

$g(r) = |r^{-1}f(r)|^2$. Now a formula for the magnetic interaction equivalent to (A4) is

$$W_m = - \int \mathbf{H} \cdot \mathbf{M} dv,$$

where \mathbf{M} is the nuclear magnetization density. Putting in (A13) and performing one partial integration, we have the effective evaluation of the electronic matrix element (A7) for these special cases. Thus, for an $s_{\frac{1}{2}}$ electron,

$$A_1 = \frac{2}{3}\mu_0 g(0)M_1; \quad (\text{A14})$$

and for a $p_{\frac{3}{2}}$ electron,

$$A_3 = - (4/35)\mu_0 g(0)M_3. \quad (\text{A15})$$

This last result is identical with the evaluation given by Casimir and Karreman²³ in their original investigation of the octupole interaction in iodine.

For the calculation of second order effects between doublet states, the forms (A7), (A8) of the dipole and quadrupole operators are used. Assuming that both doublet states have identical radial wave functions, the final result is just Eq. (42) with $\xi = \eta = 1$.

²³ H. B. G. Casimir and G. Karreman, *Physica* **9**, 494 (1942).

Shape of Collision-Broadened Spectral Lines*

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(Received August 24, 1954)

Van Vleck and Weisskopf and Fröhlich have derived a micro-wave line shape by studying the interruption by collisions of the motion of a classical oscillator. They assume that after the instantaneous impact the oscillator variables are distributed according to a Boltzmann distribution appropriate to the value of the applied field at collision. In contrast to the earlier theory of Lorentz, they obtain the correct static polarization. The procedure involves an assumption of very large velocity during collision. This is criticized on the grounds that the duration of collision is short compared to the resonant period and energy exchanges are of the order of kT . We have derived a line-shape formula assuming that the positions are unchanged after impact. Two extreme models are studied. In one, the oscillators have a Maxwellian

distribution of velocities after impact; the second is a Brownian motion treatment. The resulting line shape in both cases is that of a friction-damped oscillator. For collision frequency much less than the resonant frequency, the polarization postulated by the above authors is reached as a result of kinematic motion between collisions, and the line shapes agree. However, to obtain equal line widths and peak absorptions, the collision frequency is twice as large for the present theory. For collision frequency comparable to resonant frequency a less distorted line shape results. For testing the theories, experiments on foreign-gas broadening in the micro-wave region at pressures of the order of an atmosphere are required. Differences between the theories are small for conditions accessible experimentally at present.

1. INTRODUCTION

THE theoretical determination of the shape of a spectral line, broadened by interactions between the radiating molecule and other systems, is an exceedingly complicated problem. The general case involves a study of the types of interaction possible, treatment of the exchange of energy between internal degrees of freedom and translational motions, questions of coherence, of radiation, etc. In addition, for broad lines one may encounter the characteristic complexities of many-body problems. A clear understanding of the physical processes involved has been gained only in certain limiting cases. There, the consideration of simple models has been useful in calling attention to the ingredients which must enter into more general treatments. The present paper deals with some models which shed light on the processes responsible for the shapes of the

spectral lines in gases (chiefly rotational), in the microwave region.

For microwave wavelengths, the energy $\hbar\omega_0$, corresponding to a spectral line of angular frequency ω_0 , is usually small compared to the thermal energy kT . This implies that collision-induced transitions between states are important. Indeed, saturation measurements indicate that most collisions involve energy exchanges between the rotational and translational degrees of freedom. If consideration is restricted to foreign-gas broadening (thus excluding the long-range resonance forces), the duration of collision is short compared to the resonant period of the line. It is then useful to introduce for each line a quantity τ , which measures the time between those collisions involving exchanges of energy between translational motions and the relevant internal states. In treatments less schematic than the ones with which we deal, τ is computed in terms of the intermolecular forces. This question is not discussed here; the present work deals with the analysis of some kinetic-statistical aspects of the line-broadening problem. It is of course somewhat arbitrary to split up the problem in

* Sponsored by the U. S. Office of Naval Research, the Army Signal Corps, and the Air Force.

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this manner; a complete treatment would, however, be involved.

Our considerations are in the spirit of previous work by Van Vleck and Weisskopf¹ and also Fröhlich.² These treatments are most appropriate for foreign-gas broadening when the nonradiating molecules are more numerous than the radiating ones and form an inert reservoir. It is then permissible to neglect effects which may occur in a purely polar gas, and which have to do with definite correlations between the radiations of two colliding molecules. In addition, the problem of representing the irreversible nature of the absorption process is made simple by the presence of the nonradiating reservoir. In practice correlation considerations probably lead to new results only for highly compressed polar gases. The probable effect of a collision on the state of the radiating molecule is, in general, dependent on the mass ratio of radiating and nonradiating molecules, the type of interaction, the nature of the dynamic order of the reservoir molecules, etc. Study of these factors is important for the understanding of the differences in the dielectric behavior of compressed gases and liquids. Some of these questions will be treated in a communication to follow. For the present we limit ourselves to a criticism and analysis of certain general features of previously proposed models of the collision process. We discuss several alternative approaches. One is a strong-collision model which is perhaps appropriate when radiating and nonradiating molecules have comparable masses, and when, as in a gas, the dynamic ordering of the reservoir molecules is unimportant. The second approach is a Brownian motion treatment of a system of oscillators which is perhaps more appropriate for radiating molecules more massive than those forming the reservoir. More general models can easily be constructed.

In the development of the mathematical theory it has been useful to study the effects of collisions on the absorption or emission of radiation by a classical charge vibrating harmonically. With the help of the concept "virtual oscillator" it is possible to use the classical formulas to find the quantum-mechanical result for a general molecule. This procedure will be followed in the present paper. A more direct quantum treatment, along the lines of the work of Karplus and Schwinger,³ will be given later. If the absorption and dispersion of electromagnetic radiation is studied in the vicinity of a pure rotation line, four quantities with the dimensions of a frequency enter naturally. These are: the resonant frequency ν_0 of the line; the frequency ν of the applied field; the collision frequency ν_c ; and a quantity which is the reciprocal of the duration of collision. The duration of collision is approximately the spatial extent of the

interaction divided by the translational velocity, i.e., for foreign-gas broadening, of the order of 10^{-12} sec. The collision duration is thus short compared to the other three periods for microwave rotational lines in the centimeter range.

Van Vleck and Weisskopf¹ have discussed harmonic-oscillator models where collisions are instantaneous, and have derived a line-shape formula [Eq. (22)] which has found wide use in the interpretation of microwave spectra. The line-shape formula has, however, not been adequately checked by experiment when the line width is comparable to the resonant frequency of the line, i.e., at pressures of the order of an atmosphere. Extensive published results exist only for pure NH_3 and ND_3 . The ammonia case is complicated by line shifts arising from statistical broadening and inversion splitting, and does not provide a test of the Van Vleck-Weisskopf line shape under the conditions upon which the derivation is based. It is therefore desirable that experiments be performed on the line broadening of simple molecules (e.g., CO_2) by foreign gases at pressures in the vicinity of an atmosphere. The present paper deals with harmonic oscillators and also makes the assumption of instantaneous collisions. It is believed that the model of the collision process presented here is more realistic for gas broadening. One is led to an alternative line-shape formula which is simply the spectrum emitted by a radiating oscillator moving under the influence of a viscous resistance. The line shape agrees with that of reference 1 when the collision frequency is small compared to the resonant frequency. The discussion of Sec. 4 indicates that the differences between the formulas in the high-pressure region may be measurable, in spite of the contributions of neighboring lines.

2. ASSUMPTIONS OF EARLIER TREATMENTS

The theory of the absorption of energy by a harmonically bound particle is well known. Let e be the charge and m the mass of the particle, ω_0 the resonant angular frequency, $E_0 e^{i\omega t}$ the external field and $-m\gamma\dot{x}$ the friction force. Then the steady-state polarization $P(t)$ is given by Eq. (20c) with the resistance $r=1/\tau$. There are three limiting cases of interest. If ω tends to zero, one finds the correct static polarization for a system of N oscillators, i.e., $P = Ne^2 E / m\omega_0^2$. All reference to r has disappeared; the static polarization is independent of the rate and mechanism of approach to equilibrium. A second case is r small compared to ω and ω_0 ; the well-known anomalous dispersion and absorption line shapes result. For r comparable to ω and ω_0 the absorption line shape is asymmetrical and possesses a high frequency tail; it is however symmetrical when plotted against the logarithm of the frequency. A third limit is obtained by setting the resonant frequency equal to zero. One then obtains the simple theory of conduction and light absorption of electrons in metals or in the ionosphere. To adapt this model to describe the rotational lines of a molecule one assigns virtual oscillator

¹ J. H. Van Vleck and V. Weisskopf, *Revs. Modern Phys.* **17**, 227 (1945).

² H. Fröhlich, *Nature* **157**, 478 (1946); *Theory of Dielectrics* (Oxford University Press, London, 1949). A theory of substantially the same form was presented earlier by R. Kronig, *Physica* **5**, 65 (1938).

³ R. Karplus and J. Schwinger, *Phys. Rev.* **73**, 1020 (1948).

quantities e_{ij} , ω_{ij} , r_{ij} to each transition from level i to level j . At low foreign-gas pressures, i.e., $r_{ij} \ll \omega_{ij}$ and ω , the rotation lines are sharp, well separated, and practically symmetrical. When r_{ij} is comparable to ω and ω_{ij} , the line shape is asymmetric. For larger values one encounters overlap of lines; finally, the instantaneous collision assumption becomes invalid.

Our aim is to derive formulas for the polarization on the basis of more realistic collision models and to discuss the above cases. The principal result is that the simplest collision models give the same results as the friction-damped oscillator. For many molecules there is a range of foreign-gas pressures where individual rotation lines are still separable but where the theories predict different line shapes. In addition, different predictions in the region of strong overlap can in principle be compared with experimental absorption measurements as a function of frequency, pressure, and temperature.

Lorentz attempted to describe the process of interruption by impacts in a more physical manner. While his developments dealt with the optical region, the assumption as to the effects of an instantaneous collision can be adopted to the energy-transfer type of theory of reference 1. The key assumption is that the oscillators which suffer collisions at the same time are redistributed with positions and velocities weighted according to a Boltzmann distribution appropriate to the field-free Hamiltonian $H_0 = p^2/2m + m\omega_0^2 x^2/2$, where p and x are the momentum and position of an oscillator. Lorentz's expression for the polarization is Eq. (20a), which differs from Eq. (20c) by the presence of the term $1/\tau^2$ in the denominator. For collision frequencies much less than ω and ω_0 , the difference is negligible. However, as $\omega \rightarrow 0$ one obtains the incorrect polarization $P = N^2 e^2 E / m(\omega_0^2 + 1/\tau^2)$ and, as $\omega_0 \rightarrow 0$, one fails to obtain free-particle behavior.

The important work of Van Vleck and Weisskopf,¹ and (independently) of Fröhlich,² reopened the question of the proper treatment of collisions. These authors attempted to construct a theory which correctly describes line shapes in the microwave region where ω , ω_0 , and $1/\tau$ are comparable. To overcome the inadequacies of the Lorentz theory, they assumed that after collision at time t , the oscillator variables are distributed according to a Boltzmann distribution appropriate to the instantaneous Hamiltonian $H(t) = p^2/2m + m\omega_0^2 x^2/2 - eE_0 x \cos\omega t$. This assumption leads to the polarization of Eq. (20b), which is correct in the static limit. However, as $\omega_0 \rightarrow 0$ one does not obtain the polarization of a free electron gas, as is the case with Eq. (20c). In fact, the polarization tends to an infinite result. Van Vleck and Weisskopf justified their line shape by finding the quantum-mechanical adaptation of Eq. (20b) for the case of permanent dipoles. In the limit of an infinite moment of inertia, i.e., zero resonant frequency, they obtained the Debye formula,

$$P = \frac{N\mu^2}{3kT} / (1 + i\omega\tau),$$

where μ is the permanent dipole moment of the molecule. This was considered to be a necessary result of any correct theory. The quantum-mechanical adaptation of formula (20c) does not lead to this result. Formula (20b) has the additional consequence that the absorption tends to the finite value $\omega_p^2/\omega_0^2\tau c$ as $\omega \rightarrow \infty$; the integrated absorption over all frequencies is therefore infinite.

The experimental evidence for the Debye formula lies in dielectric relaxation experiments on liquids. Extensive measurements of the relaxation of dipoles in compressed gases have not been published.⁴ The two cases differ in the nature of the dynamic order, and it is probably to the compressed gas that the theories under consideration most nearly refer. That the liquid and compressed gas are profoundly different in their dynamical behavior can be seen, for example, from the fact that the parameter τ (if related to static viscosity) has entirely different dependences on temperature and pressure. Furthermore, measurements⁵ of supersonic absorption of compressed gases and liquids near the critical temperature indicate distinct mechanisms for the two cases. Thus we do not consider the Debye law to be a necessary result. This question will be discussed further from the theoretical point of view in a later communication. It will be shown that the Debye relaxation time is essentially different from the time between collisions, τ .

A significant advance in the understanding of the physical assumptions involved in the approaches leading to Eq. (20b) was taken by Van Vleck and Margenau.⁶ They pointed out that work is done by the electromagnetic field on the oscillator during an adiabatic collision ("impulsive work"). This is indeed necessary in a theory in which collisions induce amplitude changes since the peak amplitude after collision can differ from that before only if work has been done during the collision. The total energy absorbed from the field is the sum of the work done between and during collisions. However, a less satisfactory implication of the theory is that the oscillator velocity is instantaneously infinite for an infinitesimally short collision. This is necessary so that the mean oscillator position jumps a finite amount to reach the value appropriate to the assumed Boltzmann distribution. The present calculation is based on the conviction that this feature of the theories is not reasonable. The following arguments lead to an alternative model.

If harmonic oscillators collide with the molecules of a buffer medium, one may assume that the kinetic energies after collision have a Maxwellian distribution, since the buffer molecules have such a distribution. This procedure is followed in all the theories dealt with here

⁴ Experiments by C. S. E. Phillips of the Laboratory for Insulation Research, Massachusetts Institute of Technology, are in progress.

⁵ H. D. Parbrook and E. G. Richardson, Proc. Phys. Soc. (London) **B65**, 437 (1952).

⁶ J. H. Van Vleck and H. Margenau, Phys. Rev. **76**, 1211 (1949).

(with the exception of the Brownian motion treatment of Sec. 6). One tacitly assumes that the oscillator mass is of the same order of magnitude as the mass of the buffer molecules and that collisions are strong. Consider, on the other hand, the distribution of positions after collision. We shall argue that a reasonable assumption is that the oscillator does not alter its position during a collision.

A typical energy exchange is of the order of kT . If the duration of the collision is written as β/ω_0 , where β is a very small fraction, the distance the oscillator moves during a collision is $\simeq(kT/m)^{1/2}\beta/\omega_0$. In thermal equilibrium the mean square displacement of the oscillator is given by $m\omega_0^2\bar{x}^2/2\simeq kT$ or $(\bar{x}^2)^{1/2}=(2kT/m)^{1/2}/\omega_0$. At collision the oscillator thus moves only a small fraction of a typical amplitude. Furthermore, this distance is independent of the field E_0 , so that there can be no tendency to take up a distribution of positions determined by the external field. The action of the applied field during a collision can move the oscillator a distance of the order of $\frac{1}{2}(eE_0/m)(\beta/\omega_0)^2$. This is β^2 times the mean displacement in a static field E_0 . It therefore appears that a more reasonable assumption is that the oscillator position is unchanged as a result of collision. The impacts, however, change the velocity instantaneously, implying infinite acceleration. There is impulsive momentum change (force \times time) and impulsive work (force \times time \times particle velocity). Changes in position occur only between collisions as a result of the motion of the particle under the influence of its binding force and the external field. This picture is closely related to the description of collisions in the kinetic theory of gases. In the next section, we develop a mathematical theory embodying this idea. One finds the formula (20c) for the polarization. From the present point of view the reason for the adequacy of the Van Vleck-Weisskopf and Fröhlich formulas when $1/\tau\ll\omega_0$ and ω is the following. Consider a set of oscillators which have made collisions at the same time. The motions will then be rigorously determined by the initial conditions after collision and by the equation of motion containing the binding force and the external field. The electric field distorts the oscillator motion. If $1/\tau\ll\omega_0$ and ω , and furthermore $\omega_0>\omega$, macroscopic quantities such as the polarization have time to approach the value postulated by Van Vleck-Weisskopf and Fröhlich between collisions.⁷ No serious error is then made by assuming that the distribution in position is the Boltzmann distribution appropriate to the instantaneous value of the applied field. When $1/\tau$ is comparable to ω_0 or ω , and $\omega\gg\omega_0$, the assumption is inadequate.

3. MATHEMATICAL FORMULATION FOR HARMONIC-OSCILLATOR BROADENING

The one-dimensional harmonic oscillator is characterized by a charge e , a mass m , and a resonant frequency

⁷ See reference 2, p. 63. The subsequent development, however, does not make correct use of this insight.

ν_0 . The state of the oscillator at time t is prescribed by its position x and its velocity v . We deal with a distribution function $f(x,v,t)$,² which determines the statistical behavior of the system of oscillators. The physical interpretation is that $f(x,v,t)dx dv$ gives the number of oscillators at time t with velocities in the range $v, v+dv$ and with positions between x and $x+dx$. If the distribution function is known, it is possible to compute various other quantities of physical interest. The total number of molecules per unit volume (of ordinary, *not* x space) is N , and is independent of time. The distribution function is therefore always required to satisfy

$$N = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(x,v,t) dx dv. \quad (1)$$

The number of oscillators per unit volume at x and time t , is

$$n(x,t) = \int_{-\infty}^{+\infty} f(x,v,t) dv. \quad (2)$$

The mean electric polarization of the oscillators is

$$P(t) = e \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} x f(x,v,t) dx dv. \quad (3)$$

The mean momentum $g(x,t)$ and kinetic energy $k(x,t)$ at x and t are given, respectively, by

$$g(x,t) = m \int_{-\infty}^{+\infty} v f(x,v,t) dv,$$

$$k(x,t) = \frac{m}{2} \int_{-\infty}^{+\infty} v^2 f(x,v,t) dv.$$

We now construct the equation governing the behavior of the distribution function. $f(x,v,t)$ changes as a result of purely kinematic action and because of collisions. We write

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial x} + a \frac{\partial f}{\partial v} = \left. \frac{\delta f}{\delta t} \right|_c. \quad (4)$$

The term $v\partial f/\partial x$ represents the kinematic drift in x space, and the term $a\partial f/\partial v$, the drift in velocity space as a result of the acceleration a . The expression $\delta f/\delta t|_c$ represents the effects of collisions on the distribution function and will be discussed in detail later. To compute the acceleration we note that the Hamiltonian of the oscillator in an external electric field $E_0 \cos\omega t$ is:

$$H(t) = p^2/2m + m\omega_0^2 x^2/2 - exE_0 \cos\omega t. \quad (5)$$

We find the acceleration

$$a = d\dot{p}/mdt = -\partial H/m\partial x = -\omega_0^2 x + eE_0 \cos\omega t/m.$$

The kinetic equation for the distribution function is therefore

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial x} - \omega_0^2 x \frac{\partial f}{\partial v} + \frac{eE_0 \cos \omega t}{m} \frac{\partial f}{\partial v} = \frac{\delta f}{\delta t} \Big|_c. \quad (6)$$

In the absence of an electric field the equilibrium distribution is

$$f_0 = C_0 \exp[-(mv^2 + m\omega_0^2 x^2)/2kT]; \quad (7)$$

T is the temperature of the reservoir and k is Boltzmann's constant. Since we require $\int \int f_0 dx dv = N$, we find

$$C_0 = N\omega_0 m / 2\pi kT. \quad (8)$$

The equilibrium distribution in position is

$$n_0(x) = \int f_0 dv = N\omega_0 (m/2\pi kT)^{1/2} \exp\left(-\frac{m\omega_0^2 x^2}{2kT}\right). \quad (9)$$

If the electric field at time t , $E_0 \cos \omega t$, were frozen, the equilibrium distribution which would be reached eventually is

$$f_{eq} = C \exp[-(mv^2 + m\omega_0^2 x^2 - 2eE_0 x \cos \omega t)/2kT]. \quad (10)$$

One again requires $\int \int f_{eq} dx dv = N$. We shall be concerned with effects which are linear in the electric field strength. To this approximation $C = C_0$. More generally

$$\frac{N}{C} = \frac{2\pi kT}{m\omega_0} \exp\left(\frac{e^2 E_0^2 \cos^2 \omega t}{2kT m \omega_0^2}\right). \quad (11)$$

Let us now consider the collision term $\delta f/\delta t|_c$. Three expressions will be studied here. They are:

(1) The Lorentz assumption,

$$\frac{\delta f}{\delta t} \Big|_c = -\frac{1}{\tau} (f - f_0); \quad (12a)$$

(2) the instantaneous equilibrium assumption of Van Vleck and Weisskopf and of Fröhlich,⁸

$$\frac{\delta f}{\delta t} \Big|_c = -\frac{1}{\tau} (f - feq); \quad (12b)$$

(3) the assumption of the present report,

$$\frac{\delta f}{\delta t} \Big|_c = -\frac{1}{\tau} \left[f - n(x,t) \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv^2}{2kT}\right) \right]; \quad (12c)$$

τ is a constant independent of velocity, representing the time between collisions. We find from the kinetic equation for the above three cases that if f is normalized at

⁸ Fröhlich uses the language of distribution functions, Van Vleck and Weisskopf that of mean-free-path theory. The latter follows the history of an individual particle and is intimately connected with the characteristics of the partial differential equation satisfied by the distribution function.

any given time

$$\frac{\partial N}{\partial t} = \int \int \frac{\delta f}{\delta t} \Big|_c dx dv = 0.$$

Thus the normalization condition is maintained by the motions.

The physical content of the Lorentz assumption is that collisions make the distribution relax in a time τ to the equilibrium in the absence of a field. The Lorentz collision term is inadmissible since it leads to an incorrect equilibrium distribution for the case of a static electric field. Collisions fail to maintain the correct distribution. Assumption (2) yields the correct value of the distribution function for static fields. Left and right hand sides of the kinetic equation are separately equal to zero when $f = feq$ for static fields. The same statement holds when assumption (3) is employed. The physical content of assumption (2) is that collisions tend to make the distribution relax in a time τ to the equilibrium value characteristic of the instantaneous field at time t . This content can be expressed in another way. The number of molecules ejected from the range $x, x+dx$ and $v, v+dv$ is proportional to the number actually present in this range at time t ; this is the $-f(x,v,t)/\tau$ term. The number per second re-emitted into the range is given by feq/τ . The mathematical form of assumption (3) is somewhat different from the others; it contains the integral quantity $n(x,t) = \int f dv$. Assumption (3) states that the number per second reemitted into the velocity range $v, v+dv$ as a result of collisions has the Maxwellian form. The number re-emitted into the spatial region, $x, x+dx$, is proportional to the total number in that region before collisions.

The difference between assumption (3) and assumptions (1) and (2) may be seen by computing $\int \delta f/\delta t|_c dv$. This expression represents the change per unit time in the number of particles at x, t . It vanishes under assumption (3) but not under assumptions (1) and (2). The change per unit time due to collisions of both kinetic energy and total energy is nonzero for all three assumptions. This is indeed necessary to represent the degradative nature of the absorption process.

4. THEORY OF ABSORPTION AND DISPERSION

We investigate only processes linear in the electric field strength. Let us adopt complex notation and write

$$E = E_0 \exp(i\omega t).$$

We introduce the dimensionless quantities $\phi(x,v,t)$ and $\nu(x,t)$ defined by

$$f = f_0(1 + \phi), \quad (13)$$

$$n = n_0(1 + \nu); \quad (14)$$

ϕ and ν are proportional to the electric field strength and are small compared to unity. If terms containing products of ϕ , ν , or E are neglected, one obtains the

kinetic equation,

$$\frac{\partial \phi}{\partial t} + \frac{1}{\tau} \phi + v \frac{\partial \phi}{\partial x} - \omega_0^2 x \frac{\partial \phi}{\partial v} = \frac{eE_0 \cos \omega t v}{kT} + \Delta. \quad (15)$$

Δ takes on the following values for the three assumptions discussed above

$$(1) \quad \Delta = 0, \quad (16a)$$

$$(2) \quad \Delta = (1/\tau)(eEx/kT), \quad (16b)$$

$$(3) \quad \Delta = \nu/\tau. \quad (16c)$$

In the present section steady-state solutions will be studied. ϕ and ν are assumed to have the form $\phi = \phi_0 \exp(i\omega t)$, $\nu = \nu_0 \exp(i\omega t)$. For the discussion of this section we seek solutions of the form²

$$\phi = -(\alpha x + \beta v)E_0 \exp(i\omega t). \quad (17)$$

The values of α and β are found on inserting the expression for ϕ in the kinetic equation and equating the coefficients of x and v separately to zero. With the chosen form of ϕ the value of ν is

$$\nu = \left(\int \phi f_0 dv / \int f_0 dv \right) = -\alpha x E_0 \exp(i\omega t). \quad (18)$$

The three values of ϕ are

$$(1) \quad \phi = \frac{eE_0}{kT} e^{i\omega t} \frac{1}{(1/\tau + i\omega)^2 + \omega_0^2} \times \left[\omega_0^2 x + \left(\frac{1}{\tau} + i\omega \right) v \right], \quad (19a)$$

$$(2) \quad \phi = \frac{eE_0}{kT} e^{i\omega t} \frac{1}{(1/\tau + i\omega)^2 + \omega_0^2} \times \left[\left(\omega_0^2 + \frac{1}{\tau^2} + \frac{i\omega}{\tau} \right) x + i\omega v \right], \quad (19b)$$

$$(3) \quad \phi = \frac{eE_0}{kT} e^{i\omega t} \frac{1}{\omega_0^2 - \omega^2 + i\omega/\tau} [\omega_0^2 x + i\omega v]. \quad (19c)$$

The polarization is $P = e \int \int x f_0 \phi dx dv$ and depends only on the coefficient α . One finds

$$(1) \quad P = \frac{Ne^2 E_0}{m} \frac{e^{i\omega t}}{(1/\tau + i\omega)^2 + \omega_0^2}, \quad (20a)$$

$$(2) \quad P = \frac{Ne^2 E_0}{m\omega_0^2} \frac{[\omega_0^2 + 1/\tau^2 + i\omega/\tau] e^{i\omega t}}{(1/\tau + i\omega)^2 + \omega_0^2}, \quad (20b)$$

$$(3) \quad P = \frac{Ne^2 E_0}{m} \frac{e^{i\omega t}}{\omega_0^2 - \omega^2 + i\omega/\tau}. \quad (20c)$$

The complex dielectric constant ϵ may be written as $\epsilon = \epsilon' - i\epsilon''$. It is obtained from the formula $\epsilon - 1 = 4\pi P/E$. The absorption, a , is given by $a = \omega\epsilon''/c$, where c is the velocity of light.

The expressions for ϵ' , ϵ'' , a are (with $\omega_p^2 = 4\pi Ne^2/m$),

$$(1) \quad \epsilon' - 1 = \omega_p^2 (1/\tau^2 + \omega_0^2 - \omega^2)/D, \quad (21a)$$

$$\epsilon'' = \omega_p^2 2\omega/\tau D, \quad (21b)$$

$$a = 2\omega^2 \omega_p^2 / c\tau D; \quad (21c)$$

$$(2) \quad \epsilon' - 1 = \omega_p^2 \left[\left(\omega_0^2 + \frac{1}{\tau^2} \right) \times \left(\omega_0^2 + \frac{1}{\tau^2} - \omega^2 \right) + \frac{2\omega^2}{\tau^2} \right] / \omega_0^2 D, \quad (22a)$$

$$\epsilon'' = \omega_p^2 \omega \left(\omega_0^2 + \frac{1}{\tau^2} + \omega^2 \right) / \omega_0^2 \tau D, \quad (22b)$$

$$a = \omega_p^2 \omega^2 \left(\omega_0^2 + \frac{1}{\tau^2} + \omega^2 \right) / \omega_0^2 \tau c D,^{10} \quad (22c)$$

where the denominator D is: $D = (1/\tau^2 + \omega_0^2 - \omega^2)^2 + 4\omega^2/\tau^2$;

$$(3) \quad \epsilon' - 1 = \omega_p^2 (\omega_0^2 - \omega^2) / (\omega_0^2 - \omega^2)^2 + \omega^2/\tau^2, \quad (23a)$$

$$\epsilon'' = \frac{\omega_p^2 \omega}{\tau} / (\omega_0^2 - \omega^2)^2 + \omega^2/\tau^2, \quad (23b)$$

$$a = \frac{\omega_p^2 \omega}{\tau c} / (\omega_0^2 - \omega^2)^2 + \omega^2/\tau^2. \quad (23c)$$

Let us now compare the predictions of the theories (2) and (3). There is a variety of cases, the exact situation depending on the relations between ω , ω_0 , and $1/\tau$.

Consider, as a first case, the low-frequency wing of the line. For ω much less than both $1/\tau$ and ω_0 , the absorption according to (2), is

$$a = \omega_p^2 \omega^2 / \omega_0^2 \tau c \left(\omega_0^2 + \frac{1}{\tau^2} \right).$$

According to (3), $a = \omega_p^2 \omega^2 / c\tau \omega_0^4$. The results agree if $1/\tau \ll \omega_0$. This has an important consequence if one is considering the absorption in the microwave region at high pressures, when there are appreciable contributions from overlapping lines of high resonant frequency. For most of these lines, $1/\tau \ll \omega_0$, so that the contributions to the absorption are the same for theories (2) and (3). Of course, if the collision frequency is so great that it is comparable to the frequency of the line of maximum intensity [for a rotator of moment of inertia I , a fre-

¹⁰ This line shape was derived by R. Kronig, *Physica* 5, 65 (1938).

quency of $(kT/I)^{1/2}$] there will be important differences. Theory (2) then predicts a considerably smaller absorption than does (3). In addition, at a fixed frequency ω , the increase in absorption as $1/\tau$ increases is less rapid according to (2) than according to (3). These effects are, however, somewhat obscured by the increasing untrustworthiness of the instantaneous collision hypothesis.

As a second case, we examine the behavior in the high-frequency wing of the line. Theory (2) yields, when $\omega \gg 1/\tau$, ω_0 , the finite absorption $a = \omega_p^2/\omega_0^2\tau c$. Theory (3) yields zero for the absorption. Thus, unless a cutoff is introduced because of the failure of the instantaneous collision assumption, theory (2) leads to an infinite absorption when integrated over all frequencies. In practice, observation of the high frequency tail of one of the low lying rotation lines is difficult. Overlapping of higher rotational lines is important at collision frequencies of the order of ω_0 . It is only for such collision frequencies that the predictions of theories (2) and (3) differ significantly. Since the collision frequency may not be strictly proportional to foreign-gas pressure, and collision frequencies for higher lines differ in general from those for the lower lines, it is probably no easy task to find clearcut verifications of any theory.

A third case is $1/\tau \ll \omega$ and ω_0 . This will occur at low pressures when one finds narrow lines. Confining oneself to the body of the line, where $\omega_0^2 - \omega^2$ is of the same order of magnitude as $1/\tau^2$, we find $D \simeq (\omega_0^2 - \omega^2)^2 + 4\omega^2/\tau^2$. The absorption according to theory (2) is

$$a = \frac{\omega_p^2 2\omega^2}{\omega_0^2 \tau c} \left/ \left[(\omega_0^2 - \omega^2)^2 + 4\omega^2/\tau^2 \right] \right.$$

This has the same shape as Eq. (23c); however, to obtain the same line width the collision frequency $1/\tau$ of assumption (3) must be taken as twice that entering in assumption (2). This is an important point, since a more detailed theory expresses the collision time τ in terms of molecular properties such as dipole moment, quadrupole moment, polarizability. To compare with experiment one must obtain τ from observed line widths. It is then relevant whether the observed line width should be identified with $1/\tau$ or $2/\tau$.

For the third case (narrow lines) the peak of the absorption occurs at approximately $\omega = \omega_0$ on both theories (2) and (3). Theory (2) predicts the maximum absorption $a(\omega = \omega_0) = \omega_p^2\tau/2c$ while theory (3) yields twice this value. If the collision frequency of (3) is chosen to make the line width agree with that of (2) the absolute intensities will also be the same. However, comparing with the first case we see that the absorption in the low-frequency wing will be twice as large for theory (3).

Fourth, we consider the situation where ω , ω_0 , and $1/\tau$ are all of comparable magnitude. Formula (23c) has the important properties that the peak of the absorption always occurs at $\omega = \omega_0$ and that the absorption is

symmetric if one plots against the natural logarithm of the frequency. According to formula (22c) the position of the maximum absorption shifts to higher frequencies as $1/\tau$ becomes comparable to ω_0 . The position of maximum absorption is given by

$$\omega_{\max}^2 = \frac{(\omega_0^2 + 1/\tau^2)^2 + [(\omega_0^2 + 1/\tau^2)^4 + (\omega_0^2 + 1/\tau^2)^3(3\omega_0^2 - 1/\tau^2)]^{1/2}}{3\omega_0^2 - 1/\tau^2}$$

For $1/\tau = 0.3\omega_0$, this shift is approximately 10 percent; for $1/\tau = 0.5\omega_0$ it is 25 percent. The behavior of the maximum of the line is perhaps the most promising way of testing the theories. We must however notice that at $1/\tau = 0.3\omega_0$ the contributions of overlapping lines are also of the order of 10 percent. To add to the difficulties the contributions from the low-frequency wings of the higher rotational lines for the values of $1/\tau$ chosen, are likely to be larger according to formula (23c). This also leads to a shift towards the high frequency side. For comparison of theory and experiment the situation is more favorable for the third or fourth rotational line rather than the first. The ratio of statistical weights of the higher lines to the given line is then less, making the effects of higher lines of less importance. At $\omega = \omega_0$ the absorption according to Eq. (23c) is $a = \omega_p^2\tau/c$ aside from the effects of overlapping lines, it decreases with foreign-gas pressure. Formula (22c) has an additional factor which partially counteracts the decrease.

Finally, we examine the limit $\omega_0 \ll \omega$ and $1/\tau$, i.e., resonant frequency small compared to applied frequency and collision frequency. Such a case is difficult to realize for the rotation spectrum without the crucial intervention of overlapping lines. For $\omega_0 = 0$, assumption (3) yields the complex dielectric constant $\epsilon - 1 = \omega_p^2/(i\omega/\tau) - \omega^2$, which is characteristic of a free-electron gas. Both the real part of the dielectric constant, and the absorption $a = \omega_p^2/c\tau(\omega^2 + 1/\tau^2)$ are finite. The assumption (2) of Van Vleck and Weisskopf, on the other hand, leads to

$$\epsilon - 1 \rightarrow \frac{\omega_p^2}{\omega_0^2\tau} \left/ \left(\frac{1}{\tau} + i\omega \right) \right., \quad a = \frac{\omega_p^2\omega^2\tau}{\omega_0^2c} \left/ (1 + \omega^2\tau^2) \right.$$

Both expressions become infinite as $\omega_0 \rightarrow 0$.

5. INITIAL VALUE PROBLEM

In the preceding section, we have investigated solutions which are of the type $\phi = -(\alpha x + \beta v)E(t)$. In addition, the study has been restricted to the response to a monochromatic applied field. Let us now briefly examine, within the framework of solutions of this type, initial value problems, e.g., the decay of the polarization or distribution function to equilibrium. Writing

$$\phi = A(t)x + B(t)v, \quad (24)$$

one finds, on setting coefficients of x and v separately to

zero,

$$\frac{dA}{dt} + \frac{1}{\tau}A - \omega_0^2 B = \Delta/x, \quad (25a)$$

$$\frac{dB}{dt} + \frac{1}{\tau}B + A = \frac{eE(t)}{kT}. \quad (25b)$$

Consider a problem in which the distribution is Maxwellian at $t < 0$, i.e., $\phi = 0$, so that $A = B = 0$. At $t = 0$, a static field $E(t)$ is applied. Equation (15) has unique solutions if the distribution function $\phi(x, v, 0)$ is prescribed at $t = 0$. Thus solutions of the form $\phi = A(t)x + B(t)v$ are appropriate for those problems in which the initial distribution is also of this form. This is certainly the case when $\phi(x, v, 0) \equiv 0$ at $t = 0$. The solutions of the problem are

$$(1) \quad A(t) = \frac{eE_0\omega_0^2}{kT(\omega_0^2 + 1/\tau^2)} \left[1 + \frac{e^{-t/\tau}}{2\omega_0} \left\{ \left(\frac{i}{\tau} - \omega_0 \right) \times e^{\omega_0 t} - \left(\frac{i}{\tau} + \omega_0 \right) e^{-i\omega_0 t} \right\} \right], \quad (26a)$$

$$B(t) = \frac{eE_0}{\tau kT(\omega_0^2 + 1/\tau^2)} \left[1 + \left\{ -\frac{(1+i\omega_0 t)}{2} \times e^{i\omega_0 t} - \frac{(1-i\omega_0 t)}{2} e^{-i\omega_0 t} \right\} e^{-t/\tau} \right]; \quad (26b)$$

$$(2) \quad A(t) = \frac{eE_0}{kT} (1 - \cos\omega_0 t) e^{-t/\tau}, \quad (27a)$$

$$B(t) = \frac{eE_0}{kT} \frac{\sin\omega_0 t}{\omega_0} e^{-t/\tau}; \quad (27b)$$

$$(3) \quad A(t) = \frac{eE_0}{kT} \left(1 + \frac{e^{-t/2\tau}}{2(1/\tau^2 - 4\omega_0^2)^{1/2}} \times \left\{ -\frac{1}{\tau} [1 + (1 - 4\omega_0^2 \tau^2)^{1/2}] \times \exp \left[+\frac{t}{2\tau} (1 - 4\omega_0^2 \tau^2)^{1/2} \right] + \frac{1}{\tau} [-1 + (1 - 4\omega_0^2 \tau^2)^{1/2}] \times \exp \left[-\frac{t}{2\tau} (1 - 4\omega_0^2 \tau^2)^{1/2} \right] \right\} \right); \quad (28a)$$

$$B(t) = \frac{eE_0}{kT} \frac{-\exp[-(1/\tau^2 - 4\omega_0^2)^{1/2} t/2]}{(1/\tau^2 - 4\omega_0^2)^{1/2}}. \quad (28b)$$

It is seen that with the assumptions (1) and (2) the distribution function and polarization tend to the final values as $e^{-t/\tau} e^{\pm i\omega_0 t}$, i.e., with damped, oscillatory behavior. Assumption (3) leads to a dependence which is a linear superposition of two exponentials. For $1/\tau \ll 2\omega_0$ the decay is exactly as in assumption (2), i.e., as a damped oscillation. [Again the collision frequency must be taken as twice that of assumption (2).] If the collision frequency is so large that $1/\tau > 2\omega_0$ the decay is purely exponential. For $1/\tau \gg 2\omega_0$ one of the decay rates is $\omega_0(\omega_0\tau)$, which is much smaller than ω_0 . The high collision rate makes it difficult for the oscillator to adjust to the new equilibrium position in space.

Initial value problems of a more general nature than the one treated above may be studied by the method of characteristics. Alternatively, the problem of solving the kinetic Eq. (15) may be attacked by expanding the distribution function in Hermite polynomials. After performing a Laplace transformation with respect to the time variable one is left with simple difference equations. These may be treated by continued fraction methods. We do not undertake this analysis, which yields the exact distribution function, since the coefficient of x is unaltered. Thus the simpler approach of Secs. (4) and (5) yields the correct polarization.

6. GENERAL TREATMENTS OF OSCILLATOR BROADENING

The collision model discussed in Secs. (4) and (5) contains two separate assumptions. The first, and most essential assumption was that the position coordinate of an oscillator is unaltered by an instantaneous collision. The second assumption was that the oscillator velocities after impact were redistributed according to a Maxwellian distribution. As mentioned earlier, the second assumption does not hold for a general mass ratio of radiating and nonradiating molecules. If the first assumption is retained, one can write quite generally

$$\frac{\delta f}{\delta t} \Big|_c = \int f(v', x, t) A(v', v) dv' - f(v, x, t) \int A(v, v') dv'. \quad (29)$$

$A(v', v)$ is a transition probability which describes the effects of collisions. It is independent of time and the external field, a property which appears in keeping with the inert reservoir character of the nonpolar foreign gas. Our earlier assumption was

$$A(v, v') = A(v') = \frac{1}{\tau} \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mv^2}{2kT} \right).$$

Keilson and Storer¹¹ have considered kernels of the form

$$A(v, v') = \alpha(v' - \gamma v), \quad \text{with } 0 \leq \gamma \leq 1. \quad (30)$$

Since

$$\frac{1}{\tau} \int_{-\infty}^{+\infty} A(v, v') dv' = \int_{-\infty}^{+\infty} \alpha(\xi) d\xi, \quad (31)$$

¹¹ J. Keilson and J. E. Storer, *Quart. Appl. Math.* **10**, 243 (1952).

the collision time is independent of velocity, as has been the case for the theories of earlier sections. The particular kernel studied by Keilson and Storer is

$$A(v, v') = (1/\tau)(\beta/\pi)^{1/2} \exp[-\beta(v' - \gamma v)^2]. \quad (32)$$

Correct equilibrium is obtained with $\beta(1 - \gamma^2) = m/2kT$. The case where $\gamma = 0$ corresponds to the treatment of Sec. (4). The limit $\gamma \rightarrow 1$ is related to the Fokker-Planck equation, for which

$$\left. \frac{\delta f}{\delta t} \right|_c = \beta' \left\{ \frac{kT}{m} \frac{\partial^2 f}{\partial v^2} + \frac{\partial}{\partial v} (vf) \right\}. \quad (33)$$

Intermediate values of γ exhibit some features of the scattering of objects of different mass ratios. The complete kinetic equation is obtained by combining Eq. (6) with (33) or Eq. (29) with (32).

As in Secs. (4) and (5), we do not enter into a discussion of the complete solutions. We are interested in the behavior of the polarization, which is e times the first moment in x of the distribution

$$P = e\langle x \rangle = \int_{-\infty}^{+\infty} \int x f dx dv.$$

Equation (33) yields

$$\int \int x \left. \frac{\delta f}{\delta t} \right|_c = 0, \quad (34)$$

and

$$\int \int v \left. \frac{\delta f}{\delta t} \right|_c dx dv = -\beta' \langle v \rangle. \quad (35)$$

Forming the x moment of the left-hand side of Eq. (6) and combining with Eq. (34), we have

$$\frac{\partial}{\partial t} \langle x \rangle - \langle v \rangle = 0. \quad (36)$$

For the v moment one finds the equation

$$\frac{\partial}{\partial t} \langle v \rangle + \omega_0^2 \langle x \rangle - \frac{NeE_0}{m} \cos \omega t = -\beta' \langle v \rangle. \quad (37)$$

The x moment then satisfies the equation

$$\frac{\partial^2 \langle x \rangle}{\partial t^2} + \beta' \frac{\partial \langle x \rangle}{\partial t} + \omega_0^2 \langle x \rangle = \frac{NeE_0}{m} \cos \omega t. \quad (38)$$

The polarization is the same as Eq. (20c) with $\beta' = 1/\tau$. The more general Eqs. (29) and (32) yield

$$\int \int x \left. \frac{\delta f}{\delta t} \right|_c dx dv = 0, \quad (39)$$

$$\int \int v \left. \frac{\delta f}{\delta t} \right|_c dx dv = \frac{(\gamma - 1)}{\tau} \langle v \rangle. \quad (40)$$

One obtains the friction-damped oscillator behavior again, with a mean time between collisions of $\tau/1 - \gamma$. The Fokker-Planck limit is obtained by letting $\gamma \rightarrow 1$ and $\tau \rightarrow 0$ in such a way that limit $(\gamma - 1)/\tau = \beta'$.

The results of the present section indicate that the line shape (20c) is quite general if positions are unchanged by collisions. However, the higher moments of the distribution are sensitive to the particular model chosen. The fact that the first moment (polarization) has this behavior is peculiar to the harmonic oscillator. Other systems, such as rigid dipoles, have polarizations which depend on the precise nature of the velocity exchanges on collision.

ACKNOWLEDGMENT

The author is deeply indebted to Professor A. von Hippel for calling his attention to this problem and for many illuminating discussions. Dr. C. S. E. Phillips and Mr. J. Lebowitz have contributed critical and stimulating comments.