the value $2\pi\lambda^2$ has been chosen for ω; this means that the base of the triangle is equal to three times the shift of the maximum of $I'(\nu)$. Strictly speaking, curves 2 and 3, Fig. 1, are not comparable quantitatively because curve 2 has an "impact half width" twice that of curve 3. By taking ω in Eq. (23) to be larger the curves can be made almost to coincide. It is of interest to notice how little the statistical distribution at larger frequencies is changed by the process of diffusion. We wish to emphasize again that Eq. (23), as well as (21), breaks down when $\omega>\pi\lambda^2$, for in that case the accurate impact distribution becomes important. It would then be necessary to evaluate (18).

The position of the maximum of (23) requires comment. We state merely the results without discussing the work involved: For $\omega\ll\pi\lambda^2$ the maximum ν_0 increases with the square of the relative density, as is clear without calculation. If $\omega\gg\pi\lambda^2$ the increase of ν_0 is not strictly linear with n_1, as was found in example 1), but proportional to a power of n_1 intermediate between the first and second. In this case $(\omega\gg\pi\lambda^2)$, ν_0 is again far greater than $\frac{2}{3}\pi\lambda^2$, the position of the maximum of $I'(\nu)$. As before, the transition region in which the lower power changes into the second is defined by $\omega\approx\pi\lambda^2$.

The results of this section are definitely oversimplified. But before developing the theory further it seems well to determine whether the simple functions here derived (Eqs. (21) and (23)) agree with observations in the pressure range for which they are theoretically valid. This pressure range depends, of course, upon the gases used (cf. next section) since both ω and λ are functions of α, the parameter measuring the strength of the interactions. For the purpose of such comparison it would be necessary to measure the entire line contour rather than shift and half-width alone, as is customary. We regard as significant the fact that the maximum of the true distribution depends at small pressures largely upon the impact width, and that the position of this maximum moves toward longer wave-lengths first nearly linearly with n_1, at higher pressures with n_1^2.

§4. Comparison of Results with Experiments

The pressure shift of the line maximum is well known to be nearly proportional to the relative density of the perturbing gas. Füchtbauer and collaborators[10] have traced this linear law up to pressures of 50 atmos. Their observations are made on the 2537A-line of Hg. An essentially similar behavior is shown by the D lines of Na[11] up to relative density ≈ 10.

Recently, however, Watson and the author[12] have extended their measurements on the shift of the potassium resonance lines to relative densities above 20 and found definite departures from linearity in this region in qualitative confirmation of the theory, the perturbing gas being N_2.

The difference in the behavior of Hg and K is easily explained. The following is a list of the values of ω and $\pi\lambda^2(=4/9\pi^3 n_1^2\alpha)$ for 1 atmos. of pressure, together with the α's used in the computation of λ^2. These α's are computed for similar cases in reference 2, their numerical values are not very accurate, but the ratio of the two should not be greatly in error. The values of ω, the half-width at 1 atmos., are taken from experiment.

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[10] C. Füchtbauer, G. Joos and O. Dinkelacker, Ann. d. Physik **71**, 204 (1923).
[11] H. Margenau and W. W. Watson, Phys. Rev. **44**, 92 (1933).
[12] W. W. Watson and H. Margenau, Phys. Rev. **44**, 748 (1933).

	H_g-N_2	$K-N_2$
α	1.5×10^{-32} cm^6 sec.$^{-1}$	7×10^{-32} cm^6 sec.$^{-1}$
ω	8.3×10^{9} sec.$^{-1}$	13×10^{9} sec.$^{-1}$
$\pi\lambda^2$	1.5×10^{8} sec.$^{-1}$	7×10^{8} sec.$^{-1}$

The statement previously made, that at pressures of a few atmospheres $\omega\gg\pi\lambda^2$, and hence the impact width dominates the position of the maximum as well as the width of the line, is thus seen to be true. Since ω varies as n_1, and λ^2 as n_1^2, ω becomes equal to $\pi\lambda^2$ at about relative density 55 for the case $Hg-N_2$, at relative density 19 for $K-N_2$. It is therefore clear why strong curvature in the shift curve should not have been detected by Füchtbauer and collaborators, but should have revealed itself even at lower pressures in the other experiments referred to.

In the pressure effects of foreign gases upon the *D* lines or the resonance lines of K, the statistical intensity distribution impresses its characteristics more and more markedly upon the lines from 20 atmos. onward. At pressures of this magnitude $I'(\nu)$ is already in error for large ν, but corrections can probably be applied by single impact considerations.

As regards half-widths the theory, since it incorporates all the features of impact broadening, must be in agreement with experiment wherever the impact theories agree, that is at low and medium pressures. This has been amply tested. At higher pressures the width of the line should increase according to the statistical distribution, i.e., like n_1^2, the turning point being as before $\omega\approx\pi\lambda^2$. This fact is also verified in the experiments above considered.

The shift of the maximum is usually supposed to be independent of the temperature. This is true only for high pressures, when the statistical distribution determines the shift. For the latter depends on temperature only through the Boltzmann factor which we have here neglected, and this dependence is slight. At low pressures the maximum should exhibit much the same behavior with respect to temperature variations as does the impact width. This point has not been experimentally tested.

It has been pointed out that ω should be about twice the shift of the maximum in cases to which the theory applies. The actual half-width $\nu_{\frac{1}{2}}$ is a little larger than ω, being compounded from impact width and statistical width. We expect therefore that the ratio of $\nu_{\frac{1}{2}}$ to ν_0 (shift of maximum) exceeds 2 somewhat. Table I contains experimental values of $\nu_{\frac{1}{2}}$ and ν_0 at 1 atmos. of pressure. The first column indicates the spectral line investigated together with the perturbing gas. The four cases below the horizontal line should not follow the present rule, as we shall see.

TABLE I.

	$\nu_{\frac{1}{2}}$ PER UNIT RELATIVE DENSITY ($\times10^9$ sec.$^{-1}$)	ν_0 PER UNIT RELATIVE DENSITY ($\times10^9$ sec.$^{-1}$)	$\frac{\nu_{\frac{1}{2}}}{\nu_0}$
H_g 2537 $-$ A	9.66	3.73	2.6
H_g 2537 $-N_2$	8.26	3.73	2.2
H_g 2537 $-O_2$	7.86	3.69	2.13
Na 5890 $-$ A	17	6	2.84
Na 5890 $-N_2$	11.7	5.2	2.25
K 7665 $-N_2$	13.2	6.2	2.13
K 7699 $-N_2$	13.2	6.55	2.0
K 4044 $-N_2$	33	16.5	2.0
K 4047 $-N_2$	33	19	1.75
H_g 2537 $-CO_2$	13.1	3.2	4.1
H_g 2537 $-H_2O$	10.6	2.34	4.5
H_g 2537 $-H_2$	12.36	1.97	6.3
Na 2537 $-H_2$	19.5	4.5	4.3

Both CO_2 and H_2O have complicated molecules with permanent electric moments. Their interaction with the emitting atom calls into play additional forces which have not been considered in §1. These forces can extend the distribution $I'(\nu)$ to negative ν, thereby increasing the width and decreasing the shift. A similar situation exists with regard to H_2, although for a different reason. H_2 produces a large impact width through the factor $v^{\frac{3}{5}}$ in ω because of its lightness, which explains its efficiency in broadening the line. But the statistical distribution (7) is inadequate for this case for reasons which have been discussed in a previous communication.[13] It is there shown in connection with simple examples (Fig. 2) that, if one adds to $\Delta\nu$ of Eq. (1) a range in which $\Delta\nu$ is positive, the statistical distribution becomes nearly symmetrical and the shift of the maximum very small. Superposition of the impact width then leads to an explanation of the anomalies shown by H_2 in Table I.

Although the present treatment is restricted to resonance lines since for high series lines

[13] H. Margenau, Phys. Rev. **44**, 931 (1933).

Eq. (1) is not valid, the lines K 4044 and 4047 have been included in Table I. For higher series lines, $\Delta\nu$ may have a large positive range, and therefore $I'(\nu)$ may contain appreciable "blue" intensities. The present treatment is entirely inadequate for dealing with the highest series members of the alkali spectra, where the atom in its excited state embraces thousands of perturbers.[14]

While this work was in progress there has appeared a paper by Minkowski[15] in which the intensity distribution of the D lines perturbed by small pressures of A is investigated and compared with the results of Lenz[5] and Kuhn.[6] The agreement is found satisfactory. The considerations here presented do not conflict with these results in their respective ranges of validity (cf. in particular the remarks on the limiting form of Eq. (18)), and hence are not in disagreement with Minkowski's data. It is to be observed that for his experiments, (7) represents the accurate statistical distribution. Moreover, $\omega \gg \pi\lambda^2$. If then the center of the line is completely absorbed and measurements are confined to its wings, $|\nu| \gg \omega \gg \pi\lambda^2$. Under this condition $I \sim \nu^{-2}$ on the blue side, $I \sim \nu^{-3/2}$ on the red side of the line, as was found.

[14] A theory pertaining to these effects has been given by Fermi, Nuovo Cimento **11**, 157 (1934).

[15] R. Minkowski, Zeits. f. Physik **93**, 731 (1935).

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The Effect of Crystalline Fields on the Magnetic Susceptibilities of Sm^{+++} and Eu^{+++}, and the Heat Capacity of Sm^{+++}

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The temperature variation of the paramagnetic susceptibility of Sm^{+++} is calculated on the assumption that the ion is subject to a crystalline field which can be represented by the potential

$$V=\sum_i[D(x_i^4+y_i^4+z_i^4)+Ax_i^2+By_i^2-(A+B)z_i^2],$$

the cubic portion of this potential predominant. The susceptibility is decreased by about 25 percent with respect to that of the free ion at 74°K when the cubic potential is so chosen as to give a separation of the $J=5/2$ levels of about 200 cm^{-1} which is of the order indicated by Spedding's work on the absorption spectrum of samarium compounds. The theoretical values of the susceptibility are then in satisfactory agreement with the experimental data of Freed over a temperature range from 74°K to room temperature. The rhombic portion of the field separates the lowest excited level into two but the contribution to the susceptibility is negligible if the rhombic separation is small compared with the cubic separation. In striking contrast with Sm^{+++}, Eu behaves like the free ion even in the presence of a crystalline field. The contribution to the heat capacity of Sm^{+++} at various temperatures due to the excited levels is computed. When the levels which give good agreement with susceptibility data are used, the general shape of the curve is the same as that obtained experimentally by Ahlberg and Freed but the theoretical values are consistently lower than the experimental values.

THE EFFECT OF CRYSTALLINE FIELDS ON Sm^{+++}

Introduction

Van Vleck[1] has pointed out in his treatment of the paramagnetic susceptibilities in the rare earth ions that Sm[2] and Eu are anomalous in that some of the consecutive multiplet intervals are only of the order of kT even though the overall multiplet widths are large. This makes it necessary to consider the populations of levels other than the ground state and also second order Zeeman terms. The theoretical values thus calculated were shown in a previous paper[3] to give good agreement with experimental data on liquids and solids over a wide temperature range even though the theory is for the free ion. This theory can be applied only when the distortion by interatomic forces is negligible, that is, the energy to "turn over" an ion against interatomic

[1] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Chapter IX.

[2] Here as well as throughout the rest of the paper, the three plus signs are omitted. Whenever the chemical symbol Sm or Eu appears, it stands for the triply charged samarium or europium ion.

[3] A. Frank, Phys. Rev. **39**, 119 (1932).