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Simultaneous Effect of Doppler and Foreign Gas Broadening on Spectral Lines*

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By using the classical Fourier integral theory, an expression is given for the shape of a spectral line, broadened by phase changes due to collisions and by the actual changes in velocity of the emitting particles resulting from collisions. The result is not a simple Voigt-type folding of an exponential into a dispersion distribution; it exhibits the contraction noted by Dicke and leads to the usual formulas when the time interval between path-deflecting or phase-disturbing collisions becomes very great.

I

THE shape of spectral lines emitted by an atom or an ion in the gaseous state at high temperature is determined simultaneously by the perturbing influences of neighboring particles and by the thermal translational motion of the emitter itself. These two processes (pressure broadening and Doppler effect) are generally treated separately.

The first effect involves an analysis of the wave emitted by the atom, the amplitude and phase of which are altered by interaction with other particles of the medium. When the impacts of these particles are of short duration in comparison with the time between collisions, the perturbation can be represented as a sudden, random change in the phase of the emitted wave, and well-known analysis yields the Lorentz shape:

$$I(\omega-\omega')=\frac{1/\tau_L}{(\omega-\omega')^2+(1/\tau_L)^2}, \tag{1}$$

where ω' is the undisturbed angular frequency and τ_L the mean time between collisions which alter the radiation processes sufficiently: $1/\tau_L=nQ\bar{v}$, where n is the number density of perturbers, $\bar{v}$ their mean velocity, and Q an appropriate collision cross section. The width at half intensity is, for this shape,

$$\Delta\omega_{\frac{1}{2}}=2/\tau_L. \tag{1$'$}$$

On the other hand, the pure Doppler effect which accounts for the various frequency shifts arising from a Maxwell distribution of velocities of the emitting particles gives the following line shape:

$$I(\omega-\omega')=\exp[-(mc^2/2kT\omega'^2)(\omega-\omega')^2], \tag{2}$$

of half-width

$$\Delta\omega_{\frac{1}{2}}=2\omega'(2kT\ln 2/mc^2). \tag{2$'$}$$

To combine the two distributions a folding process is generally used in which each elementary component of the distribution (1) is assumed to be broadened in accordance with (2). This gives the following profile:

$$I(\omega-\omega')=\int_{\xi=-\infty}^{\xi=+\infty}\frac{1/\tau_L}{(\omega-\omega'-\xi)^2+(1/\tau_L)^2}\times\exp\left[-\frac{mc^2}{2kT\omega'^2}\xi^2\right]d\xi, \tag{3}$$

known as the Voigt integral.[1]

Another point of view was employed by Dicke[2] who considered collisions which induce velocity changes, but only negligible phase changes in the emitted radiation (case of atom undergoing hyperfine transitions and embodied in a buffer gas). The analysis of Dicke, presented in the work of Wittke,[3] is first concerned with the simple model of a radiating atom going back and forth with a single velocity v in a box of length a. A Fourier analysis of the radiation received by a fixed observer shows that, both in the classical and the quantum version of this model, the spectrum practically consists of a single line at the unperturbed frequency, provided the emitted wavelength λ' is much greater than a. In the opposite case ($\lambda'\ll a$), the spectrum shows the two well-known Doppler components resulting from the unperturbed line, shifted in frequency by $\pm 2\pi(c/\lambda')(v/c)$. To be closer to reality, Dicke then treats the classical model of an emitting particle moving through a gas (always without phase changes at collisions). The received wave $\exp[i(\omega' t-2\pi x/\lambda')]$ is Fourier-analyzed (x is the linear displacement of the emitter in the direction of the observer). The intensity at frequency ω so obtained,

$$\int_0^\infty\int_0^\infty e^{i(\omega-\omega')(t'-t)}\exp\left(-\frac{2\pi i}{\lambda'}[x(t')-x(t)]\right)dtdt',$$

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[1] H. C. van de Hulst and J. J. M. Reesink, Astrophys. J. **106**, 121 (1947); A. Unsöld, *Physik der Sternatmosphären* (Springer-Verlag, Berlin, 1955), p. 259.
[2] R. H. Dicke, Phys. Rev. **89**, 472 (1953).
[3] J. P. Wittke, thesis, Princeton University, 1955 (unpublished); J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620 (1956); M. Arditi and T. R. Carver, Phys. Rev. **109**, 1012 (1958); **112**, 449 (1958); F. C. Beaty and P. L. Bender, Bull. Am. Phys. Soc. **3**, 185 (1958); P. L. Bender and A. R. Chi, Phys. Rev. **112**, 450 (1958); H. Margenau, P. Fontana and L. Klein, Phys. Rev. **115**, 87 (1959).

is then averaged over an ensemble of identical and noninteracting emitters, giving

$$I(\omega-\omega')=\int_0^\infty e^{i(\omega-\omega')\tau}\times\left[\int_{\Delta x=-\infty}^{\Delta x=+\infty}\exp\left(-\frac{2\pi i}{\lambda'}\Delta x\right)W(\Delta x,\tau)d\Delta x\right]d\tau. \quad (4)$$

The probability $W(\Delta x,\tau)$ to find a displacement Δx of the particle after a time τ used by Dicke is the diffusion probability function,

$$W(\Delta x,\tau)=(4\pi D\tau)^{-\frac{1}{2}}\exp[-(\Delta x)^2/4D\tau], \quad (5)$$

where D is a diffusion coefficient for the emitter in the buffer gas. The calculation of the above integrals then leads to the following simple result for the line shape:

$$I(\omega-\omega')=\frac{4\pi^2D/\lambda'^2}{(\omega-\omega')^2+(4\pi^2D/\lambda'^2)^2}. \quad (6)$$

Dicke's result consists therefore in a Lorentzian shape of type (1), with a half-width $2.4\pi^2D/\lambda'^2$. In the microwave region this quantity is found to be much smaller than the Doppler half-width (2′) at the same temperature.[3]

The following Sec. (II) presents observations which lead to a somewhat different formulation of the problem. This formulation is extended in (III) to the condition where phase shifts at collisions are also present. Limiting cases are discussed. Finally in (IV) the spectral shape in the wings of lines is studied.

II

A first remark on the above treatment concerns the use of the probability distribution function $W(\Delta x,\tau)$, Eq. (5). It is shown by Chandrasekhar[4] that the diffusion function (4) is a limiting approximation proper for times τ such that

$$\tau\gg\beta^{-1}=mD/kT, \quad (7)$$

where β is the coefficient of the dynamical friction undergone by the moving emitting particle.

For hydrogen in argon, at 357°K and 1 atm pressure, $D=0.979$ cm²/sec.[5] The relation (7) then gives for the validity domain of (5)

$$\tau\gg 0.7\times10^{-10}\text{ sec.}$$

But in the microwave region, the periods involved are of the order of magnitude of 10^{-10} sec; therefore, Eq. (4) and the above inequality show that the use of the diffusion function (5) is not entirely justified in this instance.

Secondly, a condition analogous to $\lambda'>a$ or $\lambda'<a$ for the box model does not appear anywhere in the above diffusion treatment, though it would seem desirable for consistency. The experimental results[3] (narrowing of the lines), which agree with the theoretical prediction, seem to justify a more careful examination of this equation.

We start from a Fourier analysis of the observed amplitude $\exp[i(\omega't-2\pi x/\lambda')]$, and then consider the square modulus of the components obtained. These two operations lead to the Fourier integral formula according to which the line shape $I(\omega-\omega')$ is the Fourier transform,

$$I(\omega-\omega')=2\Re\int_0^\infty e^{i(\omega-\omega')\tau}F(\tau)d\tau, \quad (8)$$

of the correlation function:

$$F(\tau)=\lim_{T\to\infty}\frac{1}{T}\int_{-T}^{+T}\exp\left(-\frac{2\pi i}{\lambda'}[x(t_0+\tau)-x(t_0)]\right)dt_0. \quad (9)$$

The usual way to evaluate such a function[6] in the theory of pressure broadening is to apply the ergodic hypothesis, i.e., to replace the average over time contained in (9) by an average over all possible paths between time t_0 and time $t_0+\tau$. If we use the impact approximation (collisions of negligible duration), with collisions distributing the perturber paths in accordance, for example, with a Poisson law (mean time τ_D), we may write

$$F(\tau)=\sum_{m=0}^{\infty}\frac{1}{m!}\left(\frac{\tau}{\tau_D}\right)^m e^{-\tau/\tau_D}\times\exp\left(-\frac{2\pi i}{\lambda'}[\Delta x(v_0,\Delta v_1,\cdots,\tau_1,\tau_2,\cdots)]_{(m)}\right)\times P_m(v_0,\Delta v_1,\Delta v_2,\cdots,\tau_1,\tau_2,\cdots/\tau)dv_0\cdots d\tau_1\cdots. \quad (10)$$

Here, $[\ ]_{(m)}$ denotes $\Delta x=\Delta x(t_0+\tau)-\Delta x(t_0)$ for a path containing m collisions as function of the velocity[7] v_0 at time t_0, the m velocity changes Δv_i, and the m durations τ_i between the various instants of collisions starting from t_0, while P_m is the probability density of these various parameters in a path containing m collisions and described in a time τ. An evaluation of Eq. (10) is outlined by Breene[8] provided the exponent is a sum of independent phase shifts; but here the evaluation of the integral in (10) needs to be carried through completely, with retention of the exact form of P_m. Therefore, instead of keeping the exponent as in (10), the conditional probability is introduced:

$$\Pi_m(\Delta v_1,\cdots,\tau_1,\cdots/\Delta x(v_0,\Delta v_1,\cdots,\tau_1,\cdots)=\Delta x,v_0,\tau)$$

[4] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).
[5] R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1958).
[6] H. Margenau and M. B. Lewis, Revs. Modern Phys. **31**, 509 (1959).
[7] By v_0 or v_i we mean the projection of the velocity of the particles upon an axis joining it to the observer.
[8] R. G. Breene, Revs. Modern Phys. **29**, 94 (1957).

for the occurrence of a path of duration τ containing m collisions characterized by the parameters $\Delta v_1 \cdots, \tau_1 \cdots$ such that the initial velocity would be v_0 and the shift in the direction of the observer would be Δx. The quantity Π_m is related to P_m by the formulas:

$$P_m = \int_{-\infty}^{+\infty} P(v_0) P_m'(\Delta v_1, \cdots, \tau_1, \cdots / v_0, \tau) dv_0, \quad (11)$$

with

$$P_m' = \int_{-\infty}^{+\infty} W_\beta(\Delta x; v_0, \tau) \Pi_m d\Delta x. \quad (12)$$

In Eq. (11), $P(v_0)$ is the distribution function of v_0 (velocity at time t_0), and $W_\beta(\Delta x; v_0,\tau)$ is the distribution function of Δx, based on the initial velocity v_0 and the duration τ of the path. This function, extensively studied by Chandrasekhar,[4] has the following form:

$$W_\beta(\Delta x; v_0,\tau) = (A/\pi)^{\frac{1}{2}} \exp\{-A[\Delta x - v_0(1-\exp(-\beta\tau))/\beta]^2\}, \quad (13)$$

with

$$A = (m\beta^2/2kT)[2\beta\tau - 3 + 4\exp(-\beta\tau) - \exp(-2\beta\tau)].$$

Its limit for very great τ is the diffusion function (5).[4] The definitions (11) and (12) of P_m are introduced in (10). Thus, after reversing the order of the integrations and noting that

$$\int \cdots \int \Pi_m d\Delta v_1 \cdots d\tau_1 \cdots = 1,$$

one gets the following expression for the correlation function:

$$F(\tau) = \int_{-\infty}^{+\infty} P(v_0) \left[\int_{-\infty}^{+\infty} W_\beta(\Delta x; v_0,\tau) \times \exp(-2\pi i \Delta x/\lambda') d\Delta x \right] dv_0. \quad (14)$$

The integrations in Eq. (14) are performed after the change of variable $y = \Delta x - v_0[1-\exp(-\beta\tau)]/\beta$. There results, upon assuming for v_0 a Maxwellian distribution:

$$F(\tau) = \int_{-\infty}^{+\infty} \left(\frac{B}{\pi}\right)^{\frac{1}{2}} \exp(-Bv_0^2) \times \cos\{v_0[1-\exp(-\beta\tau)]/(\lambda'/2\pi)\beta\} dv_0 \times \int_{-\infty}^{+\infty} \left(\frac{A}{\pi}\right)^{\frac{1}{2}} \exp(-Ay^2) \cos[y/(\lambda'/2\pi)] dy,$$

with $B = m/2kT$. On performing the integrations and writing A and B explicitly, we obtain for the correlation function of the problem:

$$F(\tau) = \exp\left\{ -\frac{kT}{m\beta^2(\lambda'/2\pi)^2} [\beta\tau - 1 + \exp(-\beta\tau)] \right\}. \quad (15)$$

It is to be noted that this expression is obtained under the condition that the symbol m appearing in A is effectively the mass of the optically active particle itself. Strictly speaking, A is a function $A(m,m')$ of m and of the mass m' of the particles of buffer gas, and we obtain the less simple form:

$$F(\tau) = \exp\left\{ -\frac{[1-\exp(-\beta\tau)]^2}{4B(m)\beta^2(\lambda'/2\pi)^2} - \frac{1}{4A(m,m')(\lambda'/2\pi)^2} \right\}. \quad (15')$$

The line shape is the Fourier transform of Eq. (15), or of Eq. (15′).

Simple analytic forms of this line shape are immediately obtainable for limiting values of β. Since the coefficient of dynamical friction is the inverse of the relaxation time of the vector velocity of the emitter,[9] we shall take here

$$\beta \cong \tau_D^{-1};$$

τ_D is the mean free time between deflecting collisions.

(a) If τ_D is great (buffer gas at low density), the following correlation function derived from Eq. (15) is used:

$$\lim_{\beta\to 0} F(\tau) = \exp\{-[kT/2m(\lambda'/2\pi)^2]\tau^2\}, \quad (16)$$

which gives for the line shape, after taking the Fourier transform:

$$I(\omega-\omega') = [2\pi m(\lambda'/2\pi)^2/kT]^{\frac{1}{2}} \times \exp\left\{ -\frac{m(\lambda'/2\pi)^2}{2kT}(\omega-\omega')^2 \right\}. \quad (17)$$

This is the Doppler shape (2).

(b) For τ_D very small (presence of buffer gas at sufficiently high density), we use instead of Eq. (15):

$$\lim_{\beta\to\infty} F(\tau) = \exp\{-[kT/m\beta(\lambda'/2\pi)^2]\tau\}, \quad (18)$$

and the line shape becomes, by Fourier transformation,

$$I(\omega-\omega') = \frac{2(kT/m\beta)(4\pi^2/\lambda'^2)}{(\omega-\omega')^2 + (kT/m\beta)^2(4\pi^2/\lambda'^2)^2}. \quad (19)$$

According to the definition (7) of the diffusion coefficient D, this line shape is identical with Dicke's (6). Equation (6) is correct because the limit (5) of the distribution (13) for large τ has the same form as the limit, valid for every τ, of the same distribution function for large β.

We can state precisely the lower limit of $\beta = \tau_D^{-1}$ for which (18) is a good approximation to (15). It may be seen that this happens when the term $v_0[1-\exp(-\beta\tau)]$

[9] S. Chandrasekhar, Astrophys. J. 97, 255 (1943).

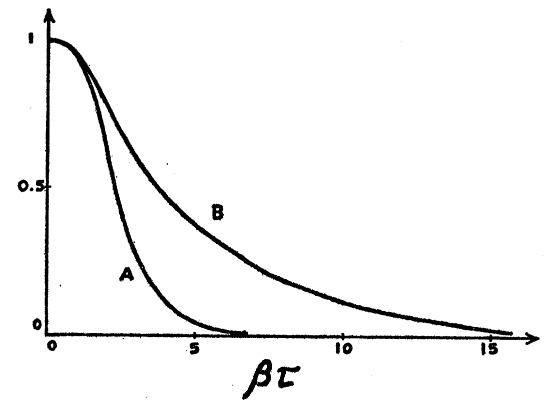

FIG. 1. Correlation functions, without phase shifts at collisions; A: Doppler type; B: present work [for $15.5(l/\lambda')^2=\frac{1}{4}$].

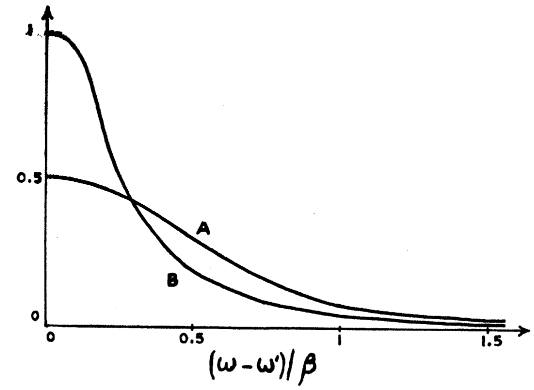

FIG. 2. Line intensities (in arbitrary units) corresponding to the correlation functions of Fig. 1.

$\times\beta^{-1}\sim v_0\beta^{-1}$ in Eq. (13) is negligible in comparison with the period of the factor $\exp(-2\pi i\Delta x/\lambda')$ appearing in Eq. (14), which is realized if $v_0\beta^{-1}\ll(\lambda'/2\pi)$. This condition may be considered as physically fulfilled if, introducing the mean velocity $\bar{V}$ of the emitter, we have $\bar{V}\beta^{-1}\ll(\lambda'/2\pi)$ or

$$\bar{V}\tau_D\cong l\ll\lambda'/2\pi.$$

Here l is the mean free path between deflecting collisions. This condition is analogous to the condition $a\ll\lambda'$ found by Dicke in his study of the box model.

Apart from the two preceding limit cases, numerical integration is necessary to obtain the line shape from the correlation function (15). The factor in the exponent in (15) may be written as $15,5(l/\lambda')^2$. This factor is taken as $\frac{1}{4}$ (which implies $\lambda'\sim 8l$). This would correspond, at $T=400°$K and for the 1771×10^6 cycles/sec hyperfine transition of Na^{23}, to a buffer gas pressure 10^{-4} mm Hg. Figure 1 shows the correlation function (15) and the Doppler correlation function (obtained for zero collision cross section for path deflection). The corresponding line shapes appear in Fig. 2 [drawn with the reduced abscissae $(\omega-\omega')/\beta$]. According to these figures, the narrowing of the line found by Dicke is apparent even for such a low density of buffer gas.

III

Thus far the perturbation of the emission mechanism at collision was not considered. We shall assume this in the simplest way, i.e., by taking account only of instantaneous phase changes in the radiation with respect to the unperturbed phase $\omega' t$ when the emitter undergoes a collision, and by neglecting any term in $(\omega+\omega')$ like that appearing in the Van Vleck-Weisskopf formula (this will force the profile to be symmetric). We take $p(\Delta\varphi)d(\Delta\varphi)$ to be the probability that, in such an encounter, the phase is shifted by a value between $\Delta\varphi$ and $\Delta\varphi+d(\Delta\varphi)$. The observed phase change will therefore be the sum of $\Delta\varphi$ and of the Doppler phase change $2\pi\Delta x/\lambda'$. Here, too, the line shape is the Fourier transform of a correlation function $F(\tau)$, and $F(\tau)$ is now

$$F(\tau)=\lim_{T\to\infty}\frac{1}{T}\int_{-T}^{+T}\exp\{-i[\Delta\varphi(t_0+\tau)-\Delta\varphi(t_0)]\}\times\exp\left[-\frac{2\pi i}{\lambda'}\Delta x(t_0,\tau)\right]dt_0. \quad (20)$$

We will assume that there is no correlation between the two exponentials above. The two ensemble averages involved in the calculation of the integral (20) may therefore be taken separately. The evaluation of the average on the first factor gives[6,8]

$$\exp[-(1-A')\tau_L^{-1}\tau-iB'\tau_L^{-1}\tau],$$

where τ_L is the mean free time between the Poisson-distributed collisions which disturb the emitted phase and

$$A'=\int_0^{2\pi}\cos(\Delta\varphi)p(\Delta\varphi)d(\Delta\varphi);$$

$$B'=\int_0^{2\pi}\sin(\Delta\varphi)p(\Delta p)d(\Delta\varphi).$$

The average over the second exponential of (20) leads to the function (14). We thus obtain for the line shape resulting from simultaneous pressure broadening (in the above way), Doppler effect, and molecular collisions:

$$I(\omega-\omega')=2\Re\int_0^{+\infty}\exp[i(\omega-\omega')\tau]e^{-iB'\tau/\tau_L}e^{-(1-A')\tau/\tau_L}\times\left[\int_{-\infty}^{+\infty}P(v_0)\int_{-\infty}^{+\infty}W_\beta(\Delta x;v_0,\tau)\times e^{-(2\pi i/\lambda')\Delta x}d\Delta x dv_0\right]d\tau, \quad (21)$$

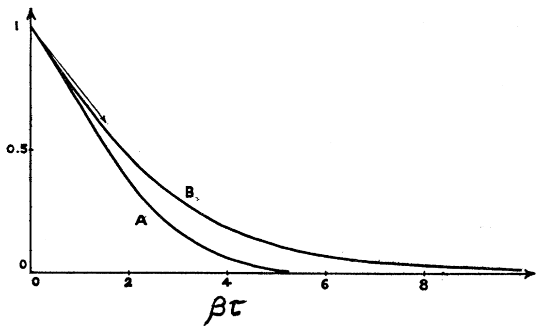

FIG. 3. Correlation functions, with phase shifts at collisions; A: Voigt type; B: present work [for $15.5(l/\lambda')^2=\frac{1}{4}$, $\tau_L=\tau_D=\beta^{-1}$, $1-A'=\frac{1}{4}$, $B'=0$]. The arrow shows the common tangent for $\beta\tau=0$.

or

$$I(\omega-\omega')=2\int_0^\infty \cos[(\omega-\omega'-B'/\tau_L)\tau]e^{-(1-A')\tau/\tau_L}$$
$$-\frac{kT}{m\beta^2(\lambda'/2\pi)^2}[\beta\tau-1+\exp(-\beta\tau)]d\tau. \quad (21')$$

This is the general expression of the line shape.

Let us examine, as before, its limiting forms for extreme values of the coefficient of dynamical friction β.

(a) For small β (low density of buffer gas), one gets from Eq. (21):

$$I(\omega-\omega')=2\int_{-\infty}^{+\infty}P(v_0)\int_0^\infty \cos\left[\left(\omega-\omega'-\frac{B}{\tau_L}-2\pi\frac{v_0}{\lambda'}\right)\tau\right]$$
$$\times\exp\left(-\frac{1-A'}{\tau_L}\tau\right)d\tau dv_0,$$

or

$$I(\omega-\omega')=2\int_{-\infty}^{+\infty}P(v_0)$$
$$\times\frac{(1-A')/\tau_L}{(\omega-\omega'-B'/\tau_L-2\pi v_0/\lambda')^2+[(1-A')/\tau_L]^2}dv_0. \quad (22)$$

If we put $2\pi v_0/\lambda'=\xi$, take for $P(v_0)$ a Maxwellian distribution, and consider the case $A'=B'=0$ [i.e., $p(\Delta\varphi)=(2\pi)^{-1}$ between $\Delta\varphi=0$ and $\Delta\varphi=2\pi$], Eq. (22) leads to the Voigt profile (3).

(b) For very large β (high density of buffer gas), we have, according so Eq. (21′):

$$I(\omega-\omega')=2\frac{(1-A')/\tau_L+(kT/m\beta)(4\pi^2/\lambda'^2)}{(\omega-\omega'-B'/\tau_L)^2+[(1-A')/\tau_L+(kT/m\beta)(4\pi^2/\lambda'^2)]^2}. \quad (23)$$

An analogous result, but based on a phenomenological damping constant to take into account the effect of phase changes at collisions, has been obtained by Wittke and Dicke.[3]

For high pressure of perturbers the Lorentzian line shape (23) replaces, therefore, the Voigt profile (22) obtained when changes of velocity at collisions are ignored.

As in Part II, we present finally a numerical application referring to a case where the above approximations are not valid and where we must use Eq. (21′) itself to get the line shape. The same value $\frac{1}{4}$ is adopted as before for the coefficient of $[\beta\tau-1+\exp(-\beta\tau)]$. We suppose moreover that $\tau_L=\tau_D=\beta^{-1}$ and we take $B'=0$ (no shift of the center of the line) and $1-A'=\frac{1}{4}$. Figure 3 shows the correlation function in this case and also the Voigt correlation function corresponding to a zero collision cross section for path-deflecting collisions. A numerical integration yields the curve B of Fig. 4. In this figure the Voigt profile A was taken from the data of reference 1. It is to be noted that, for the chosen physical conditions at least, the deflection of trajectories at collisions introduces a notable contraction of the line, relative to the Voigt profile.

IV

We study now the intensity distribution in the wings of the line, i.e., in the limiting case $|\omega-\omega'|\to\infty$.

It is possible to find the desired result by a direct application of the ergodic hypothesis to Eqs. (9) and (10), without introducing the distribution function $W_\beta(\Delta x; v_0,\tau)$. This may be seen as follows. Consider a path containing m collisions by which the velocity is altered. The probability of occurrence of such a path during a time τ is $(1/m!)(\tau/\tau_D)^m\exp(-\tau/\tau_D)$, where τ_D is the mean time between these collisions and may be identified with β^{-1}. The correlation function will therefore be

$$\exp\left(-\frac{1-A'}{\tau_L}\tau-i\frac{B'}{\tau_L}\tau\right)\sum_{m=0}^{\infty}\frac{1}{m!}\left(\frac{\tau}{\tau_D}\right)^m e^{-\tau/\tau_D}$$
$$\times\left\langle\exp\left\{i\left[-\frac{2\pi}{\lambda'}\sum_{i=1}^{m}\tau_i\Delta v_i-\frac{\tau v_0}{\lambda'}\right]\right\}\right\rangle.$$

Here we have expressed Δx in terms of the changes of velocity at collision Δv_i; the time elapsed from the ith collision till the instant $t_0+\tau$, τ_i; and the velocity before the first collision v_0. The symbol $\langle\ \rangle$ means an average over all the parameters Δv_i, τ_i, and v_0. This expression implies complete statistical independence between the perturbation of the emitted phase and the translation Δx of the emitter. By splitting off the factor $\exp(-2\pi i v_0\tau/\lambda')$, we first perform an average over all Δv_i, observing also that

$$\Delta v_i=V_{ri}(\cos\theta_i'-\cos\theta_i),$$

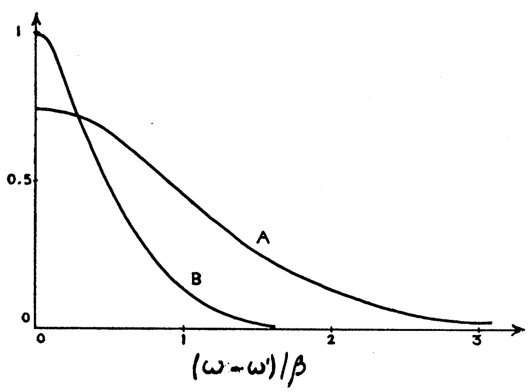

FIG. 4. Line intensities (in arbitrary units) corresponding to the correlation functions of Fig. 3.

where V_{ri} is the speed of the emitter in the center-of-gravity system of the emitter and the ith perturber; θ_i and θ_i' are the angles, before and after the collision, between the direction of the observer and the vector $\mathbf{V}_{ri}$. On knowing that in an elastic collision the angular distribution of the collision partners is spherically symmetric in the center-of-gravity system[5] and assuming statistical independence between the quantities V_{ri} we get

$$F_m(\tau)=\prod_{i=1}^{m}\left\langle\frac{\sin^2(V_{ri}\tau_i/(\lambda'/2\pi))}{(V_{ri}\tau_i/(\lambda'/2\pi))^2}\right\rangle \times\langle\exp(-2\pi i v_0\tau/\lambda')\rangle. \quad (24)$$

In averaging over the V_{ri} we note that the relative velocity $\mathcal{V}_{ri}$ of the two partners in the ith collision has a Maxwellian distribution:

$$P(\mathcal{V}_{ri})=(m^*/2\pi kT)^{\frac{3}{2}}\exp[-(m^*/2kT)\mathcal{V}_{ri}^2]4\pi\mathcal{V}_{ri}^2d\mathcal{V}_{ri},$$

provided m^* is the reduced mass of the emitter (mass m) and the perturber (mass m'). We thus have for the distribution of the V_{ri} (with $\mu=m/m^*$):

$$P(V_{ri})=(m\mu/2\pi kT)^{\frac{3}{2}}\exp[-(m\mu/2kT)V_{ri}^2]4\pi V_{ri}^2dV_{ri}.$$

The distribution of the τ_i, needed for the evaluation of (24), will be taken in such a way that the probability of occurrence of the ith collision is constant over the interval τ. In this way one finds:

$$F(\tau)=\exp\left(-\frac{1-A'}{\tau_L}\tau-i\frac{B'}{\tau_L}\tau\right)\exp\left(-\frac{\tau-C'(\tau)}{\tau_L}\tau\right) \times\langle\exp(-2\pi i v_0\tau/\lambda')\rangle, \quad (25)$$

with

$$C'(\tau)=\int_0^\tau\frac{1-\exp(-at^2)}{at^2}dt,$$

and

$$a=(2kT/m\mu)4\pi^2/\lambda'^2.$$

This correlation function cannot be considered as correct for all values of τ since the same distribution function was taken for all the relative velocities, disregarding the persistence of the initial v_0, which is taken into account in the distribution (13); but (25) may be expected to be correct if we have zero or very few collisions during the time interval τ, in which case the above incorrect hypothesis concerning the velocity distribution is of little importance. This happens obviously when τ is very small. In this case the correlation function (25) has the following limit, which corresponds therefore to $|\omega-\omega'|\to\infty$:

$$F(\tau)=\left\langle\exp\left(-\frac{1-A'}{\tau_L}\tau-i\frac{B'}{\tau_L}\tau\right) \times\exp\left(-\frac{2kT}{m\mu}\frac{4\pi^2}{\lambda'^2}\frac{1}{\tau_D}\frac{\tau^3}{6}-\frac{2\pi i}{\lambda'}v_0\tau\right)\right\rangle. \quad (26)$$

By means of the relation $\beta^{-1}=\tau_D$ already cited, Eq. (26) leads to the line shape:

$$I(\omega-\omega')=2\int_0^\infty\cos\left[\left(\omega-\omega'-\frac{B'}{\tau_L}\right)\tau\right] \times\exp\left(-\frac{1-A'}{\tau_L}\tau\right)\exp\left(-\frac{4\pi^2}{\lambda'^2}\frac{kT}{2m}\tau^2\right) \times\exp\left(-\frac{4\pi^2}{\lambda'^2}\frac{2}{\mu}\frac{kT\beta^2}{6m}\tau^3\right)dt. \quad (27)$$

Equation (27), apart from the $2/\mu$ factor which takes into account a possible difference between the masses of the emitter and the perturber not included in the distribution (13), is identical to the development of Eq. (21′) up to the terms in τ^3.

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