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Pressure Effects on Spectral Lines

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§1. CAUSES PRODUCING WIDTH AND DISPLACEMENT OF SPECTRAL LINES

IN the present paper we shall be concerned with intensity distributions in broadened spectral lines, and the symbol $I(\nu)$ will be used to denote such distributions. Its precise meaning should be stated at once: $I(\nu)d\nu$ is proportional to the intensity at frequencies between ν and $\nu+d\nu$ withdrawn from a light wave of uniform color distribution as it passes an infinitely thin sheet of absorbing atoms. Unless otherwise stated, the constant of proportionality will be so fixed that $\int_0^\infty I(\nu)d\nu=1$.

$I(\nu)$ is therefore an idealized quantity which is not given directly by experiment. It is not identical, for instance, with the intensity of absorption measured at frequency ν, unless the absorption is due to a very thin layer of atoms. But we shall see in §2 how $I(\nu)$ can be obtained from such empirical data.

$I(\nu)$ is proportional to the intensity of *emission* at frequency ν by a thin layer of atoms under similar conditions. By similar conditions is meant not only that the number and arrangement of atoms shall be the same, but also that the relative number of excited and unexcited atoms shall correspond to the state of equilibrium with radiation in the case of absorption. Since this condition is rarely realized in actual emission experiments, the results which will here be presented must not be applied thoughtlessly to the intensity distribution in emission lines. All theories here discussed share the assumption that the number of atoms in the excited state is so small that interactions between excited atoms may be neglected. This is not always true when electrical methods are used to excite radiation, and the situation is often further complicated by the permanent electric fields which are superposed upon the fields surrounding the moving atoms.

Whether the considerations in the present paper are applicable to emission will therefore have to be decided separately in each individual case. The criteria for applicability to emission are:

(1) The number of excited atoms must be small compared to the number of unexcited ones.
(2) The agency of excitation must act uniformly over a range of energies larger than the width of the line. Thus, for instance, if excitation is produced by irradiation with light, this light must have a uniform intensity distribution over the entire width of the fluorescent line.
(3) If external fields are present, they must be taken into proper account.

Theoretically we may, if we wish, think of $I(\nu)$ as the intensity taken out of the passing wave by a single absorbing atom. But as far as a single atom is concerned the intensity of absorption at ν is proportional to that of emission at ν if the atom were excited.[1] Hence in de-

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[1] This follows from the universal relation between Einstein's coefficients A and B.

scribing theoretically what happens to a single atom we are at liberty to apply either the point of view of absorption or that of emission, and we shall make use of this freedom whenever it is advantageous.

All frequencies used in the present paper are true, not angular frequencies, measured in sec.$^{-1}$.

A term frequently used is: "half-width" of the distribution. Because of existing ambiguity we define the meaning of half-width, $\Delta\nu_{\frac{1}{2}}$, here to be used. It is the entire frequency range in which $I(\nu)$ is larger than half its maximum. Thus, if $I(\nu)$ is symmetrical about its maximum $I(\nu_0)$,

$$I(\nu_0 \pm \tfrac{1}{2}\Delta\nu_{\frac{1}{2}}) = \tfrac{1}{2}I(\nu_0).$$

This is the meaning usually employed by experimental workers in this field.

To classify the various causes contributing to the width and shift of spectral lines is not an easy matter, nor is it entirely unambiguous. For the separate agencies interplay to an extent which makes their isolation difficult, and even the theories overlap in their conceptual structure, causing discrepancies between different investigators. In the present paper an attempt will be made at uniform formulation of the theory without too strict adherence to time-honored distinctions, and it will be shown how the various special theories, like impact broadening, resonance coupling, etc., fit into a more general scheme.

Those effects which are well understood and adequately treated in the literature will be discussed very briefly. A summary account of the work published up to 1932 is to be found in a review article by V. Weisskopf,[2] to which reference should be made for earlier papers not included in the present bibliography. As far as theories are concerned, the problem of line width often presents two aspects, one from the point of view of classical physics, and one from that of quantum mechanics. Wherever such a distinction can correctly be made, attention will be called to it as well as to the difference in the results to which the two points of view lead. Let us begin by outlining the various effects in question.

A. Radiation damping

The process of radiation damping is responsible for the fact that a spectral line emitted by an isolated atom is not infinitely sharp. Its classical mechanism is this: A vibrating, and hence radiating, electric charge continually loses energy and in consequence diminishes its amplitude of vibration, while maintaining its natural frequency ν_0. But a damped vibration of this kind is not monochromatic; its frequency distribution is found by making a Fourier analysis of the electric moment as a function of the time. This yields the result

$$I(\nu) = \frac{\gamma/2\pi}{(\nu_0-\nu)^2+(\gamma/2)^2}, \qquad (1)$$

where $\gamma = (4\pi/3)(e^2/mc^3)\nu_0^2$ sec.$^{-1}$,

m and e being, respectively, the mass and the charge of the vibrating particle. Formula (1) is obviously true both for emission and absorption since interactions between oscillators are here ignored. The constants are so adjusted that the total intensity $\int I(\nu)d\nu = 1$. In the case of absorption, this quantity is clearly proportional to the number of oscillators per unit volume, so that (1), also, must be multiplied by this number.

The half-width of the line, according to (1), is γ. If γ is expressed in terms of wave-lengths instead of frequencies it becomes independent of the wave-length of the line:

$$\gamma = (4\pi/3)(e^2/mc^2)\ \text{cm} = 1.17\times 10^{-4}\ \text{A}.$$

Experiment indicates, however, that different spectral lines have different widths on a wave-length scale. These classical considerations are therefore in need of revision.

In quantum mechanics the natural line width arises from the fact that each of the two energy levels E_1 and E_2, between which a transition occurs, is not indefinitely sharp but has a finite width ΔE_1 and ΔE_2, respectively. According to the work of Weisskopf and Wigner, and Hoyt[3] the intensity distribution within the line is then given by

$$I(\nu) = (\gamma/2\pi)/[(\nu_{21}-\nu)^2+(\gamma/2)^2] \qquad (2)$$

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[2] V. Weisskopf, Physik. Zeits. **34**, 1 (1933).

[3] V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 54 (1930); **65**, 18 (1931). F. Hoyt, Phys. Rev. **36**, 860 (1931).

which is formally identical with (1). ν_{21} is the Bohr frequency $(E_2-E_1)/h$. But the half-width γ has a different value. It is made up of the term widths of the two levels:

$$\gamma=\gamma_1+\gamma_2=\Delta E_1/h+\Delta E_2/h. \tag{3}$$

Each ΔE can be calculated from the principle of indeterminacy in the following way. If Δt_1 is the average time which the atom remains in the energy state E_1, then

$$\Delta E_1\cdot\Delta t_1\sim h/2\pi. \tag{4}$$

Now $1/\Delta t_1$ is the total number of spontaneous transitions which can occur per second when the atom is in state E_1. Let E_k be a lower energy state capable of combination with E_1. According to radiation theory the number of transitions taking place from E_1 to E_k per second is $(8\pi^2e^2/mc^3)\nu_{1k}{}^2f_{1k}$, ν_{1k} being the frequency and f_{1k} the "oscillator strength" corresponding to a passage from E_1 to E_k. Hence

$$\frac{1}{\Delta t_1}=\frac{8\pi^2e^2}{mc^3}\sum_k \nu_{1k}{}^2f_{1k},$$

the summation being extended over all energy levels lower than E_1. Thus, from (4),

$$\Delta E_1=\frac{4\pi e^2h}{mc^3}\sum_k \nu_{1k}{}^2f_{1k},$$

so that, because of (3)

$$\gamma=\frac{4\pi e^2}{mc^3}\left(\sum_k \nu_{1k}{}^2f_{1k}+\sum_l \nu_{2l}{}^2f_{2l}\right), \tag{5}$$

where every state l has an energy lower than E_2.

If the line in question is a resonance line the lower state is capable of no downward transitions, hence every $f_{1k}=0$. The second sum in (5) reduces to only one term, $\nu_{21}{}^2f_{21}$. For the D lines of Na, f_{21} has the value 1/3, so that in this case (2) and (5) reduce to the classical formulae (1). But in general γ will depend on the oscillator strength of the various possible transitions, and will not be the same on the wave-length scale for all spectral lines. For further details compare reference 2.

Although the quantum-mechanical explanation of natural line breadth makes no explicit use of the idea of damping, the term "radiation damping" is still applied to the present effect because of the similarity of the above results with those of the classical consideration.

B. Doppler effect

The thermal motion of the atoms of a gas will contribute to the diffuseness of a spectral line. Suppose that light from a continuous source of uniform intensity shines through the gas. If all atoms were at rest they would absorb a (nearly) sharp frequency ν_0. Atoms moving with speed v_x in the direction of propagation of the light will, by Doppler's principle, absorb a frequency

$$\nu=\nu_0(1-v_x/c). \tag{6}$$

The fractional number of such atoms within a range dv_x is

$$dn/n=(M/2\pi RT)^{\frac{1}{2}}e^{-(M/2RT)v_x{}^2}dv_x.$$

M is the molecular weight of the gas. This formula also represents the fraction of the total intensity which is absorbed at a frequency ν related to v_x by (6). Thus, if we express v_x in terms of ν, we obtain

$$I(\nu)=(Mc^2/2\pi RT\nu_0{}^2)^{\frac{1}{2}}e^{-(Mc^2/2RT\nu_0{}^2)(\nu-\nu_0)^2}. \tag{7}$$

It is thus seen that the Doppler effect causes the absorption (or emission) line to take on a Gauss distribution, whose half-width is easily seen to be

$$\Delta\nu_{\frac{1}{2}}=2(\log 2)^{\frac{1}{2}}(2RT/Mc^2)^{\frac{1}{2}}\nu_0 \tag{8}$$

or, on a wave-length scale,

$$\Delta\lambda_{\frac{1}{2}}=2(\log 2)^{\frac{1}{2}}(2RT/Mc^2)^{\frac{1}{2}}\lambda_0.$$

Thus, while the natural line width is approximately independent, on a wave-length scale, of the wave-length, the Doppler broadening diminishes as we pass to smaller wave-lengths. In the x-ray region the Doppler effect may indeed be neglected against the natural line width.

The two broadening effects become of equal magnitude at wave-lengths of about 100A. In the optical region the natural line width is therefore under ordinary conditions always masked by the Doppler effect. The distribution which results on combination of the two effects is in general complicated;* it is symmetrical about ν_0. In the wings of the spectral line, however, where $|\nu-\nu_0|$ is much greater than the Doppler half-width, the intensities still obey formula (2) and are unmodified by the Doppler effect, the reason being that (7) is a very close distribution which vanishes much more rapidly for large $|\nu-\nu_0|$ than does the dispersion curve (2). It is possible, therefore, to determine natural line widths in the optical region despite the interference due to the Doppler effect by making measurements in the extreme portions of the broadened line.

We now pass to the consideration of those causes of broadening which have their origin in the forces exerted upon the absorbing atom by its neighbors. While the former two effects were independent of the density of the gas in which absorption takes place, the remaining ones will depend strongly on the density.

C. Resonance between similar atoms

Let us first assume that the gas is monatomic and that its atoms are all of the same kind. The simplest classical description of the process of light absorption by such an assemblage would replace each atom by an oscillator with a single natural frequency ν_0 and then introduce a coupling force between all pairs of oscillators. The coupling force is that between two dipoles; it has the form

$$F_{ij}=\text{const.}/r_{ij}^4, \tag{9}$$

where r_{ij} is the distance between the ith and the jth oscillator. As a result of these interactions the entire assemblage of atoms will not have the single natural frequency ν_0, but a very great number of natural frequencies distributed around ν_0. If there were no thermal motion these frequencies would be discrete; actually they merge into a continuum and produce a broadened line. The breadth arising from this cause is often spoken of as due to coupling.

On somewhat closer inspection from the point of view of quantum mechanics the process presents a different aspect. The atoms of a gas, as long as they are in their normal states, have a symmetrical distribution of charge and do not interact as dipoles would. But, as will be shown in §4, forces of the type (9) are called into play between two similar atoms, one of which is excited. These forces result from a continual interchange of a light quantum between the two partners, i.e., from optical resonance. The situation is indeed more complicated than the simple picture of the foregoing paragraph would suggest. In view of the true origin of the coupling forces the line breadth now under discussion is sometimes referred to as resonance breadth. To avoid confusion we emphasize that there is no physical distinction between broadening due to resonance of similar atoms and broadening due to dipole coupling. Details will be worked out in §4 *et seq.*

D. Broadening due to forces of the van der Waals type

In many experiments an absorption line which would be sharp at very small gas pressures is distorted because the absorbing atom is under the influence of *foreign* atoms or molecules. For the present we shall suppose that the latter have spherical symmetry and hence carry no permanent poles. The presence of a foreign perturber will change the absorptive properties of the atom by altering the arrangement of its energy levels continually in time. In general the higher levels will be distorted more strongly than the normal one so that a net change in the energy differences will result. The interaction between the lowest state of the absorbing atom and a foreign perturber is described by introducing the well-known van der Waals force between neutral particles; that between higher energy states and an unexcited perturber can be described in a similar manner. The broadening effects which result from these forces give rise to interesting asymmetries in the spectral line and are experimentally capable of being traced to very high gas pressures. In discussing them in detail (cf. §§4, 8, 9) it will always be supposed that the number of foreign atoms or molecules surrounding the optically active atom is far greater than the number of neighbors of its own kind, so that resonance broadening can be neglected. In most experiments the broadening effects of this type are much greater than radiation damping and Doppler effect, so that these, also, may be ignored.

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* For discussion and references, see reference 2.

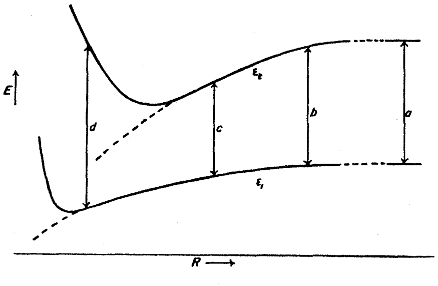

FIG. 1. Schematic trends of potential energy curves in van der Waals broadening.

A qualitative description[4] of the appearance of lines broadened by foreign gas pressures can be given in connection with Fig. 1, in which the energies of both the upper and the lower atomic states of the radiating atom (e.g., Na) are plotted (schematically) as functions of R, the distance of separation between the Na atom and a perturbing molecule. At present our interest is confined to the outer rising portions of these curves, since the inner portions are significant only for close encounters which are in general less probable than others. If all optical transitions took place at infinite separation, the line would be sharp and have the normal energy E, signified by the arrow a. But the average length of arrow is smaller than a; the mean frequency of the spectral line smaller than the normal frequency ν_0 so that the line should be shifted to the red. Moreover, the intensity within the line should lie predominantly to the red of ν_0 with but little intensity on the blue side, since transitions like d are rare.

All these features are exhibited in the microphotometer trace reproduced in Fig. 2. It represents the D_2 line, broadened in one case by 1.85 atmos., and in the other by 17.8 atmos. of argon pressure. Shift and asymmetry are clearly visible.

The main part of the present paper will be devoted to the effects C and D. But before entering upon a detailed discussion we must deal with another type of broadening.

E. Broadening by foreign perturbers carrying permanent fields

The fields in question may be due to ions, dipoles or multipoles. No complete theory of the broadening by such agencies is available. Debye[5] and Holtsmark[6] calculate the line width under the following simplifying assumptions:

(1) The broadening can be regarded as a displacement of the energy levels through a Stark effect.

(2) The effective field strength is that produced by all perturbers at the center of the radiating atom.

(3) The fields vary infinitely slowly compared with the time of emission or absorption.

Assumption (2) is questionable because the radiating electron is usually near the periphery of the atom, and the fields are very inhomogeneous. But a more detailed treatment would conjure up all the difficulties of the Stark effect in inhomogeneous fields. Assumption (3) is not serious when the density of perturbers is large and the line very broad.

The results of the theory have been subjected to quantitative experimental tests only for cases

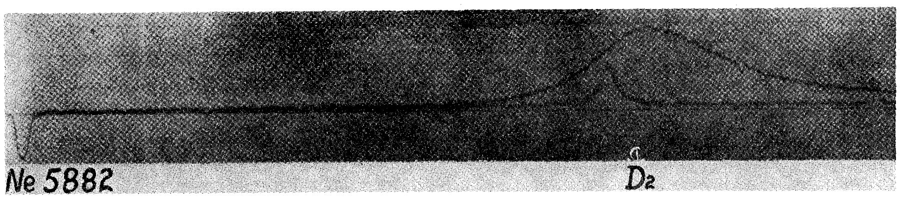

FIG. 2. Microphotometer traces of D_2 broadened by argon. *Small peak:* trace for an argon pressure of 1.85 atmos.; *large peak:* trace for a pressure of 17.8 atmos. Reference line (Ne, λ5881.896), exactly superposed on the two traces, appears on extreme left. (Lower trace is slightly out of focus in the reproduction.)

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[4] A. Jablonski, Zeits. f. Physik **70**, 723 (1931).

[5] P. Debye, Physik. Zeits. **20**, 160 (1919).

[6] J. Holtsmark, Ann. d. Physik **58**, 577 (1919); Physik. Zeits. **20**, 160 (1919); **25**, 73 (1924).

where the perturbers are ions.[7] Hence we shall limit our discussion to that case. Debye and Holtsmark have shown that the intensity distribution, which the latter author evaluates graphically, has a half-width

$$\Delta\nu_{\frac{1}{2}} = \text{const. } n_1^{\frac{2}{3}},$$

if n_1 is the number of perturbers per unit volume. The constant is related in a simple way to the width of the Stark pattern in a field of unit strength. Since we shall not return to the subject of broadening by ions, we review the experimental material relevant to it at once.

It has long been known that with spark discharges between metallic electrodes in a gas, most of the spectral lines both of the electrode material and of the gas are broadened, frequently with the center of gravity of the line shifted to the red, by intermolecular fields. Hydrogen atomic lines, as well as lines of other elements which show a first-order Stark effect, are broadened appreciably by interatomic fields even for relatively mild electrical excitation. Holtsmark and Trumpy[8] have investigated arc lines of Li, Ag, Cu and Ni which show a first-order Stark effect of known amount so that from the observed line breadths the magnitude of the mean intermolecular electric fields could be estimated. These field strengths were found to increase with arc current according to the $n^{\frac{2}{3}}$-law for ions, reaching 30,000 volts/cm for $i=17$ amperes. At this current strength the 4132A $3P-6D$ line of Li is over 8A broad.*

Interesting observations on the broadening of the Balmer lines of hydrogen by interatomic Stark effects have been made by Merton,[9] Hulburt,[10] and Finkelnburg.[11] Hulburt observed that with condensed discharges in hydrogen at 250 mm pressure the $H\beta$, $H\gamma$ and $H\delta$ lines are each broadened symmetrically for about 60A, the $H\beta$ line, however, showing the incipient division into two groups of Stark components. Finkelnburg, with capacity discharges between electrodes 1 mm apart in hydrogen at various pressures up to 30 atmos., finds as the pressure rises that the Balmer lines increase greatly in breadth, the lines nearer the beginning of the series becoming merged with the continuous background, until finally at 30 atmos. only $H\alpha$ remains as a broad intensity maximum in a continuous spectrum. At 2 atmos. the widths of the $H\alpha$, $H\beta$ and $H\gamma$ lines, the last two being reconstructed so as to have the same maximum intensity as $H\alpha$, are 550, 1680, and 2650 cm^{-1}, respectively, or almost exactly in the ratio 1 : 3 : 5. This rule, together with other facts, indicates definitely interatomic Stark effect to be the principal cause of the broadenings. If with pressure increase a line becomes so broad that it merges into the continuous spectrum, the corresponding upper state of the atom must be no longer sharply quantized. At 30 atmos. pressure, then, orbits with $n=3$ practically no longer exist.

Comparing his results with those of Rausch v. Traubenberg on the extinction of the higher members of the Balmer series with known high external electric fields, Finkelnburg concludes that at 1 atmos. the mean interatomic field must be 2×10^5 volts/cm. At 5 atmos. this mean field strength is about 5×10^5 volts/cm, while at 30 atmos. it is about 2×10^6 volts/cm. Since H_2 has no dipole moment, only ions and quadrupoles can produce these fields. The average interatomic field for 1 atmos. due to quadrupole moments is considerably less than 10^3 volts/cm, but at 100 percent ionization a mean field due to ions of 1.3×10^6 volts/cm is to be expected from the Debye and Holtsmark equations. The observed 2×10^5 volts/cm would thus indicate a 15 percent ionization in the path of the discharge. From the $n^{\frac{2}{3}}$-law of increase of field strength for ions, and assuming an equal degree of ionization at all pressures, at 30 atmos. the field strength should increase by a factor of $30^{\frac{2}{3}} \cong 10$, which again gives the 2×10^6 volts/cm estimate. The $H\beta$ line at 1 atmos. is observed to have an asymmetrical contour in agreement with the calculated lessened

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[7] Holtsmark, reference 6 explains the broadening of the $H\alpha$ line found by Michelson (Phil. Mag. **34**, 208 (1892)) as caused by the quadrupoles of the H_2 molecules, but the quadrupole moment assumed (3.2×10^{-26}) is not in agreement with the quantum-mechanical structure of the H_2 molecule, which leads to a much smaller value.

[8] J. Holtsmark and B. Trumpy, Zeits. f. Physik **31**, 803 (1925).

*A first-order Stark effect is shown only by terms with higher orbital quantum numbers, the valence electron being in a hydrogen-like orbit. Under usual excitation conditions lines involving such terms will always be somewhat broadened by intermolecular fields. Hence the name *diffuse* series, to which this Li line belongs.

[9] R. T. Merton, Proc. Roy. Soc. **A92**, 322 (1915).

[10] E. O. Hulburt, Phys. Rev. **22**, 24 (1923).

[11] W. Finkelnburg, Zeits. f. Physik **70**, 375 (1931).

intensity of the long wave-length components in the high field Stark pattern.

The reversal of the metallic lines in Finkelnburg's spectrograms results from the partial pressure of the metallic vapor. He demonstrates, however, that this partial pressure in the path of the discharge depends in turn upon the total pressure in the chamber.

Knauss and Bryan[12] have recently observed that the spectrum of a high current discharge through a narrow stream of Hg shows some of the lines to be as much as 100A broad, while others are merged entirely with the continuous background. Very strong interatomic fields must be responsible for these great line breadths.

The absorption spectra of solutions of Hg atoms in various solvents have been shown by Reichardt and Bonhoeffer[13] to give the 2537A line split into two broad components. This splitting is attributed to the action of strong interatomic electric fields. For Hg in H_2O, for example, they conclude from the size of the splitting that the effective mean field strength is 33×10^6 volts/cm, which is of the order of magnitude indicated by Finkelnburg's experiments for gas discharges at very high pressure.

§2. EXPERIMENTAL PROCEDURES FOR DETERMINING INTENSITY DISTRIBUTIONS

Before proceeding with the discussion of the several features of pressure broadening, we shall sketch very briefly the methods of determining experimentally the intensity distribution throughout the broadened spectral lines. The direct determination of this distribution may be made by the method of photographic photometry. If both the intensity of the source of continuous radiation and the sensitivity of the photographic plate do not vary sensibly with ν throughout the frequency interval considered, and if the strength of the absorption and the time of exposure are so adjusted as to cause all of the registration to be on the straight-line portion of the characteristic curve for the emulsion, the photometer trace yields directly the distribution $I(\nu)$ discussed in the previous section. For if $i(\nu)$ denotes the intensity of the transmitted light in general, i_0 that falling without absorption on the photographic plate and l the absorption path length,

$$i(\nu)=i_0 e^{-I(\nu)l}. \tag{1}$$

That is, $\log i = \text{const.} - I(\nu)l$, while for the photographic plate $\log i$ is proportional to the density D for the straight-line part of its characteristic curve. Therefore $D \propto -I(\nu)$.

In general, however, the photographic plate must be calibrated, the best method probably being to use a step filter having several steps of known transparency placed either directly in front of the slit of the spectrograph or in the plateholder just to one side of the absorption line. The first position requires equal illumination of the entire slit, a difficult problem with any of the usual sources of intense continuous radiation. The second position is therefore to be recommended, the steps of the filter lying parallel to and just far enough from the absorption line so that absorption is not interfered with. With the aid of the blackening marks so produced, the photometer trace may be readily transformed into a true absorption curve $I(\nu)$.

The ordinates of this curve are proportional to the quantity $n\kappa$, known as the index of absorption. The latter is defined by the equation

$$i(\nu)=i_0\cdot e^{-4\pi n\kappa l/\lambda}, \tag{2}$$

so that
$$n\kappa=(\lambda/4\pi l)\log(i_0/i). \tag{3}$$

The true index of absorption may thus be computed for each value of ν from the ratio i/i_0 if it is desired. For the purposes of many investigations, where interest is confined to the relative variation of the intensity across the broadened line, a knowledge of $I(\nu)$ is equivalent to that of $n\kappa(\nu)$.

To obtain the entire line contour the center of the absorption line must not show complete absorption. Trial exposures must usually be taken for each gas pressure in the absorption tube, adjusting the total absorption so that about 75 percent absorption is produced at the line maximum. The position of the absorption maximum is of course given directly by the photometer readings, for the transformation to the

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[12] H. P. Knauss and A. L. Bryan, Phys. Rev. **47**, 842 (1935).

[13] H. Reichardt and K. T. Bonhoeffer, Zeits. f. Physik **67**, 780 (1931).

true absorption curve does not shift the position of this maximum with respect to the readings for the standard lines.

A satisfactory simple numerical presentation of the amount of asymmetry in the pressure-broadened line is difficult. One can, for example, give the ratio of the area under the absorption curve on the high frequency side of the maximum to that on the low frequency side.[14] Or one can state the ratio of the red "half" to the blue "half" of the half-width of the line.[15] Obviously neither of these ratios gives much information as to the exact contour of the absorption line.

This direct method of determining the shift and asymmetry of pressure-broadened absorption lines has been employed by numerous investigators. For further details of experimental technique reference should be made especially to reports by Füchtbauer and his co-workers[16] and by Margenau and Watson.[17]

From the amount of the total absorption $\int_0^\infty (n\kappa)d\nu$, to be obtained by graphical integration of the $(n\kappa, \nu)$-curves, oscillator strengths and transition probabilities may be computed. For according to radiation theory the oscillator strength of the atoms involved is

$$f=\frac{4\nu m}{n_1 e^2}\int_0^\infty n\kappa d\nu,$$

while the transition probability A is

$$A=\frac{4\pi}{cn_1 h}\int_0^\infty n\kappa d\nu.$$

From such measurements it has been determined[18] that the oscillator strengths are approximately 1 for the resonance lines of the alkalis, while for the 2537A line of Hg the f value is but 1/35.[19] It has been found that the total absorption for this Hg line decreases with increasing pressure of foreign gas,[19] so that f becomes approximately 1/100 when the line is broadened by 36 atmospheres of CO_2 pressure, for example. The value 1/35 is computed by extrapolating to zero density of foreign gas. Trumpy[20] has observed by this method the exact manner in which the transition probabilities rapidly fall with increasing quantum number in the principal series of Na, and Waibel[21] has made similar measurements for the lines of the principal series of Cs.

Other less direct methods of measuring the half-widths and intensity distributions in spectral lines have been employed. In these methods some theoretical expression for the line contour is assumed, with unknown constants to be determined from the measurements of the total absorption. Ladenburg and Levy,[22] for example, consider the case where the light source does not give a continuous spectrum but is a column of excited gas which also absorbs the line in question. These authors give the details of the dependence of the absorption on the constants for Doppler and dispersion distributions. Also, measurement of the rotation of the plane of polarization at and near the spectral line in magneto-optic experiments may be made to yield the f values and estimates of the line breadth.[23] The relation between the line breadth and the rotation of the plane of polarization depends, however, on the nature of the assumed expression for the intensity distribution in the line.

§3. General Method of Calculating Intensity Distributions when Perturbations Depend on Time

The effects outlined in §1 C, D, and E present a common feature: the frequency of the emitting atom is disturbed by external influences, and these influences vary with the time. The classical manner of dealing with this situation is obvious. The active atom is replaced by an oscillator of natural frequency ν_0. Under the action of its

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[14] C. Füchtbauer and F. Gössler, Zeits. f. Physik **87**, 89 (1933).

[15] H. Margenau and W. W. Watson, Phys. Rev. **44**, 92 (1933).

[16] C. Füchtbauer and W. Hofmann, Ann. d. Physik **43**, 96 (1914); C. Füchtbauer, G. Joos and O. Dinkelacker, Ann. d. Physik **71**, 204 (1923); C. Füchtbauer and H. Meier, Physik. Zeits. **27**, 853 (1926).

[17] Cf. 15; also W. Watson and H. Margenau, Phys. Rev. **44**, 748 (1933).

[18] Füchtbauer and Hofmann, reference 16.

[19] Füchtbauer, Joos and Dinkelacker, reference 16; B. Trumpy, Zeits. f. Physik **40**, 594 (1926).

[20] B. Trumpy, Zeits. f. Physik **34**, 715 (1925).

[21] F. Waibel, Zeits. f. Physik **53**, 459 (1929).

[22] R. Ladenburg and S. Levy, Zeits. f. Physik **65**, 189 (1930).

[23] Cf. for example R. Minkowski, Zeits. f. Physik **23**, 69 (1922); W. Schütz, Zeits. f. Physik **45**, 30 (1927).

moving neighbors this frequency is modified into $\nu=\nu_0+\Delta\nu(t)$. The amplitude of vibration will also in general be affected by the perturbations and become a function of the time $A(t)$. Hence the electric moment at any instant t will be, if written in complex form,

$$M=A(t)\exp\left[2\pi i\int_0^t\nu(\tau)d\tau\right]. \tag{1}$$

We find the amplitude $J(\nu')$ corresponding to the frequency ν' by developing (1) in a Fourier integral

$$M(t)=\int_{-\infty}^{\infty}J(\nu')e^{2\pi i\nu't}d\nu'. \tag{2}$$

The amplitude is then given by

$$J(\nu')=\int_{-\infty}^{\infty}M(t)e^{-2\pi i\nu't}dt.. \tag{3}$$

This is, in view of (1),

$$J(\nu')=\int_{-\infty}^{\infty}A(t)\exp\left\{2\pi i\left[\int_0^t\nu(\tau)d\tau-\nu't\right]\right\}dt. \tag{4}$$

The intensity at frequency ν' finally is related to the amplitude by

$$I(\nu')=|J(\nu')|^2. \tag{5}$$

The exact way in which the amplitude of the oscillator A depends on the time is difficult to calculate. It is customary to assume A to be constant within a certain interval of time and to vanish outside this interval.

Although the treatment of the problem from the quantum-mechanical point of view is necessarily different, Lenz[24] has pointed out as early as 1924 that the final results must be the same because of the correspondence principle.

Weisskopf has shown[25] that formulae (4) and (5) are valid in quantum mechanics under certain simplifying conditions. His proof involves the use of the Kramers-Wentzel-Brillouin approximation. It is possible to establish (4) and (5) without applying this method. In the following we give a simple proof which assumes that the perturbation affects only the *energy* of the emitting atom, but not the charge distribution.* In classical terms this is equivalent to assuming constancy of the amplitude of oscillation A.

The act of emission of a photon may be regarded as the measurement of the energy of the atom in the excited state provided the energy of the lower state is known. The number of photons emitted with frequency ν', i.e., $I(\nu')$ is therefore proportional to the probability that the excited state shall have an energy $E'=h\nu'$ greater than the lower state whose energy we shall take to be 0. This probability is found by expanding the state function for the excited state in terms of pure energy functions and then picking the coefficient belonging to the energy E'. Its square will be the probability, and hence the intensity sought.

If the atom is in a pure energy state with energy E', its Ψ-function is

$$\Psi=\psi(q)e^{2\pi i(E'/h)t}. \tag{6}$$

q denotes space coordinates and E' is independent of t. Let us now assume that at $t=0$ a perturbation $\epsilon(t)$ sets in. The state function will then develop according to Schrödinger's equation

$$(h/2\pi i)(d/dt)\Psi=\epsilon(t)\Psi,$$

which has the solution

$$\psi(q)\exp\left[(2\pi i/h)\int_0^t\epsilon(\tau)d\tau\right]. \tag{7}$$

This expression must be expanded in functions like (6), that is, we must perform a Fourier analysis of (7). If we put $E'/h=\nu'$ and $\epsilon/h=\nu$, the probability amplitude becomes

$$a(\nu')=\int_{-\infty}^{\infty}\exp\left\{2\pi i\left[\int_0^t\nu(\tau)d\tau-\nu't\right]\right\}dt,$$

and this is proportional to $J(\nu')$ in (4) if $A(t)$ is considered constant. Under this condition, then, the classical method of computing intensity distributions is correct provided we replace the classical frequency $\nu(t)$ by $\epsilon(t)/h$, where ϵ is the perturbed energy as a function of the time. If the energy of the lower state also varies in time, $\epsilon(t)$ must be interpreted as the energy difference between the upper and lower state, as an inspection of the preceding argument will show.

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[24] W. Lenz, Zeits. f. Physik **25**, 299 (1924).

[25] V. Weisskopf, Zeits. f. Physik **75**, 287 (1932).

* More precisely: the matrix elements between the various atomic states are not appreciably altered.

We are thus confronted with the question of how to determine ϵ. It will depend on the space configuration of all gas atoms, and, through their motions, on the time. The next two sections will deal with the principal energy perturbations responsible for the widths of spectral lines. As a matter of nomenclature, let us write

$$\epsilon = E_2 - E_1 + \Delta\epsilon_2 - \Delta\epsilon_1, \qquad (8)$$

where E_2 and E_1 are the normal energies of the upper and lower states, respectively, $\Delta\epsilon_2$ and $\Delta\epsilon_1$ the perturbations produced in these energies by neighboring atoms. Correspondingly, we have

$$\nu = \nu_0 + \Delta\nu, \qquad (9)$$

where

$$\nu_0 = (1/h)(E_2 - E_1), \quad \text{and} \quad \Delta\nu = (1/h)(\Delta\epsilon_2 - \Delta\epsilon_1).$$

§4. VAN DER WAALS INTERACTIONS

We first turn to the problem of broadening by foreign gases, where the coupling between atoms is chiefly due to forces of the van der Waals type. Their quantum-mechanical significance has first been investigated by F. London[26] who has also derived formulas for calculating them. The two quantities to be determined are $\Delta\epsilon_1$ and $\Delta\epsilon_2$. The first of these is the additional energy possessed by the normal state of the radiating atom due to the presence of all perturbers, the second the additional energy of the excited state due to this cause. We consider at present only $\Delta\epsilon_1'$ and $\Delta\epsilon_2'$, the added energies resulting from the presence of a *single* perturber.

London's formula for the perturbation energy between one atom in state k and another (different) atom in state l is

$$\Delta\epsilon_{kl}' = -\frac{1}{R^6}\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4 \sum_{k'l'} \frac{f_{kk'}g_{ll'}}{(E_{k'}-E_k)(F_{l'}-F_l)(E_{k'}+F_{l'}-E_k-F_l)} + S. \qquad (1)$$

R is the distance between the two atoms; $f_{kk'}$ is the oscillator strength corresponding to the transition $k \rightarrow k'$ for the first atom, $g_{ll'}$ for the second. The E's and F's are the energies of the various states for the two atoms, respectively. States for which $k' = k$, or $l' = l$ must be excluded from the sum. The term containing the summation is the first one of an expansion of $\Delta\epsilon_{kl}'$ in descending powers of R^2, the remainder, S, therefore starts with const./R^8.

$\Delta\epsilon_1'$ is given by (1) if we let k refer to the ground state of the radiating atom, l to the ground state of the perturber. Since then every $E_{k'} > E_k$, and every $F_{l'} > F_l$, the term proportional to R^{-6} is certainly negative. The energy of the ground-state is therefore lowered at R values for which S may be neglected.

In discussing $\Delta\epsilon_2'$ we shall suppose the radiating atom to be in an excited P state. Most experiments on line broadening have been performed on resonance lines or on higher members of the principal series, hence this assumption seems in order. $\Delta\epsilon_2'$ is then not exactly given by formula (1) if we let k be this P state and l the ground state of the perturber; but (1) represents the average over all orientations of the excited atom. The instantaneous interaction energy depends on the magnetic quantum number of the P state,[27] and may in fact be of opposite sign for different values of this quantum number. The forces are therefore not strictly central forces, nor are they to be classed as polarization forces. To simplify matters we shall ignore this difficulty and use (1) for computing $\Delta\epsilon_2'$. As a matter of fact, we are thereby ignoring a possible cause of broadening, since we are replacing the multiplicity of $\Delta\epsilon_2'$ by a sharp average. But neither experiment nor theory is at present refined enough to warrant an investigation of these details.

$\Delta\epsilon_2'$ is not necessarily negative. To be sure, $f_{kk'}$ has always the same sign as the corresponding energy difference $E_{k'} - E_k$; hence the sign of $\Delta\epsilon_2'$ (with neglect of S) depends on the various values of $(E_{k'} - E_k + F_{l'} - F_l)$. If they are preponderantly positive, $\Delta\epsilon_2'$ will be negative. In general this will be the case, for there is only one transition which causes a negative $E_{k'} - E_k$ (namely, if k' denotes the normal state) and all $F_{l'} - F_l > 0$. Thus if the radiating atom is an alkali and the perturber a rare gas, the only

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[26] F. London, Zeits. f. Physik **63**, 245 (1930); Zeits. f. physik. Chemie **B11**, 222 (1930).

[27] H. Margenau, Phys. Rev. **40**, 392 (1932), has given the formulae for individual m values.

negative $E_{k'}-E_k$ amounts to 2 or 3 volts, while the smallest $F_{l'}-F_l$ is of the order of 10 volts (transition from normal ground state to lowest excited state). This situation is quite general when the radiating atom is a metal and the perturber a gas.

There are instances, however, where $\Delta\epsilon_2'>0$. The example of an excited sodium atom interacting with a normal K atom is a case in point,[27] for here the dominant term in the summation of (1) is the one associated with the two resonance transitions, and this is positive.[28] For this reason, ϵ (cf. $3\cdot 8$)* is greater than E_2-E_1, and the spectral line (D line) should suffer a displacement toward the blue. But experiments to verify this have not been performed. In general the shift is to the red, for it turns out that in most cases $-\Delta\epsilon_2'>-\Delta\epsilon_1'$.

For purposes of calculation formula (1) can often be simplified. Suppose, for instance, that the broadening substance is a rare gas. The energy differences $F_{l'}-F_l$ will then be grouped around the ionization energy, the smallest being the energy of resonance which is comparatively great for rare gases. The largest energy difference is of course infinite, for we must not exclude transitions to the continuous spectrum from the summation in (1); but the f values for these transitions fall rapidly beyond the ionization limit. An estimate of $\Delta\epsilon'$ can therefore be obtained by replacing all terms $F_{l'}-F_l$ by some mean energy difference $\bar{F}$ and taking this to be the ionization energy. If in this procedure we make use of a well-known formula for the polarizability α, the summation over l' can be eliminated from (1), and there results[29]

$$\Delta\epsilon'=-\frac{1}{R^6}\frac{3}{2m}\left(\frac{he}{2\pi}\right)^2\alpha\bar{F}\sum_{k'}\frac{f_{kk'}}{(E_{k'}-E_k)(\bar{F}+E_{k'}-E_k)}+S. \tag{2}$$

α and F refer, of course, to the gas. This formula is useful when the f values for the strongest lines of the radiating atom are known. For gases other than the noble ones, where there is a greater spread in the values of $F_{l'}-F_l$, its validity is very questionable, but it may still be used to determine the order of magnitude of the effects.

Numerical computations on the basis of (2),[27] while subject to the uncertainties just mentioned, show that $|\Delta\epsilon_2'|>|\Delta\epsilon_1'|$ again with the neglect of S; but $\Delta\epsilon_1'$ is not negligible compared with $\Delta\epsilon_2'$. The order of magnitude of these energies amounts to a few millivolts at distances of separation around 5A.

Next we should consider the role played by S. The first term in (1) represents the dipole-dipole interaction between the charge distributions of the two atoms in question. S contains the effects of the higher poles.[30] S is negligible when the extent of the charge distribution is considerably smaller than the distance between the atoms. Roughly speaking S will become appreciable at R values smaller than $\sim$10A in the case of $\Delta\epsilon_2'$, for $\Delta\epsilon_1'$ it may be neglected to somewhat smaller distances. The general effect of S will be to make $\Delta\epsilon'$ lower, i.e., to increase the force of attraction. At distances of separation $\sim$5A, formula (1) loses its validity altogether, for then exchange forces of the valence type set in and cause either strong repulsion or (in cases uninteresting from the point of view of this article since no atomic line could be radiated) chemical coalescence. In what follows, the effect of S will be considered only in a qualitative way.

So far we have considered interactions between two individuals, $\Delta\epsilon'$. What we wish to deal with is an assembly consisting of one radiating atom and a great number of perturbers. The transition here is simple, for the forces expressed in formula (1) possess the important property of additivity.[29] Hence $\Delta\epsilon=\sum\Delta\epsilon'$, where the sum is taken over all perturbers. With this understanding, and with neglect of S, ($3\cdot 8$) and ($3\cdot 9$) may be written

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[28] Because $E_{k'}-E_k\sim-2.1$ volts for Na, $F_{l'}-F_l\sim+1.6$ volts for K.

* In references to equations of preceding sections the first number indicates the section.

[29] Cf. F. London, Zeits. f. physik Chemie **B11**, 222 (1930).

[30] These are present even if there are no permanent poles!

$$\epsilon = E_2 - E_1 + a\sum_i (1/R_i^6) \tag{3}$$

and

$$\nu = \nu_0 + b\sum_i (1/R_i^6), \tag{4}$$

where the sum extends over all perturbers; a is the difference of the coefficients of $1/R^6$ in (1) for the excited and the normal state of the radiating atom, and $b = a/h$. b is in general negative; its order of magnitude is 10^{-32} or 10^{-31} cm^6 sec.$^{-1}$.

§5. Resonance Interactions

Let us again begin by considering the energy perturbation which takes place when only two atoms are present. $\Delta\epsilon_1'$, which, as in the last §, refers to the added energy when both atoms are in the normal state, is of the van der Waals type. The van der Waals forces in the case of metallic atoms are large; but even so they are small compared to the resonance forces which appear in $\Delta\epsilon_2'$. We shall therefore neglect $\Delta\epsilon_1$ altogether. This is proper as long as we are dealing with large distances of separation (small pressures), for the resonance perturbation energies are proportional to $1/R^3$, while $\Delta\epsilon_1 \sim 1/R^6$.

$\Delta\epsilon_2'$ depends on the orientation of the atoms, that is, on the magnetic quantum number m of the excited one. In fact we have

$$\Delta\epsilon_2' = \gamma(e^2hf_{12}/8\pi^2m\nu_0)(1/R^3), \tag{1}$$

where the numerical factor γ takes the value -2 if $m=0$, $+1$ if $m=\pm 1$.[*] f_{12} is the f value corresponding to the transition from the normal to the excited state, ν_0 the frequency of the spectral line.

To derive (1) we proceed as follows. If one of the two atoms is in the excited state ψ' and one in the normal state ψ the combined state is a superposition of the two functions

$$\psi_1 = \psi'(1)\psi(2) \quad \text{and} \quad \psi_2 = \psi(1)\psi'(2),$$

since we do not know which of the two atoms is excited. Hence the total unperturbed state function is

$$\Psi = c_1\psi_1 + c_2\psi_2, \tag{2}$$

with two possible values for c_1 and c_2, respectively. The perturbing energy is

$$V = -(e^2/R^3)(2z_1z_2 - x_1x_2 - y_1y_2) \tag{3}$$

where x_1 is the coordinate of the electron in atom 1, measured from its nucleus, and x_2 the electron coordinate in atom 2, etc. Let V_{12} be the matrix element of (3) between ψ_1 and ψ_2. Its value is easily seen to be

$$V_{12} = V_{21} = \begin{cases} -\frac{2}{3}(e^2/R^3)|r_{12}|^2 & \text{if } m=0, \\ +\frac{1}{3}(e^2/R^3)|r_{12}|^2 & \text{if } m=\pm 1, \end{cases} \tag{4}$$
$$V_{11} = V_{22} = 0.$$

r_{12} is the radial matrix element between the normal and the excited state. According to well-known rules, the perturbed energy $\Delta\epsilon_2'$ (for which we shall write Δ for the moment) is found by solving the set of equations

$$\sum_i c_j(V_{kj} - \delta_{kj}\Delta) = 0 \tag{5}$$

and this leads to

$$\begin{vmatrix} -\Delta & V_{12} \\ V_{12} & -\Delta \end{vmatrix} = 0. \tag{6}$$

Hence

$$\Delta = \pm V_{12}. \tag{7}$$

On substituting this value back into (5) we get the two sets of c's:

$$c_1 = c_2 \quad \text{and} \quad c_1 = -c_2, \tag{8}$$

showing that the combination (2) is either symmetrical or antisymmetrical. But the state (2) must be capable of optical combination (by dipole radiation) with the state in which no atom is excited, namely, $\Psi_0 = \psi(1)\psi(2)$.

If we compute the transition probabilities from Ψ_0 to the two states Ψ, we find that the transition probability to the antisymmetrical Ψ vanishes. The second possibility in (8) is therefore excluded, and there remains only

$$\Delta\epsilon_2' = +V_{12}. \tag{9}$$

Substitution of (4) into (9) leads to formula (1) if we remember that

$$|r_{12}|^2 = (3h/8\pi^2m\nu_0)f_{12}.$$

The interaction energy can have both signs, the choice depending on the value of m (not on the two possible solutions of (6)). The average over-all values of m is 0. The classical interpretation of this fact is that $\Delta\epsilon_2'$ is, on the average, just as often positive as negative. In fact one may show that, if one desires to use classical methods of averaging over angles, $\Delta\epsilon_2'$ is equal to $e^2hf_{12}/8\pi^2m\nu_0R^3$ times an angular function whose maximum value is 1 and which has a mean value 0. Eq. (1) can therefore be correctly interpreted as the analog for the classical interaction of two permanent dipoles of equal moments $\mu = (e^2hf_{12}/8\pi^2m\nu_0)^{\frac{1}{2}}$. But this analogy breaks down when the number of partners in the interaction is greater than two. The forces represented by Eq. (1) are not additive.

To see this we repeat the procedure leading to (1). Suppose there are n atoms, one of which is excited. We then have n functions

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[*] Symbol m, occurring in formulas such as (1), refers of course to the electron mass.

$$\psi_1=\psi'(1)\psi(2)\cdots\psi(n),$$
$$\psi_2=\psi(1)\psi'(2)\cdots\psi(n),$$
$$\cdots\cdots\cdots$$
$$\psi_n=\psi(1)\psi(2)\cdots\psi'(n)$$

and n linear combinations of the type

$$\Psi=c_1\psi_1+c_2\psi_2+\cdots+c_n\psi_n$$

in place of (2). V is now more complicated; it involves the angles between the various radii vectors connecting the atoms. Instead of (2) we now have the secular equation

$$\begin{vmatrix} V_{11}-\Delta & V_{12} & \cdots V_{1n} \\ V_{21} & V_{22}-\Delta & \cdots V_{2n} \\ \cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot \\ V_{n1} & V_{n2} & \cdots V_{nn}-\Delta \end{vmatrix}=0. \qquad (10)$$

The solutions Δ of this equation are irrational functions of the V_{ij}. This means that they cannot be composed additively from the V_{ij}. When (10) is solved, the n sets of coefficients c must be determined by substitution in (5). Each set must then be assigned a weight proportional to the strength of combination with the unexcited state $\Psi_0=\psi_1(1)\psi(2)\cdots\psi(n)$, and this is also the weight of the corresponding Δ. Only the antisymmetrical state will have a 0-weight. We thus obtain a weighted distribution of eigenvalues Δ which is not in general symmetrical about $\Delta=0$. Each eigenvalue Δ, finally, is capable of assuming three different values because of the three possibilities for m.

Our aim has been merely to sketch the method and to point out the difficulties involved. The problem has not been solved, although various attempts have been made.[31] These have already been discussed by Weisskopf[2] who points out that the assumption of an error curve for the distribution of the solutions Δ of Eq. (10) is misleading. The solution of (10) is clearly impossible if n is large. But the sum of the Δ's can be shown to be 0. From this circumstance Holtsmark and Frenkel conclude that the distribution of Δ's is symmetrical about $\Delta=0$. This is true, of course, but it allows no inference regarding the distribution of frequencies within the broadened line, since the Δ's are not of equal weight.

For these reasons we shall apply the theory of resonance coupling only to cases of line broadening in which the simultaneous action of several perturbers may be ignored, so that we may content ourselves with the use of Eq. (1). This is proper at small pressures if attention is confined to the wings of the line.[32] Under these simplifying conditions ($\Delta\epsilon_2=\Delta\epsilon_2'$, $\Delta\epsilon_1=0$) we may write, in view of (3·9) and (1),

$$\nu=\nu_0\pm B/R^3, \quad \text{where } B=e^2f_{12}/8\pi^2m\nu_0. \qquad (11)$$

The factor γ has here been replaced by ± 1, its "classical value."

§6. True Distribution *vs.* Statistical Distribution; Velocity Broadening.

The true intensity distribution, which is given by (3·4, 5), presents a noteworthy feature. Suppose that $\nu(\tau)$, the actual frequency absorbed or emitted, lies always in a certain range Δ. $I(\nu')$ will then not vanish in general if ν' lies outside Δ, because the Fourier analysis produces finite intensities even for frequencies which the vibrating system has never possessed. The spectral line will therefore contain frequencies ν corresponding to energies $\epsilon=h\nu$ which have never occurred as perturbation values.

This fact is most simply explained by an idea due to Oldenberg[33] who points out the possibility of conversion of kinetic energy into radiation and *vice versa*. Thus let us suppose that the configuration of perturbers is such as to produce a given ϵ-value. If we visualize the act of absorption as an instantaneous process and imagine all atoms to retain their state of motion, the only frequency which can be absorbed is ϵ/h, and the line would be sharp. The atoms may, however, lose or gain kinetic energy during the optical process, so that the frequency may be either greater or smaller than ϵ/h. Since the atom concerned—and it is plausible to suppose that the exchange takes place during a single encounter—can at most lose its thermal energy and is not likely to gain more, we expect the diffuseness of the spectral line due to this cause to be of the order of kT/h. It should be small for slowly moving atoms.

From this point of view one may regard the true intensity distribution as decomposable into two distributions.* The first is that arising from the actual presence of modified frequencies corresponding to perturbation values which the configuration of atoms has produced in the course of its motion. This distribution can be calculated by the methods of statistical mechanics and will be called the *statistical* frequency distribution. Superimposed upon this will be found the diffuseness arising from the exchange

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[31] J. Holtsmark, Zeits. f. Physik **34**, 722 (1925); J. Frenkel, Zeits. f. Physik **59**, 198 (1930); L. Mensing, Zeits. f. Physik **61**, 655 (1930).

[32] In the wings of the line the frequency shifts, being large, are caused by close encounters. For close encounters the probability of binary or higher order impacts is small.

[33] O. Oldenberg, Zeits. f. Physik **47**, 184 (1928); **51**, 605 (1928).

* Compare also reference 2.

of energy just discussed. For some purposes this may conveniently be regarded as a second distribution. We shall refer to it as "velocity broadening distribution"[34] because, as we have seen, it results from the fact that the atoms may gain or lose velocity during the act of radiation. Its more precise definition will be given shortly. The true distribution (3·4, 5) comprises both of these.

It may seem somewhat surprising that the argument which we have used in §3 to establish the true distribution, making use of a single radiating atom, should yield the velocity distribution correctly. The reason is that we have not really limited ourselves to the consideration of a single atom, for we implied, by letting ϵ be a function of the time, that the system in question is an open one whose energy is not conserved. Exchanges of energy have thus been permitted, and the effects assumed by Oldenberg figure implicitly in the result.

We shall now investigate the relation between true, statistical and velocity distributions in greater detail, following somewhat the outline of a previous paper.[35] If we combined (3.4) and (3.5) we obtain for the true distribution ($A(t)$ will be taken to be constant = 1)

$$I(\nu')=\int\int dt_1dt_2 \exp\{2\pi i[\textstyle\int_0^{t_1}\nu(\tau)d\tau-\int_0^{t_2}\nu(\tau)d\tau+\nu'(t_2-t_1)]\}. \tag{1}$$

The two integrations for which no limits are stated extend over the entire time during which the process of radiation occurs, which will for the present be regarded as infinite. If we substitute for t_2-t_1 the variable x we may write (1):

$$I(\nu')=\int dt_1\int dx \exp\{2\pi i[\nu'x-\textstyle\int_0^x\nu(\tau)d\tau]\}. \tag{2}$$

Let us now make a Taylor expansion of the integral in the exponent.

$$\begin{aligned}\int_0^x \nu(\tau)d\tau&=\nu_{x=0}\cdot x+\dot{\nu}_{x=0}\cdot x^2/2+\cdots\\&=\nu(t_1)x+\dot{\nu}(t_1)x^2/2+\cdots.\end{aligned} \tag{3}$$

The dots denote time derivatives. If the molecules of the gas moved with extreme slowness all terms but the first could be neglected in this expansion. In that case (2) would read

$$\begin{aligned}I(\nu')&=\int dt_1\int dx \exp\{2\pi i[\nu'-\nu(t_1)]x\}\\&=\lim_{a\to\infty}\int dt_1\cdot\frac{\sin 2\pi a[\nu'-\nu(t_1)]}{\pi[\nu'-\nu(t_1)]}.\end{aligned} \tag{4}$$

But what is the meaning of dt_1? It is the interval of time during which the frequency of radiation is $\nu(t_1)$. In other words, $dt_1=I_s(\nu)d\nu$, where we have written $I_s(\nu)$ for the statistical frequency distribution defined previously. With this substitution, (4) goes into

$$I(\nu')=\lim_{a\to\infty}\int I_s(\nu)\frac{\sin 2\pi a(\nu'-\nu)}{\pi(\nu'-\nu)}d\nu=I_s(\nu'). \tag{5}$$

We see, therefore, that the statistical distribution is the limiting form of the true distribution for very small velocities, and hence low temperatures. Conversely, we may say that the velocity broadening distribution, the incorporation of which into I_s produces the true distribution, must become negligible for very small velocities.[36]

The general way in which I_s must be modified at higher temperatures can also be determined by inspecting (2). The integral over x in this expression is a function of ν' and $\nu(t_1)$, say $F(\nu', \nu)$. Hence, in view of what has been said about dt_1, (2) takes the form

$$I(\nu')=\int I_s(\nu)F(\nu', \nu)d\nu. \tag{6}$$

The function F in this expression is the velocity broadening distribution; its only rigorous definition is by means of this integral. An exact evaluation of $F(\nu', \nu)$ on a theoretical basis has

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[34] The use of the term "impact distribution" which might seem more appropriate, is preempted, for it is almost universally applied to a special type also known as Lorentz distribution (cf. §7).

[35] H. Margenau, Phys. Rev. **48**, 755 (1935).

[36] In this connection compare also H. Kuhn and F. London, Phil. Mag. **18**, 983 (1934).

not been carried through and is not likely to succeed because of the difficulties in determining $\int_0^x \nu(\tau)d\tau$ in (2). The quantity $\nu(\tau)$ in this integral represents the instantaneous perturbation (on a frequency scale) due to all atoms. One may show, however, that the function $F(\nu', \nu)$ is symmetrical with respect to ν', and hence that impacts produce a symmetrical spreading of the frequencies at every ordinate of the I_s curve; but this spreading is not the same for all ordinates. In the next sections we shall discuss a few practical approximative methods of dealing with the F distribution in specific cases of broadening.

Some further insight into the factors on which $F(\nu', \nu)$ depends may be gained by utilizing the first two terms of the expansion (3). We then find after simple calculation for the real part of $F(\nu', \nu)$ (the imaginary part is of no importance, for it must vanish in the integration over dt_1, a real quantity, in (2))

$$\Re F(\nu', \nu)$$

$$= \left(\frac{1}{2|\nu|}\right)^{\frac{1}{2}} \left[\cos\frac{\pi(\nu'-\nu)^2}{|\dot{\nu}|} + \sin\frac{\pi(\nu'-\nu)^2}{|\dot{\nu}|}\right]. \quad (7)$$

$|\dot{\nu}|$ will in general be a function of ν. A crude idea of the width of $F(\nu', \nu)$ can be obtained by supposing $|\dot{\nu}|$ to be independent of ν over the range in which F is appreciable. The function (7) is plotted in Fig. 3. Its width $w \approx 2(|\dot{\nu}|/\pi)^{\frac{1}{2}}$. The negative portions of F are of course meaningless, if we think of the function as an actual intensity distribution, yet they are present. This feature shows that the decomposition of $I(\nu')$ into I_s and F, which has been made, is possible only in a formal way, as indicated by Eq. (6), and that F gains physical meaning only if combined properly with some statistical distribution. Nevertheless the two aspects of statistical broadening and velocity broadening are so suggestive that the distinction may well be retained.

The width of the F distribution, as we have seen, is about $|\dot{\nu}|^{\frac{1}{2}}$. Since we have assumed $|\dot{\nu}|$ to be constant, this quantity must refer to some average value which is by no means uniquely defined. This average will increase, however, if the number of impacts increases. We may conclude, therefore, that the width of the impact distribution will grow in some way with the density of the gas. Furthermore, since $\dot{\nu}$ during a single impact is $(\partial\nu/\partial r)v_i \cos(v_i, r)$ we see that $|\dot{\nu}|^{\frac{1}{2}}$ is approximately proportional to the square root of the speed of the molecules, although the terms in (3) which have been neglected may well produce proportionality to a power of v somewhat greater than 1/2.

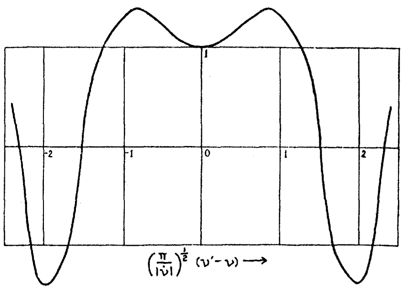

FIG. 3. Graph of the function (7).

The foregoing considerations of a fundamental nature, while not readily adaptable to practical purposes of calculation, are helpful in gaining a correct perspective and in judging the validity of simpler calculations. In order to turn them to useful account we must start with far simpler initial hypotheses. Lenz[37] has evaluated expression (1) with some rigor. His results are interesting, but claim validity only for a small range of pressures because of the complexity of the calculation. The usual procedure is to do violence either to I_s,[38] or to F.[39] In the first group of papers, the calculations involve the simplifying assumption that the statistical distribution is negligible, i.e., that $I_s(\nu)$ may be regarded as 0 for every ν except in a very small range where it is large; in the latter group $F(\nu', \nu)$ is taken to be 0 unless $\nu = \nu'$. The details will be discussed in simple terms in the next section. As to terminology, we remark that theories of the first type are usually classified as impact theories; for the latter we propose to use the term statistical theories. Neither can be complete by itself. The

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[37] W. Lenz, Zeits. f. Physik **80**, 423 (1933).

[38] H. A. Lorentz, Proc. Amst. Acad. **8**, 591 (1906); V. Weisskopf, Zeits. f. Physik **75**, 287 (1932); H. Kallmann and F. London, Zeits. f. physik Chemie **B2**, 207 (1929).

[39] H. Margenau, Phys. Rev. **40**, 387 (1932); **43**, 129 (1933); **44**, 931 (1933); M. Kulp, Zeits. f. Physik **79**, 495 (1932); **87**, 245 (1933).

difference between them is one of method rather than substance, although it is sometimes erroneously supposed that impact theories describe a type of broadening physically different from others. All interactions produce both statistical and impact broadening.

§7. Impact Theories and Their Experimental Verification

The simplest premise upon which a theory of pressure broadening can be constructed is to assume a constant frequency perturbation together with a finite radiation time. This procedure leads to the formula describing what is commonly known as Lorentz[40] broadening, a formula which we shall now derive. The physical mechanism assumed by Lorentz is this: An atom absorbs or emits the sharp frequency ν_0 during the time between two collisions. Each collision stops the radiation process completely, the energy of vibration being wholly converted into kinetic energy. The theory is therefore an impact theory in its purest form.

Let the time between two collisions be T. The function $A(t)$ will then be a constant within the interval $-T/2<t<T/2$ and 0 outside. Furthermore, $\nu(\tau)=\nu_0=\text{const.}$ Hence (3.4) becomes

$$J(\nu')=\text{const.}\int_{-T/2}^{T/2} e^{2\pi i(\nu_0-\nu')t}dt = \text{const.}\,\frac{\sin \pi(\nu_0-\nu')T}{\pi(\nu_0-\nu')}.$$

$I(\nu')$, according to (3.5), is the square of this expression. But T is not the same for all collisions. It is therefore necessary to average $I(\nu')$ over all radiation times. The probability that T shall lie between T and $T+dT$ is proportional to $e^{-T/\tau}dT$, where τ is the mean time between collisions. Hence

$$\overline{I(\nu')}=\text{const.}\int_0^\infty \frac{\sin^2[\pi(\nu_0-\nu')T]}{\pi^2(\nu_0-\nu')^2}e^{-T/\tau}dT = \frac{\text{const.}}{(\nu'-\nu_0)^2+(1/2\pi\tau)^2}. \quad (1)$$

This is Lorentz' formula. It defines a dispersion curve of half-width

$$\Delta\nu_{\frac{1}{2}}=1/\pi\tau. \quad (2)$$

By putting $\int\overline{I(\nu')}d\nu'=1$, the const. in Eq. (1) is seen to have the value $1/2\pi^2\tau$.

The impact distribution thus derived has therefore the same form as the natural spectral line (whose shape is discussed in §1A). In the present derivation natural line width has been disregarded. It can be shown, however, that if radiation damping is included in the calculation in accordance with its classical mechanism, formula (1) remains unaltered, except that one must write in place of $1/\pi\tau$ the quantity $1/\pi\tau+\gamma$, where γ is the same as in (1·1). The half-width of a line affected by radiation damping and Lorentz broadening is therefore the sum of the half-widths of the two separate effects.

The Doppler effect produces greater confusion and alters the line shape. But, as was pointed out in (1·2), the Doppler modification is inappreciable in the extreme wings of the line.

The quantity $1/\tau$ is the number of collisions per second, which is known from kinetic theory to be $\pi\rho^2\bar{v}n_1$. In this expression $\bar{v}$ is the root-mean-square velocity of impact, n_1 the number of atoms per unit volume. ρ is known as the "optical collision diameter," that is, the average distance between the centers of two colliding atoms at which the radiative process stops. In view of this relation, (2) takes the form

$$\Delta\nu_{\frac{1}{2}}=\rho^2\bar{v}n_1. \quad (3)$$

This formula is applied both to the case of broadening by foreign atoms and by atoms of the same kind, only $\bar{v}$ has to be calculated differently for the two cases as is well known from kinetic theory. If the half-width of the line is measured, ρ can be computed from (3) provided one takes the values of $\bar{v}$ and n_1 from gas theory. ρ is not necessarily the same as the kinetic collision diameter, although it might be expected to be of the same order of magnitude. Before discussing the experimental material which has been collected in support of formulas (1) and (3), and their defects, it seems well to point out how $\overline{I(\nu)}'$ of (1) fits into the general scheme of the last section.

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[40] H. A. Lorentz, reference 38. Compare also J. Q. Stewart, Astrophys. J. 59, 32 (1934).

This is fairly obvious. $I_s(\nu)$ has in Lorentz' theory been assumed to be different from zero only in a very small range about $\nu=\nu_0$. Inspection of (6.6) then shows that $\overline{I(\nu')}$ is to be identified with F in such a way that $F(\nu'\nu)=\text{const.}/[(\nu'-\nu)^2+1/(2\pi\tau)^2]=I(\nu'\nu)$, which will cause (6.6) to read

$$I(\nu')=\int I_s(\nu)\overline{I(\nu',\,\nu)}d\nu=\text{const.}\ \overline{I(\nu',\,\nu_0)}.$$

We now pass to an examination of the experiments bearing on Lorentz' theory. Most of the measurements on the width and shape of absorption lines at low gas pressures have been made either on the 2537A Hg line or on the Na D lines. Minkowski,[41] Schütz,[23] Korff[42] and Weingeroff[43] all agree that the D lines become broader than the natural line width at a Na vapor pressure slightly less than 10^{-2} mm. The theoretical value of the natural width of the D lines as computed with Eq. (1.1) is 1.012×10^7 sec.$^{-1}$ (0.64×10^8 sec.$^{-1}$ in angular frequency units). This value is actually obtained by Minkowski, Schütz and Weingeroff, each using a different experimental method, at pressures of about 10^{-3} mm. Minkowski measured directly the intensity in the wings of the lines much broadened because of a long absorption path in order to make inappreciable the effect of Doppler broadening (cf. §1). For the case of the D lines this experimental verification of the theoretical natural line width is a check on the correctness of the f values 1/3 and 2/3. (Although subject to no pressure broadening at these low vapor pressures, the observed intensity distribution may be expected to depart somewhat from the dispersion form because of insufficient resolution and the influence of anomalous dispersion.)

Contours of the D lines obtained with low Na vapor pressures have been measured by Korff.[44] His measurements show that the opacity throughout the line varies inversely as the square of the wave-length distance from resonance, as is to be expected from Eq. (1) when the half-width can be neglected as compared to $(\nu-\nu_0)$. The contours show the variation of the total width of the line with the square root of the number of atoms in the line of sight,[45] and the correct natural line width is indicated.

Almost without exception investigators find the expected linear increase of the half-width with density of atoms in the absorption tube. The reported approximate variation of the half-widths of several lines of the principal series of Na with the square root of the number of absorbing atoms by Harrison and Slater[46] is questionable[41] because of possible sources of error in their procedure. Trumpy[19, 20] has similarly reported a proportionality between line width and the square root of the number of absorbing atoms both for the Na and the Hg lines. He used, however, a rather high pressure of a foreign gas in these experiments—CO_2 pressures up to 36 atmospheres in the Hg 2537A absorptions, for example—, and reports indeed that the line breadths for several different CO_2 pressures extrapolated to zero Hg vapor pressure are approximately proportional to the total pressure. But with increasing Hg vapor pressure the increasing line widths are produced by simultaneous foreign gas broadening and resonance broadening, and the half-widths due to these two effects are not additive. Therefore no conclusion as to the variation of line width with the number of Hg atoms may be drawn from these measurements.

If the density of absorbing atoms is so low tha broadening by like atoms is negligible, the breadths of the Hg 2537 line and of several alkali atom absorption lines have been shown to be proportional to the density of foreign gas atoms up to quite high foreign gas pressures. Füchtbauer, Joos and Dinkelacker,[16] for example, have observed this linear dependence for the Hg-line up to a maximum of 50 atmospheres. Fig. 4 is reproduced from their plot showing the linear variation of the half-widths of the line with

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[41] R. Minkowski, Zeits. f. Physik **36**, 839 (1926).

[42] S. A. Korff, Astrophys. J. **76**, 124 (1932).

[43] M. Weingeroff, Zeits. f. Physik **67**, 679 (1931).

[44] S. A. Korff, Phys. Rev. **38**, 477 (1931); Astrophys. J. **76**, 124 (1932).

[45] This is in agreement with Eq. (1), for the const. of the numerator includes $1/\tau$ and hence n_1. The total width is determined by Korff as the frequency interval between two points on the contour where the opacity is a constant (5 percent of its maximum). At these points, the second term in the denominator of (1) may be neglected. Then

$$n_1/(\nu'-\nu_0)^2=\text{const.},\ (\nu'-\nu_0)\propto n_1^{\frac{1}{2}}.$$

[46] G. R. Harrison and J. C. Slater, Phys. Rev. **26**, 176 (1925).

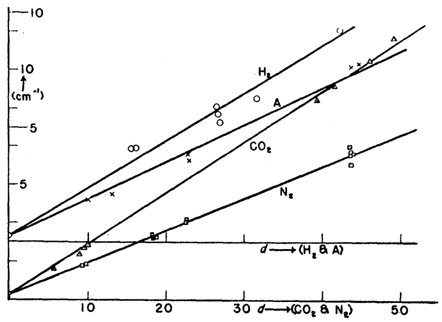

FIG. 4. Half-widths of the Hg 2537A line *vs.* relative density of perturbing gases. (After Füchtbauer, Joos and Dinkelacker.)

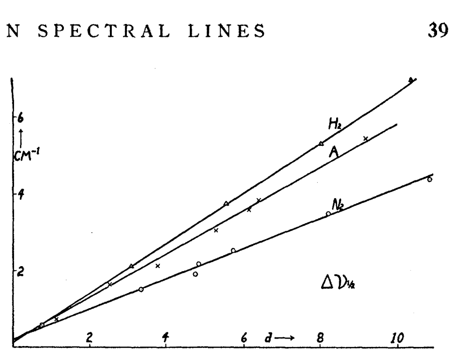

FIG. 5. Half-widths of the D lines (averages for D_1 and D_2) *vs.* relative density of perturbing gases.

relative density (the density of the amount of perturbing gas at 0°C and 1 atmos.) of H_2, A, CO_2 and N_2. A similar linear relationship for the D lines of Na broadened by H_2, A and N_2 is displayed in Fig. 5, taken from the work of Margenau and Watson.[15] This direct proportionality between the width of the D lines and the density of the perturbing gas has been observed for a smaller pressure range by Füchtbauer and Schell,[47] Minkowski[41] and Korff[44] and for other alkali lines by Füchtbauer and his co-workers[16] and by Watson and Margenau.[17] However, the latter find for the K resonance lines broadened by N_2 an increase in half-width more rapid than linearly with N_2 density when the perturbing gas is at about relative density 20 (cf. discussion in §9).

The optical collision diameters determined from the observed line half-widths vary considerably depending upon the experimental methods and theories used. They are always, however, consistently larger than the atomic diameters as given by the kinetic theory. Substituting the kinetic theory value of $\bar{v}$ in Eq. (3) and solving for ρ^2 we obtain the formula

$$\rho^2=\frac{\pi\Delta\nu_{\frac{1}{2}}}{2n_1(2\pi kT)^{\frac{1}{2}}}\left(\frac{mM}{m+M}\right)^{\frac{1}{2}}, \qquad (4)$$

where m is the mass of the absorbing atom, M that of the perturbing molecule. In addition to the direct determination of the line half-width from the line contour this width may be found under certain conditions from measurement of the total absorption.[48] Zemansky[49] and Kunze[50] have determined the width of the Hg line broadened by foreign gases by total absorption measurements. Schütz[23] has measured the width of the Na D lines broadened by a number of foreign gases with the method of magnetic rotation. Optical collision diameters may also be computed from the amount of the quenching of resonance radiation by certain gases.[51] Such determinations have been made for the Hg line by Stuart[52] and for the Na lines for H_2, N_2 and CO_2 as the foreign gases by Mannkopff,[53] von Hamos,[54] Kisilbasch, Kondratjew and Leipunsky[55] and Winans.[56] We list in Table I some of the optical collision diameters for Na with several foreign gases as determined from observed half-widths of the broadened D lines. For comparison we include the values from the experiments on the quenching of Na resonance radiation together with theoretical values to be derived later (cf. Eq. (7.7)). A similar table of

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[47] C. Füchtbauer and C. Schell, Physik. Zeits. **14**, 1164 (1913); cf. also F. Waibel, Zeits. f. Physik **53**, 459 (1929); F. Gössler and H. E. Kundt, Zeits. f. Physik **89**, 63 (1934); C. Füchtbauer and F. Gössler, Zeits. f. Physik **93**, 648 (1935); C. Füchtbauer and H. J. Reimers, Zeits. f. Physik **95**, 1 (1935).

[48] R. Ladenburg and F. Reiche, Ann. d. Physik **42**, 181 (1913).

[49] M. W. Zemansky, Phys. Rev. **36**, 219 (1930).

[50] P. Kunze, Ann. d. Physik **8**, 500 (1931).

[51] Cf. Mitchell and Zemansky, *Resonance Radiation and Excited Atoms*, p. 206.

[52] H. A. Stuart, Zeits. f. Physik **32**, 262 (1925).

[53] R. Mannkopff, Zeits. f. Physik **36**, 315 (1926).

[54] L. Z. von Hamos, Zeits. f. Physik **74**, 379 (1932).

[55] B. Kisilbasch, V. Kondratjew and A. Leipunsky, Physik. Zeits. Sowjetunion **2**, 201 (1932).

[56] J. G. Winans, Zeits. f. Physik **60**, 631 (1930).

TABLE I. *Optical collision diameters for Na with various foreign gases in A units.*

	H_2	He	N_2	Ne	A
Füchtbauer and Schell			12.0		
Minkowski			7.7		7.9
Margenau and Watson	5.6		6.5		8.7
Schütz	5.8	5.6	8.3	6.2	9.0
Quenching diameter: Mannkopff	4.1		7.8		
Quenching diameter: von Hamos			5.4		
Quenching diameter: Kisilbasch *et al.*			2.5		
Quenching diameter: Winans	2.5		3.1		
Theoretical value		4	7	6	7

collision diameters for the 2537A Hg line is given by Weisskopf.[2]

It is well known that all absorption lines are broadened to a much greater extent by increase of pressure of the same atoms than by foreign gas pressure. Optical collision diameters computed from the measured widths of these very much broadened lines are much larger than those given in Table I. Korff,[42] for example, computes from his measurement of the pressure at which the Na lines become broader than the radiation damping width that the distance for Na–Na interaction is about 200A. Orthmann and Pringsheim,[57] by indirect measurement of the width of the Hg line, find that a rise of Hg vapor pressure from 0.0001 mm to 7.3 mm produces the same broadening as does the addition of 250 mm of a mixture of He and Ne. This pressure difference would indicate that ρ is about 50A for Hg–Hg interaction. Similar measurements have been made by Waibel[21] on the absorption lines of Cs. It is very doubtful, however, whether these very large collision diameters have any significance (cf. §8 below).

Pressure broadening experiments on the near infrared band spectra of HCl, H_2O and CO_2 have shown that Lorentz' theory is largely capable of accounting for the line breadths. All of the rotational lines are broadened to about the same extent, with approximate proportionality between breadth and pressure, and with intensity distributions of the dispersion curve form. The breadths produced by different foreign gases as well as by the absorbing gas itself are all of the same order of magnitude. Becker[58] has measured the half-width of a line of the 1.74μ HCl band at pressures of 3, 5, 7, 9 and 11 atmos. as 8.65, 14.0, 17.1, 21.75 and 25.1A, respectively. These widths indicate an optical collision diameter for HCl against HCl of 13.6A.

Interesting pressure broadening data for the lines of the HCN band at 1.04μ have been reported by Herzberg and Spinks.[59] The broadening for 1 atmos. of HCN gas pressure is considerably greater than that in the HCl bands at the same pressure of HCl. The line width increases rapidly with pressure, is far less when an equal amount of air is substituted for part of the HCN, and decreases with increasing molecular rotation. These facts indicate that the effect cannot be described solely as Lorentz broadening. Furthermore, the indicated strong interaction of the HCN molecules cannot be due only to the large dipole moment of HCN, for the H_2O and HCl bands do not show this very large pressure broadening. Herzberg and Spinks mention that an additional necessary condition for the effect would seem to be the relatively easy deformability of the molecule, shown by a small vibration frequency.[60] The lowest frequency of HCN is 713 cm^{-1}, while for H_2O it is $\sim 1600\ \text{cm}^{-1}$ and for HCl$\sim 3000\ \text{cm}^{-1}$.

Lorentz' theory, if taken literally, implies that the broadening is caused by collisions of the second kind. If this were true, the process of broadening should invariably be accompanied by a diminution of the total intensity of radiation, as measured by $\int_0^\infty n\kappa d\nu$, that is, there should be "quenching" of the radiation.

But quenching has been observed in relatively few cases.[61] Clearly, then, the mechanism cannot be understood in that way. Lenz[24] and Kallmann and London[38] have indicated how the essential features of Lorentz' theory can be maintained in the face of this apparent contradiction, if only the meaning of the impact diameter ρ is changed. They point out that it is not necessary to assume

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[57] W. Orthmann and P. Pringsheim, Zeits. f. Physik **46**, 106 (1927).

[58] H. Becker, Zeits. f. Physik **59**, 583 (1930).

[59] G. Herzberg and J. W. T. Spinks, Proc. Roy. Soc. **A147**, 434 (1934).

[60] HCN polymerizes easily, as Dr. Herzberg has pointed out to the writers in conversation. This also shows the existence of strong interatomic forces.

[61] The *D* lines are quenched by H_2, N_2, Br_2 and CO_2 and the Hg line 2537 by H_2, O_2, and CO. See H. A. Stuart, reference 52; Mitchell and Zemanski, *Resonance Radiation and Excited Atoms;* R. Mannkopf, reference 53; J. G. Winans, reference 56.

the process of radiation to terminate abruptly on collision, but that a phase change of sufficient magnitude is equivalent to such determination because it makes sections of an uninterrupted wave train incoherent. Correspondingly, they define ρ as the distance of separation between two atoms at which the phase of the radiation has undergone a change of about π radians, as a result of the frequency changes which have taken place in the motion. Weisskopf[25] has given a simple method for calculating the collision diameter thus defined. The phase φ is related to the $\Delta\nu$ appearing in (3.9) by

$$\varphi = \int 2\pi\Delta\nu dt. \tag{5}$$

Let us assume that the frequency change is due to the passage of a *single* perturber. Then $\Delta\nu$ is a function of R, the distance between the partners, and through R of the time t. The perturber may be taken to fly along a straight line of distance d from the radiating atom with uniform speed v, so that $R = (\overline{v^2}t^2 + d^2)^{\frac{1}{2}}$. We now distinguish two cases:

(a) The perturber is a foreign atom. Then $\Delta\nu$ is given approximately by (4.4);

$$\Delta\nu = b/R^6 = b/(\overline{v^2}t^2 + d^2)^3.$$

The total phase change during the flight is, according to (5),

$$\varphi = 2\pi b \int_{-\infty}^{\infty} \frac{dt}{(\overline{v^2}t^2 + d^2)^3} = \frac{3\pi^2}{4} \frac{b}{\bar{v}d^5}.$$

φ is seen to depend very strongly on d. Weisskopf takes for ρ that value of d which makes $\varphi \approx 1$. Hence[62]

$$\rho \cong ((3\pi^2/4)(b/\bar{v}))^{1/5}. \tag{6}$$

(b) If the perturber is an atom of the same kind, $\Delta\nu$ is given by (5.11), and

$$\varphi = 2\pi B \int_{-\infty}^{\infty} \frac{dt}{(\overline{v^2}t^2 + d^2)^{\frac{3}{2}}} = \frac{4\pi B}{\bar{v}d^2}.$$

Putting $\varphi \approx 1$ for $d = \rho$, we obtain

$$\rho \cong (4\pi B/\bar{v})^{\frac{1}{2}}.$$

We put the values (6) and (7) into the Lorentz formula (3) and obtain

$$\Delta\nu_{\frac{1}{2}} \cong 2.2 b^{2/5}(\bar{v})^{3/5} n_1$$

$$\text{for broadening by foreign gases,} \tag{8}$$

$$\Delta\nu_{\frac{1}{2}} \cong 4\pi B n_1$$

$$\text{for broadening by similar atoms.} \tag{9}$$

In view of (3.11), the last equation may be written

$$\Delta\nu_{\frac{1}{2}} \cong (e^2 f_{12}/2\pi m \nu_0) n_1. \tag{10}$$

Formulae (6) and (7) agree well, as to order of magnitude, with the values of ρ derived from the experimental half-widths (using Eq. (3)). But the experimental values agree rather poorly among themselves, as was noted; an exact verification of the theory is therefore difficult.

Formula (10), however, permits an interesting check. We have already noted that the half-width of the D lines becomes greater than the natural line width at pressures somewhat below 10^{-2} mm. The natural width of the D lines is 1.1×10^7 sec.$^{-1}$. The value of n_1 for which (6) becomes equal to this comes out to be about 10^{14}, which corresponds to a pressure of about 3×10^{-3} mm.

Well established is also the fact that $\Delta\nu_{\frac{1}{2}}$ is proportional to n_1, as already mentioned in the discussion of the experimental material. This feature is common to all impact theories. The various results differ, however, in their dependence on the mean velocity $\bar{v} \equiv (\overline{v^2})^{\frac{1}{2}}$.

In the simple Lorentz theory the half-width is proportional to $\bar{v}$ since ρ is regarded as a constant. But in Weisskopf's formulae (8) and (10) this is no longer true. In (10) the quantity $\bar{v}$ has indeed dropped out. We have seen in the previous section that the velocity width must vanish as $\bar{v} \rightarrow 0$. Since Eq. (10) does not satisfy this requirement it is clear that it expresses more than what we have termed the effect of velocity broadening. Weisskopf seems to regard it as representing impact width. This nomenclature is unfortunate because, to put the matter forcibly, Eq. (10) predicts a width even if the atoms are stationary, that is if there are no impacts.

This at once indicates that Eq. (10) includes

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[62] H. Kuhn, Phil. Mag. **28**, 987 (1935) modifies this procedure by putting $\varphi = \pi$ and determining ρ, which introduces a different numerical factor in (6). We feel that such refinements are unimportant, because there is no sharp value of φ beyond which wave trains are to be regarded as distinct.

somehow the effect of the statistical distribution I_s. In fact we shall show in the next section that it represents essentially the statistical half-width for the case of resonance interactions. The formula is of course correct, but the way in which it is here derived, though it is simple and elegant, obscures its meaning.[63]

§8. STATISTICAL THEORIES

The statistical distribution of frequencies was defined in §6 as the distribution $I_s(\nu)$ which results if the intensity at frequency ν is regarded as proportional to the time interval during which ν is radiated. This time interval in turn is proportional to the relative volume of configuration space in which the frequency perturbation is ν. Let there be one radiating atom and n perturbers. If the radiating atom is fixed at the origin of the coordinate system the element of configuration space is the product $(4\pi/V)^n R_1^2 dR_1 R_2^2 dR_2 \cdots R_n^2 dR_n$ where V is the volume of the gas. Hence

$$I_s(\nu')d\nu' = (4\pi/V)^n \int \cdots \int R_1^2 R_2^2 \cdots R_n^2 dR_1 \cdots dR_n. \qquad (1)$$

The integration here is to be extended over the range of all R's in which

$$\nu' - d\nu'/2 < \nu(R_1R_2\cdots R_n) < \nu' + d\nu'/2.$$

We consider first again the case of broadening by foreign gases, where $\nu(R_1R_2\cdots R_n)$ is given approximately by (4.4):

$$\nu = \nu_0 + b \sum_{i=1}^{n} \frac{1}{R_i^6}.$$

Eq. (1) can be evaluated by the methods of statistical mechanics.[64] We shall state here only the result:

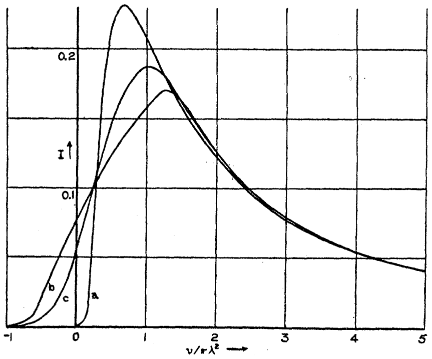

FIG. 6. Curve *a*, statistical distribution $I_s(\nu)$, Eq. (8.2); curve *b*, I_s modified by uniform diffusion, Eq. (9.4) with $\Delta = 2\pi\lambda^2$; curve *c*, I_s modified by a different diffusing function of smaller half-width. Abscissae are in units $\pi\lambda^2$; the area under each curve is unity.

$$I_s(\nu) = \begin{matrix} 0 & \text{if } (\nu_0-\nu)<0 \\ \lambda(\nu_0-\nu)^{-3/2}e^{-\pi\lambda^2/(\nu_0-\nu)} & \text{if } (\nu_0-\nu)>0, \end{matrix} \qquad (2)$$

where $$\lambda = \tfrac{2}{3}\pi(-b)^{\frac{1}{2}} n_1. \qquad (2')$$

As was remarked in §4, b is usually a negative constant. n_1 is again the number of foreign atoms per unit volume. Expression (2) is plotted in Fig. 6. Its derivation involves the assumption that (4.4) is valid all the way into the origin of R. As a consequence, it is in error for those frequencies which correspond to close encounters, that is for large values of $(\nu_0-\nu)$. In fact the tail in Fig. 6a is too long. The error increases as n_1 becomes larger; it creeps inward from the external portions of the distribution curve. Eq. (2) should be valid, except for the tail, far above atmospheric pressures. Its validity is discussed more in detail in the last reference.[64]

H. Kuhn[62] has previously given the formula

$$I_s(\nu) \cong \text{const. } (-b)^{\frac{1}{2}}(\nu_0-\nu)^{-\frac{3}{2}}$$

as valid for the wing of the broadened line. It is seen to be the form taken by (2) if $(\nu_0-\nu) \gg 10|b|n_1^2$. The maximum of $I_s(\nu)$ is given by

$$\nu_0 - \nu = \tfrac{2}{3}\pi\lambda^2 = (\tfrac{2}{3}\pi)^3|b|n_1^2. \qquad (3)$$

Hence the shift of the maximum of I_s is proportional to the *square* of the relative density of the foreign gas. The half-width of I_s is $1.85\pi\lambda^2$, and

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[63] The meaning of ρ, Eq. (7), must likewise not be taken too literally, for it is seen that $\rho \to \infty$ as $\bar{v} \to 0$, which is difficult to interpret. The trouble may be traced to the definition (5) and the subsequent substitution for $\Delta\nu$. Suppose, for instance, that $\Delta\nu$ is constant. There will then be no impact width and hence a vanishing optical collision diameter because the radiation is coherent. Nevertheless the procedure outlined leads to an infinite ρ.

[64] H. Margenau, Phys. Rev. **48**, 755 (1935).

hence proportional to n_1^2. The interesting feature of I_s is its asymmetry, which is qualitatively that observed experimentally at very high pressure. But before comparison with experiment is made (cf. next §) I_s must be augmented by an inclusion of the velocity broadening distribution.

Next we discuss the statistical distribution for the example of resonance broadening. Here we are forced to limit our considerations to the broadening effects at very small pressures (cf. §5) where only two atoms may be supposed to interact at any time. By more detailed calculations than those which will be presented in this paper it can be shown that the resulting statistical distribution, derived on the condition of additivity of the interactions, is of the dispersion type. The half-width of this distribution can be determined by the following simple analysis.

According to (5.11), $\nu = \pm B/R^3$ if ν is measured from ν_0 as origin. Any atom is equally likely to produce a blue or a red shift. Hence we divide all perturbers into two equal groups, one producing blue, the other red shifts. In a volume $2/n_1$ there will be on the average one atom of group I. Let us call this volume V_0. Thus

$$V_0 = 2/n_1. \tag{4}$$

Eq. (1) now takes the simple form

$$I_s(\nu)d\nu = \frac{4\pi}{V_0}\int_{\nu}^{\nu+d\nu} R^2 dR = \frac{4\pi}{V_0}R^2(\nu)\frac{dR}{d\nu}. \tag{5}$$

Now since $|\nu| = B/R^3$, $R(\nu) = (B/\nu)^{\frac{1}{3}}$. If we substitute this value and its derivative in (5), the result is[65]

$$I_s(\nu) = \frac{4\pi}{3V_0}\frac{B}{\nu^2} = \frac{2\pi}{3}n_1\frac{B}{\nu^2}. \tag{6}$$

Because we have dealt with single impacts only, (6) is the statistical distribution for large ν. It is so normalized that $\int I_s(\nu)d\nu = 1$.[66] We know the correct form of $I_s(\nu)$ to be of the dispersion type[67]

$$(\Delta\nu_{\frac{1}{2}}/2\pi)/[\nu^2 + (\tfrac{1}{2}\Delta\nu_{\frac{1}{2}})^2]. \tag{7}$$

This is also normalized. For $\nu \gg \Delta\nu_{\frac{1}{2}}$, (7) takes the form $\Delta\nu_{\frac{1}{2}}/2\pi\nu^2$. Comparing this with (6) we find

$$\Delta\nu_{\frac{1}{2}} \cong (4\pi^2/3)Bn_1. \tag{8}$$

Upon inserting the value of B from (5.11) it is thus found that

$$\Delta\nu_{\frac{1}{2}} \cong (e^2 f_{12}/6m\nu_0)n_1. \tag{9}$$

It is interesting to observe that this expression is identical, except for a factor $6/2\pi$, with formula (7.10). The latter has been derived on the basis of impact theory with the use of the optical diameter ρ. The present deduction shows that the use of optical diameters is entirely superfluous, and that the real meaning of (9), or (7.10), regards the statistical distribution of frequencies. This may offer an explanation of the fact that the values of ρ calculated by numerous investigators from resonance broadening of spectral lines diverge widely. Our conclusion is that they have very little significance, and that the use of optical collision diameters in connection with resonance broadening should be discouraged.

Formula (9) does not include what we have termed velocity broadening. This is probably small compared to the width given by (9). At any rate (9) should be regarded as the *minimum breadth* of the line due to the effect of resonance.

The literature contains numerous statements about "coupling breadths." Logically, this cannot be separated from the effects expressed by (9). It arises when the presence of numerous atoms is taken into proper consideration, as was pointed out in §5. The exact calculation then becomes impossible, but Weisskopf[25] has shown on the basis of simple classical considerations that deviations from (9) are negligible for sufficiently large values of $(\nu_0 - \nu)$, that is for those portions of the distribution curve from which half-widths have been experimentally derived.

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[65] Numerically this formula is uncertain by a factor 2 as a result of the crude manner in which we have dealt with the double sign in $\nu = \pm B/R^3$.

[66] The lower limit of this integral is of course not 0, but $\nu' = B/R_0^3$ where $(4\pi/3)R_0^3 = 1/n_1$.

[67] The reader will observe that there is no definite *experimental* evidence for this statement. The experimental half-width is mostly found by assuming (7) and making measurements for large ν, and then obtaining $\Delta\nu_{\frac{1}{2}}$ by finding the coefficient of ν^2, guided by (7). This is precisely the process which we are here employing to determine $\Delta\nu_{\frac{1}{2}}$.

§9. Asymmetries and Shifts

In the present § we shall limit ourselves for the most part to examples of broadening by foreign gases, where asymmetries and shifts are most pronounced. There are a few instances of strongly asymmetrical broadening and of shifts due to pressures of the same gas (cf. below); but in general, lines broadened by atoms of the same kind are symmetrical, at least sufficiently far from the center of absorption, as the discussion above has shown. Let us first review some of the experimental features of asymmetrically broadened lines. The existence of pressure shifts of spectral lines, mostly towards the red, has been known for many years.[68] Quantitative study of the intensity distribution throughout an absorption line broadened by a considerable pressure of a foreign gas seems to have been first made by Füchtbauer and Hoffmann[69] for the blue Cs lines. Using N_2 gas pressures up to 2360 mm they obtained the true line contours by the method of photographic photometry. The asymmetrical nature of the broadened lines is clearly indicated by their photometer curves, the decrease of absorption being less rapid on the red side of the maximum.

Detailed study of the shifts and asymmetries produced in the Hg 2537A line by pressures up to 50 atmospheres of six different foreign gases has been made by Füchtbauer, Joos and Dinkelacker.[16] Their finding that over this entire pressure range the line half-widths are directly proportional to the relative density of the foreign gas had already been mentioned (§7). The shift of the maximum of absorption, towards the red for every gas, also varies linearly with the density of the perturbing gas. Fig. 7 reproduces F. J. and D.'s figure giving the measured shifts plotted against relative density. H_2, although producing almost the greatest half-width, effects the smallest shift, the line contour having but very little asymmetry to the blue. The contours of the N_2 and A-broadened lines are markedly asymmetrical to the red, and these are just the gases producing the largest shift of the maximum of absorption. The values of the half-widths and shifts of the Hg line per unit relative density of these several foreign gases are assembled in Table II.

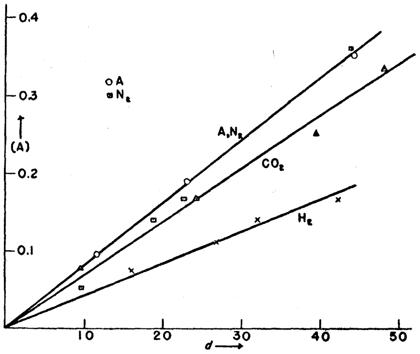

Fig. 7. Shifts of the Hg 2537A line *vs.* relative density of perturbing gases. (After Füchtbauer, Joos and Dinkelacker.)

Similar measurements of the effects of foreign gases (A, N_2 and H_2) on the *D* lines of Na have been made by Margenau and Watson.[15] Foreign gas pressures up to 17 atmospheres were used, the Na vapor pressure being kept so low as to make resonance broadening negligible. The line contours reveal (1) the red shift of the absorption maximum as well as the half-widths varying linearly with the density of the perturbing gas, (2) marked asymmetries, most pronounced near the base of the line, and to the red for A and N_2, but slightly to the blue for H_2, (3) both *D* lines showing approximately the same broadening and

Table II. *Half-widths $\Delta\nu_{\frac{1}{2}}$ and shifts $\Delta\nu$ of Hg, Na and K resonance lines per unit relative density of perturbing gas ($sec.^{-1}\times 10^9$).*

Line	Foreign Gas	$\Delta\nu_{\frac{1}{2}}/d$	$\Delta\nu/d$	Ratio
Hg 2537	A	9.66	3.73	2.6
"	N_2	8.26	3.73	2.2
"	O_2	7.86	3.69	2.13
Na 5890	A	17	6	2.84
"	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
Hg 2537	CO_2	13.1	3.2	4.1
"	H_2O	10.6	2.34	4.5
"	H_2	12.36	1.97	6.3
Na 5890	H_2	19.5	4.5	4.3

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[68] Cf. W. J. Humphreys and Mohler, Astrophys. J. **3**, 114 (1896).

[69] C. Füchtbauer and W. Hoffmann, Physik. Zeits. **14**, 1168 (1913); Ann. d. Physik **43**, 96 (1914).

shift. The *D* lines are broadened by a given gas almost twice as strongly (in freq. units) as is the Hg line. Values of the shifts and half-widths per unit relative density are listed in Table II.

Pressure effects of N_2 up to 30 atmos. pressure on the K resonance lines have been investigated by Watson and Margenau.[17] The lines are broadened very asymmetrically to the red, the shifts and half-widths increasing linearly with the density to about relative density 10. Above this pressure, however, there is definite indication of a more rapid than linear increase. The initial rates of shift and broadening are given in Table II. It is interesting to note the approximate constancy of the ratio of half-width to shift, the ratio being slightly larger than 2 for most perturbing gases. The significance of this ratio will be considered below. A discussion of the details of the pressure broadening of the higher members of the principal series of the alkalis is to be found in §10.

Minkowski[70] has investigated the intensity distribution in the *D* lines broadened by H_2, He, Ne, N_2, A and several hydrocarbon gases, all at pressures below 200 mm. The method of long absorption path length, giving complete opacity for the centers of the lines, was used in order to avoid modifications due to the Doppler effect (cf. §1). Therefore the entire line contour was not obtained. The asymmetrical character of the intensity distribution in the broadened lines was determined, however, with H_2 and He producing slight asymmetry to the violet and A and the hydrocarbons the greatest red asymmetry.

By assembling measurements on the intensity distribution on both sides of the *D* lines broadened by various pressures of A up to about 100 mm from a large number of spectrograms Minkowski[71] has recently shown that the intensity decrease on the long wave-length side of the lines is proportional to $(\nu_0-\nu)^{-\frac{3}{2}}$ while on the short wave-length side it is approximately proportional to $(\nu-\nu_0)^{-2}$.

These experimental facts can be understood rather simply in terms of the theoretical concepts developed in the preceding sections. Let us first consider the role of the statistical distribution $I_s(\nu)$, given by (8.2). Its half-width, as was noted, is $1.85\pi\lambda^2\approx 25|b|n_1^2$. Now for the Hg line 2537, $|b|$ is about 1.5×10^{-32} cm^6 sec.$^{-1}$. Hence, at atmospheric pressure, the half-width of I_s is $\sim 2.5\times 10^8$ sec.$^{-1}$. But the half-width measured by Füchtbauer and his collaborators[16] is 8.26×10^9 sec.$^{-1}$. It is thus seen that the statistical distribution contributes at this pressure only a very small portion of the broadening, which is therefore *almost entirely due to the velocity effect.* Indeed if we assume the entire width to be given by (7.8) which describes essentially this effect, we find for $\Delta\nu_{\frac{1}{2}}$ the value $\approx 8\times 10^9$ sec.$^{-1}$, and this is in agreement with the experimental one. (This good agreement is probably accidental!)

Since the velocity breadth increases with n_1 the line width should be proportional to the relative density of the perturbing gas as long as the velocity breadth is the predominant one. However, the statistical width grows with n_1^2, so that a point will be reached at which the two are equal. As we pass from this point to still higher relative densities a curvature in the graph of $\Delta\nu_{\frac{1}{2}}$ *vs.* n_1 should set in indicating a change to the statistical n_1^2-law. This transition occurs when

$$\Delta\nu_{\frac{1}{2}}\approx\pi\lambda^2 \qquad (1)$$

where we may regard $\Delta\nu_{\frac{1}{2}}$ as given by (7.8), or else take it directly from experiment. For the Hg line this condition is realized for a relative density of about 50. Measurements have not been carried beyond such pressures; it is therefore understandable that deviations from the linear law have not been observed for the Hg line. The K resonance lines present a more favorable case for the detection of the departure, as will be shown below in another connection (cf. Table III). Here the departure has been observed[17] at relative densities around 15.

Before proceeding to details, let us give some attention to the true intensity distribution within the line. If we knew the exact velocity broadening distribution, *F*, we could find $I(\nu)$ by compounding $I_s(\nu)$, as given by (8.2), with *F* in accordance with (6.6). Two cases may here be distinguished.

First, suppose the pressure of the foreign gas to be low, so that $\pi\lambda^2\ll\Delta\nu_{\frac{1}{2}}$. It is then the velocity

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[70] R. Minkowski, Zeits. f. Physik **55**, 16 (1929).

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

broadening distribution which impresses its features predominantly upon the line. But this distribution is given with reasonable accuracy by the impact theories; we know that it is approximately a dispersion function whose half-width is given by (7.8). Because this is not now the complete half-width (although very nearly so) we will call it Δ. On these premises the true intensity distribution will be[72]

$$I(\nu')=\text{const.}\int_{-\infty}^{\infty}\frac{I_s(\nu)d\nu}{(\nu'-\nu)^2+(\Delta/2)^2}. \tag{2}$$

The value of this integral for two limiting cases can be determined at once. If $\nu'\gg\Delta\gg\pi\lambda^2$, that is, for the extreme blue wing of the spectral line, $I(\nu')$ varies nearly as $(\nu')^{-2}$; i.e. it behaves like the dispersion curve. On the other hand, if $-\nu'\gg\Delta$, (2) takes on the features of I_s because I_s falls off less rapidly than the dispersion curve. But the behavior of I_s on the extreme red side of the line is given by $(\nu')^{-\frac{3}{2}}$. Experimental verification of these relations by Minkowski has already been noted.

Formula (2), if calculated graphically, reveals in general the features of a simpler expression derived by Lenz[37] by carrying out the Fourier analysis *in extenso*.

Next we proceed to the case where $\pi\lambda^2\geqq\Delta\nu_{\frac{1}{2}}$. The characteristics of the true distribution are now chiefly those of I_s, and the exact form of F is no longer so important. For the sake of simplicity let us assume that F scrambles the frequencies uniformly within a range Δ. One can then show[64] that

$$I(\nu')=\frac{1}{\Delta}\int_{\nu'-\Delta/2}^{\nu'+\Delta/2}I_s(\nu)d\nu \tag{3}$$

$$=\frac{1}{\Delta}\left[\phi\left(\frac{\pi\lambda^2}{\nu'-\Delta/2}\right)^{\frac{1}{2}}-\phi\left(\frac{\pi\lambda^2}{\nu'+\Delta/2}\right)^{\frac{1}{2}}\right] \tag{4}$$

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

This expression is plotted in Fig. 6, curve b. An exact comparison of this curve with experimental line contours has not yet been made, but it shows in a qualitative way most of the experimental features. There is now, of course, an appreciable intensity at ν values on the blue side of ν_0. We observe that the position of the maximum is different from the maximum of I_s.

A word of caution is necessary in this connection. The condition $\pi\lambda^2\approx\Delta\nu_{\frac{1}{2}}$ is usually verified only at pressures around 20 atmos. or more. But at such high densities I_s is already strongly in error on the red side. We must therefore expect (4) to be inaccurate on the red wing of the line.

Fortunately, however, as Kuhn[62] has pointed out and as the figure shows, the effect of F in this region is unimportant, and I agrees practically with I_s. Hence conclusions may be drawn as to the correct form of the interaction law (4.4) by observing the intensities in the extreme red wing of the line (cf. reference 64). This is true also for the former case of low pressures. On the basis of such considerations Minkowski[71] has determined the value of $|b|$ in (4.4) to be about 6×10^{-32} cm^6 sec.$^{-1}$.

The position of the intensity maximum in asymmetrical distributions is now to be investigated. Its displacement with respect to ν_0 is known as the shift of the line. Some theories have identified this shift with the mean, $\overline{(\nu-\nu_0)}$, of the frequency distributions. This mean is easily calculated; it is always strictly proportional to n_1 and depends in a sensitive manner upon the distance of closest approach. Also, it turns out that the mean of the true distribution is equal to the mean of $I_s(\nu)$. In reference 27 Margenau has calculated approximate distances of closest approach in this manner, by identifying the measured shift with $\overline{(\nu-\nu_0)}$. This procedure has been rightly criticized by Kuhn[62] who points out that the measured shift, which is the displacement of the maximum and not the mean, is largely independent of the distance of closest approach.

A theoretical estimate of the variation of the shift with n_1 can be obtained easily.[73] We suppose again that the velocity effect diffuses every ordinate of $I_s(\nu)$ in a uniform manner. The true distribution is then given by (3). On setting its derivative with respect to ν' equal to 0 we have for the shift, ν_m, the relation

$$I_s(\nu_m+\Delta/2)=I_s(\nu_m-\Delta/2), \tag{5}$$

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[72] Again we measure frequencies from ν_0 as origin.

[73] A more detailed discussion is found in reference 64.

Δ being the "velocity breadth." According to this equation, ν_m can be determined by the simple graphical procedure of finding where the I_s curve (Fig. 6a) has a horizontal width Δ. The mean of the two abscissae defining this width is ν_m.

Now suppose that $\Delta \gg \pi\lambda^2$, which is the case up to pressures of several atmos. Then, since I_s rises very rapidly at $\nu = 0$, the abscissa bounding the range of width Δ on the left lies practically at $\nu = 0$; the limit on the right is about Δ, and

$$\nu_m \approx \Delta/2. \tag{6}$$

This is true regardless of the precise behavior of $I_s(\nu)$ for large ν.

We see that ν_m in this case bears very little relation to the maximum of I_s. Moreover, since Δ varies linearly with n_1, ν_m also does because of (6). At low pressures the shift of the observed maximum is thus entirely occasioned by the increasing velocity width (here equivalent to the usual impact width) of the line. Relation (6) is well substantiated by the values in Table II. The quotient $\Delta\nu_{\frac{1}{2}}/\nu_m$ is somewhat greater than 2 because $\Delta\nu_{\frac{1}{2}}$ is a little larger than Δ, being compounded from velocity breadth and statistical breadth. It is to be noted that the gases CO_2, H_2O, H_2, if used as broadening agents, do not follow this rule. This is because their interactions with a radiating atom are not adequately described by the theory of §4, in the case of CO_2 and H_2O because of the complexity and polarity of the molecules, in the case of H_2 chiefly because of the neglect of R and exchange forces in (4.4).

In arriving at the relation (6) we have made use of the fact that $I_s(\nu)$ rises very steeply at $\nu = \nu_0$ and has no intensities for $\nu > \nu_0$. This is of course only an approximation; it ceases to be valid for lines which involve higher atomic states. In Fig. 1 we have drawn schematically the curves ϵ_1 and ϵ_2. In deriving I_s we have assumed the curves to follow the dotted lines, whereas really each has a minimum. Thus we have considered only transitions like *b* and *c*, which involve less energy than *a*, and excluded transitions like *d* which involve more. If the upper minimum lies sufficiently near the origin the region of phase space in which transitions like *d* are possible is small, and their occurrence may be neglected. The fact that (6) is approximately valid for resonance lines shows that this is the case. But if the upper state of the line is a higher excited state, ϵ_2 may have no minimum at all (in which case there results a blue shift, cf. reference 27) or, if it has a minimum, this may lie so far from the origin that transitions of type *d* cannot be neglected. Rule (6) will then certainly not be valid.

If $\Delta \ll \pi\lambda^2$, which is true for high pressures, ν_m coincides with the maximum of I_s, and hence varies with n_1^2. The region in which the linear law gradually changes into the square law is again given by $\Delta \approx \pi\lambda^2$.

An upward curvature in the plot of ν_m *vs.* n_1 has been found for the K lines 7665 and 7699A, perturbed by N_2,[17] not for Hg 2537A under similar conditions. In the former case departures became noticeable at relative densities around 15, in the latter they were still absent at the highest pressures (relative densities ≈ 50). Table III offers an explanation of these facts. It contains the values of b, computed from (4.2); of $\Delta\nu_{\frac{1}{2}}$, the empirical half-width (by which Δ may be replaced) for unit relative density; and of $\pi\lambda^2$ (cf. 8.2), for the two cases above.

TABLE III.

	Hg−N	K−N
b	1.5×10^{-32} cm^6 sec.$^{-1}$	7×10^{-32} cm^6 sec.$^{-1}$
$\Delta\nu_{\frac{1}{2}}$	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 values of b are quite uncertain, but their ratio should not be strongly in error. The table shows that $\Delta\nu_{\frac{1}{2}}$, which varies as n_1, and $\pi\lambda^2$ which varies as n_1^2, become equal at relative density 19 for $K-N_2$, at relative density 55 for $Hg-N_2$. The experimental results are therefore not surprising.

At low pressures the shift of the maximum should not be independent of the temperature, as is usually supposed, for the velocity breadth varies with the temperature. This point has not been tested experimentally.

At very high pressures ($\pi\lambda^2 \gg \Delta\nu_{\frac{1}{2}}$) the asymmetries of the true distribution are practically those of I_s. But here I_s is not correctly given by (8.2). It becomes necessary to consider the nature of the interaction curves (Franck-Condon curves) in greater detail. The calculation of I_s is then in general difficult; but a simplified (one-dimensional) consideration[74] shows qualitative agreement between the experimental types of asymmetry and the expected tendency of the Franck-Condon curves.

Several striking examples of very much broadened, asymmetrical resonance lines in emission have been reported. Hopfield[75] has observed the He resonance line at 585A to be broadened asymmetrically to the high frequency side for some 500 cm^{-1}. Weizel[76] has explained this by showing that in the upper state of the resonance line the electronic energy always increases on the approach of another He atom. The average translational energy of the excited He atoms in the arc is probably high enough so that the resonance transition may take place from points well upon the repulsion $^1\Pi_u$ and $^1\Sigma_u$ potential energy curves, thus producing the large broadening of the resonance line. This broadening is then experimental evidence for the existence of these two predicted terms of the He_2 molecule.

Oldenberg[77] has produced asymmetrical broadening of the Hg 2537A line by Hg and by pressures of A and Kr. The resonance level of the Hg atom is shifted by the quasi-binding with the foreign gas atom, while the very large broadenings observed by Oldenberg in the fluorescence spectrum of these $Hg-A$ and $Hg-Kr$ mixtures are evidence of the interchange between atomic kinetic energy and radiation (cf. §6 above). Strong evidence for the existence of fairly stable Cs-polarization molecules is to be found in the experiments of H. Kuhn[78] whose spectrograms of the absorption by Cs vapor at fairly high pressures show weak bands accompanying the very broad, asymmetrical Cs atomic lines.

§10. SHIFTS OF THE HIGHER SERIES MEMBERS OF THE ALKALIS

To predict in detail the behavior of the higher members of the principal series under pressures of foreign gases requires a much more precise knowledge of the interaction curve ϵ_2 than can at present be obtained. One can draw one qualitative inference from London's formula (4.2), which of course is still valid, for large R. If k refers to one of the higher P states, say the second or third, transitions from this state to near lying S and D states have large probabilities, and hence large f values. Hence there will be terms in the sum of (4.2) for which $f_{kk'}$ is large and which have at the same time small denominators since $E_{k'}-E_k$ is small. For this reason we may expect larger shifts for higher series members. But on the whole no regularities regarding shifts or half-widths can be predicted.

The contours of the second and third doublets of the principal series of caesium broadened by a number of foreign gases at pressures up to 4700 mm have been studied in considerable detail by Füchtbauer and Gössler.[79] Gössler and Kundt[80] have extended this investigation to the fourth member of the Cs series. The second doublet in the principal series of potassium broadened by N_2 and H_2 has been examined by H. Petermann,[81] while Watson and Margenau[17] have measured the contours of both the second and third doublets of K broadened by N_2 through a greater range of pressures. All of these pressure-broadened lines show the expected larger shifts and half-widths. In addition interesting variations either in the direction or the amount of the asymmetry of the line contour are displayed.

Table IV, summarizing the findings for the Cs lines, is taken from the paper by Gössler and Kundt.[80] The columns headed *Asym.* give the ratio of the area under the line contour to the red of the absorption maximum to that to the violet of the maximum. $\Delta\lambda$ is the shift of the maximum of absorption in A units, while $\Delta\nu_{\frac{1}{2}}$ is the half-width in sec.^{-1} reduced to $T=400$ abs. and 760 mm pressure. For all the foreign gases the breadth of the lines increases as one proceeds to higher members of the series, but the rate of increase would indicate a constant value of the pressure broadening for still higher series mem-

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

[75] J. J. Hopfield, Astrophys. J. **72**, 133 (1930).

[76] W. Weizel, Phys. Rev. **38**, 642 (1931).

[77] O. Oldenberg, Zeits. f. Physik **47**, 184 (1928); **51**, 605 (1928); **55**, 1 (1929).

[78] H. Kuhn, Zeits. f. Physik **76**, 782 (1932).

[79] C. Füchtbauer and F. Gössler, Zeits. f. Physik **87**, 89 (1933).

[80] F. Gössler and H. E. Kundt, Zeits. f. Physik **89**, 63 (1934).

[81] H. Petermann, Diss. Rostock, 1930.

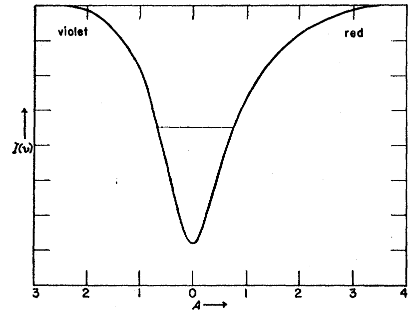

Fig. 8. Contour of the Cs 4555A line (second member of principal series) perturbed by N_2 (pressure 3984 mm). Note red asymmetry. (After Füchtbauer and Gössler.)

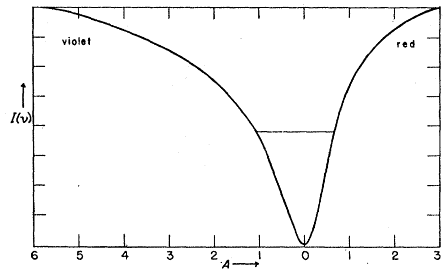

Fig. 9. Contour of the Cs 3876A line (third member of principal series) perturbed by N_2 (pressure 4196 mm). Note strong violet asymmetry. (After Füchtbauer and Gössler.)

bers. With the exception of argon all the gases used produce pressure shifts changing in direction from red to violet in passing to the higher series members. Also the lessened rate of increase of the shift in going from the third to the fourth series member is a harbinger of a constant value for the shift for the highest members of the series. The asymmetry of the broadened lines, which initially for all gases is changing from red to violet, seems also to be tending towards a constant value for the higher series members. It is of interest that for one case, that of the 3876A line broadened by N_2, a red shift of the maximum of absorption is accompanied by a violet asymmetry. According to our theoretical discussion this seemingly anomalous pressure effect is quite understandable. Figs. 8 and 9 illustrate the change of asymmetry from red (Cs 4555A) to violet (Cs 3876A) for nitrogen pressure broadening.

Table IV. *Asymmetry, shift and half-width for the second, third and fourth members of the principal series of caesium broadened by He, Ne, A and N_2.*

Cs Line	Asym.	Δλ(A)	$\Delta\nu_{\frac{1}{2}}\times(10^{-11})$	Asym.	Δλ(A)	$\Delta\nu_{\frac{1}{2}}\times(10^{-11})$
	Helium			Neon		
4555A	0.84 violet	0.0804 violet	3.55	1.03 slight red	0.0232 red	1.31
3876A	0.47 very strong viol.	0.269 violet	7.96	0.54 strong viol.	0.0502 violet	2.53
3612A	0.64 strong viol.	0.375 violet	8.27	0.56 strong viol.	0.070 violet	2.62
	Argon			Nitrogen		
4555A	1.80 very strong red	0.109 red	3.52	1.30 red	0.120 red	2.49
3876A	1.59 strong red	0.319 red	7.42	0.56 strong viol.	0.0745 red	4.24
3612A	1.26 red	0.470 red	8.81	0.60 strong viol.	0.0515 violet	7.41

The pressure effects of foreign gases for the Cs resonance lines have not been investigated. For the *K* series, however, Watson and Margenau[17] have observed the considerable increase in shift and half-width in passing from the resonance lines to the second and third members of the series. Table V summarizes these observations for the lowest densities. There is a slight difference in the size of the shifts for the $^2\Pi_{\frac{1}{2}}$ and the $^2\Pi_{3/2}$ components, but the widths of the two components are in each case about equal. Comparing the effect of N_2 and H_2 on the second doublets only, the broadening is according to Füchtbauer about 25 percent greater for the Cs lines than for the *K* lines. For both of these doublets Petermann found the short wave-length component to be broadened by H_2 about 20 percent more than is the long wave-length component. These variations of pressure effects as between the two components of the doublets, as

Table V. *Summary of pressure shifts Δν and broadenings $\Delta\nu_{\frac{1}{2}}$ per unit relative density for potassium doublets.*

λ	7665	7699	4044	4047	3446	3447
$\Delta\nu/d(\text{cm}^{-1})$	0.206	0.219	0.55	0.64	0.49	0.45
$\Delta\nu_{\frac{1}{2}}/d(\text{cm}^{-1})$	0.44	0.44	1.10	1.10		

well as the indicated and predicted departures of the shifts for high pressures from the usual linear increase with density of foreign gas deserve further investigation.

As we pass to the highest members of the principal series in the alkalis theory again affords guidance. Fermi[82] has calculated the shifts to be expected for such lines in an interesting manner and correlated them with the collision cross sections of slow electrons in the respective gases. We now present Fermi's theory.

When the valence electron of an alkali atom is excited to a state with principal quantum number ≈ 30 the radius of its Bohr orbit is 500A; it encloses a sphere which, at atmospheric pressure, contains about 13,000 foreign atoms. Moreover, the valence electron moves through these atoms rather slowly, its de Broglie wave-length being around 100A. Its motion resembles therefore very much the motion of a slow free electron through a gas.

A change from the normal energy of the valence electron can be ascribed to two causes:

(1) The atom core polarizes all foreign atoms within the orbit of the valence electron, and this effect diminishes the total energy of the system.

(2) The valence electron, in the aggregate of its encounters with the foreign atoms, either gains or loses energy. Whether the system gains or loses energy depends on the charge distribution of the foreign atoms. These two effects will now be discussed in order.

(1) Let α be the atomic polarizability of the perturbers, and F_i the field at the position of the ith perturber due to the core of the alkali atom. The change in energy will then be

$$\Delta\epsilon = -\sum_i \frac{\alpha}{2} F_i^2.$$

But F_i is simply e/R_i^2, hence

$$\Delta\epsilon = -\frac{\alpha e^2}{2} \sum_i \frac{1}{R_i^4}. \qquad (1)$$

Because the sum converges rapidly for large R it may be extended over *all* perturbers instead of limiting it to the atoms inside the electron orbit. Thus there corresponds a value of $\Delta\epsilon$ to every configuration of atoms, i.e., to every set of R_i. The value of $\Delta\epsilon$ corresponding to the intensity maximum in the line (if the present effect alone were responsible for the broadening) will be that associated with the most probable configuration, which is a uniform distribution of perturbers. When it prevails, every volume of size $1/n_1$ contains one perturber. Let us assume them to be arranged in spherical shells. The first perturber will then be a distance R_1 away from the origin, where

$$(4\pi/3)R_1^3 = 1/n_1,$$

and from there on outward we consider them spread uniformly and continuously over all volume with density n_1. This procedure is not rigorous, but gives an answer which is nearly right. We have on the basis of these assumptions

$$\sum_i \frac{1}{R_i^4} = 4\pi n_1 \int_{R_1}^{\infty} \frac{R^2 dR}{R^4} = \frac{4\pi n_1}{R_1}$$

$$= 4\pi n_1 (4\pi n_1/3)^{1/3} \approx 20 n_1^{4/3} \qquad (2)$$

in view of the preceding equation. Combining (1) and (2) we obtain

$$\Delta\epsilon = -10 e^2 \alpha n_1^{4/3},$$

so that the frequency shift due to this cause is

$$\Delta\nu_1 = -10(e^2/h)\alpha n_1^{4/3}.$$

For convenience we may replace α by the dielectric constant D according to

$$D = 1 + 4\pi n_1 \alpha.$$

The result is then

$$\Delta\nu_1 = -2.8 \times 10^7 (D-1) n_1^{\frac{1}{3}}. \qquad (3)$$

(2) Next we consider the change in the energy which occurs as a result of the impacts of the valence electron with the foreign atoms. The valence electron moves in a potential composed of two parts: (1) U, the potential due to its nucleus, (2) $\sum_i V_i$, the potential due to all the foreign atoms. The spatial extent of V_i (potential due to the ith perturber) is small compared to the electron's de Broglie wave-length. The Schrödinger equation is

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[82] E. Fermi, Nuovo cim. **11**, 157 (1934).

$$\nabla^2\psi+(8\pi^2m/h^2)(\epsilon-U-\sum_i V_i)\psi=0. \qquad (4)$$

Let us introduce a function $\bar{\psi}$, defined as the space average of ψ over a domain whose linear dimensions are small compared to the de Broglie wave-length, but sufficiently large to contain numerous perturbers. U may be considered constant in such a range. This function satisfies an equation obtained from (4) by carrying out the space integration over the above domain:

$$\nabla^2\bar{\psi}+\frac{8\pi^2m}{h^2}(\epsilon-U)\bar{\psi}-\frac{8\pi^2m}{h^2}\overline{\sum_i V_i\psi}=0. \qquad (5)$$

We turn to the evaluation of the last term of this equation. Consider a coordinate system whose origin is fixed at the center of the ith perturber. In this system, $V_i=V_i(r)$ (provided the charge distribution of a perturbing molecule has spherical symmetry, as we shall suppose). The variation in V_i is large within a small range about $r=0$, so large in fact that $\epsilon-U$ is negligible compared to V_i. In the neighborhood of $r=0$, therefore,

$$\nabla^2\psi=(8\pi^2m/h^2)V_i\psi,$$

or if we put $\psi=u(r)/r$,

$$u''=(8\pi^2m/h^2)V_iu. \qquad (6)$$

Far away from the origin, where $V_i=0$, the solution of (6) is

$$u=c_1+c_2r. \qquad (7)$$

But far away from a perturber where the variation in ψ is due only to U and therefore small, $\psi=\bar{\psi}$, and $u=r\bar{\psi}$. We must therefore identify the coefficient c_2 in (7) with $\bar{\psi}$ which we may here regard as constant. For c_1 we may write $a\bar{\psi}$ so that (7) becomes

$$u=(a+r)\bar{\psi}. \qquad (8)$$

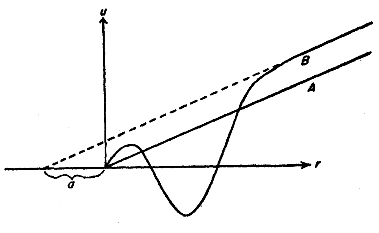

FIG. 10. Graph of u, Eq. (6).

Fig. 10 shows the meaning of the length a: it is the distance through which the electron wave is displaced with respect to the origin by the presence of V_i. If no perturbers were present the u-function would be the straight[83] line A. V_i causes it to be represented by B. The *phase change* δ which occurs as a result of V_i is related to a by

$$a/\lambda=\delta/2\pi, \qquad (9)$$

where λ is the de Broglie wave-length.

From (6) we have

$$\frac{8\pi^2m}{h^2}\int V\psi d\tau=4\pi\cdot\frac{8\pi^2m}{h^2}\int Vurdr=4\pi\int u''rdr$$
$$=4\pi\left|u'r-u\right|_0^r=-4\pi a\bar{\psi}.$$

The last step follows if we remember that u is given by (8) at the upper limit, and vanishes for $r=0$ because $\psi=u/r$ has to remain finite. Since there are n_1 perturbers per unit volume,

$$\frac{8\pi^2m}{h^2}\overline{\sum_i V_i\psi}=-4\pi n_1a\bar{\psi}.$$

On inserting this in Eq. (5) there results

$$\nabla^2\bar{\psi}+\frac{8\pi^2m}{h^2}\left(\epsilon+\frac{h^2an_1}{2\pi m}-U\right)\bar{\psi}=0. \qquad (10)$$

This, however, is simply Schrödinger's equation for the electron in the potential of the atom core, but with $\epsilon+h^2an_1/2\pi m$ in place of ϵ. The eigenvalues of (10) are the eigenvalues in the absence of the foreign atoms, diminished by $h^2an_1/2\pi m$. Hence

$$\begin{aligned}\Delta\epsilon&=-h^2an_1/2\pi m,\\ \Delta\nu_2&=-han_1/2\pi m.\end{aligned} \qquad (11)$$

The constant a is related to the collision cross section of slow electrons in the foreign gas. If the wave-length λ of the electrons is large compared to the obstacle with which they collide, the collision cross section is given by[84]

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[83] Straight because the de Broglie wave-length is large compared to the dimensions of the figure.

[84] G. Wentzel, *Handbuch der Physik*, Vol. 24, 1 (1933), p. 711.

$$\sigma=(\lambda^2/\pi)\sin^2\delta.$$

Now δ is small and given by (9). Therefore

$$\sigma=4\pi a^2. \qquad (12)$$

The quantity a may be either positive or negative; its sign is not given by (12). But Reinsberg[85] shows that the shift given by (11) is toward the red if the collision cross section plotted against electron velocities, has a minimum for low velocities; otherwise it is toward the blue.

Fermi finally assumes the two shifts, $\Delta\nu_1$ and $\Delta\nu_2$, to be additive. Hence the result, on combining (3) and (11) and using numerical constants, is

$$\nu_0-\nu_m=-2.8\times10^7(D-1)n_1^{\frac{1}{3}}\pm0.33\sigma^{\frac{1}{2}}n_1. \qquad (13)$$

Fermi's theory is essentially a statistical one and does not include the broadening effect due to atomic motions. But since the shifts represented by (13) are very large indeed they are not likely to be modified appreciably by the inclusion of this effect.

Experimental determinations of the pressure shifts of the highest members of the principal series of the alkalis have been made by Amaldi and Segrè[86] (Na and K perturbed by H_2, N_2, He, A), Füchtbauer, Schulz and Brandt[87] (Na and K perturbed by N_2, He, Ne, A), Füchtbauer and Gössler[88] (Cs perturbed by Hg and Xe), and Füchtbauer and Reimers[89] (Cs perturbed by Kr). The first two of these papers show that the amount of the shift of the lines is independent of the kind of absorbing alkali atoms, depending only on the nature of the perturbing foreign gas, as the preceding theory shows. The shifts are constant in each case for all lines after about the fifteenth in the series, again in agreement with theory. Reduced to 0°C and 1 atmos. they are about 9.8 cm^{-1} red for A, 0.2 cm^{-1} violet for Ne and 5.8 cm^{-1} violet for He. $\Delta\nu_2$ as computed from the observed shifts at the series end and reduced to 0°C and 760 mm is 9.82 cm^{-1} violet for Hg, 31.6 cm^{-1} red for Xe, 17.20 cm^{-1} red for Kr, 8.5 cm^{-1} violet for N_2, and 5.47 cm^{-1} red for H_2.

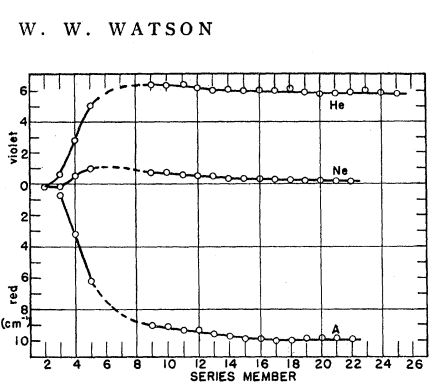

FIG. 11. Shifts of the Cs principal series lines perturbed by He, Ne, and A. (After Füchtbauer, Schulz and Brandt.)

Fig. 11, giving the shifts of all the Cs series lines when perturbed by He, Ne and A at 0°C and 1 atmos., is taken from the report by Füchtbauer, Schulz and Brandt.[87] The values for the second, third and fourth series members are taken from the earlier measurements of Füchtbauer and his co-workers, whereas those from the ninth member to the end are their values for Na and K which should be quite the same for Cs. To be noted are the change in sign of the shift at the first lines for He and Ne, the maxima formed by the He and Ne curves and the lack of a maximum for the A curve. These higher series lines are of course broadened and have an asymmetrical intensity distribution. The constant pressure shift for the lines near the limit of these series is accompanied by a constant value for the line breadths. Those gases producing the largest shifts cause the greatest half-breadths, the but little shifted lines for the case of Ne being therefore the sharpest. Füchtbauer[90] gives a curve representing the variations in the half-widths of Cs and Na lines up to $3S-22P$ broadened by He which we reproduce in Fig. 12. The large maximum at the fifth member of the series and the approach to a constant end value are interesting features of this curve. All of the higher series members after the fifth retain the same asymmetrical character to the series end; slightly asymmetrical to the

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[85] C. Reinsberg, Zeits. f. Physik **93**, 416 (1935).

[86] E. Amaldi and E. Segrè, Nature **133**, 141 (1934), Nuovo cim. **11**, 145 (1934).

[87] C. Füchtbauer, P. Schulz and A. F. Brandt, Zeits. f. Physik **90**, 403 (1934).

[88] C. Füchtbauer and F. Gössler, Zeits. f. Physik **93**, 648 (1935).

[89] C. Füchtbauer and H. J. Reimers, Zeits. f. Physik **95**, 1 (1935).

[90] C. Füchtbauer, Physik. Zeits. **35**, 975 (1934).

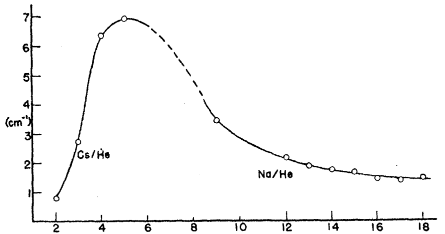

FIG. 12. Half-widths, reduced to 0°C and 1 atmos., of members of the principal series of Cs (lines 2 to 6) and Na (lines 9 to 19) perturbed by helium. (After Füchtbauer.)

violet for the He broadening, strongly asymmetrical to the red for A broadening.

In Table VI are collected the values of the effective cross sections for the several foreign gases used in these pressure-broadening experiments, calculated from the constant pressure shifts for the lines near the end of the alkali series with the aid of Eqs. (3) and (11). They are the effective cross sections for all the atoms in a cm^3 at 1 mm pressure, obtained by multiplying the collision cross sections σ for the single atoms of the perturbing gas by $n_1/760=3.553\times10^{16}/\text{cm}^3$. In these calculations the value of $\Delta\nu_1$, Eq. (3), is computed from the known dielectric constant or polarizability of the perturbing gas and the pressure and temperature holding for the spectrogram in question. This "red" contribution is then subtracted from the observed shift in order to obtain $\Delta\nu_2$ which is usually much the larger of the two parts.

TABLE VI. *Effective cross sections of gases for electrons of very low velocity.*

GAS	FROM EQ. (1013)	REF.	BY ELECTRICAL EXP.	ELEC. VELOCITY	REF.
He	15.5 cm^2/cm^3	87	15.3 cm^2/cm^3	0.03 volt	91
Ne	0.23	87	——		
A	25.2	87	26.0	0.03 volt	91
Kr	121.3	89	20	$v<0.6$ volt	93
Xe	412	88	58	0.2 volt	93
Hg	37.2	88	250–300	$v<1$ volt	92
N_2	~5	87	10		91
H_2	12.3	86	24.4		91

The comparison of the spectroscopic and electrical values in Table VI needs some explanation. For Ar, Kr and Xe only, of the gases used, the Ramsauer cross section for small electron velocities has a minimum, so that the $\Delta\nu_2$ of Eq. (11) should cause a red shift according to Reinsberg.[85] These are just the perturbing gases that produce red shifts, all the others are to the violet. For Xe, for example, the Ramsauer curve shows for small electron velocities a very steep rise. An electrical measurement with electrons of say 0.03 volt, which is about the orbital velocity of the valence electron for the term 20P, would probably yield about the spectroscopic value 412 cm^2/cm^3. The same explanation holds for the discrepancy between the two values for Kr. The good agreement between the values of the effective cross sections for He and for A by the two methods is apparently due to the exceptionally low electron velocities used by Wahlin. This optical method yields the first determination of this quantity for Ne. The value 37.2 for Hg as compared to the much larger value by electrical methods is interesting, indicating that the last part of the Ramsauer curve (for low electron velocities) may have a maximum after which it sinks to the value 37 for the very lowest velocities. Hence even though this curve has a minimum for larger electron velocities, the pressure shift produced by Hg is to the violet. A similar explanation may be used for the rather large difference between the two values for N_2. For N_2, as a matter of fact, a falling of the Ramsauer curve in the range of lowest electron velocities has been noted.

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[91] H. B. Wahlin, Phys. Rev. **37**, 260 (1931).

[92] R. B. Brode, Proc. Roy. Soc. **A105**, 397 (1925).

[93] C. Ramsauer and R. Kollath, Ann. d. Physik **3**, 536 (1929).

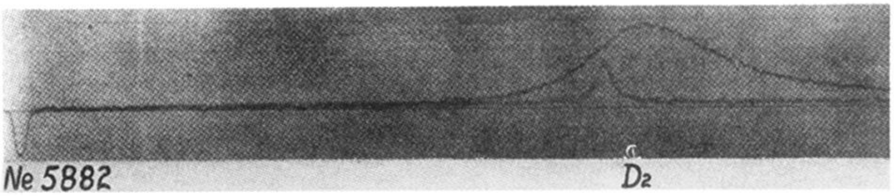

FIG. 2. Microphotometer traces of D_2 broadened by argon. *Small peak:* trace for an argon pressure of 1.85 atmos.; *large peak:* trace for a pressure of 17.8 atmos. Reference line (Ne, λ5881.896), exactly superposed on the two traces, appears on extreme left. (Lower trace is slightly out of focus in the reproduction.)