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THE EFFECT OF COLLISIONS ON THE DOPPLER BROADENING OF SPECTRAL LINES

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1. INTRODUCTION

THE Doppler effect is one of the fundamental causes of broadening of spectral lines. The traditional treatment of broadening caused by the Doppler effect amounts to the following (see, e.g. [1]). If an oscillator having an intrinsic vibration frequency ω_0 is moving with respect to the observer at a velocity **v**, then in the observer's coordinate system its frequency will be $\omega = \omega_0 + \mathbf{kv}$, where **k** is the wave vector of the radiation. Hence it is assumed that the shape of the emission line of a set of moving oscillators is determined by their velocity distribution W(v) dv in the ray direction:

$$I(\omega)\,d\omega = W\left(\frac{\omega-\omega_0}{k}\right)\frac{d\omega}{k} = W\left(c\,\frac{\omega-\omega_0}{\omega_0}\right)\frac{c}{\omega_0}\,d\omega. \qquad (1.1)$$

Strictly speaking, this approach is correct only when the velocity of each oscillator remains constant for an infinite time. Actually, in deriving the formula (1.1) for the intensity distribution $I(\omega)d\omega$, the assumption was made implicitly that the spectrum of an oscillator of velocity v in the ray direction contains only the single frequency $\omega_0[1 + (v/c)]$. However, if the oscillator is not in free motion, and its velocity remains constant only for a finite time τ, then the emission from the oscillator over the interval τ will give a spectrum having a width $\Delta\omega \sim 1/\tau$ about $\omega_0[1 + (v/c)]$. In order that we may apply Eq. (1.1), evidently, the width of this spectrum must be small in comparison with the mean Doppler shift: $1/\tau \ll \omega_0(\overline{v}/c)$. This inequality can be rewritten in the form $2\pi l \gg \lambda$, where $l = \overline{v}c$ is the mean free path, and $\lambda = 2\pi c/\omega_0$ is the wavelength of the light. For the visible region of the spectrum, $\lambda \simeq 5 \times 10^{-5}$ cm. Hence this condition fails only at relatively high pressures, of the order of atmospheric. Thus, for most astrophysical applications and many light sources, such as low-pressure gas-discharge lamps, Eq. (1.1) describes the Doppler broadening with enough accuracy for practical purposes.

However, we can point out a whole series of other examples in which Eq. (1.1) is inapplicable. For example, whenever the wavelength λ is large (the far infrared and the millimeter and centimeter ranges), the relation $2\pi l \gg \lambda$ fails to hold even at very low pressures. In addition, conditions can occur in which the wavelength λ is greater than the dimensions of the vessel holding the gas. In other words, if the free motion of the atom is restricted for any reason, the influence of the Doppler effect on spectral lines can become essentially different. A well-known example of this sort is the Mössbauer effect, which is due to the localization of the emitting particle within a region small in comparison with $\lambda/2\pi$ (see, e.g. [2]). In essence, Doppler broadening plays practically no role in the spectra of molecules in a liquid for the same reason.

As a rule, the interaction of an emitting atom with surrounding particles is taken into account only as a perturbation of the internal motion of the oscillator, i.e., as a change in the phase and amplitude of its vibrations. There is an extensive literature on this problem (see, e.g. [1]). However, what we have said above implies that the role of collisions in broadening spectral lines is considerably more complex in the general case. The reason for this is that collisions can change the nature of the translational motion of the oscillator, while simultaneously perturbing its vibrations. Both of these effects of collisions are closely connected together, and must be treated jointly.

We should note that all this set of problems is of interest not only in atomic and molecular spectroscopy, but also in understanding a number of subtle phenomena of the physics of gas lasers (see Sec. 8).

This article is devoted to a detailed analysis of the effect of collisions on Doppler broadening and the relation of impact broadening to the Doppler effect.

We shall first take up the general method of treating the effect of collisions on pure Doppler broadening, neglecting any possible interference with the vibrations of the oscillator. In this case, the amplitude of the light wave radiated by the moving oscillator depends on the time as follows:

$$E(t) \sim e^{-i\omega_0 t + i\mathbf{kr}(t)}, \quad \mathbf{r}(t) = \int_{-\infty}^{t} \mathbf{v}(t')\,dt'. \qquad (1.2)$$

If the oscillator undergoes collisions with resultant change of velocity, then **v**(t) and **r**(t) will be random functions of the time. Then the spectrum E(t) from (1,2) will contain a certain set of frequencies. The intensity distribution $I(\omega)$ in this case can be found by the general formulas of Fourier analysis (see, e.g., [1]):

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty \Phi(\tau)\,e^{i\omega\tau}\,d\tau, \qquad (1.3)$$

where $\Phi(\tau)$ is the correlation function for the amplitude of emission E(t):

$$\Phi(\tau) = \langle e^{-ik\mathbf{r}(\tau)} \rangle,$$

$$\mathbf{r}(\tau) = \int_t^{t+\tau} \mathbf{v}(t')\, dt'. \quad (1.4)$$

Here $\mathbf{r}(\tau)$ is the displacement of the oscillator during the time τ, and the angle brackets denote averaging over the ensemble of oscillators.

If the oscillators do not collide, and have a Maxwell velocity distribution,

$$\mathbf{r}(\tau) = \mathbf{v}(\tau), \quad W_M(v) = \frac{1}{\sqrt{\pi}\,\bar{v}} e^{-v^2/\bar{v}^2}, \quad \bar{v}^2 = \frac{2kT}{m}, \quad (1.5)$$

then

$$\Phi(\tau) = \int_{-\infty}^{\infty} e^{-ikv\tau} W_M(v)\, dv = e^{-(k\bar{v}\tau)^2 \cdot \frac{1}{4}}. \quad (1.6)$$

Substituting (1,6) into (1,3), we easily obtain

$$I(\omega) = \frac{1}{\sqrt{\pi}\Delta\omega_D} e^{-\left(\frac{\omega}{\Delta\omega_D}\right)^2}, \quad \Delta\omega_D = k\bar{v} = \omega_0 \frac{\bar{v}}{c}, \quad (1.7)$$

which is a special case of (1,1). Here and everywhere below, the frequency ω is referred to the position of the unshifted frequency ω_0.

In agreement with (1.4), the width of the distribution $\Phi(\tau)$ is determined by the characteristic time τ_k which it takes for the oscillator to move a distance of the order of $1/k = \lambda/2\pi$, where λ is the wavelength of the radiation. When (1,6) holds, this time is of the order of $1/k\bar{v}$.

Any factor restricting or hindering the movement of the oscillators must broaden the distribution $\Phi(\tau)$, and hence narrow the contour of $I(\omega)$. Evidently, the collisions of the atoms of a gas will increase the mean time taken for an atom to move a distance $\lambda/2\pi$. Hence, collisions must be manifested in a decrease in the width of the spectrum* in comparison with $\Delta\omega_D$. Such an effect must be quite substantial when the mean free path l is much shorter than $\lambda/2\pi$. In this limiting case, the time for an atom to move the distance $\lambda/2\pi$ is determined by the law of diffusion, and is approximately equal to $\tau_k \cong (l/\bar{v})(\lambda/2\pi l)^2$. Hence, for a line width of $1/\tau_k$ we find

$$\frac{1}{\tau_k} \cong \frac{\bar{v}}{l}\left(\frac{2\pi l}{\lambda}\right)^2 = \Delta\omega_D \frac{2\pi l}{\lambda} \ll \Delta\omega_D. \quad (1.8)$$

Thus, at a high gas density, when the number of collisions per distance $\lambda/2\pi$ is great, the Doppler contour must be narrowed in comparison with (1.7) by a factor of $2\pi l/\lambda$.

These qualitative ideas agree with the calculation of the Doppler contour $I(\omega)$ made in [4]. In the special case of the Brownian-movement model[3] used in [4], the following expression was derived for the correlation function:

$$\Phi(\tau) = e^{-\frac{k^2}{2}\langle x^2 \rangle}, \quad \langle x^2 \rangle = \frac{\bar{v}^2}{\nu_d^2}\left[\nu_d\tau - 1 + e^{-\nu_d\tau}\right], \quad (1.9)$$

where $\langle x^2 \rangle$ is the mean-square displacement in the direction of $\mathbf{k}$ over the time τ, and ν_d is the effective frequency of the collisions, involving the diffusion coefficient through the relation $\nu_d = \bar{v}^2/2D$.

In the limiting case when $\nu_d \to 0$, Eq. (1.9) goes over into (1.6). When $\nu_d \neq 0$ for $\nu_d\tau \gg 1$,

$$\Phi(\tau) = e^{-\left(\frac{k^2\bar{v}^2}{2\nu_d}\right)\tau} = e^{-(\Delta\omega_D^2\tau/2\nu_d)}, \quad (1.10)$$

and in the region $\omega \ll \nu_d$,

$$I(\omega) \simeq \frac{\gamma_d}{\pi}\frac{1}{\omega^2 + \gamma_d^2}, \quad \gamma_d = \frac{\Delta\omega_D^2}{2\nu_d} = \frac{1}{2}\Delta\omega_D\frac{2\pi l}{\lambda}. \quad (1.11)$$

Thus, the central region of the line is described by a dispersion contour having a width $2\gamma_d$ (cf. (1.8)). At high enough pressures, when $l \ll \lambda/2\pi$, most of the intensity is concentrated in the region $\omega \ll \nu_d$ in which Eq. (1.11) is valid. This result was derived for the first time in [5]. We shall return to a more detailed analysis of the intensity distribution corresponding to the correlation function of (1.9) in Sec. 2.

We shall now consider other causes of broadening: radiative decay and broadening due to interaction of the emitting atom with surrounding particles. A simultaneous account of radiative decay and the Doppler effect involves no difficulties, since these causes of broadening are statistically independent. As we know,[1] the correlation function in this case equals the product of the correlation functions describing each of the causes of broadening individually:

$$\Phi(\tau) = \Phi_1(\tau)\Phi_2(\tau), \quad (1.12)$$

while the intensity distribution $I(\omega)$ is determined by the convolution

$$I(\omega) = \int_{-\infty}^{\infty} I_1(\omega - \omega') I_2(\omega')\, d\omega'. \quad (1.13)$$

Here, $I_1(\omega)$ and $I_2(\omega)$ are expressed in terms of $\Phi_1(\tau)$ and $\Phi_2(\tau)$ by using Eq. (1.3).

Conversely, as we remarked above, broadening due to interaction and that due to the Doppler effect are statistically dependent in the general case. Broadening due to interactions involves a phase shift of the atomic oscillator when the atom collides with surrounding particles. Obviously, both the phase of the oscillations and the velocity of translational motion of the atom can be altered in the same collision. Furthermore, the changes in phase and velocity can be interrelated.[1] The very fact of the statistical dependence of Doppler broadening and broadening due to interactions had been noted even earlier,[6-8] but has never been taken into account in concrete calculations.

A combined account of broadening due to interactions and to the Doppler effect leads to the correlation function

*We emphasize that we are speaking only of collisions in which only the velocity of the oscillator is changed, but not its phase. See below on the subject of collisions with a phase change.

$$\Phi(\tau) = \langle e^{-i\varphi(\tau)}e^{-i\mathbf{kr}(\tau)}\rangle, \quad (1.14)$$

where $\varphi(\tau)$ is the phase shift of the atomic oscillator due to collisions over the time τ (the phase φ is complex in the general case: $\varphi = \eta - i\beta$, where the quantity β determines the rate of decay of the oscillations). We shall denote by τ_φ the characteristic time that it takes for the phase φ to increase by an amount of the order of π, and by τ_V the time that it takes for the velocity of the atom to vary substantially. The role played by the statistical dependence of the two factors in (1.14) depends essentially on the relation between the times τ_φ and τ_V. If $\tau_\varphi \ll \tau_V$, i.e., the phase change in the collisions occurs with a much greater efficiency than the velocity change, then the effect of collisions on the Doppler effect can be generally neglected. Then the resulting contour is given to a good enough approximation by the convolution of the Doppler contour [(1.1), (1.7)] with the contour describing the effect of interactions. An example of collisions of this type is those of an emitting atom with electrons. Owing to their small mass, the electrons practically do not alter the velocity of the atom, even in collisions substantially changing the phase.

However, if $\tau_\varphi \sim \tau_V$ or $\tau_\varphi > \tau_V$, there are no grounds for considering the first and second factors in (1.14) to be statistically independent. We note that the most favorable case for manifestation of the narrowing effect discussed above is when $\tau_\varphi \gg \tau_V$. Then this narrowing is not masked by broadening due to interactions. In fact, in agreement with (1.9)—(1.11), the narrowing effect begins to be manifested when $\nu_d \sim 1/\tau_V > \Delta\omega_D$. However, this effect can be observed only when the broadening due to perturbation of the phase of the oscillator, which is of the same order of magnitude as $1/\tau_\varphi$, is less than $\Delta\omega_D$, i.e., when $1/\tau_\varphi < 1/\tau_V$.

Such a relation between the times τ_φ and τ_V can actually occur. Often the collisions of heavy particles are not accompanied by quenching. That is, the imaginary component of the phase shift $\beta = 0$. The real component η of the phase shift is determined by the difference in the shifts of the combining levels arising from interaction. Whenever the shifts in these levels are almost the same, η is small. Another example of this sort is Rayleigh scattering in a gas. As we know, a Rayleigh scattering line is not broadened by interaction, since this scattering is due to forced, rather than intrinsic, vibrations of the oscillator.

Thus, the effect of collisions on pure Doppler broadening is of interest in a number of physical problems. However, this problem has been discussed heretofore only within the framework of the Brownian-movement model.[3] Here we cannot consider even this treatment to be exhaustive, especially in the part dealing with the intensity distribution in the outer wings of the line. Besides, in a number of applications, the strong-collision model is of greater interest than the Brownian-movement model used in [4].

This entire set of problems involving the effect of collisions on pure Doppler broadening is discussed in Secs. 2 and 3 of this article. It has proved extremely convenient here to use the kinetics-equations method. This method permits us to treat highly differing collision models in a unified manner. Most important of all, it permits us to generalize to the general case in which the broadenings due to the Doppler effect and to interaction are statistically dependent. This generalization is the subject of Secs. 4—7.

3. DOPPLER BROADENING (BROWNIAN-MOVEMENT MODEL)

In pure Doppler broadening the phase shift $\varphi(\tau)$ of the atomic oscillator due to interaction is zero. Hence the problem of calculating the correlation function is reduced, according to (1.14), to finding the mean value of the function $\exp[-i\mathbf{k}\cdot\mathbf{r}(\tau)]$, where $\mathbf{r}(\tau)$ is the distance that the atom moves in time τ.

Let us introduce the distribution function $f(\mathbf{r}, \mathbf{v}, t; \mathbf{v}_0)$. This function gives the relative number of atoms which move over a distance $\mathbf{r}$ and acquire a velocity $\mathbf{v}$ in the time t, when located at the point $\mathbf{r} = 0$ and having the velocity $\mathbf{v}_0$ at the time $t = 0$. This distribution function satisfies the ordinary kinetic equation

$$\frac{\partial f}{\partial t} + \mathbf{v}\nabla f = S, \quad (2.1)$$

where S is the collision integral. In the problem under discussion, the solution of Eq. (2.1) must satisfy the initial conditions

$$f(\mathbf{r}, \mathbf{v}, 0; \mathbf{v}_0) = W(\mathbf{v}_0)\,\delta(\mathbf{v}-\mathbf{v}_0)\,\delta(\mathbf{r}), \quad (2.2)$$

where $W(\mathbf{v}_0)$ is the velocity distribution of the atoms $t = 0$. By using the function f, Eq. (1.4) can be rewritten in the form

$$\Phi(\tau) = \langle e^{-i\mathbf{kr}(\tau)}\rangle = \int d\mathbf{v}\,d\mathbf{v}_0 \int e^{-i\mathbf{kr}} f(\mathbf{r}, \mathbf{v}, \tau; \mathbf{v}_0)\,d\mathbf{r}. \quad (2.3)$$

We assume in Eqs. (2.3) and (2.2) that the medium is spatially homogeneous. In addition, we assume that a constant excitation source is acting, so that the problem is stationary in time. Evidently, the concentration of excited atoms is determined by the intensity of the excitation source and by the rate of decay of the excited states. Since in this section we are neglecting quenching due to collisions, the decay is determined only by radiative transitions. Owing to the statistical independence of radiative and Doppler broadenings, radiative decay can be taken into account in the last stage of the calculations.

The method presented here can be extended to problems that are inhomogeneous both in space and in time. For example, we can treat the problem of emission from atoms enclosed in a space of dimensions comparable with the wavelength λ.[5] In problems like this, we must change the initial condition (2.2), and introduce the appropriate boundary conditions. However, we shall limit ourselves below to treating homogeneous problems.

We can neglect the collision of excited atoms with one another in treating the problem of broadening of spontaneous emission lines. Hence the collision integral S is a linear integral operator:

$$S = -\int [A(\mathbf{v}, \mathbf{v}') f(\mathbf{r}, \mathbf{v}, t; \mathbf{v}_0) - A(\mathbf{v}', \mathbf{v}) f(\mathbf{r}, \mathbf{v}', t; \mathbf{v}_0)]\, d\mathbf{v}', \tag{2.4}$$

where $A(\mathbf{v},\mathbf{v}')$ is the probability per unit time of collisions involving a velocity change $\mathbf{v} \rightarrow \mathbf{v}'$. It is the form of the function $A(\mathbf{v},\mathbf{v}')$ in particular that determines the kinetics of the collisions, and hence, the nature of the spectrum $I(\omega)$. Often the collision integral of (2.4) is written in a somewhat different form. Let the collision be characterized by the set of parameters g. These parameters might be the impact distance (closest distance of approach), or the angles specifying the orientation of the colliding particles, or the velocities, etc. We shall denote by $P(g)\,dg$ the number of collisions having their parameters g in the range from g to g+dg, and by $\Delta\mathbf{v}(g)$ the velocity change in these collisions. In this notation the collision integral S has the form

$$S = -\int P(g)\, [f(\mathbf{r}, \mathbf{v}, t; \mathbf{v}_0) - f(\mathbf{r}, \mathbf{v} - \Delta\mathbf{v}(g), t; \mathbf{v}_0)]\, dg. \tag{2.4'}$$

We see from Eqs. (2.1)–(2.4) that we can carry out the averaging over the initial velocities $\mathbf{v}_0$ in the general form before solving Eq. (2.1). Let us introduce the new distribution function

$$f(\mathbf{r}, \mathbf{v}, t) = \int f(\mathbf{r}, \mathbf{v}, t; \mathbf{v}_0)\, d\mathbf{v}_0. \tag{2.5}$$

Averaging over $\mathbf{v}_0$ does not change the form of the kinetic equation (2.1). However, the initial conditions are changed hereby. Hence, we finally obtain

$$\Phi(\tau) = \int d\mathbf{v} \int e^{-i\mathbf{k}\mathbf{r}} f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{r}. \tag{2.6}$$

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty e^{i\omega\tau} \Phi(\tau)\, d\tau = \frac{1}{\pi} \operatorname{Re} \int dv \int e^{i(\omega\tau - \mathbf{k}\mathbf{r})} f(\mathbf{r}, \mathbf{v}, \tau)\, d\mathbf{r}\, d\tau, \tag{2.7}$$

$$\frac{\partial f}{\partial t} + \mathbf{v}\nabla f = -\int [A(\mathbf{v}, \mathbf{v}') f(\mathbf{r}, \mathbf{v}, t) - A(\mathbf{v}', \mathbf{v}) f(\mathbf{r}, \mathbf{v}', t)]\, d\mathbf{v}', \tag{2.8}$$

$$f(\mathbf{r}, \mathbf{v}, 0) = W(\mathbf{v})\, \delta(\mathbf{r}). \tag{2.9}$$

We see from (2.7) that the spectrum $I(\omega)$ that we are interested in is determined by the space-time Fourier component $F(\mathbf{k},\mathbf{v},\omega)$ of the function $f(\mathbf{r},\mathbf{v},t)$:

$$F(\mathbf{k}, \mathbf{v}, \omega) = \frac{1}{\pi} \int e^{i(\omega t - \mathbf{k}\mathbf{r})} f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{r}\, dt, \tag{2.10}$$

$$I(\omega) = \operatorname{Re} \int F(\mathbf{k}, \mathbf{v}, \omega)\, d\mathbf{v}. \tag{2.11}$$

In a number of cases, it is considerably simpler to find the function $F(\mathbf{k},\mathbf{v},\omega)$ than to find the distribution function $f(\mathbf{r},\mathbf{v},t)$ itself.

When there are no collisions, S = 0, and we can derive the ordinary Doppler distribution from (2.8)–(2.11). In fact, in this case (2.8) and (2.9) imply that

$$f(\mathbf{r}, \mathbf{v}, t) = W(\mathbf{v})\, \delta(\mathbf{r} - \mathbf{v}t). \tag{2.12}$$

Upon substituting (2.12) into (2.6) and assuming $W(\mathbf{v})$ to be a Maxwell distribution, we obtain

$$\Phi(\tau) = \int W(\mathbf{v})\, e^{-i\mathbf{k}\mathbf{v}\tau}\, d\mathbf{v} = e^{-(k\bar{v}\tau)^2 \frac{1}{4}}, \tag{2.13}$$

which agrees with (1.6).

We shall now treat the case of Brownian movement within the framework of the model studied in detail in [3].

As we know, this model can be used in the case of "weak" collisions. An example of this type of collisions might be the scattering of a heavy emitting atom by light perturbing particles. In addition, this model gives a good description of collisions involving small-angle scattering. We can use the diffusion approximation for the collision integral of (2.4) in such cases.[3,9] Then Eq. (2.8) acquires the form

$$\frac{\partial f}{\partial t} + \mathbf{v}\nabla_{\mathbf{r}} f = \nu_d \operatorname{div}_{\mathbf{v}} (\mathbf{v} f) + q\Delta_{\mathbf{v}} f. \tag{2.14}$$

Here it is assumed that the coefficients ν_d and q do not depend on the velocity, and satisfy the relation

$$q = \frac{\bar{v}^2}{2} \nu_d, \quad \bar{v}^2 = \frac{2kT}{m}.$$

In its physical meaning, ν_d is the effective frequency of the collisions. This frequency defines the time $\tau_v = 1/\nu_d$ that it takes for a particle to lose track of its initial velocity (see Eq. (1.61) in [3]):

$$\langle \mathbf{v} \rangle = \mathbf{v}_0 e^{-\nu_d \tau}.$$

Equation (2.14) is discussed in [3]. However, for further generalizations, it is convenient to solve Eq. (2.14) by the Fourier-transform method, in distinction from [3]. Let us introduce the function

$$\Psi(\mathbf{k}, \boldsymbol{\varkappa}, t) = \int f(\mathbf{r}, \mathbf{v}, t)\, e^{-i(\mathbf{k}\mathbf{r} + \boldsymbol{\varkappa}\mathbf{v})}\, d\mathbf{r}\, d\mathbf{v}. \tag{2.15}$$

According to (2.14) and (2.9), this function satisfies the equation

$$\frac{\partial \Psi}{\partial t} + (\nu_d \boldsymbol{\varkappa} - \mathbf{k}) \frac{\partial \Psi}{\partial \boldsymbol{\varkappa}} = -q\varkappa^2 \Psi \tag{2.16}$$

and the initial conditions

$$\Psi(\mathbf{k}, \boldsymbol{\varkappa}, 0) = \int W(\mathbf{v})\, e^{-i\boldsymbol{\varkappa}\mathbf{v}}\, d\mathbf{v}. \tag{2.17}$$

Equations (2.6) and (2.15) imply that

$$\Phi(\tau) = \Psi(\mathbf{k}, 0, \tau). \tag{2.18}$$

Thus, (2.16) is essentially an equation for the correlation function. This is the essence of the convenience

*For brevity, we shall use the term "probability" below, although A(v, v') is a probability density per unit time.

of solving the kinetic equation by the Fourier-transform method.

If we solve Eq. (2.16) under the initial conditions (2.17), we find for a Maxwell distribution of the atomic velocities:

$$\Psi(\mathbf{k}, \varkappa, t) = \exp\left\{-\frac{1}{2}\left[G\varkappa^2 + 2H\varkappa\mathbf{k} + P\mathbf{k}^2\right]\right\}, \qquad (2.19)$$

where

$$G = \bar{v}^2/2, \quad H = \frac{\bar{v}^2}{2\nu_d}\left[1 - e^{-\nu_d t}\right], \quad P = \frac{\bar{v}^2}{\nu_d^2}\left[\nu_d t - 1 + e^{-\nu_d t}\right]. \qquad (2.20)$$

If we set $\kappa = 0$ in accord with (2.18), we obtain the expression of [4] for the correlation function (see Eq. (1,9)):

$$\Phi(\tau) = \exp\left[-\frac{\Delta\omega_D^2}{2\nu_d^2}\left(\nu_d\tau - 1 + e^{-\nu_d\tau}\right)\right], \quad \Delta\omega_D = k\bar{v}. \qquad (2.21)$$

The intensity distribution $I(\omega)$ can be found by using (2.7). For the correlation function of (2.21), it is expressed in terms of a confluent hypergeometric function:[10]

$$I(\omega) = \operatorname{Re} J(\omega); \qquad (2.22)$$

$$J(\omega) = \frac{1}{\pi}\int_0^\infty \exp\left[i\omega\tau - \frac{\Delta\omega_D^2}{2\nu_d^2}\left(\nu_d\tau - 1 + e^{-\nu_d\tau}\right)\right]d\tau$$

$$= \frac{1}{\pi}\,\frac{1}{\dfrac{\Delta\omega_D^2}{2\nu_d} - i\omega}\,\Phi\left[1,\ 1 + \frac{\Delta\omega_D^2}{2\nu_d^2} - i\frac{\omega}{\nu_d};\ \frac{\Delta\omega_D^2}{2\nu_d}\right], \qquad (2.23)$$

where

$$\Phi[\alpha, \gamma; z] = 1 + \frac{\alpha}{\gamma}\frac{z}{1!} + \frac{\alpha(\alpha+1)}{\gamma(\gamma+1)}\frac{z^2}{2!} + \frac{\alpha(\alpha+1)(\alpha+2)}{\gamma(\gamma+1)(\gamma+2)}\frac{z^3}{3!} + \ldots \qquad (2.24)$$

If we set $\nu_d = 0$ in (2.21) and (2.23), then again we obtain the ordinary Doppler intensity distribution for a Maxwell distribution of the atomic velocities:

$$\Phi(\tau) = e^{-(\Delta\omega_D\tau)^2\frac{1}{4}}, \quad I(\omega) = \frac{1}{\sqrt{\pi}\Delta\omega_D}e^{-\left(\frac{\omega}{\Delta\omega_D}\right)^2}. \qquad (2.25)$$

Let us trace the changes in $I(\omega)$ that result at low collision frequencies, where $\nu_d \ll \Delta\omega_D$. At the center of the line at $\omega = 0$, we find

$$I(0) = \frac{1}{\sqrt{\pi}\Delta\omega_D}\left\{1 + \frac{2}{3\sqrt{\pi}}\frac{\nu_d}{\Delta\omega_D}\right\}. \qquad (2.26)$$

In the outer wing of the line, the asymptotic expansion for $I(\omega)$ has the form

$$I(\omega) = \frac{e^{-\left(\frac{\omega}{\Delta\omega_D}\right)^2}}{\sqrt{\pi}\Delta\omega_D}\left\{1 - \frac{2\pi}{3}\left(\frac{\nu_d}{\Delta\omega_D}\right)^2\left(\frac{\omega}{\Delta\omega_D}\right)^2\right\}$$

$$+ \frac{\nu_d\Delta\omega_D^2}{2\pi\omega^4}\left[1 + \frac{5\Delta\omega_D^2}{\omega^2} - \left(\frac{\nu_d}{\omega}\right)^2\right]. \qquad (2.27)$$

At high enough values of ω, we can drop the first term containing the exponential, and keeping the fundamental term, we get

$$I(\omega) \cong \frac{1}{\sqrt{\pi}\Delta\omega_D}\,\frac{\nu_d\,\Delta\omega_D^3}{2\sqrt{\pi}\omega^4} \quad (\omega \gg \Delta\omega_D \gg \nu_d). \qquad (2.28)$$

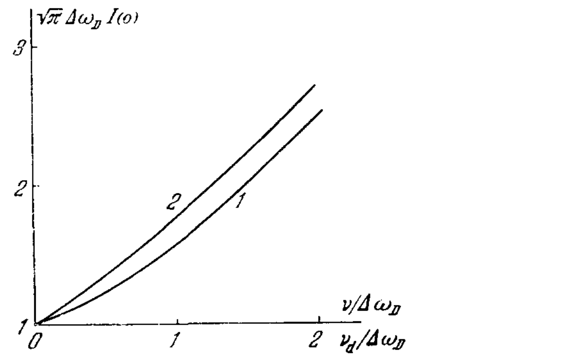

FIG. 1. Relation of the intensity at the center of the line ($\omega = 0$) at the frequency of elastic collisions. Curve 1 corresponds to the weak-collision model (Sec. 2), and curve 2 to the strong-collision model (Sec. 3).

Thus, the existence of collisions enhances the intensity of the line in the center and in the wings, the latter declining as ω^{-4}.

As the frequency of collisions increases, the intensity of the line at the center ($\omega = 0$) increases monotonically (Fig. 1, curve 1). In the intermediate case where $\nu_d \sim \Delta\omega_D$, and when $\nu_d \gg \Delta\omega_D$, we can conveniently use the following expansion of $I(\omega)$:

$$I(\omega) = \frac{1}{\pi}\operatorname{Re}\left\{\frac{1}{\gamma_d - i\omega}\left[1 + \frac{\gamma_d}{\gamma_d + \nu_d - i\omega}\right.\right.$$

$$\left.\left. + \frac{\gamma_d^2}{(\gamma_d + \nu_d - i\omega)(\gamma_d + 2\nu_d - i\omega)} + \ldots\right]\right\}$$

$$= \frac{e^{\gamma_d/\nu_d}}{\pi}\left\{\frac{\gamma_d}{\gamma_d^2 + \omega^2} - \frac{\nu_d + \gamma_d}{\omega^2 + (\nu_d + \gamma_d)^2}\cdot\frac{\gamma_d}{\nu_d}\right.$$

$$\left. + \frac{2\nu_d + \gamma_d}{\omega^2 + (2\nu_d + \gamma_d)^2}\cdot\frac{1}{2!}\left(\frac{\gamma_d}{\nu_d}\right)^2 - \ldots\right\}. \qquad (2.29)$$

Figure 2 shows graphs of $I(\omega)$ calculated for certain values of $\nu_d/\Delta\omega_D$. The narrowing of the central part of the line and the appearance of wings of greater than Gaussian intensities are clearly marked. The dotted curve in Fig. 2 corresponds to a dispersion line having the same width as curve 3. Comparison with curve 3 shows that the actual contour of the line has less intense wings than the dispersion curve. This reflects the more rapid decline of the intensity with increasing frequency (as ω^{-4} rather than ω^{-2}).

In the limiting case in which $\nu_d \gg \Delta\omega_D$, we can limit the expansion in (2,29) to the first two terms. Since here $\gamma_d = \frac{1}{2}\Delta\omega_D\cdot(\Delta\omega_D/\nu_d) \ll \Delta\omega_D \ll \nu_d$, the expression for $I(\omega)$ takes on the form

$$I(\omega) = \frac{1}{\pi}\,\frac{\gamma_d\nu_d^2}{[\omega^2 + \gamma_d^2][\omega^2 + \nu_d^2]}. \qquad (2.30)$$

Near the center of the line, $\omega^2 \ll \nu_d^2$, and we can drop

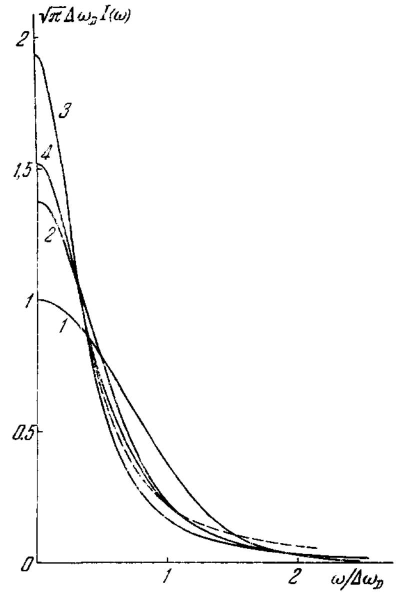

FIG. 2. The contour of a Doppler-broadened line for the following values of the parameters: Curve 1: $\nu_d = 0$; curve 2: $\nu_d = 0.7\,\Delta\omega_D$; curve 3: $\nu_d = \sqrt{2}\,\Delta\omega_D$; curve 4 is plotted for the strong-collision model with $\nu = 0.7\,\Delta\omega_D$; the dotted curve is a disperson contour having a width equal to that of curve 3.

ω^2 in comparison with ν_d^2. Then (2.30) gives

$$I(\omega)=\frac{1}{\pi}\frac{\gamma_d}{\omega^2+\gamma_d^2}, \qquad (2.31)$$

That is, the line has a simple dispersion form with a width

$$2\gamma_d=\frac{\Delta\omega_D^2}{\nu_d}. \qquad (2.32)$$

Since the mean free path $l \simeq v/\nu_d$,

$$2\gamma_d=\Delta\omega_D\frac{2\pi l}{\lambda}, \qquad (2.33)$$

That is, the central part of the line is $2\pi l/\lambda$ times narrower than the pure Doppler width $\Delta\omega_D$, in complete accord with the qualitative discussion of Sec. 1.

At high frequencies where $\omega \gg \nu_d \gg \gamma_d$, Eq. (2.30) goes over into the asymptotic formula (2.28), which consequently proves valid for all values of ν_d.

At a fixed frequency ω, the intensity of the wing first increases with increasing frequency of collisions, and then declines, reaching its maximum at $\nu_d \cong \omega$. Thus, as ν_d increases, an ever greater part of the emission spectrum is described by Eq. (2.31), while the wing described by Eq. (2.28) is shifted over into the region of higher frequencies.

We must note that the relative intensity of the wings is comparatively small. Nevertheless, in an entire set of problems (astrophysical, in particular), the existence of a wing proportional to ω^{-4} must be taken into account, since the absolute intensity may be sufficiently large.

The intensity distribution in the wings of the line found above differs from that derived in [4] (see also [1]):

$$I(\omega)\sim\exp\left\{-\frac{\omega^2}{\Delta\omega_D^2}\right\},\quad \omega>\nu_d. \qquad (2.34)$$

The ideas adduced in [4] to favor (2.34) amount to the following, Since the integrand in the expression (2.7) for $I(\omega)$ contains the oscillating factor $\exp(i\omega\tau)$, the value of $I(\omega)$ will be determined by the behavior of the correlation function at small τ. If we expand the argument of the exponential in Eq. (2.21) as a power series in τ, and keep only the first non-vanishing term ($\sim\tau^2$), we arrive at Eq. (3.34). An analogous argument has also been used in [11] in analyzing the limiting expressions for the spectrum $I(\omega)$. At the same time, it was shown above that $I(\omega) \sim \omega^{-4}$ in the wings of the line, independently of the relation between ν_d and $\Delta\omega_D$. The latter result is indeed implicit in the general theorems of Fourier analysis. Actually, for steady-state random processes, the correlation function is a function of $|\tau|$.* On the other hand, the expansion of (2.21) as a power series in $|\tau|$ has the following form when $\tau \to 0$:

$$\Phi(\tau)=1-\frac{\Delta\omega_D^2}{2}\left[\frac{\tau^2}{2!}-\nu_d\frac{|\tau|^3}{3!}+\dots\right]. \qquad (2.35)$$

We see from (2.35) that the third derivative of the function $\Phi(\tau)$ is discontinuous at the point $\tau = 0$. According to a well-known theorem on the rate of decline of the coefficients of a Fourier series,[12] the Fourier components of the function $\Phi(\tau)$, i.e., $I(\omega)$, must decline no faster than ω^{-4}. Thus, the variation of the intensity at high frequencies depends on the behavior (as $\tau \to 0$) of the derivatives of the correlation function, rather than the correlation function itself. This same result can also easily be derived directly from (1.2). If the collisions are instantaneous, and the velocity changes discontinuously, then the first derivative of the emission field $E(t)$ shows a discontinuity. Hence, the Fourier components of E_ω decline no faster than ω^{-2}, and $I(\omega) \sim E_\omega^2$ declines no faster than ω^{-4}.

The arguments given here show that the power law of decline of the intensity in the wings of the line is not connected with the concrete model used in deriving Eq. (2.21), but is valid in all cases when the collisions are considered instantaneous. The question naturally arises of how valid the instantaneous-collision hypothesis is in analyzing the intensity distribution in the wings of the line. Actually the collisions are characterized by a finite time $\delta\tau$. This time is equal in order of magnitude to the ratio of the effective radius of interaction to the velocity. As we can easily show, the finite nature of $\delta\tau$ is manifested in the intensity distribution at frequencies $\omega \gtrsim 1/\delta\tau$. Thus, all that we have said above about the intensity distribution in the wings of the line holds for frequencies $\omega \ll 1/\delta\tau$. The intensity distribution in the region $\omega \gtrsim 1/\delta\tau$ is deter-

*In calculating $I(\omega)$, this fact has been reflected in the limits of integration over t in Eq. (2,7).

mined by the concrete mechanism of the collisions. As a rule, $\delta\tau \lesssim 10^{-13}$ sec, while $1/\delta\tau \gg \nu_d$, $\Delta\omega_D$. Hence the formulas (2.28) and (2.30) for the wings, which are applicable when $\omega \gg \nu_d$, $\Delta\omega_D$, cover a very broad range of frequencies.

The broadening of emission lines is the topic of discussion in this paper. It is interesting to note that collisions also give rise to wings having a gradual intensity decline in the Doppler contour of Rayleigh scattering lines in a gas. This was demonstrated in [7]. However, in this case $I(\omega) \sim \omega^{-6}$ at high frequencies. The different exponent in the power law involves the specific nature of Rayleigh scattering. Since the total momentum of the colliding particles is conserved, and both particles take part in the scattering, there is a discontinuity in the second derivative, rather than the first, of the scattering field $E(t)$ of these particles.

3. DOPPLER BROADENING. THE STRONG-COLLISION MODEL

It is assumed in the Brownian-movement model discussed above that a substantial change in velocity is the result of a large number of collisions.[3] It is not evident a priori how applicable this approximation is to the case of strong collisions. Hence, let us return to the general equation (2.8). We shall write the first term of the collision integral in (2.8) in the form $-\nu f$, where ν is the effective collision frequency:

$$\nu(\mathbf{v}) = \int A(\mathbf{v}, \mathbf{v}')\, d\mathbf{v}'.$$

From (2.8), we can derive the following Fredholm integral equation of the second kind for the space-time Fourier components $F(\mathbf{k}, \mathbf{v}, \omega)$ of the distribution function (see (2.10)):

$$F(\mathbf{k}, \mathbf{v}, \omega) = \frac{1}{\nu + i(\mathbf{kv} - \omega)} \int A(\mathbf{v}', \mathbf{v}) F(\mathbf{k}, \mathbf{v}', \omega)\, d\mathbf{v}' + \frac{W(\mathbf{v})}{\nu + i(\mathbf{kv} - \omega)}. \quad (3.1)$$

The second term on the right-hand side of Eq. (3.1) takes into account the initial conditions of (2.9).

In order to solve (3.1), we must know the concrete form of the kernel $A(\mathbf{v}', \mathbf{v})$. We shall use a relatively simple strong-collision model that permits us to find the spectrum in closed form. The model is based on assuming that $A(\mathbf{v}', \mathbf{v})$ is independent of $\mathbf{v}'$. That is, $A(\mathbf{v}', \mathbf{v}) = A(\mathbf{v})$. In other words, we assume that the velocity $\mathbf{v}$ of the particle after collision is independent of its velocity $\mathbf{v}'$ before collision. In distinction from the Brownian-movement model of (2.14), this model reflects the fundamental qualitative characteristics of scattering of light particles by heavy ones.[9,13,14]

The concrete form of the function $A(\mathbf{v})$ is unambiguously determined by the condition $S = 0$ at statistical equilibrium. In particular, we can easily show that $A(\mathbf{v})$ must be determined by the formula

$$A(\mathbf{v}) = \nu W_M(\mathbf{v}), \quad W_M(\mathbf{v}) = \frac{1}{[\sqrt{\pi}\,\bar{v}]^3} e^{-v^2/\bar{v}^2}, \quad (3.2)$$

where ν is independent of the velocity. This form of the collision integral implies that the probability of various values of the velocity of an atom is determined by the equilibrium distribution even after the first collision, and that an arbitrary initial distribution $W(\mathbf{v})$ transforms into an equilibrium distribution in a time of the order of $1/\nu$. Consequently, the quantity ν has the same physical meaning as ν_d which enters in Sec. 2: the quantities $1/\nu$ and $1/\nu_d$ determine the time that it takes for an atom to forget completely its initial velocity.

With this type of kernel $A(\mathbf{v})$, the equations for the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ and its Fourier components $F(\mathbf{k}, \mathbf{v}, \omega)$ acquire the form:

$$\frac{\partial f}{\partial t} + \mathbf{v}\nabla f = -\nu \left[f - W_M(\mathbf{v}) \int f(\mathbf{r}, \mathbf{v}', t)\, d\mathbf{v}' \right], \quad (3.3)$$

$$F(\mathbf{k}, \mathbf{v}, \omega) = \frac{\nu W_M(\mathbf{v})}{\nu + i(\mathbf{kv} - \omega)} \int F(\mathbf{k}, \mathbf{v}', \omega)\, d\mathbf{v}' + \frac{W(\mathbf{v})}{\nu + i(\mathbf{kv} - \omega)}. \quad (3.1')$$

By integrating the right and left-hand sides of Eq. (3.1′) over $\mathbf{v}$ and using (2.11) and (2.22), we derive

$$I(\omega) = \frac{\frac{1}{\pi} \int \frac{W(\mathbf{v})\, d\mathbf{v}}{\nu + i(\mathbf{kv} - \omega)}}{\left[1 - \nu \int \frac{W_M(\mathbf{v})\, d\mathbf{v}}{\nu + i(\mathbf{kv} - \omega)} \right]}. \quad (3.4)$$

We can interpret Eq. (3.4) as follows. The numerator in (3.4) involves the fact that the emission from the oscillator is broken up into a sequence of incoherent trains of duration $1/\nu$, and within each train a frequency is emitted that is displaced by the amount of the Doppler shift $\mathbf{kv}$. However, the actual trains that the emission is separated into by the velocity change of the atom upon collision cannot be considered incoherent. As we have said above (see Sec. 1), coherence is lost in a time τ_k, which corresponds to motion of the atom over a distance $\lambda/2\pi$. Hence, all emission within the time τ_k can interfere, regardless of how many trains it is divided into. The role of this interference is reflected in the denominator of (3.4). Interference between successive trains can be neglected only when the train length $l \gg \lambda/2\pi$. However, this means that $\nu \ll \Delta\omega_D$. Under this condition, the second term in the denominator is much smaller than unity, while the numerator goes over into the ordinary Doppler intensity distribution corresponding to the initial velocity distribution of the atoms. However, if ν is not small but comparable with $\Delta\omega_D$, the interference of different trains is substantial.

We shall assume that $W(\mathbf{v})$ is an equilibrium distribution function. Then (3.4) implies that

$$I(\omega) = \frac{1}{\sqrt{\pi}\Delta\omega_D} \operatorname{Re} \left[\frac{w\left(\frac{\omega}{\Delta\omega_D}, \frac{\nu}{\Delta\omega_D}\right)}{1 - \sqrt{\pi}\frac{\nu}{\Delta\omega_D} w\left(\frac{\omega}{\Delta\omega_D}, \frac{\nu}{\Delta\omega_D}\right)} \right], \quad (3.5)$$

where the function

$$w(x, y) = \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}\, dt}{x + iy - t} = \frac{1}{\sqrt{\pi}} \int_0^{\infty} e^{-z^2 + i(x+iy)z}\, dz \quad (3.6)$$

can be expressed in terms of the probability integral of a complex argument*

$$w(x, y) = e^{-(x+iy)^2}\left\{1-\frac{2}{\sqrt{\pi}}\int_0^{i(x+iy)} e^{-t^2}\,dt\right\}. \qquad (3.7)$$

We can easily see from (3.6) and (3.5) that we get the Gaussian intensity distribution (2.25) in the limiting case where $\nu \to 0$. When $\nu \neq 0$, but $\nu \ll \Delta\omega_D$, we can easily derive an expansion of $I(\omega)$ in powers of $\nu/\Delta\omega_D$ and $\omega/\Delta\omega_D$. At the center of the line, $\omega = 0$, and from (3.6) and (3.5) we have

$$I(0) \simeq \frac{1}{\sqrt{\pi}\,\Delta\omega_D}\left\{1+\frac{\pi-2}{\sqrt{\pi}}\frac{\nu}{\Delta\omega_D}\right\}. \qquad (3.8)$$

This expression differs from (2.26) only in the numerical coefficient of the $\nu/\Delta\omega_D$ term, which is about twice as large in Eq. (3.8). Therefore, when $\nu = \nu_d$, strong collisions are about twice as effective in narrowing the line than weak collisions. One can show that the intensity at the point $\omega = 0$ increases monotonically with increasing $\nu/\Delta\omega_D$ (curve 2 in Fig. 1).

We can elucidate the behavior of the intensity in the wings of the line by using the asymptotic expansion of the probability integral for large values of the modulus of the argument:

$$I(\omega) \simeq \frac{1}{\sqrt{\pi}\,\Delta\omega_D}\,\frac{1}{2\sqrt{\pi}}\,\frac{\nu\Delta\omega_D^3}{\omega^2\,[\omega^2+\nu^2]+\frac{1}{4}\Delta\omega_D^4} \qquad (\omega^2+\nu^2 \gg \Delta\omega_D^2). \qquad (3.9)$$

When $\omega \gg \nu$, we can drop the term $\omega^2\nu^2$ in the denominator of (3.9). Upon taking into account the conditions for applicability of Eq. (3.9), we can also drop the term $\frac{1}{4}\Delta\omega_D^4$. Thereupon, (3.9) coincides with (2.28). Hence, the strong-collision model gives the same intensity distribution in the wings of the line as the Brownian-movement model does.

In the limiting case where $\nu \gg \Delta\omega_D$, Eq. (3.9) is valid for all values of ω. In the region $\omega > \nu$ the line contour has a dispersion form with a width $2\gamma_d = \Delta\omega_D^2/\nu$. As is implied in what we have said above, when $\omega > \nu$, the dispersion is replaced by a wing having $I(\omega) \sim \omega^{-4}$.

Thus, both models discussed here and in Sec. 2 lead to the same line shape in all frequency ranges at high collision frequencies (ν, $\nu_d \gg \Delta\omega_D$). When the values of ν or ν_d are not too high, the wings of the lines are also the same. However, the central part of the line proves to differ somewhat for identical values of the parameters ν and ν_d. One can see this by comparing Eqs. (2.26) and (3.8), as has been discussed above. One can see the general character of the distinction in Fig. 2, where curves 2 and 4 are calculated for $\nu = \nu_d = 0.7\,\Delta\omega_D$.

In order to reveal what is involved in the similarity of the results in the strong- and weak-collision models, we shall compare the firts and second moments of the displacement **r** and the velocity **v**. We see from (2.19) that in the Brownian-movement model **r** and **v** are normally-distributed random variables (see, e.g. [1], Sec. 58) with second moments equal to

$$\langle \mathbf{r}^2\rangle = 3\frac{\bar{v}^2}{\nu_d^2}[\nu_d t - 1 + e^{-\nu_d t}],$$

$$\langle \mathbf{r}\mathbf{v}\rangle = 3\frac{\bar{v}^2}{2\nu_d}[1-e^{-\nu_d t}],$$

$$\langle \mathbf{v}^2\rangle = 3\frac{\bar{v}^2}{2}; \qquad (3.10)$$

As for the first moments, we have assumed that $\langle \mathbf{r}\rangle = \mathbf{r}_0 = 0$, and

$$\langle \mathbf{v}\rangle = \mathbf{v}_0 e^{-\nu_d t}. \qquad (3.10')$$

In the strong-collision model, the quantities **r** and **v** are generally not distributed normally. However, as we can easily show, the first and second moments in this case are also given by Eqs. (3.10) and (3.10′), with ν_d replaced therein by ν. Thus, the two models under discussion correspond to different distributions for **r** and **v**, but give identical mean values, variances and correlational moments for these quantities. Since with a large number of collisions any distribution approaches a normal one, it is quite understandable that when $\nu \gg \Delta\omega_D = k\bar{v}$, i.e., $l \ll \lambda/2\pi$, both models lead to identical results. Conversely, we should expect the greatest difference when $\nu \ll \Delta\omega_D$, i.e., when collisions are relatively infrequent, as is the case,

The relation between the strong- and weak-collision models can be taken up in further detail by specifying a kernel $A(\mathbf{v}, \mathbf{v}')$ that will contain both these models as limiting cases. Following [9], we shall set

$$A(\mathbf{v}, \mathbf{v}') = a(\mathbf{v}' - \gamma\mathbf{v}). \qquad (3.11)$$

The vanishing of the collision integral for the equilibrium distribution provides an explicit expression for $a(\mathbf{v}' - \gamma\mathbf{v})$:

$$a(\mathbf{v}'-\gamma\mathbf{v}) = \frac{\mu}{[\pi(1-\gamma^2)\bar{v}^2]^{3/2}}\exp\left[-\frac{(\mathbf{v}'-\gamma\mathbf{v})^2}{(1-\gamma^2)\bar{v}^2}\right]. \qquad (3.12)$$

The physical meaning of the parameter can be easily established by calculating the mean value of the velocity $\{\mathbf{v}'\}$ after collision

$$\{\mathbf{v}'\} = \frac{1}{\mu}\int \mathbf{v}'\,a(\mathbf{v}'-\gamma\mathbf{v})\,d\mathbf{v}' = \gamma\mathbf{v}.$$

Hence, γ is the ratio of the mean velocity after collision to the velocity of the particle before collision. Thus, the fundamental assumption of the model of (3.12) is that this ratio is independent of **v**. The size of the constant γ must be chosen in accord with the specific nature of the collisions. If a light particle is being scattered by a heavy one, then $\gamma \cong 0$, corresponding to the model discussed in this section. For collisions of a heavy particle with light ones, γ is close to unity. As is shown in [9], when $1-\gamma \ll 1$, the collision integral corresponds to the Brownian-

*There is a detailed analysis of the properties and a table of this function in [15].

movement model to an accuracy of terms of the order of $(1-\gamma)^2$.

It is easy to calculate the second moments of **r** and **v** for the model of (3.12). They prove to be

$$\langle r^2\rangle = 3\frac{\bar{v}^2}{\mu(1-\gamma)}\left[t-\frac{1-e^{-\mu(1-\gamma)t}}{\mu(1-\gamma)}\right],$$
$$\langle rv\rangle = \frac{3}{2}\frac{\bar{v}^2}{\mu(1-\gamma)}\left[1-e^{-\mu(1-\gamma)t}\right],$$
$$\langle v^2\rangle = \frac{3}{2}\bar{v}^2. \quad (3.13)$$

Hence, in this more general model as well, the variances and the correlational moment have the same form as before (cf. (3.10)). The difference consists only in the fact that the quantity $\mu(1-\gamma)$ acts as the effective collision frequency $1/\tau_v$ in (3.13). It is specifically this quantity that is equivalent to the parameters ν and ν_d in the strong-collision model ($\gamma = 0$) and the Brownian-movement (i.e., weak-collision) model ($1-\gamma \ll 1$).

We shall now discuss the case in which both strong and weak collisions occur simultaneously. Since we are restricting our treatment only to pair collisions, the collision integral S can be written in the form

$$S = \nu_d\left[\operatorname{div}_v(\mathbf{v}f)+\frac{\bar{v}^2}{2}\Delta_v f\right]-\nu\left[f-W_M(\mathbf{v})\int f(\mathbf{r},\mathbf{v}',t)\,d\mathbf{v}'\right]. \quad (3.14)$$

We can find the solution of the kinetic equation with the collision integral of (3.14) by using the same methods as above. The final result for the function $I(\omega)$ has the form

$$I(\omega)=\frac{1}{\pi}\,\frac{\dfrac{1}{\nu+\nu_d-i\omega}\Phi\left[1,1+\dfrac{\nu+\nu_d-i\omega}{\nu_d};\dfrac{\nu_d}{\nu_d}\right]}{1-\dfrac{\nu}{\nu+\nu_d-i\omega}\Phi\left[1,1+\dfrac{\nu+\nu_d-i\omega}{\nu_d};\dfrac{\nu_d}{\nu_d}\right]}. \quad (3.15)$$

This general expression contains as special limiting cases (2.23) and (3.4), which may be derived from (3.15) with $\nu \to 0$ and $\nu_d \to 0$, respectively.*

When ν, $\nu_d \ll \Delta\omega_D$, the first non-vanishing correction term to the intensity in the center of the line ($\omega = 0$) has the form

$$I(0) \simeq \frac{1}{\sqrt{\pi}\,\Delta\omega_D}\left\{1+\frac{\pi-2}{\sqrt{\pi}}\frac{\nu}{\Delta\omega_D}+\frac{2}{3\sqrt{\pi}}\frac{\nu_d}{\Delta\omega_D}\right\}. \quad (3.16)$$

We see by comparing (3.16) with Eqs. (2.26) and (3.8) that the strong and weak collisions made additive contributions with the same coefficients as when they are treated separately. In the outer wings, the intensity is determined by the sum $\nu + \nu_d$:

$$I(\omega)=\frac{1}{\sqrt{\pi}\Delta\omega_D}\,\frac{1}{2\sqrt{\pi}}\,\frac{(\nu+\nu_d)\,\Delta\omega_D^3}{\omega^4}. \quad (3.17)$$

The same thing happens when $\nu^2+\omega^2 \gg \Delta\omega_D^2$, or $\nu_d \gg \Delta\omega_D$. In the first case, for example, $I(\omega)$ is given by the formula

$$I(\omega)=\frac{1}{\sqrt{\pi}\,\Delta\omega_D}\,\frac{1}{2\sqrt{\pi}}\,\frac{(\nu+\nu_d)\,\Delta\omega_D^3}{\omega^2[\omega^2+(\nu+\nu_d)^2]+\Delta\omega_D^4/4}, \quad (3.18)$$

which is analogous to Eq. (3.9). As we should have expected from general considerations of the statistics of the variables **r** and **v**, the essential thing in these limiting cases is the total effective collision frequency.

Thus, both models of strong and weak collisions, as well as the joint treatment of strong and weak collisions, lead to very similar results. The decideing factor in correctly describing the narrowing of the Doppler contour is the choice of the characteristic quantity τ_v. The fact of what determines the quantity τ_v, weak or strong collisions or both together, plays a secondary role. For strong collisions, τ_v is the time of flight between two successive collisions. For weak collisions, the atom undergoes a large number of collisions in the time τ_v, the velocity varying slightly each time (by the amount $(1-\gamma)\mathbf{v}$, where $(1-\gamma) \ll 1$). However, the essential factor in both cases is the time required for an appreciable change in velocity.

4. BROADENING DUE TO INTERACTION

Before going on to generalizing the results derived above to the case of broadening due to interaction and the Doppler effect, it seems expedient to formulate a theory of impact broadening in terms of the kinetic equation.

We shall assume that the emitting atom is at rest. Then, in accord with (1.14) we must calculate the correlation function

$$\Phi(\tau)=\langle e^{-i\varphi(\tau)}\rangle, \quad \varphi=\eta-i\beta. \quad (4.1)$$

Here $\varphi(\tau)$ is the phase shift of the atomic oscillator resulting from collisions within the time τ. A calculation of (4.1) in the impact-theory approximation gives the following results:[1,16]

$$\Phi(\tau)=e^{-(\Gamma+i\Delta)\tau}, \quad (4.2)$$

$$I(\omega)=\frac{1}{\pi}\frac{\Gamma}{(\omega-\Delta)^2+\Gamma^2}. \quad (4.3)$$

Here Γ and Δ are the width and displacement of the line, as determined by the formula

$$\Gamma+i\Delta=\int P(g)\left[1-e^{-i\psi(g)}\right]dg, \quad (4.4)$$

where g denotes the set of collision parameters, $P(g)\,dg$ is the number of collisions of type g per unit time, and $\psi(g)$ is the phase shift in a collision having the parameters g.

We shall now show how we can derive Eqs. (4.2)—(4.4) by using the kinetic-equation method. For sim-

*Eq. (3.15) implies the following asymptotic representation of the hypergeometric function in terms of the probability integral:

$$\frac{1}{\gamma-1}\Phi(1,\gamma;z)=\sqrt{\frac{\pi}{2z}}\,w\left(\frac{\gamma-1-z}{\sqrt{2z}}\right),$$

if γ, $z\to\infty$, with $(\gamma-1-z)/\sqrt{2z}$ remaining finite. The function w is defined by Eq. (3.6) or (3.7).

plicity, we shall begin with a model of a one-dimensional harmonic oscillator having the characteristic frequency ω_0. We shall denote by q and p the generalized coordinates and momentum of the oscillator. The correlation function of (4.1) can be written in the form

$$\langle e^{-i\varphi(\tau)}\rangle = \int e^{-i\varphi} f(q, p, \tau)\, dq\, dp, \qquad (4.5)$$

where $f(q, p, \tau)$ is a distribution function satisfying the kinetic equation

$$\frac{\partial f}{\partial t} + \left\{\frac{\partial H}{\partial p}\frac{\partial f}{\partial q} - \frac{\partial H}{\partial q}\frac{\partial f}{\partial p}\right\} = S. \qquad (4.6)$$

The quantity $f(q, p, \tau)\,dq\,dp$ determines the relative number of oscillators having coordinates and momenta at the instant t within the ranges from q to $q+dq$ and from p to $p+dp$; $H(q,p)$ is the Hamiltonian of the oscillator; S is the collision integral.

Such an approach was used in [13] in the theory of impact broadening. Here they used the Cartesian coordinate and the corresponding momentum as the variables q and p. However, a difficulty arises with this choice of generalized coordinates. It involves the fact that in the general case both q and p vary in the collision process. In the translational-motion case discussed in the previous sections, the atomic coordinate changes by an amount considerably less than the wavelength (10^{-8} cm) during the time of the collision $\delta\tau$ ($\delta\tau \sim 10^{-13}$ sec). Hence it was possible in the collision integral to neglect all but the change in the velocity of translational motion. The situation differs when treating the motion of an atomic oscillator. The optical region of the spectrum corresponds to periods of vibration of the atomic electrons (10^{-15} sec) considerably shorter than the duration $\delta\tau$ of the collisions. Hence one must take into account both the change in the velocity and in the coordinate of the oscillator. This fact greatly complicates the calculations.

In the study [13] cited above, the problem was simplified, since the variation of the coordinate during the collision was neglected. Thus the results obtained in [13] can be used only in the far infrared and radio regions, where the vibration period of the oscillator becomes longer than the duration of the collision.

The mentioned difficulties in using the kinetic-equation method involve the faulty choice of variables in [13]. In this problem it is natural to choose as the variables the action J and its canonical conjugate, the angle w. The phase shift $\psi = \eta - i\beta$ is most easily expressed in terms of these variables. Namely, η is simply the change in the variable w over the time of the collision, $\Delta w = w - w_0$, and β is determined by the change in the variable J: $J = J_0 e^{-\beta}$. If we write Eq. (4.6) in terms of the variables J and w, and then transform here, as well as in (4.5), to the variables η and β, we can obtain

$$\Phi(\tau) = \langle e^{-i\varphi(\tau)}\rangle = \int e^{-i\varphi} f(\varphi, \tau)\, d\varphi, \qquad (4.7)$$

Here the distribution function $f(\varphi, \tau)$, which gives the relative number of oscillators having the given phase φ, satisfies the kinetic equation

$$\frac{\partial f}{\partial t} = -\int P(g)\,[f(\varphi, t) - f(\varphi - \psi(g), t)]\, dg. \qquad (4.8)$$

As one always does in the theory of impact broadening, we assume in (4.8) that every collision of type g corresponds to a change $\psi(g)$ in the phase of the oscillator that is independent of the value φ of the phase before the collision. Hence,

$$P(g)\,dg = A(\varphi - \varphi')\,d\varphi', \quad \Gamma + i\Delta = \int A(\psi)\,[1 - e^{-i\psi}]\, d\psi, \qquad (4.9)$$

where $A(\varphi - \varphi')$ is the probability per unit time of a change of the phase φ' (the phase before collision) to φ (the phase after collision). After this, Eq. (4.8) can also be written in the form

$$\frac{\partial f}{\partial t} = -\int [A(\varphi' - \varphi) f(\varphi, t) - A(\varphi - \varphi') f(\varphi', t)]\, d\varphi'. \qquad (4,10)$$

The function $f(\varphi, t)$ must satisfy the initial condition

$$f(\varphi, 0) = \delta(\varphi) \qquad (4,11)$$

(cf. (2.9)).

Multiplying (4.8) by $e^{-i\varphi}$, integrating over φ, and using (4.4), we obtain the following equation for the correlation function:

$$\frac{\partial \Phi}{\partial t} = -\Phi \int P(g)\,[1 - e^{-i\psi(g)}]\, dg = -(\Gamma + i\Delta)\,\Phi. \qquad (4.12)$$

By integrating (4.12), we obtain the formula (4.2) for the correlation function.

Thus, the kinetic-equation method permits one to derive very easily the general expressions of the impact theory of broadening of spectral lines. Here the hypothesis on the collision mechanism used in [13], which limits the region of applicability of the results of this study, proves to be superfluous.

5. JOINT TREATMENT OF INTERACTION AND THE DOPPLER EFFECT

We shall introduce the distribution function $f(\mathbf{r}, \mathbf{v}, \varphi, t)$ of the oscillators with respect to velocities, coordinates, and phases. This function satisfies the kinetic equation

$$\frac{\partial f}{\partial t} + \mathbf{v}\nabla f = S \qquad (5.1)$$

and the initial conditions

$$f(\mathbf{r}, \mathbf{v}, \varphi, 0) = W(\mathbf{v})\,\delta(\mathbf{r})\,\delta(\varphi). \qquad (5.2)$$

Using the distribution $f(\mathbf{r}, \mathbf{v}, \varphi, t)$, we can write the general expression for the correlation function (1.14) in the form

$$\Phi(\tau) = \langle e^{-i\mathbf{kr}(\tau) - i\varphi(\tau)}\rangle = \int e^{-i\mathbf{kr} - i\varphi} f(\mathbf{r}, \mathbf{v}, \varphi, \tau)\, d\mathbf{r}\, d\mathbf{v}\, d\varphi. \qquad (5,3)$$

Let us introduce the symbol

$$\tilde{f}(\mathbf{r}, \mathbf{v}, t) = \int e^{-i\varphi} f(\mathbf{r}, \mathbf{v}, \varphi, t)\, d\varphi \qquad (5.4)$$

and express the correlation function $\Phi(\tau)$ in terms of $\tilde{f}$:

$$\Phi(\tau) = \int e^{-i\mathbf{kr}} \tilde{f}(\mathbf{r}, \mathbf{v}, \tau)\, d\mathbf{r}\, d\mathbf{v}. \quad (5.5)$$

This expression has exactly the same form as (2.6). The only difference is that $f(\mathbf{r}, \mathbf{v}, \tau)$ from (5.4) occurs in place of the distribution function $f(\mathbf{r}, \mathbf{v}, \tau)$.

We shall begin with discussing the simplest model, which, however, permits us to elucidate all the qualitative features of the phenomenon. We shall characterize the collision by a single parameter, the impact distance ρ. Let the phase of the oscillator change by the same amount ψ_0 whenever a perturbing particle passes by at an impact distance $\rho \leq \rho_0$. Also let its velocity change in such a way that the velocity distribution after collision is an equilibrium distribution, regardless of the velocity before collision. We shall also assume that when $\rho > \rho_0$, neither the phase nor the velocity of the oscillator changes.

The collision integral in (5.1) has the form

$$S = -\int P(\rho)\, d\rho\, [f(\mathbf{r}, \mathbf{v}, \varphi, t) - f(\mathbf{r}, \mathbf{v} - \Delta\mathbf{v}(\rho), \varphi - \Delta\varphi(\rho), t)], \quad (5,6)$$

where $\Delta\mathbf{v}(\rho)$ and $\Delta\varphi(\rho)$ are the changes in velocity and phase resulting from collision at an impact distance of ρ. This expression is a natural generalization of (2.4′) and (4.8) to the case in which both the velocity and phase of the oscillator are changed simultaneously upon collision. Within the framework of the adopted model, $\Delta\mathbf{v}(\rho) = 0$ and $\Delta\varphi(\rho) = 0$ when $\rho > \rho_0$, and the expression within the square brackets in (5.6) vanishes. Hence the integration in (5.6) is performed between the limits 0 and ρ_0. The first term in (5.6) can be written in the form $-\nu f$, where

$$\nu = \int_0^{\rho_0} P(\rho)\, d\rho$$

is the number of collisions having impact distances $\rho \leq \rho_0$. The second term in Eq. (5.6) can be represented in the form

$$\nu W_M(\mathbf{v}) \int f(\mathbf{r}, \mathbf{v}', \varphi - \psi_0, t)\, d\mathbf{v}',$$

This is because we have assumed in this model that every collision leads to a phase change of ψ_0 and to the establishment of a Maxwellian velocity distribution $W_M(\mathbf{v})$ of the atoms, regardless of the values of the velocity and the impact distance. Thus, the collision integral of (5.6) proves to be

$$S = -\nu \left[f(\mathbf{r}, \mathbf{v}, \varphi, t) - W_M(\mathbf{v}) \int f(\mathbf{r}, \mathbf{v}', \varphi - \psi_0, t)\, d\mathbf{v}' \right]. \quad (5.7)$$

If we multiply (5.1), (5.2), and (5.7) by $e^{-i\varphi}$ and integrate over φ, we can derive the following equation for the function $\tilde{f}$:

$$\frac{\partial \tilde{f}}{\partial t} + \mathbf{v}\nabla\tilde{f} = -\nu \left[\tilde{f} - W_M(\mathbf{v}) \int \tilde{f}(\mathbf{r}, \mathbf{v}', t)\, d\mathbf{v}' e^{-i\psi_0} \right],$$
$$\tilde{f}(\mathbf{r}, \mathbf{v}, 0) = W(\mathbf{v})\, \delta(\mathbf{r}). \quad (5.8)$$

Equation (5.8) differs from the kinetic equation (3.3) in the strong-collision model only in the factor $e^{-i\psi_0}$ in the second term of the collision integral. The quantity $e^{-i\psi_0}$ determines what the broadening due to the phase change of the oscillator upon collision would be if the collisions were not accompanied by a velocity change. Actually, in the adopted model the width Γ and the shift Δ in (4.4) are related to $e^{-i\psi_0}$ by the relation

$$\Gamma + i\Delta = \nu(1 - e^{-i\psi_0}). \quad (5.9)$$

Hence, it is convenient to write the right-hand side of (5.8) in a somewhat different form by adding and subtracting the term $\nu\tilde{f}e^{-i\psi_0}$:

$$\frac{\partial \tilde{f}}{\partial t} + \mathbf{v}\nabla\tilde{f} = -(\Gamma + i\Delta)\tilde{f} - \nu e^{-i\psi_0} \left[\tilde{f} - W_M(\mathbf{v}) \int \tilde{f}(\mathbf{r}, \mathbf{v}', t)\, d\mathbf{v}' \right]. \quad (5.10)$$

If different collisions were responsible for the phase change and the velocity change, then the function $\tilde{f}$ would satisfy the equation

$$\frac{\partial \tilde{f}}{\partial t} + \mathbf{v}\nabla\tilde{f} = -(\Gamma + i\Delta)\tilde{f} - \nu \left[\tilde{f} - W_M(\mathbf{v}) \int \tilde{f}(\mathbf{r}, \mathbf{v}', t)\, d\mathbf{v}' \right], \quad (5.11)$$

where the collision integral S is the sum of two independent terms of the same form as that entering into Eqs. (3.3) and (4.12).

We see by comparing Eqs. (5.10) and (5.11) that the introduction of a phase discontinuity that occurs simultaneously with the velocity change has the result, from the formal standpoint, that the frequency ν of the elastic collisions in (5.10) is replaced by the complex quantity $\nu e^{-i\psi_0}$, where $|\nu e^{-i\psi_0}| = \nu e^{-\beta} < \nu$. It follows from (5.9) that

$$\nu e^{-i\psi_0} = \nu - \Gamma - i\Delta.$$

Thus, in distinction from (5.11), the right-hand side of (5.10) cannot be expressed as two independent terms, each describing different broadening effects; this is a direct reflection of the statistical dependence of the changes in the velocity and phase. As we shall see below, this fact can lead not only to quantitative changes, but also to certain qualitative changes in the spectrum. In particular, the line contour can prove to be asymmetric (see Sec. 7).

The characteristics of the collision integral involving the statistical dependence of the phase and velocity changes can also be revealed without recourse to the simplifications used above. In the general case, the collision integral taking into account both the phase increment and the velocity change can be written in the form

$$S = -\int [A(\mathbf{v}, \mathbf{v}', \varphi' - \varphi) f(\mathbf{r}, \mathbf{v}, \varphi, t)$$
$$- A(\mathbf{v}', \mathbf{v}, \varphi - \varphi') f(\mathbf{r}, \mathbf{v}', \varphi', t)]\, d\mathbf{v}'\, d\varphi'. \quad (5.12)$$

If the change in the phase $(\varphi \to \varphi')$ and in the velocity $(\mathbf{v} \to \mathbf{v}')$ occur during different collisions, then

$$A(\mathbf{v},\ \mathbf{v}',\ \varphi'-\varphi)=A_1(\mathbf{v},\ \mathbf{v}')\,\delta(\varphi'-\varphi)+A_2(\mathbf{v},\ \varphi'-\varphi)\,\delta(\mathbf{v}'-\mathbf{v}). \tag{5.13}$$

Here one can easily derive the following equation for the function $\tilde{f}$:

$$\frac{\partial\tilde{f}}{\partial t}+\mathbf{v}\nabla\tilde{f}=-(\Gamma+i\Delta)\tilde{f}-\int[A_1(\mathbf{v},\ \mathbf{v}')\tilde{f}-A_1(\mathbf{v}',\ \mathbf{v})\tilde{f}(\mathbf{r},\ \mathbf{v}',\ t)]\,d\mathbf{v}', \tag{5.14}$$

$$\Gamma+i\Delta=\int A_2(\mathbf{v},\ \psi)\,e^{-i\psi}\,d\psi. \tag{5.15}$$

The right-hand side of Eq. (5.14) contains terms analogous to those existing in the description of pure Doppler broadening and of broadening due to interaction (cf. (3.3) and (4.12), and also (5.11)).

If the phase and velocity changes are produced in the same collisions, then one can also distinguish in the collision integral $\tilde{S}$ a term $-(\Gamma+i\Delta)\tilde{f}$, in analogy to the way in which this has been done in (5.10). However, here the remaining part of $\tilde{S}$ proves to depend not only on the velocity change, but also on the phase change. In particular, we can easily derive the following equation for the function $\tilde{f}$:

$$\frac{\partial\tilde{f}}{\partial t}+\mathbf{v}\nabla\tilde{f}=-(\Gamma+i\Delta)\tilde{f}-\int[\tilde{A}(\mathbf{v},\ \mathbf{v}')\tilde{f}(\mathbf{r},\ \mathbf{v},\ t)-\tilde{A}(\mathbf{v}',\ \mathbf{v})\tilde{f}(\mathbf{r},\ \mathbf{v}',\ t)]\,d\mathbf{v}', \tag{5.16}$$

where

$$\tilde{A}(\mathbf{v},\ \mathbf{v}')=\int A(\mathbf{v},\ \mathbf{v}',\ \psi)\,e^{-i\psi}\,d\psi,$$

$$\Gamma+i\Delta=\int A(\mathbf{v},\ \mathbf{v}',\ \psi)\,[1-e^{-i\psi}]\,d\psi\,d\mathbf{v}'. \tag{5.17}$$

Equations (5.16) and (5.14) have the same structure, but the kernel of the integral term in (5.16) is the complex function $\tilde{A}(\mathbf{v},\mathbf{v}')$, whose form generally depends on the distribution of discontinuities in the phase ψ.

Equation (5.14) contains the real probability of the velocity change $\mathbf{v}\to\mathbf{v}'$, which doesn't involve the nature of the phase change in any way. As we see from the definition of the function $\tilde{A}(\mathbf{v},\mathbf{v}')$, this distinction is analogous to the appearance of the factor $e^{-i\psi_0}$ in (5.10). The difference consists only in the fact that the phase shift ψ_0 was assumed to be constant for all collisions in the simpler model for which Eq. (5.10) was written while arbitrary phase increments are assumed in (5.16). Consequently, the collision integral contains a certain averaged characteristic, namely, the Fourier transform of $A(\mathbf{v},\mathbf{v}',\psi)$ averaged over ψ.

Above we have discussed two types of collisions. In collisions of the first type, both the phase and velocity change simultaneously. In collisions of the second type, either the phase alone, or the velocity alone changes. Whenever both types of collisions occur, the collision integral S will be a linear combination of the right-hand sides of Eqs. (5.14) and (5.16).

The corresponding generalization of the kinetic equation is so obvious that we shall not write it out.

6. BROADENING DUE TO INTERACTION AND THE DOPPLER EFFECT (STATISTICAL INDEPENDENCE)

First we shall discuss the strong-collision model (i.e., we shall take (3.2) to express the function $A_1(\mathbf{v},\mathbf{v}')$ in Eq. (5.14)). Then Eq. (5.14) takes on the form

$$\frac{\partial\tilde{f}}{\partial t}+\mathbf{v}\nabla\tilde{f}=-(\Gamma+i\Delta)\tilde{f}-\nu\left\{\tilde{f}-W_M(\mathbf{v})\int\tilde{f}(\mathbf{r},\ \mathbf{v}',\ t)\,d\mathbf{v}'\right\}. \tag{6.1}$$

We can easily find the intensity distribution $I(\omega)$ in the spectral line from (6.1) by the same method as in Sec. 3:

$$I(\omega)=\frac{1}{\pi}\,\mathrm{Re}\left\{\frac{\int\frac{W(\mathbf{v})\,d\mathbf{v}}{\nu+\Gamma-i(\omega-\Delta-\mathbf{kv})}}{1-\nu\int\frac{W_M(\mathbf{v})\,d\mathbf{v}}{\nu+\Gamma-i(\omega-\Delta-\mathbf{kv})}}\right\}. \tag{6.2}$$

This expression differs from Eq. (3.4) (pure Doppler broadening) in the terms $\Gamma+i\Delta$ in the resonance denominators. When Γ and Δ do not depend on the velocity of the emitting atom, we can represent (6.2) as the convolution of a dispersion curve and the function (3.4), which defines the line contour when $\Gamma=\Delta=0$:

$$I(\omega)=\int_{-\infty}^{\infty}\frac{\Gamma/\pi\,d\omega'}{\Gamma^2+(\omega-\Delta-\omega')^2}\,\mathrm{Re}\left\{\frac{1}{\pi}\,\frac{\int\frac{W(\mathbf{v})\,d\mathbf{v}}{\nu-i(\omega'-\mathbf{kv})}}{1-\nu\int\frac{W(\mathbf{v})\,d\mathbf{v}}{\nu-i(\omega'-\mathbf{kv})}}\right\}. \tag{6.3}$$

Actually, the integrand of the integral over ω' has a single pole in the upper half-plane of the complex frequency: $\omega'=\omega-\Delta+i\Gamma$. We can convince ourselves that (6.3) and (6.2) are identical by using the subtraction theorem.

We emphasize that the arguments given here essentially make use of the independence of Γ and Δ of $\mathbf{v}$. In the opposite case, the line contour is not expressible as a convolution. Thus, broadenings due to interaction and the Doppler effect are statistically independent (even in the case of (5.13)) only when Γ and Δ are independent of the velocity of the emitting atom. This is easy to understand from simple physical considerations. If $\Gamma=\Gamma(\mathbf{v})$ and $\Delta=\Delta(\mathbf{v})$, then the phase change on collision will depend on what velocity the atom acquired from the previous elastic collision. It is evident from symmetry considerations that $\Gamma(\mathbf{v})$ and $\Delta(\mathbf{v})$ can be only even functions of $\mathbf{v}$. Hence, as we can easily show, the line contour (6.2) will generally be asymmetric.

Let us discuss expression (6.2) for constant Γ and Δ in greater detail. In this case, the line contour will be symmetric with respect to the point $\omega=\Delta$. That is to say, the size of Δ determines the shift of the line peak. We shall assume hereinafter that the frequency is referred to this point, i.e., we shall assume that

$\Delta = 0$. We see from Eq. (6.2) that the phase changes during the collisions diminish the line-narrowing effect due to elastic collisions (see Secs. 2. 3). Formally, this is due to the fact that, for a given value of the sum $\nu + \Gamma$, the integral term in the denominator of (6.2) is diminished by a factor of $1+\Gamma/\nu$ as compared with (3.4). In the limiting case where $\Gamma \gg \nu$, we can drop it completely, and Eq. (6.2) goes over into the ordinary convolution of a Gaussian with a dispersion distribution:

$$I(\omega) = \frac{\Gamma}{\pi^{3/2}\bar{v}} \int_{-\infty}^{\infty} \frac{e^{-v^2/\bar{v}^2}\,dv}{\Gamma^2 + (\omega - kv)^2}. \qquad (6.4)$$

In order to analyze the case where $\Gamma \gtrsim \nu$, let us examine the expressions for $I(\omega)$ when $\omega = 0$ and $\nu, \Gamma \ll \Delta\omega_D$, and when $\omega^2 + (\Gamma + \nu)^2 \gg \Delta\omega_D^2$:

$$I(0) \simeq \frac{1}{\sqrt{\pi}\,\Delta\omega_D}\left\{1 + \frac{1}{\sqrt{\pi}\,\Delta\omega_D}[(\pi-2)\nu - 2\Gamma]\right\} \quad (\nu, \Gamma \ll \Delta\omega_D), \qquad (6.5)$$

$$I(\omega) \simeq \frac{1}{\pi} \frac{\frac{1}{2}\frac{\Delta\omega_D^2(\nu+\Gamma)}{\omega^2+(\nu+\Gamma)^2} + \Gamma}{\left[\frac{1}{2}\frac{\Delta\omega_D^2(\nu+\Gamma)}{\omega^2+(\nu+\Gamma)^2} + \Gamma\right]^2 + \omega^2} \quad (\omega^2 + (\nu+\Gamma)^2 \gg \Delta\omega_D^2). \qquad (6.6)$$

We can easily see the following from Eqs. (6.5) and (6.6): at low collision frequencies, $\nu, \Gamma \ll \Delta\omega_D$, and the line center maintains an approximately Gaussian form, but is somewhat narrowed if $\Gamma < [(\pi-2)/2]\,\nu$, or is broadened in the opposite case. When $\omega \to \infty$, the intensity decreases as ω^{-2}, independently of the values of ν, Γ, or $\Delta\omega_D$. However, the boundary of the region in which $I(\omega) \sim \omega^{-2}$ is determined by the relation between these parameters. Specifically,

$$I(\omega) \simeq \frac{\Gamma}{\pi}\frac{1}{\omega^2}, \qquad (6.7)$$

if

$$\omega^2 + (\nu+\Gamma)^2 \gg \frac{\nu+\Gamma}{\Gamma}\Delta\omega_D^2. \qquad (6.8)$$

If $\nu \lesssim \Gamma \ll \Delta\omega_D$, then the wing of the line for which $I(\omega) \sim \omega^{-2}$ will begin at $\omega \gtrsim \Delta\omega_D$. However, if $\nu \gg \Gamma$, then this region will be shifted to higher frequencies, while in the frequency range $\nu \ll \omega \ll \sqrt{\nu/\Gamma}\,\Delta\omega_D$ the intensity distribution will obey the law

$$I(\omega) \simeq \frac{1}{\sqrt{\pi}\,\Delta\omega_D}\frac{\nu\Delta\omega_D^3}{2\sqrt{\pi}\,\omega^4}, \qquad (6.9)$$

just as when there are no phase discontinuities (cf. (2.28)).

At higher collision frequencies when $\nu + \Gamma \gg \Delta\omega_D$, the central part of the line will have a dispersion shape analogous to (2.31), but with a different width:

$$I(\omega) \simeq \frac{1}{\pi} \frac{\frac{1}{2}\frac{\Delta\omega_D^2}{\nu+\Gamma} + \Gamma}{\left[\frac{1}{2}\frac{\Delta\omega_D^2}{\nu+\Gamma} + \Gamma\right]^2 + \omega^2}. \qquad (6.10)$$

When $\nu + \Gamma \gg \Delta\omega_D^2/\Gamma$, the line width is determined only by the phase change in the collisions. This is quite understandable physically, since the stated condition implies that the atom travels a distance considerably shorter than $\lambda/2\pi$ in the time $1/\Gamma$ corresponding to a substantial phase change:

$$\frac{\bar{v}}{\Gamma} \ll \frac{\nu+\Gamma}{\Delta\omega_D}\frac{1}{k} \ll \frac{\lambda}{2\pi}. \qquad (6.11)$$

Naturally, the Doppler effect exerts no influence here on the line contour.

If ν and Γ are proportional to each other, then the term $\Delta\omega_D^2/(\nu+\Gamma)$ will decrease with increasing Γ. The minimum value of the width in (6.10) is 2Γ, which is attained when $\Gamma(\Gamma+\nu) = \Delta\omega_D^2/2$.

Figures 3 and 4 show the results of numerical calculations of the line contour, peak intensity, and line width for intermediate values of the parameters. We see from these plots that when $\nu \gtrsim \Delta\omega_D$, the peak intensity of the line rapidly declines with increasing Γ, even when Γ amounts to a small fraction of ν (of the order of several tenths). Thus, broadening due to interactions highly effectively masks the effect of narrowing of the Doppler contour. Nevertheless, when $\nu \sim \Gamma$, the narrowing effect is still quite noticeable (see curves 1 and 3 in Fig. 3).

Very similar results are obtained also in the weak-collision model. Here Eq. (5,14) for the function $\tilde{f}$ has the form

$$\frac{\partial\tilde{f}}{\partial t} + \mathbf{v}\nabla\tilde{f} = -(\Gamma + i\Delta)\tilde{f} + \nu_d\,\mathrm{div}_{\mathbf{v}}(\mathbf{v}\tilde{f}) + q\Delta_{\mathbf{v}}\tilde{f}. \qquad (6.12)$$

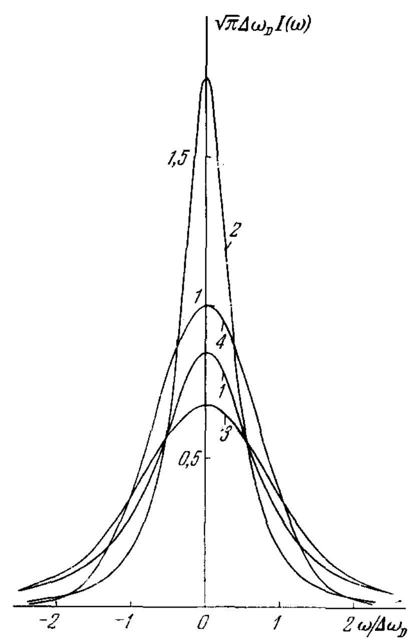

FIG. 3. The contour of lines broadened by interaction and the Doppler effect (case of statistical independence). Curve 1: $\nu = \Delta\omega_D$, $\Gamma = 0.4\Delta\omega_D$; curve 2: $\nu = \Delta\omega_D$, $\Gamma = 0$; curve 3: $\nu = 0$, $\gamma = 0.4\Delta\omega_D$; curve 4: $\nu = \Gamma = 0$.

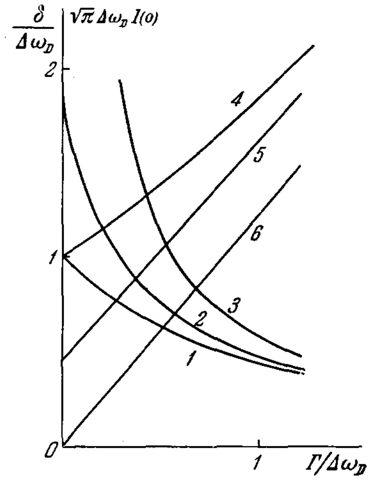

FIG. 4. Relation of the peak intensity (curves 1–3) and the width δ(4–6) of the line to $\Gamma/\Delta\omega_D$ when the broadenings due to interaction and the Doppler effect are statistically independent. Curves 1 and 4: $\nu = 0$; 2 and 5: $\nu = \Delta\omega_D$; 3 and 6: $\nu = \infty$.

By solving this equation and using (5.5), we find the correlation function (for constant Γ, Δ, ν_d, and q):

$$\Phi(\tau) = \exp\left\{-(\Gamma + i\Delta)\tau - \frac{\Delta\omega_D^2}{2\nu_d^2}[\tau\nu_d - 1 + e^{-\nu_d\tau}]\right\}. \quad (6.13)$$

Thus, $\Phi(\tau)$ is the product of the correlation functions figuring in the analysis of broadening due to interactions and the Doppler effect separately (cf. Eqs. (4.2) and (2.21)). Since the pure Doppler broadenings are very similar tin the strong- and weak-collision models, the resulting contours will also be similar. Consequently, we shall not analyze Eq. (6.13) in detail.

7. BROADENING DUE TO INTERACTION AND THE DOPPLER EFFECT (STATISTICAL DEPENDENCE)

We shall analyze Eq. (5.16) and the corresponding line contour with the following form for the kernel $A(\mathbf{v}, \mathbf{v}', \psi)$:

$$A(\mathbf{v}, \mathbf{v}', \psi) = A(\mathbf{v}, \mathbf{v}')B(\psi). \quad (7.1)$$

This expression means that the velocity and phase changes are produced in the same collision, but the values of these changes are in no way interrelated. Without loss of generality, we can assume that

$$\int B(\psi)\, d\psi = 1. \quad (7.2)$$

Here the function $A(\mathbf{v}, \mathbf{v}')$ has the meaning of the probability per unit time of a velocity change $\mathbf{v} \rightarrow \mathbf{v}'$, regardless of the phase change. We shall make the same assumptions about this function as we did in Secs. 2 and 3. Then, Eq. (5.16) for $\tilde{f}$ in the strong-collision model will become

$$\frac{\partial\tilde{f}}{\partial t} + \mathbf{v}\nabla\tilde{f} = -(\Gamma + i\Delta)\tilde{f} - \nu\tilde{B}\left[\tilde{f} - W_M(\mathbf{v})\int\tilde{f}(\mathbf{r}, \mathbf{v}', t)\, d\mathbf{v}'\right], \quad (7.3)$$

Here, in accordance with (5.17), (7.1), and (7.2),

$$\nu\tilde{B} = \nu\int B(\psi)e^{-i\psi}\, d\psi = \nu - \Gamma - i\Delta, \quad (7.4)$$

while in the weak-collision model,

$$\frac{\partial\tilde{f}}{\partial t} + \mathbf{v}\nabla_r\tilde{f} = -(\Gamma + i\Delta)\tilde{f} + \nu_d\tilde{B}\left[\operatorname{div}_{\mathbf{v}}(v\tilde{f}) + \frac{\bar{v}^2}{2}\Delta_v\tilde{f}\right],$$
$$\nu_d\tilde{B} = \nu_d\left[1 - \frac{\Gamma + i\Delta}{\nu}\right]. \quad (7.5)$$

Thus, in both models, the effect of the phase shifts in the collisions amounts to replacing the effective collision frequencies ν and ν_d by the complex quantities $\nu\tilde{B}$ and $\nu_d\tilde{B}$. In this regard, (7.3) and (7.5) are analogous to Eq. (5.10).

We shall first take up the strong-collision model. Repeating the calculation of Sec. 3, we find

$$I(\omega) = \frac{1}{\pi}\operatorname{Re}\left\{\frac{\int\frac{W(\mathbf{v})\, d\mathbf{v}}{\nu - i(\omega - \mathbf{k}\mathbf{v})}}{1 - \nu\tilde{B}\int\frac{W_M(\mathbf{v})\, d\mathbf{v}}{\nu - i(\omega - \mathbf{k}\mathbf{v})}}\right\}. \quad (7.6)$$

In distinction from Eq. (6.2), the resonance denominator in (7.6) contains only ν, but not $\nu + \Gamma$ or Δ. This is quite understandable, since the real part of the resonance coefficients is determined, roughly speaking, by the mean length of the wave trains into which the emission from the oscillator is broken by collisions (see the discussion of Eq. (3.4)). In the case of Sec. 6, the individual trains result both from phase changes and velocity changes. However, in the given case, the phase and velocity changes arise in the same collision, so that the mean number of trains per unit time is ν, just as when phase discontinuities are absent. Hence, the resonance coefficients in (7.6) are the same as in (3.4). The effect of the phase changes in the collisions was manifested in the coefficient $\tilde{B}$ in (7.6). We recall that the denominator of (7.6) reflects the role of interference of trains, which narrows the contour of the Doppler-broadened line. On the other hand, we can easily see from (7.2) and (7.4) that $|\tilde{B}| < 1$. Hence, the appearance of $\tilde{B}$ in Eq. (7.6) can be interpreted as the decrease in coherence between different trains.

We assume that $\tilde{B}$ is a real quantity. For example, this is true in resonance broadening. Then a simple redefinition of the parameters of Eq. (7.6) leads to (6.2). In fact, according to (7.4), when $\Delta = 0$, Eq. (7.6) coincides with (6.2) to an accuracy defined by the replacement in (6.2): $\nu \rightarrow \nu - \Gamma$. Thus, when $\Delta = -\nu\operatorname{Im}\tilde{B} = 0$, the line contour proves to be qualitatively the same, regardless of whether the phase and velocity changes occur in the same or different collisions.

A considerably more interesting situation arises when $\Delta \neq 0$. Then the line contour proves to be not simply shifted (as was the case when the phase and velocity changes took place at different times; cf. Eq. (6.2)), but is asymmetric. This is quite visible in Fig. 5, where the intensity distributions are given for different values of the parameters $\nu/\Delta\omega_D$, Δ/ν, and Γ/ν.

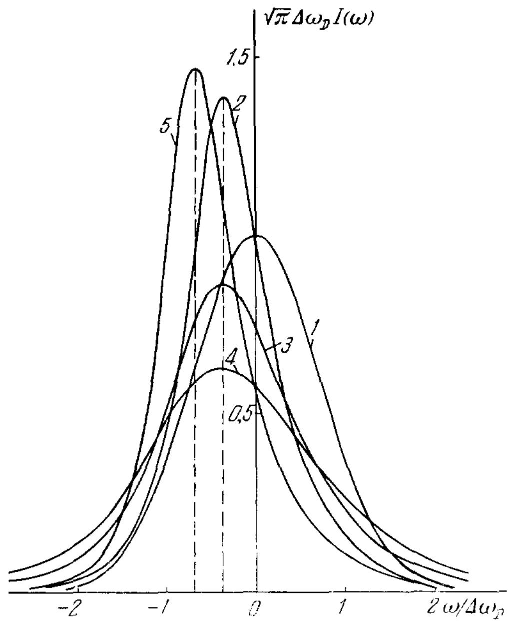

FIG. 5. The contour of lines when the broadenings due to interaction and to the Doppler effect are statistically dependent. Curve 1: $\nu = \Gamma = 0$; curve 2: $\gamma = \frac{1}{2}\Delta\omega_D$, $\Gamma = 0$, $\Delta = -\frac{1}{4}\Delta\omega_D$; curve 3: $\nu = \frac{1}{2}\Delta\omega_D$, $\Gamma = -\Delta = +\frac{1}{4}\Delta\omega_D$; curve 4: $\gamma = \Gamma = \frac{1}{2}\Delta\omega_D$, $\Delta = -\frac{1}{4}\Delta\omega_D$; curve 5: $\nu = -\Delta = \frac{1}{2}\Delta\omega_D$, $\Gamma = 0$.

We know from the general theory of the spectral intensity of random steady-state processes that the center of gravity of the intensity distribution $I(\omega)$ involves the derivative of the correlation function (see, e.g., [16]):

$$\langle\omega\rangle = \int_{-\infty}^{\infty} \omega I(\omega)\, d\omega = i\left(\frac{d\Phi}{d\tau}\right)_{\tau=0}. \qquad (7.7)$$

Using the general expression (1.14) for $\Phi(\tau)$, we get

$$\langle\omega\rangle = \left\{\frac{d}{d\tau}\langle\varphi + \mathbf{kr}\rangle\right\}_{\tau=0}. \qquad (7.8)$$

Since

$$\frac{d}{d\tau}\langle\mathbf{r}\rangle = \langle\mathbf{v}\rangle = 0, \quad \frac{d}{d\tau}\langle\varphi\rangle = \Delta, \qquad (7.9)$$

Equation (7.8) gives

$$\langle\omega\rangle = \Delta. \qquad (7.10)$$

Hence, the shift in the center of gravity of the line depends in no way on the elastic-scattering model, and is determined exclusively by the processes that give rise to broadening by interaction. On the other hand, we can easily show for the case $\nu \ll \Delta\omega_D$ that the shift in the maximum of the contour, as defined by (7.6), is

$$\omega_{\max} = 2\Delta. \qquad (7.11)$$

Thus, the asymmetry of the line is caused by the fact that the peak is shifted farther than the center of gravity of the contour.

We shall show that asymmetry of the line contour involves the fact that the random quantities $\mathbf{r}$ and φ are not normally distributed. Let us assume the opposite. Then, according to the definition of normally-distributed random quantities, we have [11]

$$\Phi(\tau) = \langle\exp[-i(\varphi + \mathbf{kr})]\rangle$$
$$= \exp\left\{-i\langle\varphi\rangle - \frac{1}{2}\left[\langle(\mathbf{kr})^2\rangle + 2\langle\mathbf{kr}\varphi\rangle + \langle\varphi^2\rangle\right]\right\}. \qquad (7.12)$$

Evidently, in our problem $\langle\mathbf{k}\cdot\mathbf{r}\varphi\rangle = 0$, since shifts $\mathbf{r}$ of the atom in opposite directions will correspond to identical phase shifts. Thus, the assumption that $\mathbf{r}$ and φ are normally distributed automatically implies that broadenings due to interaction and to the Doppler effect are statistically independent. Hence, the line contour would be symmetrical with respect to the frequency $\omega = \Delta$. What we have said implies that line asymmetry can arise only because $\mathbf{r}$ and φ deviate from normal statistics.

The statement given here can be illustrated well in the weak-collision model. We showed above (see Eq. (2.19) and the discussion of (3.10)) that in this model the displacement $\mathbf{r}$ is a normally-distributed quantity. This remains valid even when we take into account phase shifts. However, the two-dimensional probability distribution for $\mathbf{r}$ and φ will no longer be normal. We can see this from the expression for the correlation function, which we can find from Eq. (7.5) and (5.5):

$$\Phi(\tau) = \exp\left\{-(\Gamma + i\Delta)\tau - \frac{\Delta\omega_D^2}{2\tilde{\nu}_d^2}\left[\tilde{\nu}_d\tau - 1 + e^{-\tilde{\nu}_d\tau}\right]\right\},$$

$$\tilde{\nu}_d = \nu_d\tilde{B} = \nu_d\left[1 - \frac{\Gamma + i\Delta}{\nu}\right]. \qquad (7.13)$$

We see from the definition (1.3) of the function $I(\omega)$ that the only reason why $I(\omega)$ will be a symmetric function of $\omega - \Delta$ when the correlation function is complex is the factor $\exp(-i\Delta\tau)$. This is not true for (7.13) when $\Delta \neq 0$, since $\tilde{\nu}_d$ is a complex quantity. Hence, the line contour will be asymmetric, and this implies that the distribution for $\mathbf{r}$ and φ differs from normal.

The statistics for $\mathbf{r}$ and φ must approach a normal distribution when the number of collisions is large. Hence, the line contour must become symmetric as $\nu \to \infty$. If we assume that $\nu \gg \Delta\omega_D$, and restrict our treatment to the region of not too great frequencies ($\nu > \omega$) where most of the energy is concentrated, we get the following expression for $I(\omega)$:

$$I(\omega) \cong \frac{1}{\pi}\frac{\dfrac{\Delta\omega_D^2}{2\nu} + \Gamma}{\left[\dfrac{\Delta\omega_D^2}{2\nu} + \Gamma\right]^2 + (\omega - \Delta)^2}. \qquad (7.14)$$

Thus, the line is actually symmetric in this case.

8. EXPERIMENTAL VERIFICATION OF THE THEORY

In closing, we shall take up the problem of experimentally testing the theory developed above. As concerns the effect of narrowing of lines by elastic collisions, we shall have to consider, of course, not demonstrating the effect per se (it has been observed in many studies), but elucidating its role under various conditions characteristic of the optical region of the spectrum, where it has never been taken into account. As was shown above, the narrowing effect can be manifested even when $\nu \sim \Gamma$, and in a number of cases this situation must occur.

However, the most interesting consequence of the theory seems to us to be that the line contour becomes asymmetric when we take into account the statistical dependence of broadening due to interaction and that due to the Doppler effect. In certain experiments, line asymmetry has been observed at pressures at which there was not yet any reason to expect a high intensity of the statistical wing. We have in mind the study [17], which showed asymmetry in the neon line at $\lambda = 3.3913\,\mu$ $(5s'[{}^1\!/_2]^0_1 - 4p'[{}^3\!/_2]_2)$ at pressures of the order of 1 mm Hg. Possibly, the asymmetry of the lines found in [17] is due to the effect discussed above, although we cannot state this quite definitely without more studies.

In addition, according to the reports [18,19], an asymmetric frequency-dependence of the intensity has been found in gas lasers. This effect is closely connected with the problem of the symmetry of the contour of spectral lines. However, a detailed discussion of it would require analysis of the non-linear phenomena in lasers, and hence, cannot be carried out within the limits of this article, which is devoted to the linear theory of broadening of spectral lines.

Still, it is à propos to mention the following. As in the cases treated above, the treatment of non-linear phenomena can be divided into two problems: deriving the expression to be averaged over the collisions, and the averaging process itself. Of course, in the non-linear theory one must average an expression differing from the correlation function of (1.14). However, the entire procedure of averaging over the collisions presented in this article can be extended to a broad class of non-linear problems without any changes in principle. On this basis, calculations were made in [20] of the intensity of laser action $P(\omega)$ of gas lasers, and the following was shown: if one assumes that the Doppler and impact broadenings are statistically independent, then $P(\omega)$ is an even function of $\omega - \Delta$, regardless of the elastic-scattering model. However, if one takes into account the statistical dependence of these mechanisms of broadening, then $P(\omega)$ proves to be an asymmetric function of the frequency in either the strong- or weak-collision model. Thus, the results of [18,19] can be considered to be an experimental confirmation of the conception developed above in the theory of broadening of spectral lines.

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