

On the Shape of Collision-Broadened Lines

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INTRODUCTION

THE three most common causes of the breadth of spectral lines are the Doppler effect, radiation damping, and interruption by collisions. The last of these three effects is usually the most important at high pressures in the visible spectral region. At infra-red and longer wave-lengths it is predominant even at comparatively low pressures. The assumption made in the present paper that the breadth is due to collisions is hence often warranted for ordinary light, and always for microwaves.

The literature of collision broadening is dominated by two names—those of Lorentz¹ and Debye,² who treated respectively resonant and nonresonant absorption. It is true that Debye's "relaxation" theory of dispersion and absorption is probably not usually thought of as relating to the subject of broadening by collision. It can, nevertheless, be regarded as a theory of spectral shape for a non-resonant line, i.e., one which would be of zero frequency except for the interruptions due to collisions. Clearly, the distinction between resonant and nonresonant absorption is in a certain sense a purely artificial one, inasmuch as zero frequency is merely a special case of a finite frequency. Hence one might expect the Debye theory to be merely a special case of the Lorentz one. However, this is not the case, and one of the first points we would like to make in the present paper is that in consequence a single, integrated theory has been lacking. Namely, the Lorentz formulas give no absorption at all, instead of the Debye result, if the resonant frequency is put equal to zero. We shall later see that this dilemma has arisen because Lorentz incorrectly assumed that after each collision the

mean distribution was, on the average, an unpolarized one. Actually the application of Boltzmann statistics favors orientations or phases in which the molecule is so oriented as to have a low energy in the field, and when allowance for this is made, a unified theory is obtained. Of course, Lorentz was essentially right for the case which he meant to consider, *viz.*, that in which the line breadth is small compared to the resonant frequency, as is always true for lines in the visible region. In the Debye case, however, the resonance frequency is zero. The interest in the formulas which we derive does not lie merely in internal consistency and the satisfaction of having a single theory that comprises both the limiting cases of a proper frequency very high or negligible compared to the line breadth. In the microwave region the line breadth can be of the same order of magnitude as the resonant frequency. This, for instance, is the case of the famous line in ammonia, measured by Cleeton and Williams³ and located at about 1.3 cm, which is associated with the "turning inside out" of the ammonia molecule. Hence it is no longer of academic interest to have a theory applicable to all values of the ratio of the line breadth to resonant frequency.

STRONG VS. WEAK COLLISIONS

The various items mentioned in the preceding paragraph become much more succinct when expressed in mathematical form. Before doing so, however, we must say something about the different types of assumptions which can be made concerning collisions. There are two limiting cases which may be delineated. These we shall call, respectively, strong and weak colli-

¹ H. A. Lorentz, *The Theory of Electrons*, note 57.

² P. Debye, *Polar Molecules*, Chap. V.

³ C. E. Cleeton and H. H. Williams, *Phys. Rev.* **45**, 234 (1934).

sions. A strong collision may be defined as one in which the impact is so powerful that the molecule has no "hangover" or memory regarding its orientation or other distributional properties before collision. In addition, as is usually tacitly done, the assumption may be made that the collision is adiabatic, i.e., takes place over an interval of time which is short compared to the period of oscillation in the impressed field. If the collisions are both strong and adiabatic the molecules can be regarded as distributed after impact in accordance with the Boltzmann law appropriate to the instantaneous value of the field at collision.⁴

We shall ourselves suppose that the collisions are adiabatic. Consequently after a strong collision, the probability of a molecule of electrical moment μ making an angle ψ with an applied field $E \cos \omega t$ will be taken proportional to $\exp[-\mu \cos \psi E \cos(\omega t_0)/kT]$, where t_0 is the value of the time at collision. The adiabatic assumption is essentially that the quantity t_0 has a meaning.

The other case is that of weak collisions. Here the assumption is made that any individual collision has but little effect in disturbing the original orientation or polarization of the molecule, so that an appreciable change in distribution is obtained only as the result of a large number of

impacts, which hence have to be bountiful. The well-known theory of Debye² on the relaxation behavior of dielectric liquids may be regarded as the embodiment of the weak collision mechanism for the non-resonant case. The viscous resistant force proportional to the rotational velocity in his theory may be considered as representing the damping due to the pattering of a large number of feeble impacts. A number of variants of Debye's calculations should be mentioned, which lead to the same final result. In an interesting article, Kauzmann⁵ shows how the redistribution at collision can be interpreted in terms of reaction rates such as are used in chemical kinetics, instead of in terms of a Brownian motion. Kauzmann includes calculations for both weak and strong collisions. In the appendix we extend his results to include the general intermediate case. The derivation of the analogue of the Debye formula in paramagnetic relaxation given by Kronig⁶ is substantially a quantum-mechanical adaptation of the reaction-rate model, in which the possible orientations are discrete rather than continuous. Kronig assumes essentially weak collisions, since he supposes that at each collision the magnetic quantum number can change by only one unit. At the end of the appendix his model will be amplified to include collisions of arbitrary strength.

A SIMPLE DERIVATION OF THE DEBYE FORMULA

In comparing the Debye theory of nonresonant rotators with the Lorentz calculations on resonant oscillators it is clearly advisable to have a collision mechanism which is as similar as possible in the two cases. We shall therefore adopt the strong collision viewpoint, as it is the easiest to handle, as well as being a reasonable model for impacts in gases. We shall begin by giving a particularly simple derivation of the Debye formula, which is considerably shorter than the usual calculations based on weak collisions and Brownian motion.

Let us suppose that after each collision the probability of distribution of a dipole is distributed in accordance with the Boltzmann law. Let us consider the mean polarization per molecule, at time t ,

⁴ It may be objected that by supposing that after collisions the molecules are distributed in accord with the Boltzmann law, we assume that the transition probability $A_{m \rightarrow m'}$ between two orientations m, m' is influenced only by the energy $W_{m'}$ of the final state, whereas that W_m of the initial might also enter, as for instance in connection with the activation energy necessary to surmount an intervening potential hill. In other words, we suppose that $A_{m \rightarrow m'} = A \exp(-W_{m'}/kT)$, where A is a constant; on the other hand, detailed balancing requires only that $A_{m \rightarrow m'}/A_{m' \rightarrow m} = \exp(-(W_{m'} - W_m)/kT)$. This relation demands only that $A_{m \rightarrow m'} = \varphi(m, m', T)e^{-W_{m'}/kT}$ where φ is symmetrical in m and m' . However, we show in the appendix (cf. remarks after Eq. (24)) that the results with this more general assumption are precisely the same, for strong collisions, as though only the terminal energy were to enter. We, therefore, consider the end result of a strong collision as in accord with the Boltzmann law, as this picture is easier to visualize.

⁵ W. Kauzmann, *Rev. Mod. Phys.* **14**, 12 (1942).

⁶ C. J. Gorter and R. de L. Kronig, *Physica* **3**, 1009 (1936); also especially, Kronig, *ibid.* **5**, 65 (1938).

for the class of molecules whose last preceding collision was at time t_0 . If the applied field is $E \cos \omega t$, the relevant Boltzmann factor is obtained by using the potential energy $-\mu E \cos(\omega t_0)$ appropriate to time t_0 , so that the mean polarization per molecule is

$$\frac{\mu \int_0^\pi \cos \psi \exp [\mu E \cos \psi \cos(\omega t_0)/kT] \sin \psi d\psi}{\int_0^\pi \exp [\mu E \cos \psi \cos(\omega t_0)/kT] \sin \psi d\psi} \quad (1)$$

Here we assume that the inertia of the molecule is so large that the latter can be regarded as stationary between collisions. The supposition is warranted if the frequency of our strong collisions is high compared to the molecular rotational frequency, and is the analogue of Debye's treatment of the resistance as viscous rather than inertial. When only terms of the lowest non-vanishing order in E are retained, (1) becomes

$$\frac{\mu^2 E \cos(\omega t_0) \int_0^\pi \cos^2 \psi \sin \psi d\psi}{kT \int_0^\pi \sin \psi d\psi} = \frac{\mu^2 E}{3kT} \Re \exp(i\omega t_0). \quad (2)$$

Here and elsewhere the symbol \Re means that only the real part of the following complex expression is to be used. To obtain the polarization P per cc, we must multiply by the number N of molecules/cc, and average over the various times of last collision. With random collisions the probability that the last collision experienced before t was in the interval $t-\theta-d\theta$, $t-\theta$ is $(1/\tau)e^{-\theta/\tau}d\theta$ where τ is the mean interval between collisions. The mean polarization per unit volume is hence

$$P = \frac{NE\mu^2}{3kT} \Re \frac{1}{\tau} \int_0^\infty e^{i\omega(t-\theta)} e^{-\theta/\tau} d\theta = \frac{NE\mu^2}{3kT} \Re \frac{e^{i\omega t}}{1+i\omega\tau}. \quad (3)$$

This is the same as the usual expression of Debye. If now we write this formula for P as $E\Re(a-ib)e^{i\omega t}$, the absorption coefficient α is $4\pi b\omega/c$, inasmuch as this is the same as the mean work $\langle EdP/dt \rangle_\omega$ done on the molecule divided by the energy flow $cE^2/8\pi$ in the incident radiation. Thus

$$\alpha = \frac{\omega}{c} \frac{4\pi N\mu^2}{3kT} \frac{\omega\tau}{1+\omega^2\tau^2}. \quad (4)$$

This expression gives the absorption per unit length. The corresponding expression for the imaginary part of the dielectric constant, which is the same as the absorption over a path of $(1/2\pi)$ times a wave-length, is like (4) except that the factor ω/c is wanting.

Although we have given a classical derivation, it is easy to give the corresponding quantum-mechanical proof. This differs only in that the orientations are discrete rather than continuous, so that we must average by summing over the various quantum states rather than integrating over a sphere as in (1). However, the theorem of spectroscopic stability in quantum mechanics shows that $\langle \cos^2 \theta \rangle_{av} = \frac{1}{3}$, as in classical theory, and so the result is the same as before.

The case in which the collisions are not perfectly strong, i.e., do not restore equilibrium after each encounter, will be considered in the appendix.

THE LORENTZ OSCILLATOR THEORY

We now turn to the Lorentz theory¹ of line-broadening for a harmonic oscillator. Let ω be the angular frequency of the incident wave, and let ω_0 be that of the oscillator, whose charge and mass

we denote by e and m , respectively. If $E \cos \omega t$ be the electric field, the equation of motion is

$$m \left(\frac{d^2 x}{dt^2} + \omega_0^2 x \right) = eE \cos \omega t, \quad (5)$$

of which the solution is

$$x = \mathfrak{B} \left\{ \frac{eEe^{i\omega t}}{m(\omega_0^2 - \omega^2)} + C_1 \exp(i\omega_0 t) + C_2 \exp(-i\omega_0 t) \right\}. \quad (6)$$

Suppose now that at a time $t - \theta$, the oscillator has last experienced a collision. Then the transient amplitudes C_1 , C_2 are determined by the values of x and dx/dt immediately after collision. Different oscillators will have different values of x , dx/dt created by the collisions, as no two of the latter are alike. Lorentz assumes that positive and negative values of x and of dx/dt are equally probable, so that on the average one has immediately after collision $x = dx/dt = 0$. Since the averaging of the polarizations of the various oscillators is a linear process, the net result is the same as though one had a single oscillator, and determined C_1 , C_2 so that it has $x = dx/dt = 0$ at time $t_0 = t - \theta$. Then (6) becomes

$$x = \mathfrak{B} \left[\frac{eEe^{i\omega t}}{m(\omega_0^2 - \omega^2)} \left\{ 1 - \frac{1}{2} \left(1 + \frac{\omega}{\omega_0} \right) \exp(i(\omega_0 - \omega)\theta) - \frac{1}{2} \left(1 - \frac{\omega}{\omega_0} \right) \exp(-i(\omega_0 + \omega)\theta) \right\} \right]. \quad (7)$$

We must now average this expression over the various times of last collision. If the collisions occur at random, with a mean interval τ , we multiply, as before, by $(1/\tau)e^{-\theta/\tau}$ and integrate over θ from 0 to ∞ . The result is

$$x = \mathfrak{B} \left[\frac{eEe^{i\omega t}}{m(\omega_0^2 - \omega^2)} \left\{ 1 - \frac{1 + (\omega/\omega_0)}{2\tau[-i(\omega_0 - \omega) + (1/\tau)]} - \frac{1 - (\omega/\omega_0)}{2\tau[i(\omega_0 + \omega) + (1/\tau)]} \right\} \right]. \quad (8)$$

If we write the bracketed factor of (8) as $Ee^{i\omega t}(x' - ix'')$ then the absorption coefficient α and refractive index n are (assuming $n^2 - 1 \ll 1$) given by $\alpha = 4\pi N\omega e x''/c$, $n^2 - 1 = 4\pi N e x'$. Thus it follows that

$$\alpha = \frac{2\pi N e^2}{mc} \left(\frac{\omega}{\omega_0} \right) \left[\frac{1/\tau}{(\omega - \omega_0)^2 + (1/\tau)^2} - \frac{1/\tau}{(\omega + \omega_0)^2 + (1/\tau)^2} \right], \quad (9)$$

$$n^2 - 1 = \frac{4\pi N e^2}{m(\omega_0^2 - \omega^2)} \left[1 - \frac{\frac{1}{2} + \frac{1}{2}(\omega/\omega_0)}{\tau^2[(\omega - \omega_0)^2 + (1/\tau)^2]} - \frac{\frac{1}{2} - \frac{1}{2}(\omega/\omega_0)}{\tau^2[(\omega + \omega_0)^2 + (1/\tau)^2]} \right]. \quad (10)$$

We must now seek to generalize this result to the general quantum-mechanical system. This can be done by making use of the fact that each transition between stationary states can be identified with a certain equivalent or "virtual" classical oscillator, whose effective charge is correlated with the transition probability. Namely, the quantum theory of dispersion⁷ shows that the adaptation is achieved by replacing e^2/m by $8\pi^2\nu_{ij}|\mu_{ij}|^2/3h$ and ω_0 by $2\pi\nu_{ij}$. Here $\nu_{ij} = (W_i - W_j)/h$ is the characteristic frequency associated with a transition between the states i and j . The corresponding moment matrix element μ_{ij} may be either electric or magnetic, the reaction in the latter case being, of course, with H rather than E . One must also distribute the molecules among the various stationary states in accord with the Boltzmann law, and sum over the various possible transitions. One thus obtains

$$\alpha = \left(\frac{8\pi^3\nu N}{3hc} \right) \frac{\sum_j \sum_i |\mu_{ij}|^2 f(\nu_{ij}, \nu) e^{-W_j/kT}}{\sum_j e^{-W_j/kT}}. \quad (11)$$

⁷ Cf. W. Heitler, *The Quantum Theory of Radiation*, Eq. (19), p. 40 vs. Eq. (19), p. 108. His quantity eX_{ab} is the same as our μ_{ij} , and his ν corresponds to our ω .

Where $\nu = \omega/2\pi$ is the incident frequency and f is a "shape factor"

$$f(\nu_{ij}, \nu) = \frac{1}{\pi} \left[\frac{\Delta\nu}{(\nu_{ij} - \nu)^2 + \Delta\nu^2} - \frac{\Delta\nu}{(\nu_{ij} + \nu)^2 + \Delta\nu^2} \right], \quad \text{with } \Delta\nu = \frac{1}{2\pi\tau}. \quad (12)$$

Substantially the same result can also be derived by means of quantum-mechanical radiation theory,⁸ as given, for instance, in Heitler's book,⁹ when allowance is made for transitions in which ν and ν_{ij} are opposite in sign, corresponding to the possibility that excitation of the atom is accompanied by the emission rather than absorption of a quantum. (In this connection the law of conservation of energy need not superficially be satisfied, as energy balance is taken care of by the mechanism responsible for the damping.) The theory is usually assumed to be for radiation, rather than collision damping, but this does not affect general questions of line form.

A common case is one where the resonance frequencies of the molecule are small compared with kT/h . In the microwave region, for instance, this condition is always fulfilled. Since

$$\nu_{ji} = -\nu_{ij}, \quad f(\nu_{ij}, \nu) = -f(\nu_{ji}, \nu), \quad |\mu_{ij}| = |\mu_{ji}|,$$

and

$$(e^{-\nu} - e^{-x-\nu}) \sim \frac{1}{2}x(e^{-\nu} + e^{-x-\nu}) \quad \text{if } x \ll 1,$$

we may then replace (11) by

$$\alpha = \left(\frac{8\pi^3 \nu N}{6hc} \right) \frac{h}{kT} \frac{\sum_i \sum_j |\mu_{ij}|^2 \nu_{ij} f(\nu_{ij}, \nu) e^{-W_{ij}/kT}}{\sum_j e^{-W_{ij}/kT}}. \quad (13)$$

The advantage of (13) is that it involves no nearly compensating terms or negative factors, as $\nu_{ij} f(\nu_{ij}, \nu)$ is always positive.

To compare with the Debye formula for absorption due to a rotating dipole, we must specialize (13) in the following way: the molecule has a permanent moment of magnitude μ for all stationary states, and in addition the rotational energy is considered to be negligible. Stated in equation form, these two conditions mean that

$$\sum_i |\mu_{ij}|^2 = \mu^2, \quad \nu_{ij} = 0. \quad (14)$$

When we substitute (14) in (13), however, we obtain zero rather than the expression (4).

REVISION OF THE LORENTZ FORMULA

The fact that (14) does not reduce (13) to (4) is the contradiction between the Debye and Lorentz theories referred to at the beginning of the article. What is the explanation of the discrepancy? It is that there is a fallacy in the Lorentz calculation, which we have embodied in our Eqs. (5)–(10), when there is thermal equilibrium. Then the values of x and dx/dt after collision should be regarded as distributed not randomly for the oscillator, but instead according to the Boltzmann distribution law for a Hamiltonian function

$$H(t) = (p^2/2m) + \frac{1}{2}m(\omega_0 x)^2 - exE \cos \omega t, \quad (p = dx/dt).$$

Hence the constants C_1 , C_2 in (6) have been incorrectly determined in obtaining (7), and when one introduces a Boltzmann distribution after collision at time $t_0 = t - \theta$, the effect is to increase C_1 , C_2

⁸ E. Wigner and V. Weisskopf, *Zeits. f. Physik* **63**, 54; **65**, 18 (1930); V. Weisskopf, *ibid.* **75**, 287 (1932).

⁹ W. Heitler, *The Quantum Theory of Radiation*, p. 113, Eq. (12). In adding the term in $\nu + \nu_0$ which corresponds to the second member of our Eq. (12), a minus sign must be used because the excitation of the molecule is here accompanied by emission rather than absorption of a light quantum. Heitler interprets $4\pi\Delta\nu$ as the transition probability, but the latter becomes $2\pi\Delta\nu$ when one allows for the possibility of interruptions in both initial and final states.

by amounts ΔC_1 , ΔC_2 , where

$$\Delta C_1 \exp(i\omega_0 t_0) = \Delta C_2 \exp(-i\omega_0 t_0) = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x \exp[-H(t_0)kT] dx dp}{2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[-H(t_0)kT] dx dp} = \frac{Ee \cos \omega t_0}{m\omega_0^2}.$$

Correspondingly there is added to (7) the term

$$(Ee/m\omega_0^2) \cos(\omega t_0) \cos \omega_0(t-t_0) = (Ee/2m\omega_0^2) \mathfrak{B}[e^{i\omega(t-t_0)}(\exp(i\omega_0\theta) + \exp(-i\omega_0\theta))]. \quad (15)$$

When we average, as before, over θ with weighting factor $(1/\tau)e^{-\theta/\tau}$, (15) becomes

$$\frac{Ee}{2m\omega_0^2\tau} \mathfrak{B}\left[e^{i\omega t} \left\{ \frac{1}{(1/\tau) - i(\omega_0 - \omega)} + \frac{1}{(1/\tau) + i(\omega_0 + \omega)} \right\}\right]. \quad (16)$$

When (16) is added, (8) is changed to

$$x = \mathfrak{B}\left[\frac{eEe^{i\omega t}}{m(\omega_0^2 - \omega^2)} \left\{ 1 - \frac{(\omega_0 + \omega)\omega/\omega_0^2\tau}{2[(1/\tau) - i(\omega_0 - \omega)]} + \frac{(\omega_0 - \omega)\omega/\omega_0^2\tau}{2[(1/\tau) + i(\omega_0 + \omega)]} \right\}\right].$$

Correspondingly we have in place of (9) and (10)

$$\alpha = \frac{2\pi Ne^2}{mc} \left(\frac{\omega}{\omega_0}\right)^2 \left[\frac{1/\tau}{(\omega - \omega_0)^2 + (1/\tau)^2} + \frac{1/\tau}{(\omega + \omega_0)^2 + (1/\tau)^2} \right], \quad (17)$$

$$n^2 - 1 = \frac{4\pi Ne^2}{m(\omega_0^2 - \omega^2)} \left[1 - \frac{\frac{1}{2}(\omega/\omega_0) + \frac{1}{2}(\omega/\omega_0)^2}{\tau^2[(\omega - \omega_0)^2 + (1/\tau)^2]} + \frac{\frac{1}{2}(\omega/\omega_0) - \frac{1}{2}(\omega/\omega_0)^2}{\tau^2[(\omega + \omega_0)^2 + (1/\tau)^2]} \right]. \quad (18)$$

The extension to the quantum-mechanical system still gives (11) and (13), but with the difference that the shape factor f has the significance

$$f(\nu_{ij}, \nu) = -f(\nu_{ij}, \nu) = \frac{1}{\pi} \frac{\nu}{\nu_{ij}} \left[\frac{\Delta\nu}{(\nu_{ij} - \nu)^2 + \Delta\nu^2} + \frac{\Delta\nu}{(\nu_{ij} + \nu)^2 + \Delta\nu^2} \right] \quad (19)$$

instead of (12). When we use (19) rather than (12), Eq. (13) reduces to (4) if we make the specializations (14). The paradox is thus removed.¹⁰ It should, however, be emphasized that the modifications which we have introduced in the standard Lorentz theory are of no importance in the optical resonance region in which Lorentz himself was interested, where the second members of formulas such as (12) or (19) are of no interest, and where one has both $\Delta\nu/\nu \ll 1$ and $|\nu_{ij} - \nu|/\nu \ll 1$. In much of the microwave region, or in the limiting case of the Debye theory, these inequalities are not satisfied, and the modifications are considerable. In the limit $\nu_{ij} \ll \nu$, for instance, use of (19) in (11) gives a finite absorption, whereas (12) gives zero, as previously mentioned. In the other limit $\nu_{ij} \gg \nu$, Eq. (19) gives half as much absorption as (12).

As a further indication that our modifications of the Lorentz formula are correct, it may be noted that according to (18), the static dielectric constant obtained as the limit of n^2 as $\nu \rightarrow 0$, has the correct value $1 + 4\pi Ne^2/m\omega_0^2$ appropriate to a harmonic oscillator, regardless of the collision frequency.

¹⁰ Another phrasing, somewhat more quantum-mechanical in language, of the discrepancy between (4) and (13) which results when we use the shape factor (12) is the following. If we treat diagonal matrix elements by means of the Kronig-Gorter theory, which is essentially the quantum-mechanical transcription of the Debye calculation, and if we treat the off-diagonal elements by means of the form factor (12) rather than (19), then the diagonal and non-diagonal elements do not enter symmetrically. Namely, the non-diagonal effect does not agree with the diagonal in the special case of zero proper frequency, which is contrary to the general stability characteristic of quantum mechanics. For instance, if we consider a moment vector precessing about an axis to which it is coupled by some internal field (e.g. the axis of figure in a diatomic molecule), the components perpendicular to the axis would make no contribution to the absorption in the limiting case that the coupling energy is very small. On the other hand, when (19) is used, the perpendicular components will in the limit contribute twice as much as the parallel, as should be the case.

With the unmodified formula (10), the correct limit is obtained only if the collision frequency $1/\tau$ is negligibly small compared to the proper frequency of the line. The fact that experimentally the dielectric constants of gases are not influenced by pressure (except insofar as the latter alters the number of molecules or the local field) may be regarded as an empirical confirmation of the fact that in the limit $\nu=0$ the formulas for the polarization should not involve the collision frequency.

REMARKS ON THE LIMITS OF VALIDITY OF THE FORMULAS

In closing, it should be emphasized that our proofs have all assumed that the collisions are sufficiently rapid, that the alternations of the field during a collision can be regarded as negligible. This supposition is usually referred to as the adiabatic hypothesis, and the statistical distribution problem is treated as essentially that appropriate to a static field equal to the instantaneous value of the field at collision. In this connection it should be emphasized that the validity of the adiabatic hypothesis does not require that the incident frequency ν be small in comparison with the line breadth parameter $\Delta\nu$. If so, the theory would not be usable at all in much of the microwave region. The idea that the theory fails whenever ν is comparable with $\Delta\nu$ is incorrect, for, with strong collisions, $1/2\pi\Delta\nu$ is of the order of magnitude of the mean time τ between collisions, which is much longer than the duration τ_c of a collision. Hence $\Delta\nu \sim \nu$ does not imply $1/\tau_c \sim \nu$. With weak collisions the mean free time between impacts is even smaller than $1/2\pi\Delta\nu$, as many weak collisions are required to produce the same damping as a strong one. Ultimately, with any model, when the frequency is so high that the phase oscillates a great deal during a collision, i.e. when $\nu \sim 1/\tau_c$, the impacts are probably ineffective in creating thermal equilibrium, and the extra term omitted by Lorentz should not be added. The correct formulas are then presumably more nearly (9)–(10) than (17)–(18). In consequence, at extremely high frequencies, the absorption probably approaches zero rather than a finite limit as given by our formulas. However, one is presumably far short of this limit in any microwave region. It should be cautioned that the modified formulas discussed in the present paper do not apply to the theory of the dielectric polarization due to free electrons in the upper atmosphere. Here one is dealing with free particles rather than charges bound to a given position, and the

concept of statistical distribution of moment vectors after collision loses meaning. Hence the conventional theory of the refraction, etc., of the ionosphere is unaffected.

It should be also emphasized that throughout the article we have assumed that there is a single relaxation time τ , or in other words that on the average all molecules have the same mean collision intervals. If one can separate the totality of molecules into different classes such that the subdivisions have unlike values of τ , then one has a phenomenon which is usually spoken of as a "dispersion of relaxation times."¹¹ The parameter τ can then not be regarded as a constant, and the final formulas must be integrated over a distribution of values of τ . The effect of such a dispersal in τ is to make the absorption of the wings of the line more intense than one would expect from the behavior in the center, inasmuch as by (19) the absorption in the center is proportional to $\langle\tau\rangle_{Av}$, and that in the wings to $\langle 1/\tau \rangle_{Av}$ since $\tau = 1/2\pi\Delta\nu$. Clearly one has $\langle 1/\tau \rangle_{Av} > 1/\langle\tau\rangle_{Av}$ if τ is distributed over a range of values. There is some evidence experimentally that the shape does not conform to (19) and that the deviations are of the general character to be expected if there is a dispersion of relaxation times.¹² If the rotational structure is not resolved, as for example in the ammonia resonance, such a dispersion can, perhaps, be explained on the ground of resonance effects, which make the collision cross sections larger for impacting molecules in like than in unlike rotational states. The molecules in highly populated rotational

¹¹ Cf., for instance, R. Fuoss and J. Kirkwood, *J. Am. Chem. Soc.* **63**, 385 (1941) or Kauzmann, reference (5), p. 26.

¹² It is often hard to tell whether apparent discrepancies between theoretical and experimental line forms are due to distribution of relaxation times or to incorrect assumptions concerning the "line strength," or intensity of the dipole matrix element. In this connection it is always well to examine the experimental value of $\int_0^\infty (\alpha/\nu^2) d\nu$ as this integral is independent of τ and so is unaffected by the assumption of dispersion in τ . Any anomalies in this integral hence cannot be attributed to distributed relaxation times.

states will have more counterparts and will hence experience more frequent resonant collisions than do the less inhabited ones, and so will have smaller effective values of τ . This explanation obviously does not apply when the rotational structure has been resolved. Then the only distinction between molecules which can make them differ in τ appears to be the diversity in translational energy. Clearly, fast molecules will experience more collisions per second than slow ones. With the conventional hard sphere model, the resulting dispersion in collision in-

tervals can be shown to be too small to have much influence on line-form. If, however, the force fields of the molecules vary slowly with distance, then the fast molecules may penetrate to regions where the intermolecular forces are sufficient to cause frequent reorientation of the dipole moments, whereas the slow molecules may have inadequate translational energy to make them come near other molecules. In this way, it is possible that an appreciable dispersion of relaxation time can be obtained. The subject is one which needs further investigation.

APPENDIX. DERIVATION OF THE DEBYE FORMULA FOR COLLISIONS OF ARBITRARY STRENGTH

In his interesting paper, Kauzmann⁵ shows how the Debye formula can be obtained for collisions which are either weak or strong, i.e., which alter the orientation of the dipole moment but little, or else destroy all traces of the previous arrangement. He uses what he calls the activation model, in which he considers that to switch from one orientation to another at collision, it is necessary for the molecule to receive rotational energy to surmount some sort of intervening potential hill. He thus stresses the parallelism to the activation theory of the breaking of bonds, etc. in chemical kinetics. As a matter of fact, his considerations are more general than any specific picture of the activation process and require only that the transition probabilities satisfy detailed balancing when there is thermal equilibrium, like, for instance, the absorption and emission probabilities in the Einstein derivation of the radiation law.

In this appendix we shall show that Kauzmann's procedure, or one closely related to it, can readily be extended to include "intermediate collisions" which are not of the limiting weak or strong categories. Let $A_{\omega \rightarrow \omega'} d\omega'$ be the probability that at collision a dipole originally in an element of solid angle $d\omega$ be transferred to another element $d\omega'$. It is only necessary to suppose that

(a) In the absence of the applied field $E \cos \omega t$, the probability $A_{\omega \rightarrow \omega'}^0$ is a function $f(\theta)$ only of the angle θ between the vectors specifying $d\omega$ and $d\omega'$. This assumption is trivial, as obviously in the absence of the field, only the amount of angular change, and not the direction, is of significance. The special cases of strong and weak collisions correspond, respectively, to $f(\theta)$ being independent of θ and to $f(\theta)$ being negligible except for small θ . Here and elsewhere the zero superscript attached to A indicates that the value is that without the applied field.

(b) In the absence of E , there is detailed balancing without preferential weighting of any given orientation, so that $A_{\omega \rightarrow \omega'}^0 = A_{\omega' \rightarrow \omega}^0$.

(c) In the presence of the field, detailed balancing is preserved when the states are weighted in accordance with appropriate Boltzmann factors. This means that

$$A_{\omega \rightarrow \omega'} \exp(\mu E \cos \psi \cos \omega t / kT) = A_{\omega' \rightarrow \omega} \exp(\mu E \cos \psi' \cos \omega t / kT). \quad (20)$$

Here ψ and ψ' are the angles between the applied field E and the elements of solid angle $d\omega$ and $d\omega'$, respectively. In accordance with the adiabatic hypothesis, we use in the Boltzmann factors the instantaneous value of the field at collision, which is assumed to take place at time t .

(d) Higher powers than the first in the field strength can be neglected. These various assumptions collectively imply that

$$A_{\omega \rightarrow \omega'} = A_{\omega \rightarrow \omega'}^0 [1 + (\mu E \cos \psi' \cos \omega t / kT)] + EA^{(1)}_{\omega \rightarrow \omega'}(t, T), \quad (21)$$

with

$$A_{\omega' \rightarrow \omega}^0 = A_{\omega \rightarrow \omega'}^0, \quad A^{(1)}_{\omega' \rightarrow \omega} = A^{(1)}_{\omega \rightarrow \omega'}. \quad (22)$$

The equation expressing the change in the number of molecules in any element of solid angle $d\omega$ is

$$dN_\omega/dt = - \int \int A_{\omega \rightarrow \omega'} N_\omega d\omega' + \int \int A_{\omega' \rightarrow \omega} N_{\omega'} d\omega'. \quad (23)$$

In the absence of the field, orientations are equally probable, and in the presence of the field, only the linear terms in E need be included because of (d), so that we can take

$$N_\omega = (N/4\pi) + EN_\omega^{(1)}.$$

When we neglect higher powers of E , Eq. (23) becomes

$$dN_\omega^{(1)}/dt = - \int \int A_{\omega \rightarrow \omega'}^{(0)} (N_\omega^{(1)} - N_{\omega'}^{(1)}) d\omega' + [N\mu \cos(\omega t)/4\pi kT] \int \int A_{\omega \rightarrow \omega'}^{(0)} (\cos \psi - \cos \psi') d\omega'. \quad (24)$$

The fact that $A_{\omega \rightarrow \omega'}^{(0)}$ has cancelled out entirely from (24), owing to the symmetry (22), furnishes the proof of the statement made in footnote 4 essentially to the effect that no generality is added by including the last term in (21). Now multiply (24) by $\mu E \cos \psi$ and integrate over ω . Since the polarization P is

$$\mu E \int \int N_\omega^{(1)} \cos \psi d\omega,$$

we have

$$dP/dt = -\mu E \int \int \int A_{\omega \rightarrow \omega'}^{(0)} (N_\omega^{(1)} - N_{\omega'}^{(1)}) \cos \psi d\omega' d\omega \\ + [N\mu^2 E \cos(\omega t)/4\pi kT] \int \int \int A_{\omega \rightarrow \omega'}^{(0)} (\cos^2 \psi - \cos \psi' \cos \psi) d\omega d\omega'. \quad (25)$$

Now, by an elementary transformation formula, we have

$$\cos \psi = \cos \psi' \cos \theta + \sin \psi' \sin \theta \cos \varphi, \quad (26)$$

where θ, φ are the polar coordinates of the vector specifying $d\omega$ in a frame whose axis is the vector specifying $d\omega'$ and whose meridian plane contains E .

Now by (a) and (22) we have

$$\int \int A_{\omega \rightarrow \omega'}^{(0)} d\omega' = \int \int f(\theta) d\omega = \gamma, \quad \int \int A_{\omega \rightarrow \omega'}^{(0)} \cos \theta d\omega = \int \int f(\theta) \cos \theta d\omega = \delta, \\ \int \int A_{\omega \rightarrow \omega'}^{(0)} \sin \theta \cos \varphi d\omega' = \int \int f(\theta) \sin \theta \cos \varphi d\omega = 0, \quad (27)$$

where γ and δ are constants independent of the position on the sphere. We now use the substitution (26) for the second or negative term of the integrands in (25). Then in virtue of (27) we have

$$dP/dt = -\gamma\mu E \int \int N_\omega^{(1)} \cos \psi d\omega + \delta\mu E \int \int N_{\omega'}^{(1)} \cos \psi' d\omega' \\ + [N\mu^2 E \cos(\omega t)/4\pi kT] [\gamma \int \int \cos^2 \psi d\omega - \delta \int \int \cos^2 \psi' d\omega'],$$

or

$$dP/dt = -(\gamma - \delta)P + [N\mu^2 E(\gamma - \delta) \cos(\omega t)/3kT]. \quad (28)$$

The solution of this differential equation is

$$P = \frac{N\mu^2 E}{3kT} \Re \left[\frac{e^{i\omega t}}{1 + i\omega/(\gamma - \delta)} \right]. \quad (29)$$

This result is similar to the Debye formula (3), which is thus established. The constant $\gamma - \delta$ is equal to the reciprocal of the relaxation time τ . The assumption of strong collisions is that $A_{\omega \rightarrow \omega'}$ is independent of ω' , so that $\delta = 0$. With weak collisions, the values of $\cos \theta$ which are most heavily weighted in (27) are those near unity, and then δ is nearly as large as γ .

The procedure which has given the generality to the proof is obviously the use of (26). If quantum mechanics is used, so that the orientations are discrete rather than continuous, the results are still valid. We of course then have sums rather than integrals, but the spectroscopic stability of quantum mechanics insures that the transformation properties are similar to those of classical theory. The simplest quantum-mechanical illustration is the atomic magnetic case where the moment in the direction of the field is $mg\beta$, where β is the Bohr magneton, g is the Landé factor, and m is the magnetic quantum number. This model has been treated by Kronig⁶ and Kauzmann⁵ for weak and strong collisions, respectively. In place of (24), we would have for collisions of arbitrary strength

$$dN_m^{(1)}/dt = -\sum_{m'} A_{m \rightarrow m'}^0 (N_m^{(1)} - N_{m'}^{(1)}) + [Ng\beta \cos(\omega t)/kT(2j+1)] \sum_{m'} (m - m') A_{m \rightarrow m'}^0, \quad (30)$$

where j is the inner quantum number. The polarization P is $H \sum_m N_m^{(1)} g\beta m$. The relations corresponding to (26)–(27) are

$$\sum_{m'} A_{m \rightarrow m'}^0 = \gamma, \quad \sum_{m'} m' A_{m \rightarrow m'}^0 = m\delta. \quad (31)$$

The first relation of (31) merely expresses the fact or “sum-rule” that the total transition probability is independent of m . The second is less readily demonstrated but can, for instance, be established in the following way. Let \mathbf{a} be a matrix whose square determines the transition probability. Then the second sum in (31) is, except for a constant factor, proportional to a diagonal element of the matrix $\mathbf{q}_z = \mathbf{a} \mathbf{j}_z \mathbf{a}$ where \mathbf{j}_z is the component of angular momentum in the direction of the applied field. If capital letters denote another choice of the axis of quantization and the λ 's are the direction cosines, then

$$\mathbf{a} \mathbf{J}_z \mathbf{a} = \mathbf{A} \mathbf{J}_z \mathbf{A} = \mathbf{S}^{-1} \mathbf{a} [\lambda_{zx} \mathbf{j}_x + \lambda_{zy} \mathbf{j}_y + \lambda_{zz} \mathbf{j}_z] \mathbf{a} \mathbf{S}. \quad (32)$$

The relation $\mathbf{a} = \mathbf{A}$ which we have used expresses the fact that, in the absence of the field, the transition probabilities obviously cannot depend on how the axis of quantization is selected. Equation (32) shows that \mathbf{q}_z transforms like the z component of a vector, and, this being the case, group theory¹³ shows that its diagonal elements are proportional to m . Thus the second part of (31) is established. By use of the relation $\sum m^2 = \frac{1}{3} j(j+1)(2j+1)$, and by following a procedure analogous to the one we have given in more detail in the classical case, the result (28) is finally obtained with, of course, H in place of E , and with $\mu^2 = g^2 \beta^2 j(j+1)$.

¹³ Cf., for instance, H. A. Kramers, Proc. Amsterdam Acad. Sci. **33**, 953 (1930).