Pressure Broadening Effects on the Output of a Gas Laser*†

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A model for a laser oscillator in which the atoms of the active medium do not collide during their radiative lifetimes has been used by Lamb. His theory predicts that as the cavity frequency is tuned through atomic resonance, there can be a dip in the intensity of the laser radiation. In the present work this model is generalized by allowing the atoms to collide while they radiate. The general formulation of the collision problem is presented for thermally moving neutral atoms interacting with a standing-wave cavity mode, and it is then applied to the calculation of the intensity profile for some simple collision models. It is found that as the pressure increases, not only is the "dip" broadened and made less deep, but it is also shifted and becomes asymmetric. Some observations by Cordover on pressure effects are found to be in satisfactory accord with this theory.

I. INTRODUCTION

THE model for a laser oscillator used recently by Lamb[1] consisted of an optical cavity of the Fabry-Perot type containing an active atomic medium. The atoms of this medium were assumed to have only two levels a and b concerned in the laser action. Radiative decay to lower states was described phenomenologically by two damping constants γ_a and γ_b. An assumed classical optical field in the cavity induced a polarization in the medium. The amplitudes and frequencies of the different modes of oscillation were determined by requiring that this polarization should be the source for the field in accordance with the macroscopic Maxwell equations. The atoms were allowed to move without collisions and to have a thermal equilibrium velocity distribution. Motion of the radiating atoms played an important role in the theory because they could move through several wavelengths of the optical field before they decayed.

In many qualitative respects, the above theory gave a very satisfactory account of observed gas laser behavior. In practice, however, the gas pressure was too high for the neglect of collisions to be a good approximation. For example, in the case where only a single mode was excited, the theory predicted that for a sufficiently high power level the intensity should go through a "dip" as the cavity was tuned through resonance with the atomic transition frequency. Such behavior was, in fact, subsequently observed by various workers,[2,3] but the magnitude and shape of the dip was found to be a sensitive function of pressure. The purpose of the present paper is to treat a generalized model for a gas laser which takes into account the collisions experienced by the active atoms during their lifetimes. The end result is a theoretical expression [Eq. (118)] for the pressure dependence of the intensity versus cavity tuning curve.

The calculations are similar to those found in discussions of pressure broadening of emission or absorption lines.[4] There are, however, a number of differences: (1) Nonlinear properties of the active dielectric medium play an essential role in our case, but they are not usually considered in pressure-broadening theory. (2) We are here concerned with the theory of a self-sustained oscillator. The collisional effects of interest to us do not produce a finite linewidth of the laser radiation but rather affect the laser output and its dependence on cavity tuning. In usual pressure-broadening theory, the spectral lines already have a Doppler width much larger than their natural radiative width. As a result, an additional broadening or an asymmetry can only be seen experimentally at perturbing gas pressures which are rather high, and the desirable assumption that binary collisions play a dominant role may not be well justified. On the other hand, in the case of a gas laser, the intrinsic width of the tuning dip is of the order of the radiative linewidth. Collisional effects can then be studied at much lower pressures. (3) A further very important difference is that in a Fabry-Perot laser we are concerned with a standing-wave electromagnetic field. A radiating atom can move an appreciable number of optical wavelengths during its lifetime, interacting at each point with a field of different amplitude. If the

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motion of the atom is disturbed by collisions, the history of its interactions is changed, the atom sees a field which is amplitude modulated in an irregular fashion, and its contribution to the state of laser oscillation is modified. If one were concerned with a traveling electromagnetic wave as is the case in pressure-broadening theories, the effect of the atomic motion would be a phase modulation and not an amplitude modulation.

II. TYPES OF COLLISIONS

Theories of collision broadening can be quite complicated and it is therefore useful to make some preliminary remarks about different kinds of collisions and their relative importance.

A He-Ne laser oscillating at 0.63 μ wavelength might have a partial pressure at room temperature of 2 Torr of helium and 0.2 Torr of neon. Under these conditions, a typical active atom of neon would be about 2.34×10^{-6} cm away from its nearest neighbor. If we take $v=10^5$ cm/sec as the effective atomic speed, a collision with a distance of closest approach of $b=10^{-8}$ cm lasts about $b/v=10^{-13}$ sec, and may be regarded as reasonably adiabatic with respect to the mixing of levels a and b whose frequency separation is 6×10^{14} Hz for the laser under consideration. The rate of such close collisions $b<10^{-8}$ cm experienced by an active atom is 2.44×10^6 sec^{-1}. More distant encounters would satisfy the condition for adiabaticity even better.

In a real laser, the atomic levels a and b may have magnetic sublevels. Since our present calculations are limited to the case of two-level atoms, we are not going to give an explicit treatment of the effect of inelastic transitions between magnetic sublevels in this paper. However, they should be important only in the closest encounters. For these, and any other inelastic collisions, the atomic state is drastically changed due to electrical interactions and there will be little correlation between the radiation emitted before and after the impact. It seems very plausible to allow for inelastic collisions and magnetic reorientation by simply adding quantities G_aP and G_bP, proportional to pressure, to the radiative damping constants γ_a and γ_b. For the purposes of this paper we will also ignore the possibility that resonant interactions are important. In such collisions an exchange of excitation would take place between the active atom and an atom of the same kind in a state of different excitation. It is planned to deal with this problem on a later occasion. In the present treatment, we consider all the perturbers to be helium atoms.

We see from the above discussion that except for the closest encounters which are described by pressure-dependent damping constants, the effect of a perturber on a radiating atom can largely be regarded as a van der Waals interaction. As the perturbers move around with respect to the active atom, the atomic transition frequency ω between the levels a and b can be considered to change adiabatically with time, becoming a function $\omega(t)$. There will also be forces on the active atom which cause it to follow a zig-zag path of some complexity. Let this be denoted by $\mathbf{r}(t)$, with velocity $\mathbf{v}(t)=d\mathbf{r}/dt$ and let $v(t)$ be the component of this velocity vector along the laser axis.

In Sec. III we are going to generalize the discussion of Ref. 1 by taking into account the time dependence of $\omega(t)$ and $v(t)$. The dipole moment acquired by an atom having a particular history will be calculated and then the polarization of the medium as a whole will be obtained by summing up the contributions of the atoms in which all possible histories are properly taken into account. We will obtain a quite general expression for the single-mode intensity versus tuning frequency [Eq. (30)] and the following sections, IV–VI, will be devoted to making suitable simplifying approximations so that the expression can be evaluated in reasonably simple algebraic form.

III. FORMAL CALCULATION OF THE INTENSITY PROFILE

We assume that for single-mode operation the cavity field and the polarization induced by it in the active medium have the following general form:

$$E(z,t)=E(t)\cos\{\nu t+\varphi(t)\}\sin Kz, \tag{1}$$

$$P(z,t)=[C(t)\cos\{\nu t+\varphi(t)\} + S(t)\sin\{\nu t+\varphi(t)\}]\sin Kz, \tag{2}$$

where $E(t)$, $C(t)$, $S(t)$, and $\varphi(t)$ are slowly varying functions of time. It was shown in Ref. 1 that the self-consistency requirement, namely that $E(z, t)$ and $P(z, t)$ satisfy the macroscopic Maxwell equations, leads to the following set of differential equations:

$$(\nu+\dot{\varphi}-\Omega)E=-\tfrac{1}{2}(\nu/\epsilon_0)C, \tag{3}$$

$$\dot{E}+\tfrac{1}{2}(\nu/Q)E=-\tfrac{1}{2}(\nu/\epsilon_0)S, \tag{4}$$

where Ω is the cavity frequency and Q represents the losses of the cavity. The quantities $C(t)$ and $S(t)$ are functionals of the slowly varying amplitude $E(t)$ and phase $\varphi(t)$. In order to determine these functional relations we must find the quantum-mechanical density matrix which describes the time evolution of each atom while it interacts with the cavity field $E(z, t)$, compute the corresponding dipole moment, then the macroscopic polarization $P(z, t)$, and finally determine $C(t)$ and $S(t)$ according to Eq. (2).

The equation of motion for the density matrix which describes an excited atom moving with uniform velocity v and interacting with the electric field $E(z, t)$ was derived in Ref. 1. In order to make these equations applicable to the present case we have merely to replace v by $v(t)$ and ω by $\omega(t)$ and to write an expression for the perturbation $V(t)$ which properly recognizes the instantaneous location of the atom in question. We have

$$\dot{\rho}_{ab}=-i\omega(t)\rho_{ab}-\gamma_{ab}\rho_{ab}+iV(t)(\rho_{aa}-\rho_{bb}),$$
$$\dot{\rho}_{aa}=-\gamma_a\rho_{aa}+iV(t)(\rho_{ab}-\rho_{ba}),$$
$$\dot{\rho}_{bb}=-\gamma_b\rho_{bb}-iV(t)(\rho_{ab}-\rho_{ba}),$$
$$\rho_{ba}=\rho_{ab}^*, \tag{5}$$

where

$$\gamma_{ab}=\tfrac{1}{2}(\gamma_a+\gamma_b) \tag{6a}$$

and

$$V(t)=-\wp\hbar^{-1}E(\{z_0+\int_{t_0}^{t}d\hat{t}\,v(\hat{t})\},t), \tag{6b}$$

with $\wp$ denoting the dipole matrix element between the states a and b.

From here on the calculation proceeds in exactly the same manner as in Ref. 1 except now, when the macroscopic polarization $P(z,t)$ is obtained, it must be averaged over all possible histories of the variables $v(t)$ and $\omega(t)$ before the Fourier components $C(t)$ and $S(t)$ are substituted in Eqs. (3) and (4).

As in Ref. 1, we sum up the individual dipole moments with all possible initial conditions, weighted according to the rate of production of atoms with such initial conditions. We write

$$P(z,t)=\wp\sum_{\alpha=a,b}\int_{-\infty}^{t}dt_0\int_0^L dz_0\int_{-\infty}^{\infty}dv_0\,\lambda_\alpha(z_0,v_0,t_0)\times[\rho_{ab}(\alpha,z_0,v_0,t_0,t)+\rho_{ba}(\alpha,z_0,v_0,t_0,t)]\times\delta\left(z-z_0-\int_{t_0}^{t}d\hat{t}\,v(\hat{t})\right), \tag{7}$$

where $\lambda_\alpha(z_0,v_0,t_0)$ is the rate at which atoms appear in state $\alpha=a,b$ in the phase-space volume element dz_0dv_0 at the phase-space point z_0, v_0 at time t_0. As in Ref. 1 we assume that the rate $\lambda_\alpha(z_0,v_0,t_0)$ may be factored as follows:

$$\lambda_\alpha(z_0,v_0,t_0)=\Lambda_\alpha(z_0,t_0)P_0(v_0), \tag{8}$$

where $P_0(v_0)$ is the initial velocity distribution.

We must solve Eq. (5) by iteration to third order in the electric field amplitude, once with the initial condition

$$\rho=\begin{pmatrix}1&0\\0&0\end{pmatrix}, \tag{9a}$$

and again with the initial condition

$$\rho=\begin{pmatrix}0&0\\0&1\end{pmatrix}. \tag{9b}$$

The expression for $\rho(\alpha,z_0,v_0,t_0)$ are then inserted into Eq. (7) in order to calculate the polarization $P(z,t)$.

We assume that the excitation rates $\Lambda_\alpha(z_0,t_0)$ are slowly varying functions of z_0 and t_0 and may be replaced by $\Lambda_\alpha(z)$. The following expression for the induced atomic polarization is then obtained:

$$P(z,t)=P^{(1)}(z,t)+P^{(3)}(z,t), \tag{10}$$

where, for atoms with a symmetric velocity distribution $P_0(v_0)=P_0(-v_0)$,

$$P^{(1)}(z,t)=-\tfrac{1}{2}i\wp^2\hbar^{-1}N(z)E(t)\exp\{-i(\nu t+\varphi)\}\times\int_{-\infty}^{\infty}dv_0\,P_0(v_0)\int_{-\infty}^{t}dt'\exp\left\{-\gamma_{ab}(t-t')-i\int_{t'}^{t}d\hat{t}[\omega(\hat{t})-\nu]\right\}\cos\left\{K\int_{t'}^{t}d\hat{t}\,v(\hat{t})\right\}\times\sin Kz+\text{c.c.}, \tag{10'}$$

and in the "Doppler limit" of Ref. 1,

$$\begin{aligned}P^{(3)}(z,t)=&\tfrac{1}{32}i\wp^4\hbar^{-3}N(z)E(t)^3\exp\{-i(\nu t+\varphi)\}\\&\times\int_{-\infty}^{\infty}dv_0\,P_0(v_0)\sum_{\alpha=a,b}\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\\&\times\int_{-\infty}^{t''}dt'''\Big[\exp\Big\{-\gamma_{ab}(t-t')-i\int_{t'}^{t}d\hat{t}\\&\times[\omega(\hat{t})-\nu]-\gamma_\alpha(t'-t'')-\gamma_{ab}(t''-t''')\\&-i\int_{t'''}^{t''}d\hat{t}[\omega(\hat{t})-\nu]\Big\}+\exp\Big\{-\gamma_{ab}(t-t')\\&-i\int_{t'}^{t}d\hat{t}[\omega(\hat{t})-\nu]-\gamma_\alpha(t'-t'')\\&-\gamma_{ab}(t''-t''')+i\int_{t'''}^{t''}d\hat{t}[\omega(\hat{t})-\nu]\Big\}\Big]\\&\times\cos\left\{+K\int_{t'}^{t}d\hat{t}\,v(\hat{t})-K\int_{t'''}^{t''}d\hat{t}\,v(\hat{t})\right\}\\&\times\sin Kz+\text{c.c.},\end{aligned} \tag{10''}$$

where $N(z)$ is given by

$$N(z)=[\Lambda_a(z)/\gamma_a]-[\Lambda_b(z)/\gamma_b]. \tag{11}$$

In order to average the polarization over the histories of the functions $\omega(t)$ and $v(t)$, one must evaluate the following expectation values:

$$\left\langle\exp\left\{\pm iK\int_{t'}^{t}d\hat{t}\,v(\hat{t})-i\int_{t'}^{t}d\hat{t}\,\Delta\omega(\hat{t})\right\}\right\rangle, \tag{12}$$

$$\left\langle\exp\left\{\pm iK\left[\int_{t'}^{t}d\hat{t}\,v(\hat{t})-\int_{t'''}^{t''}d\hat{t}\,v(\hat{t})\right]-i\int_{t'}^{t}d\hat{t}\,\Delta\omega(\hat{t})\mp i\int_{t'''}^{t''}d\hat{t}\,\Delta\omega(\hat{t})\right\}\right\rangle, \tag{13}$$

where $\Delta\omega(t)$ is defined by the relation

$$\omega(t)=\omega+\Delta\omega(t), \tag{14}$$

and the bracket $\langle\cdots\rangle$ indicates an averaging over all possible histories $v(t)$ and $\Delta\omega(t)$ during the appropriate time intervals. The ordering of the different times appearing as limits of the integrals in (12) and (13) is given by $t'''<t''<t'<t$. The above averages are rather complicated and difficult to evaluate, and it would be very desirable to be able to assume that the changes in v and $\Delta\omega$ are uncorrelated. Since in a specific collision the integrated values of $\Delta\omega$ and the change in the velocity vector are interrelated, it is clear that the above assumption cannot be strictly valid. However, the function $v(t)$ is only one Cartesian component of the velocity vector and thus the assumption is not so unreasonable, though its validity is hard to check.[5]

By assuming that $\Delta\omega$ and v are uncorrelated it is possible to average over v and over $\Delta\omega$ separately and the quantities to be evaluated are

$$\Delta^{\pm}(t',t)=\left\langle \exp\left\{\pm iK\int_{t'}^{t} d\hat{t}\, v(\hat{t})\right\}\right\rangle, \tag{15}$$

$$\Delta^{\pm}(t''',t'',t',t)=\left\langle \exp\left\{\pm iK\left[\int_{t'}^{t} d\hat{t}\, v(\hat{t})-\int_{t'''}^{t''} d\hat{t}\, v(\hat{t})\right]\right\}\right\rangle, \tag{16}$$

$$\Gamma^{\pm}(t',t)=\left\langle \exp\left\{\pm i\int_{t'}^{t} d\hat{t}\, \Delta\omega(\hat{t})\right\}\right\rangle, \tag{17}$$

$$\Gamma^{\pm}(t''',t'',t',t)=\left\langle \exp\left\{-i\int_{t'}^{t} d\hat{t}\, \Delta\omega(\hat{t})\pm i\int_{t'''}^{t''} d\hat{t}\, \Delta\omega(\hat{t})\right\}\right\rangle. \tag{18}$$

Generalizing a nomenclature used in pressure-broadening theories we shall call these quantities characteristic functions. As is apparent from the previous discussion, the first two of these functions allow for the fact that the collisions change the amplitude modulation of the effective field seen by the emitting atom, and the second two describe the effect of the frequency modulation which occurs while an atom undergoes a collision.

Before discussing the method of calculating these characteristic functions, we proceed, at least formally, to solve for the intensity profile. We first write the spatial Fourier projection of the average polarization on the cavity mode in terms of the characteristic functions

$$\langle P^{(1)}(t)\rangle=-\tfrac{1}{2}i\wp^2\hbar^{-1}\bar{N}E(t)\exp\{-i(\nu t+\varphi)\}\times\int_{-\infty}^{t}dt'\exp\{-[\gamma_{ab}+i(\omega-\nu)](t-t')\}\times\Delta(t',t)\Gamma^{-}(t',t)+\text{c.c.}, \tag{19}$$

$$\begin{aligned}\langle P^{(3)}(t)\rangle=&\tfrac{1}{32}i\wp^4\hbar^{-3}\bar{N}E(t)^3\exp\{-i(\nu t+\varphi)\}\\&\times\sum_{\alpha=a,b}\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\int_{-\infty}^{t''}dt'''\\&\times[\exp\{-[\gamma_{ab}+i(\omega-\nu)](t-t')-\gamma_\alpha(t'-t'')\\&-[\gamma_{ab}+i(\omega-\nu)](t''-t''')\}\\&\times\Delta(t''',t'',t',t)\Gamma^{-}(t''',t'',t',t)\\&+\exp\{-[\gamma_{ab}+i(\omega-\nu)](t-t')-\gamma_\alpha(t'-t'')\\&-[\gamma_{ab}-i(\omega-\nu)](t''-t''')\}\Delta(t''',t'',t',t)\\&\times\Gamma^{+}(t''',t'',t',t)]+\text{c.c.},\end{aligned} \tag{20}$$

where

$$\Delta=\tfrac{1}{2}(\Delta^{+}+\Delta^{-}) \tag{21}$$

and

$$\bar{N}=L^{-1}\int_0^L dz\,N(z). \tag{22}$$

The amplitude equation (4) now becomes

$$dE/dt=\langle\alpha\rangle E-\langle\beta\rangle E^3. \tag{23}$$

The coefficients $\langle\alpha\rangle$ and $\langle\beta\rangle$ are generalizations of the constants α and β in Ref. 1 and may be written as

$$\langle\alpha\rangle=[\tfrac{1}{2}(\nu/Q)/\mathfrak{J}_i(\gamma_{ab})][\mathfrak{N}\mathfrak{J}_i(\mu)-\mathfrak{J}_i(\gamma_{ab})] \tag{24}$$

and

$$\langle\beta\rangle=\tfrac{1}{32}\wp^2\mathfrak{N}(\gamma_a\gamma_b)^{-1}\hbar^{-2}[(\nu/Q)/\mathfrak{J}_i(\gamma_{ab})][\mathfrak{J}_i^{-}(\mu,\mu)+\mathfrak{J}_i^{+}(\mu,\mu^*)], \tag{25}$$

where

$$\mathfrak{N}=\bar{N}/\bar{N}_T \tag{22'}$$

is the relative excitation of Ref. 1, Eq. (84); and the complex quantity μ is given by

$$\mu=\gamma_{ab}+i(\omega-\nu). \tag{26}$$

The functions $\mathfrak{J}(\mu)$, $\mathfrak{J}^{\pm}(\mu_1,\mu_2)$ are defined by the following relations:

$$\mathfrak{J}(\mu)=iKu\int_{-\infty}^{t}dt'\exp\{-\mu(t-t')\}\Delta(t',t)\Gamma^{-}(t',t) \tag{27}$$

and

$$\begin{aligned}\mathfrak{J}^{\pm}(\mu_1,\mu_2)=&iKu\gamma_a\gamma_b\sum_{\alpha=a,b}\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\int_{-\infty}^{t''}dt'''\\&\times\exp\{-\mu_1(t-t')-\gamma_\alpha(t'-t'')\\&-\mu_2(t''-t''')\}\Delta(t''',t'',t',t)\\&\times\Gamma^{\pm}(t''',t'',t',t),\end{aligned} \tag{28}$$

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[5] S. Rautian and I. Sobel'man [J. Quantum Electron. 2, 446 (1966)] consider the v and $\Delta\omega$ correlations to be the cause of any asymmetry of the tuning dip curve. In contrast, our explanation of this phenomenon as given in Sec. V(c) involves a statistical distribution of van der Waals interactions. See Eq. (124).

whose imaginary parts are $\mathfrak{J}_i(\mu)$ and $\mathfrak{J}_i^{\pm}(\mu_1, \mu_2)$, respectively. The steady-state solution of Eq. (23) is

$$E^2 = \langle\alpha\rangle / \langle\beta\rangle \quad (29)$$

which, in terms of a dimensionless intensity I, takes the form

$$I(\omega - \nu) \equiv (\wp^2 E^2/\hbar^2\gamma_a\gamma_b) = 16[\mathfrak{J}_i(\mu) - \mathfrak{N}^{-1}\mathfrak{J}_i(\gamma_{ab})] \times [\mathfrak{J}_i^-(\mu, \mu) + \mathfrak{J}_i^+(\mu, \mu^*)]^{-1}. \quad (30)$$

This expression for the intensity profile is a very general one and involves no other major approximations than the ones implied by the use of perturbation theory, assumption of the Doppler limit, and our idealization of the collision process. The rest of the paper will be devoted to the evaluation of Eq. (30) in more explicit terms employing various approximations, and comparing the results with experiments.

IV. AVERAGING OVER THE HISTORIES OF v(t)

As a first step in evaluation of the functions $\mathfrak{J}(\mu)$ and $\mathfrak{J}^{\pm}(\mu_1, \mu_2)$ we shall develop a formalism which allows us to calculate the characteristic functions defined by Eqs. (15) and (16).

(a) *General Formulation of the Averaging Procedure*

If we describe the position and velocity of an atom by vectors $\mathbf{r}$ and $\mathbf{v}$, respectively, the characteristic function defined by Eq. (15) may be written as

$$\begin{aligned}\Delta^{\pm}(t', t) &= \left\langle \exp\left\{\pm iK \int_{t'}^{t} d\hat{t}\, v(\hat{t})\right\}\right\rangle \\ &= \left\langle \exp\left\{\pm i\mathbf{K}\cdot \int_{t'}^{t} d\hat{t}\, \mathbf{v}(\hat{t})\right\}\right\rangle \\ &= \langle \exp\{\pm i\mathbf{K}\cdot[\mathbf{r}(t) - \mathbf{r}(t')]\}\rangle, \quad (31)\end{aligned}$$

where the vector $\mathbf{K}$ points along the laser tube ($+z$ axis) and has a magnitude K given by

$$K = \Omega/c = 2\pi n/L, \quad (31')$$

where n is the mode number and L is the length of the cavity.

It may be worthwhile to show how our equations reduce to those of Ref. 1 in the case where the atoms do not suffer collisions. In that case we may set

$$\mathbf{r}(t) - \mathbf{r}(t') = \mathbf{v}(t - t'). \quad (32)$$

Since each atom follows a definite path, completely defined by its initial position and velocity, the averaging over all the radiating atoms may be carried out trivially, and we have

$$\begin{aligned}\Delta^{\pm}(t', t) &= \pi^{-1/2}u^{-1} \int_{-\infty}^{\infty} dv \exp\{\pm iKv(t-t') - v^2/u^2\} \\ &= \exp\{-\tfrac{1}{4}K^2u^2(t-t')^2\}, \quad (33)\end{aligned}$$

where we have assumed that the velocity distribution of the radiating atoms is Maxwellian. Since in a collisionless theory there are no frequency variations, the quantities $\Gamma^{\pm}(t', t)$ and $\Gamma^{\pm}(t''', t'', t', t)$ are here equal to unity. In the large Doppler velocity limit ($\gamma_{ab}/Ku \ll 1$), but not making the "δ-function approximation," Eq. (30) may be reduced by a series of simple integrations to the form

$$I(\omega - \nu) = 8[1 - \mathfrak{N}^{-1} \exp\{(\omega-\nu)^2/(Ku)^2\}] \times [1 + \mathfrak{L}(\omega - \nu)]^{-1}, \quad (34)$$

with the Lorentzian function

$$\mathfrak{L}(\omega - \nu) = \gamma_{ab}^2[\gamma_{ab}^2 + (\omega-\nu)^2]^{-1}. \quad (34')$$

This expression for $I(\omega - \nu)$, which is somewhat more accurate than Eq. (96) of Ref. 1, also implies a dip in intensity as the cavity frequency $\Omega \simeq \nu$ passes through resonance, provided one is sufficiently far above threshold.

In order to treat the case where some of the atoms undergo collisions during the interval (t', t) let us introduce the conditional probability density $P(\mathbf{v}', \mathbf{r}', t' \mid \mathbf{v}, \mathbf{r}, t)$ that if an atom were at the phase-space point $\mathbf{v}', \mathbf{r}'$, at the time t' it would be in the volume element $d^3v\, d^3r$ located at $\mathbf{v}, \mathbf{r}$ at time t. For simplicity, we will assume that all conditional probability densities, such as $P(\mathbf{v}', \mathbf{r}', t' \mid \mathbf{v}, \mathbf{r}, t)$, are the same irrespective of the state of the active atom. We may now write the characteristic functions $\Delta^{\pm}(t', t)$ in the following form:

$$\begin{aligned}\Delta^{\pm}(t', t) = &\int d^3v' \int d^3v \int d^3r' \int d^3\Delta r \\ &\times P(\mathbf{v}', \mathbf{r}', t' \mid \mathbf{v}, \mathbf{r}' + \Delta\mathbf{r}, t)\, P(\mathbf{v}', \mathbf{r}', t') \\ &\times \exp\{\pm i\mathbf{K}\cdot\Delta\mathbf{r}\}, \quad (35)\end{aligned}$$

where $P(\mathbf{v}', \mathbf{r}', t')$ is the distribution function of the radiating atoms at t',

$$\Delta\mathbf{r} = \mathbf{r} - \mathbf{r}', \quad (36)$$

and the space integrations are over the volume of the laser cavity.

Let us further introduce Fourier transforms $G_\kappa(\mathbf{v}', \mathbf{r}', t' \mid \mathbf{v}, t)$ defined by the following relations[6]:

$$G_\kappa(\mathbf{v}', \mathbf{r}', t' \mid \mathbf{v}, t) = \int d^3\Delta r\, P(\mathbf{v}', \mathbf{r}', t' \mid \mathbf{v}, \mathbf{r}' + \Delta\mathbf{r}, t) \times \exp\{i\kappa\mathbf{K}\cdot\Delta\mathbf{r}\}, \quad (37)$$

where the parameter κ may take on the values $+1$, -1, 0. Clearly, once the functions $G_K(\mathbf{v}', \mathbf{r}', t' \mid \mathbf{v}, t)$ are known, the characteristic functions $\Delta^{\pm}(t', t)$ can be

[6] These quantities are often referred to as Wiener integrals; see, for example, E. W. Montroll, *Rendiconti della Scuola Internazionale de Fisica Enrico Fermi* (Nicola Zanichelli-Editore, Bologna, 1959), X Corso.

calculated from

$$\Delta^{\pm}(t',t)=\int d^3v'\int d^3v\int d^3r'\ P(\mathbf{v}',\mathbf{r}',t')\times G_{\pm1}(\mathbf{v}',\mathbf{r}',t'\mid\mathbf{v},t). \quad (38)$$

It is doubtful whether the dilute gaseous active medium in gas lasers is in thermodynamic equilibrium with respect to atomic velocities. Nevertheless, for reasons of mathematical convenience, we will assume that the distribution $P(\mathbf{v}',\mathbf{r}',t')$ is just a steady-state Maxwell distribution for some temperature, i.e.,

$$P(\mathbf{v}',\mathbf{r}',t')=V^{-1}P_0(\mathbf{v}'),$$

where

$$P_0(\mathbf{v}')=\pi^{-3/2}u^{-3}\exp\{-|\mathbf{v}'|^2/u^2\}, \quad (39)$$

and furthermore conjecture that the transition probability density $P(\mathbf{v}',\mathbf{r}',t'\mid\mathbf{v},\mathbf{r}'+\Delta\mathbf{r},t)$ depends on the relative position vector $\Delta\mathbf{r}$, but not on the location of the point $\mathbf{r}'$ in the laser volume V. We then define

$$f(\mathbf{v}',t'\mid\mathbf{v},\Delta\mathbf{r},t)=P(\mathbf{v}',\mathbf{r}',t'\mid\mathbf{v},\mathbf{r}'+\Delta\mathbf{r},t) \quad (40)$$

and

$$G_\kappa(\mathbf{v}',t'\mid\mathbf{v},t)=G_\kappa(\mathbf{v}',\mathbf{r}',t'\mid\mathbf{v},t), \quad (41)$$

so that we may write in place of Eq. (37),

$$G_\kappa(\mathbf{v}',t'\mid\mathbf{v},t)=\int d^3\Delta r\, f(\mathbf{v}',t'\mid\mathbf{v},\Delta\mathbf{r},t)\times\exp\{i\kappa\mathbf{K}\cdot\Delta\mathbf{r}\}. \quad (42)$$

The characteristic function $\Delta^{\pm}(t',t)$ may now be calculated as

$$\Delta^{\pm}(t',t)=\int d^3v'\int d^3v\ P_0(\mathbf{v}')G_{\pm1}(\mathbf{v}',t'\mid\mathbf{v},t). \quad (43)$$

We must now find a method for determining the transition probability $f(\mathbf{v}',t'\mid\mathbf{v},\Delta\mathbf{r},t)$ of Eq. (40). To this end let us consider a radiating atom at the phase-space point $\mathbf{r}',\mathbf{v}'$ at the time t' and introduce a representative ensemble for that atom which describes all of its possible future motions. It can easily be shown that the phase-space density $f(\mathbf{v},\mathbf{r},t)$ of such an ensemble must be a solution of the following Boltzmann equation:

$$(\partial/\partial t)f(\mathbf{v},\mathbf{r},t)=-\mathbf{v}\cdot\nabla f(\mathbf{v},\mathbf{r},t)-\int d^3v'\ W(\mathbf{v}\mid\mathbf{v}')f(\mathbf{v},\mathbf{r},t)+\int d^3v''\ W(\mathbf{v}''\mid\mathbf{v})f(\mathbf{v}'',\mathbf{r},t), \quad (44)$$

whose collision kernel $W(\mathbf{v}\mid\mathbf{v}')$ has the property that $W(\mathbf{v}\mid\mathbf{v}')d^3v'$ is the probability per unit time that an atom *changes* its velocity from $\mathbf{v}$ to the velocity range $(\mathbf{v}',\mathbf{v}'+d\mathbf{v}')$. Consequently, the integral of $W(\mathbf{v}\mid\mathbf{v}')$ over all final velocities $\mathbf{v}'$ (with exclusion of a small region about $\mathbf{v}$) is the probability per unit time that an atom of velocity $\mathbf{v}$ will experience a collision and hence we write

$$(T(\mathbf{v}))^{-1}=\int d^3v'\ W(\mathbf{v}\mid\mathbf{v}'), \quad (45)$$

whose $T(\mathbf{v})$ is the average collision time for an atom of velocity $\mathbf{v}$. Equation (44) may then be written in the following simplified form:

$$(\partial/\partial t)f(\mathbf{v},\mathbf{r},t)=-\mathbf{v}\cdot\nabla f(\mathbf{v},\mathbf{r},t)-(T(\mathbf{v}))^{-1}f(\mathbf{v},\mathbf{r},t)+\int d^3v''\ W(\mathbf{v}''\mid\mathbf{v})f(\mathbf{v}'',\mathbf{r},t). \quad (46)$$

Since we want the ensemble to be concentrated in the volume element $d^3v'\,d^3r'$ at the phase-space point $\mathbf{v}',\mathbf{r}'$ at time t' we should solve Eq. (46) with the normalized initial condition

$$f(\mathbf{v}',\mathbf{r}',t'\mid\mathbf{v},\mathbf{r},t')=\delta(\mathbf{r}-\mathbf{r}')\delta(\mathbf{v}-\mathbf{v}'). \quad (47)$$

Clearly such a solution will be just the transition probability density $f(\mathbf{v}',t'\mid\mathbf{v},\Delta\mathbf{r},t)$ which we seek to calculate since $f(\mathbf{v}',\mathbf{r}',t'\mid\mathbf{v},\mathbf{r},t)$ is properly normalized to unity.

Instead of trying to solve Eq. (46) as it stands, we multiply both sides by the exponential factor $\exp\{i\kappa\mathbf{K}\cdot\Delta\mathbf{r}\}$ and integrate them over the position variables $\Delta\mathbf{r}$. This leads to integro-differential equations for the quantities $G_\kappa(\mathbf{v}',t'\mid\mathbf{v},t)$,

$$(\partial/\partial t)G_\kappa(\mathbf{v}',t'\mid\mathbf{v},t)=(i\kappa\mathbf{K}\cdot\mathbf{v}-[T(\mathbf{v})]^{-1})\times G_\kappa(\mathbf{v}',t'\mid\mathbf{v},t)+\int d^3v''\ W(\mathbf{v}''\mid\mathbf{v})\times G_\kappa(\mathbf{v}',t'\mid\mathbf{v}'',t), \quad (48)$$

where we have made use of the definition (42). We must solve this equation with a δ-function initial condition

$$G_\kappa(\mathbf{v}',t'\mid\mathbf{v},t')=\delta(\mathbf{v}-\mathbf{v}'). \quad (49)$$

For any given interaction potential the collision kernel $W(\mathbf{v}'\mid\mathbf{v})$ is well defined and thus we have reduced the problem of finding $G_\kappa(\mathbf{v}',t'\mid\mathbf{v},t)$, and therefore the characteristic functions $\Delta^{\pm}(t',t)$ which are related to $G_{\pm1}(\mathbf{v}',t'\mid\mathbf{v},t)$ by Eqs. (43), to the solution of an integro-differential equation.

Before attempting to solve Eq. (48) let us turn to the calculation of the higher-order characteristic functions which are defined by Eqs. (16). Proceeding along the lines of the previous discussion we write

$$\Delta^{\pm}(t''',t'',t',t)=\left\langle \exp\left\{\pm iK\int_{t'}^{t} d\hat{t}\, v(\hat{t}) \mp iK\int_{t'''}^{t''} d\hat{t}\, v(\hat{t})\right\}\right\rangle$$
$$=\left\langle \exp\left\{\pm i\mathbf{K}\cdot\left[\int_{t'}^{t} d\hat{t}\, \mathbf{v}(\hat{t}) - \int_{t'''}^{t''} d\hat{t}\, \mathbf{v}(\hat{t})\right]\right\}\right\rangle$$
$$=\langle \exp\{\pm i\mathbf{K}\cdot[\mathbf{r}(t)-\mathbf{r}(t')-\mathbf{r}(t'')+\mathbf{r}(t''')]\}\rangle. \quad (50)$$

We define a generalization of the transition probability $P(\mathbf{v}',\mathbf{r}',t' \mid \mathbf{v},\mathbf{r},t)$ by letting

$$P(\mathbf{v}''',\mathbf{r}''',t''' \mid \mathbf{v}'',\mathbf{r}'',t'';\mathbf{v}',\mathbf{r}',t';\mathbf{v},\mathbf{r},t) \times d^3v''d^3r''d^3v'd^3r'd^3vd^3r$$

be the conditional probability that an atom which was at the phase-space point $(\mathbf{v}''',\mathbf{r}''')$ at the time t''' will be at $(\mathbf{v}'',\mathbf{r}'')$, $(\mathbf{v}',\mathbf{r}')$, and $(\mathbf{v},\mathbf{r})$ at the later times t'', t', t, respectively. The characteristic functions $\Delta^{\pm}(t''',t'',t',t)$ may then be written as

$$\Delta^{\pm}(t''',t'',t',t)=\int d^3v'''\int d^3v''\int d^3v'\int d^3v \times\int d^3r'''\int d^3r''\int d^3r'\int d^3r \times P(\mathbf{v}''',\mathbf{r}''',t''') \times P(\mathbf{v}''',\mathbf{r}''',t''' \mid \mathbf{v}'',\mathbf{r}'',t''; \times \mathbf{v}',\mathbf{r}',t';\mathbf{v},\mathbf{r},t) \times\exp\{\pm i\mathbf{K}\cdot[\mathbf{r}-\mathbf{r}'-\mathbf{r}''+\mathbf{r}''']\}. \quad (51)$$

It seems reasonable to assume that the collisions constitute a Markoff process. As shown in Appendix I, one can then factor the complicated four time conditional probability as

$$P(\mathbf{v}''',\mathbf{r}''',t''' \mid \mathbf{v}'',\mathbf{r}'',t'';\mathbf{v}',\mathbf{r}',t';\mathbf{v},\mathbf{r},t) = P(\mathbf{v}''',\mathbf{r}''',t''' \mid \mathbf{v}'',\mathbf{r}'',t'')P(\mathbf{v}'',\mathbf{r}'',t'' \mid \mathbf{v}',\mathbf{r}',t') \times P(\mathbf{v}',\mathbf{r}',t' \mid \mathbf{v},\mathbf{r},t). \quad (52)$$

In analogy with Eq. (37), the generalized G functions, $G_{\pm1}(\mathbf{v}''',\mathbf{r}''',t''' \mid \mathbf{v}'',t'';\mathbf{v}',t';\mathbf{v},t)$ may now be defined as

$$G_{\pm1}(\mathbf{v}''',\mathbf{r}''',t''' \mid \mathbf{v}'',t'';\mathbf{v}',t';\mathbf{v},t) =\int d^3\Delta r\int d^3\Delta r'\int d^3\Delta r'' \times P(\mathbf{v}''',\mathbf{r}''',t''' \mid \mathbf{v}'',\mathbf{r}'''+\Delta\mathbf{r}'',t'') \times P(\mathbf{v}'',\mathbf{r}'''+\Delta\mathbf{r}'',t'' \mid \mathbf{v}',\mathbf{r}'''+\Delta\mathbf{r}''+\Delta\mathbf{r}',t') \times P(\mathbf{v}',\mathbf{r}'''+\Delta\mathbf{r}''+\Delta\mathbf{r}',t' \mid \mathbf{v},\mathbf{r}'''+\Delta\mathbf{r}''+\Delta\mathbf{r}'+\Delta\mathbf{r},t) \times\exp\{\pm i\mathbf{K}\cdot[\Delta\mathbf{r}-\Delta\mathbf{r}'']\}, \quad (53)$$

where

$$\Delta\mathbf{r}''=\mathbf{r}''-\mathbf{r}''', \quad \Delta\mathbf{r}'=\mathbf{r}'-\mathbf{r}'', \quad \text{and} \quad \Delta\mathbf{r}=\mathbf{r}-\mathbf{r}'.$$

From (42) and the spatial homogeneity of

$$P(\mathbf{v}',\mathbf{r}',t' \mid \mathbf{v},\mathbf{r},t),$$

it follows that the quantity (53) factors as follows:

$$G_{\pm1}(\mathbf{v}''',t''' \mid \mathbf{v}'',t'';\mathbf{v}',t';\mathbf{v},t)=G_{\mp}(\mathbf{v}''',t''' \mid \mathbf{v}'',t'') \times G_0(\mathbf{v}'',t'' \mid \mathbf{v}',t')G_{\pm1}(\mathbf{v}',t' \mid \mathbf{v},t). \quad (54)$$

(b) *Solution of the Velocity Averaging Problem for a Simple Collision Model*

We first replace Eq. (48) by its one-dimensional form

$$(\partial/\partial t)G_\kappa(v',t' \mid v,t)=(i\kappa Kv-[T(v)]^{-1})G_\kappa(v',t' \mid v,t) +\int dv''\, W(v'' \mid v)G_\kappa(v',t' \mid v'',t). \quad (48')$$

Let us further define the collision model by assuming that the kernel of Eq. (48′) has the form

$$W(v' \mid v)=(\pi^{1/2}uT)^{-1}\exp\{-v^2/u^2\}, \quad (55)$$

where T is the average time between collisions independent of v and $u\pi^{-1/2}$ is the average speed along the cavity axis. The above transition kernel $W(v' \mid v)$ implies that no matter what value v' the axial velocity had initially, the probability of finding it in the range v, $v+dv$ after the collision is given by the equilibrium distribution, that is to say, we know no more about that atom than any of the others. Since we knew so little about it initially, i.e., only one component of its velocity, this does not seem to be an unreasonable assumption.

Equation (48′) now takes the form

$$(\partial/\partial t)G_\kappa(v',t' \mid v,t)=(i\kappa Kv-T^{-1})G_\kappa(v',t' \mid v,t) +(\pi^{1/2}uT)^{-1}\exp\{-v^2/u^2\}\int_{-\infty}^{\infty} dv''\, G_\kappa(v',t' \mid v'',t), \quad (56)$$

with

$$G_\kappa(v',t' \mid v,t')=\delta(v-v').$$

Integrating the above equation formally, we obtain

$$G_\kappa(v',t' \mid v,t)=\exp\{(i\kappa Kv-T^{-1})(t-t')\}\delta(v'-v) +(\pi^{1/2}uT)^{-1}\exp\{-v^2/u^2\}\int_{t'}^{t} d\hat{t} \times\exp\{(i\kappa Kv-T^{-1})(t-\hat{t})\}\int_{-\infty}^{\infty} dv'' \times G_\kappa(v',t' \mid v'',\hat{t}). \quad (57)$$

If the perturbing atoms are in thermal equilibrium we may assume that the changes in v form a stationary random process and the functions $G_\kappa(v',t' \mid v,t)$ depend only on the time difference $t-t'=\tau'$. Multiplying Eq. (57) by

$$(\pi^{1/2}u)^{-1}\exp\{-v'^2/u^2\},$$

changing the time integration variable from $\hat{t}$ to $\tau=\hat{t}-t'$, and then integrating both sides of the equation over v and v', the following equality emerges for $\kappa=\pm1$:

$$(\pi^{1/2}u)^{-1}\int_{-\infty}^{\infty}dv'\exp\{-v'^2/u^2\}\int_{-\infty}^{\infty}dv\,G_{\pm1}(v',t'\mid v,t)$$
$$=\exp\{-\tfrac{1}{4}(Ku\tau')^2-\tau'/T\}+(\pi^{1/2}uT)^{-1}\int_0^{\tau'}d\tau$$
$$\times\exp\{-\tfrac{1}{4}K^2u^2(\tau'-\tau)^2-(\tau'-\tau)/T\}$$
$$\times\left[\int_{-\infty}^{\infty}dv'\int_{-\infty}^{\infty}dv''\exp\{-v'^2/u^2\}G_{\pm1}(v',t'\mid v'',t'+\tau)\right].\quad(58)$$

One may note that

$$(\pi^{1/2}u)^{-1}\int_{-\infty}^{\infty}dv'\exp\{-v'^2/u^2\}\int_{-\infty}^{\infty}dv\,G_{\pm1}(v',t'\mid v,t)$$
$$=\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dv'\,P_0(v')G_{\pm1}(v',t'\mid v,t),\quad(59)$$

which are the characteristic functions $\Delta^{\pm}(t',t)$ defined by Eq. (43). Hence Eq. (58) may be written as integral equations for the characteristic functions $\Delta^{\pm}(t',t)\equiv\Delta^{\pm}(\tau')$,

$$\Delta^{\pm}(\tau')=\exp\{-\tfrac{1}{4}(Ku\tau')^2-\tau'/T\}+(T)^{-1}\int_0^{\tau'}d\tau$$
$$\times\exp\{-\tfrac{1}{4}K^2u^2(\tau'-\tau)^2-(\tau'-\tau)/T\}\Delta^{\pm}(\tau).\quad(60)$$

Since Eq. (60) is manifestly independent of the sign of κ, it is clear that for this collision model the characteristic functions Δ^+, Δ^-, and $\Delta=\frac{1}{2}(\Delta^++\Delta^-)$ are all equal.

We recall at this point that a quantity which appears in Eq. (30) for the intensity I is the imaginary part $\mathfrak{Z}_i(\mu)$ of the function $\mathfrak{Z}(\mu)$ defined by Eqs. (26) and (27). For the moment, we neglect the variations in the transition frequency by setting $\Delta\omega(t)=0$ and consequently $\Gamma(t',t)=1$. Multiplication of Eq. (60) by $\exp\{-\mu\tau'\}$ and integration over the variable τ' from 0 to ∞ leads to a simple algebraic relation for $\mathfrak{Z}(\mu)$,

$$\mathfrak{Z}(\mu)=Z(\mu')+(iTKu)^{-1}\mathfrak{Z}(\mu)Z(\mu'),\quad(61)$$

where the convolution theorem has been used to carry out the integration over the second term in Eq. (60) and $Z(\mu')$ is the plasma dispersion function defined in Ref. 1 as

$$Z(\mu')=iKu\int_0^{\infty}d\tau'\exp\{-\mu'\tau'-\tfrac{1}{4}(Ku\tau')^2\},\quad(62)$$

with complex argument

$$\mu'=\mu+(1/T)=\gamma_{ab}+(1/T)+i(\omega-\nu).\quad(63)$$

The function $\mathfrak{Z}(\mu)$ may now be found trivially as

$$\mathfrak{Z}(\mu)=Z(\mu')[1+i\epsilon Z(\mu')]^{-1},\quad(64)$$

where the dimensionless parameter ϵ is given by

$$\epsilon=(KuT)^{-1}$$
$$\approx(\text{optical wavelength})/(\text{collision mean free path}).\quad(64')$$

For sufficiently low pressures, ϵ is a small quantity, and $\mathfrak{Z}(\mu)$ may be expanded in the form

$$\mathfrak{Z}(\mu)=Z(\mu')-i\epsilon[Z(\mu')]^2+\cdots.\quad(65)$$

We now turn to the calculation of $\mathfrak{Z}^{\pm}(\mu_1,\mu_2)$ given by Eq. (28) for the case of $\Gamma^{\pm}(t''',t'',t',t)=1$. At first, let us consider the characteristic functions $\Delta^{\pm}(t''',t'',t',t)$ which, by the use of Eqs. (51)–(54) may be written as

$$\Delta^{\pm}(t''',t'',t',t)$$
$$=(\pi^{1/2}u)^{-1}\int_{-\infty}^{\infty}dv'''\exp\{-(v''')^2/u^2\}$$
$$\times\int_{-\infty}^{\infty}dv''\int_{-\infty}^{\infty}dv'\int_{-\infty}^{\infty}dv\,G_{\mp}(v''',t'''\mid v'',t'')$$
$$\times G_0(v'',t''\mid v',t')G_{\pm}(v',t'\mid v,t).\quad(66)$$

We now note that for $\kappa=0$, Eq. (56) is solved by

$$G_0(v',t'\mid v,t)$$
$$=\delta(v'-v)\exp\{-(t-t')/T\}+(\pi^{1/2}u)^{-1}$$
$$\times\exp\{-v^2/u^2\}(1-\exp\{-(t-t')/T\}),\quad(67)$$

since the integral over v'' in (57) is then equal to unity. In (67), we replace v', t' by v'', t'' and v, t by v', t' and rewrite Eq. (66) in the form

$$\Delta^{\pm}(t''',t'',t',t)$$
$$=(\pi^{1/2}u)^{-1}\int_{-\infty}^{\infty}dv'''\exp\{-(v''')^2/u^2\}\int_{-\infty}^{\infty}dv''\int_{-\infty}^{\infty}dv$$
$$\times G_{\mp}(v''',t'''\mid v'',t'')G_{\pm}(v'',t'\mid v,t)$$
$$\times\exp\{-(t'-t'')/T\}+(\pi^{1/2}u)^{-2}\int_{-\infty}^{\infty}dv'''$$
$$\times\exp\{-(v''')^2/u^2\}\int_{-\infty}^{\infty}dv''\int_{-\infty}^{\infty}dv'\exp\{-(v')^2/u^2\}$$
$$\times\int_{-\infty}^{\infty}dv\,G_{\mp}(v''',t'''\mid v'',t'')G_{\pm}(v',t'\mid v,t)$$
$$\times[1-\exp\{-(t'-t'')/T\}],\quad(68)$$

where the integration over the variable v' has already been carried out in the first term on the right. Integrals of the form

$$D_{\kappa\kappa'}(\tau''',\tau')=(\pi^{1/2}u)^{-1}\int_{-\infty}^{\infty}dv'''\exp\{-(v''')^2/u^2\}$$
$$\times\int_{-\infty}^{\infty}dv\,X_{\kappa\kappa'}(v''',v;\tau''',\tau'),\quad(69)$$

where the quantity

$$X_{\kappa\kappa'}(v''',v';\tau''',\tau')$$

is defined by

$$X_{\kappa\kappa'}(v''',v';\tau''',\tau')=\int_{-\infty}^{\infty}dv''\,G_\kappa(v''',0;v'',\tau''')$$
$$\times G_{\kappa'}(v'',0;v,\tau'),\quad(69')$$

are considered in Appendix I. It is shown there that the quantity (69) obeys the integral equation

$$D_{\kappa\kappa'}(\tau''',\tau')=\exp[-\{(\tau'+\tau''')/T\}-\tfrac{1}{4}(Ku)^2$$
$$\times(\kappa'\tau'+\kappa\tau''')^2]+(1/T)\int_0^{\tau'''}d\hat{t}\,\Delta_\kappa(\hat{t})$$
$$\times\exp[-\{(\tau'+\tau'''-\hat{t})/T\}-\tfrac{1}{4}(Ku)^2$$
$$\times(\kappa'\tau'+\kappa\tau'''-\kappa\hat{t})^2]+(1/T)\int_0^{t'}d\hat{t}$$
$$\times D_{\kappa\kappa'}(\tau''',\hat{t}')\exp[-\{(\tau'-\hat{t})/T\}$$
$$-\tfrac{1}{4}(Ku)^2(\kappa')^2(\tau'-\hat{t})^2].\quad(70)$$

For $\kappa'=\kappa=\pm1$ it is found that Eq. (70) has the solution

$$D_{\pm1\pm1}(\tau''',\tau')=\Delta^{\pm}(\tau'+\tau'''),\quad(70')$$

which corresponds to the intuitively obvious Smoluchowski equation,[6a]

$$\int_{-\infty}^{\infty}dv''\,G_{\pm1}(v''',0\,|\,v'',\tau''')G_{\pm}(v'',0\,|\,v,\tau')$$
$$=G_{\pm1}(v''',0\,|\,v,\tau'+\tau''').\quad(69'')$$

However, for $\kappa'=-\kappa=+1$, the quantity

$$D^{\mp}(\tau''',\tau')\equiv D_{-1+1}(\tau''',\tau')=D_{+1-1}(\tau',\tau''')\quad(70'')$$

has a more complex structure. It is shown in Appendix II that its double Laplace transform

$$S(\mu_1,\mu_2)=iKu\int_0^\infty d\tau'\int_0^\infty d\tau'''$$
$$\times\exp\{-\mu_1\tau'-\mu_2\tau'''\}D^{\mp}(\tau''',\tau')\quad(71)$$

has the value

$$S(\mu_1,\mu_2)=\mathfrak{Z}(\mu_1)\mathfrak{Z}(\mu_2)(\mu_1'+\mu_2')^{-1}\{[Z(\mu_1')]^{-1}$$
$$+[Z(\mu_2')]^{-1}\}.\quad(71')$$

[6a] M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 233 (1945).

Then, by recalling the definitions of the characteristic functions

$$\Delta^{\pm}(t',t)\equiv\Delta^{\pm}(\tau')\quad(43')$$

of Eq. (43), one may write Eq. (68) in the following rather transparent form:

$$\Delta^{\pm}(\tau''',\tau'',\tau')\equiv\Delta^{\pm}(t''',t'',t',t)$$
$$=\exp\{-\tau''/T\}D^{\pm}(\tau''',\tau')$$
$$+(1-\exp\{-\tau''/T\})\Delta^{\mp}(\tau''')\Delta^{\pm}(\tau').\quad(72)$$

The first term on the right-hand side of Eq. (72) may be interpreted as the product of the characteristic function for the case where the velocity of the atom at the end of the interval τ''' is the same as at the beginning of the interval τ', and the probability that no collision occurred in the interval τ''. The second term may be thought of as the characteristic function for the case where the velocities at the end of the interval τ''' and the beginning of the interval τ' are uncorrelated, multiplied by the probability that at least one collision occurred in the interval τ''. Since the collision kernel Eq. (55) implies that all memory of the previous velocity is lost during a collision, the possibility of such an interpretation for Eq. (72) is reassuring.

We now proceed to the calculation of $\mathfrak{Z}^{\pm}(\mu_1,\mu_2)$ by setting $\Gamma^{\pm}(t''',t'',t',t)=1$ and substituting Eq. (72) into Eq. (28), we find that

$$\mathfrak{Z}^{\pm}(\mu_1,\mu_2)=iKu\gamma_a\gamma_b[\{(1/\gamma_a')+(1/\gamma_b')\}\int_0^\infty d\tau'\int_0^\infty d\tau'''$$
$$\times\exp\{-\mu_1\tau'-\mu_2\tau'''\}D^{\mp}(\tau''',\tau')$$
$$+\{(1/\gamma_a)+(1/\gamma_b)-(1/\gamma_a')-(1/\gamma_b')\}$$
$$\times\int_0^\infty d\tau'\,\Delta^{\pm}(\tau')\exp\{-\mu_1\tau'\}$$
$$\times\int_0^\infty d\tau'''\,\Delta^{\mp}(\tau''')\exp\{-\mu_2\tau'''\}],\quad(73)$$

where the τ'' integration has already been carried out and we have introduced the notation

$$\gamma_a'=\gamma_a+(1/T),$$
$$\gamma_b'=\gamma_b+(1/T),$$
$$\gamma_{ab}'=\gamma_{ab}+(1/T).$$

Recalling the definition of the $\mathfrak{Z}(\mu)$ function as given by Eq. (27) for ($\Gamma=1$), and also substituting (71) and (71′) into Eq. (73), we find

$$\mathfrak{Z}^{\pm}(\mu_1,\mu_2)=2\gamma_{ab}'[(\gamma_a\gamma_b)/(\gamma_a'\gamma_b')]$$
$$\times[\mathfrak{Z}(\mu_1)\mathfrak{Z}(\mu_2)(\mu_1'+\mu_2')^{-1}\{[Z(\mu_1')]^{-1}$$
$$+[Z(\mu_2')]^{-1}\}$$
$$-i\{[(\gamma_{ab}\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)]-1\}(Ku)^{-1}$$
$$\times\mathfrak{Z}(\mu_1)\mathfrak{Z}(\mu_2)].\quad(73')$$

The function $\mathfrak{I}(\mu)$ is given exactly by Eq. (64) so we have obtained an exact solution for $\mathfrak{I}^{\pm}(\mu_1, \mu_2)$ also, subject only to the assumption that Eq. (55) gives the correct collision kernel.

To make a proper test of our theory it will be necessary to work with numerically evaluated values of the plasma dispersion function $Z(\mu)$. For the present paper, however, we merely assess the qualitative effects of our model collisions on the intensity profile by expanding Eqs. (65) and (73′) in the high Doppler limit where the plasma dispersion function is approximated by

$$Z(\mu)\simeq i\pi^{1/2}\exp\{-(\omega-\nu)^2/(Ku)^2\}. \qquad (62')$$

Terms which can give corrections of first order in ϵ are kept, but in them the Gaussian exponential factor and the relative excitation $\mathfrak{N}$ are not distinguished from unity. The intensity (30) then becomes

$$\begin{aligned} I(\omega-\nu)=A[1-\mathfrak{N}^{-1}\exp\{(\omega-\nu)^2/(Ku)^2\}] \\ \times[1+\mathcal{L}'(\omega-\nu)+2\pi^{1/2}(\gamma_{ab}'/Ku) \\ \times\{(\gamma_{ab}\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)-1\}]^{-1}, \quad (74) \end{aligned}$$

$$A=8[(\gamma_a'\gamma_b')/(\gamma_a\gamma_b)](1+2\pi^{1/2}\epsilon)^{-1} \qquad (75\text{a})$$

and

$$\mathcal{L}'(\omega-\nu)=(\gamma_{ab}')^2/[(\gamma_{ab}')^2+(\omega-\nu)^2]. \qquad (75\text{b})$$

When Eq. (74) is compared to the collisionless intensity profile given by Eq. (34) it is seen that the main effect of changing atomic velocities during collisions is to contribute an additive term in the denominator, and to add a term $(1/T)$ to the width parameter γ_{ab} of the Lorentzian function in the denominator.

Before attempting to compare the above result with experiments we turn to the calculation of the characteristic functions $\Gamma^{\pm}(t', t)$ and $\Gamma^{\pm}(t''', t'', t', t)$. This is done in order to determine the effects on the intensity function $I(\omega-\nu)$ of adiabatic variations of transition frequency $\Delta\omega(t)$ during a collision.

V. AVERAGING OVER THE HISTORIES OF $\Delta\omega$ (t)

(a) *General Remarks*

In this discussion we assume that the interaction potential between two colliding atoms is a van der Waals potential,

$$V_\alpha(r)=\hbar B_\alpha/r^6, \qquad (76)$$

where r is the distance of a perturber from the radiating atom and B_α is the van der Waals coefficient corresponding to the αth state of the radiating atom. It should be a good approximation to assume that the combined effect of all perturbers is a sum of such expressions $V_\alpha=\sum_j V_\alpha(r_j)$. Because the perturbers are moving, the V_α will be functions of time $V_\alpha(t)$ and will produce adiabatic changes $\Delta\omega(t)=\hbar^{-1}[V_a(t)-V_b(t)]$ in the resonant frequency. At the low densities of interest to us, it will suffice to consider that only one perturber at a time is close enough to produce a significant time-dependent contribution to $\Delta\omega$ and that the other more distant background perturbers produce a very slowly varying modulation of the atomic transition frequency. For the latter contribution we replace the time averaging by a statistical average [see Sec. V(c)].

If we approximate the relative motion of the nearest perturber by a straight line, the time-dependent modulation of the transition frequency may be written as

$$\Delta\omega(t)=[V_a(t)-V_b(t)]\hbar^{-1}=B(b^2+v^2t^2)^{-3}, \quad (77)$$

where v is the speed of the perturber in the rest frame of the radiating atom, b is the distance of closest approach (impact parameter), and $B=B_a-B_b$ is the difference of the two van der Waals constants. The "duration" of a collision τ_c may be defined as the solution of the algebraic equation

$$\tfrac{1}{2}\Delta\omega(0)=\Delta\omega(\tau_c), \qquad (78)$$

which is $\tau_c\cong 0.512(b/v)$. The average number of encounters per unit time with a range db of impact parameters b is given by $2\pi b db\rho\bar{v}$, where ρ is the density of perturbers and $\bar{v}$ is their mean speed.

The modulation of $\Delta\omega$ due to such a close collision are short-lasting and infrequent, so that the integral

$$\int_{t'}^{t} d\hat{t}\,\Delta\omega(\hat{t})$$

may be replaced by a sum of all the individual phase shifts due to different collisions in the interval (t', t). The approximation is characteristic of interruption theories of pressure broadening.

In effect, for the purpose of the calculation, we assume the existence of a critical impact parameter b^* and treat all collisions with $b<b^*$ in the interruption theory limit and all other collisions in the statistical limit. Such a separation of close and distant encounters is rather artificial and thus the value of b^* is somewhat arbitrary. However, it turns out that the results of our calculation depend only slightly on b^* and hence an uncertainty about its value is of little importance.

We now write $\Delta\omega$ in the form

$$\Delta\omega=\Delta\omega_c+\Delta\omega_d, \qquad (79)$$

where $\Delta\omega_c$ is the modulation due to the *close* collisions and $\Delta\omega_d$ is the frequency shift due to the *distant* collisions. It is reasonable to assume that two such markedly different types of collision events act independently, and write (17) in factored form

$$\Gamma^{\pm}(\tau')\equiv\Gamma^{\pm}(t', t)=\Gamma_c^{\pm}(\tau')\,\Gamma_d^{\pm}(\tau'). \qquad (80)$$

Hence, we may proceed to calculate $\Gamma_c^{\pm}(\tau')$ and $\Gamma_d^{\pm}(\tau')$, separately.

(b) *Interruption Theory Limit*

As mentioned above, in this limit we replace integrals of the sort

$$\int_{t'}^{t} d\hat{t}\, \Delta\omega(\hat{t})$$

by the sum of the phase shifts due to $N(t-t')$ individual collisions in the interval (t', t). If one characterizes each phase shift $\chi(v, b)$ by an impact parameter b and a relative speed v, and assumes that the various collisions are independent, then the two-time characteristic function for close collisions may be written as

$$\Gamma_c^+(t', t) = \langle \exp\{\pm i \sum_{j=1}^{N(t-t')} \chi(v_j, b_j)\}\rangle, \tag{81}$$

where $N(t-t')$ is the number of collisions in time interval $t-t'$ for a particular history. The average over all histories may now be calculated in the following manner:

$$\begin{aligned}\Gamma_c^+(t', t) = P_0(t, t') &+ \int_{t'}^{t} dt_1 \int_0^{b^*} db_1 \int_{-\infty}^{\infty} dv_1 \\ &\times P_0(t, t_1)\, P(t_1, v_1, b_1) \exp\{i\chi(b_1, v_1)\}\, P_0(t, t') \\ &+ \int_{t'}^{t} dt_2 \int_{t'}^{t_2} dt_1 \int_0^{b^*} db_1 \int_{-\infty}^{\infty} dv_1 \int_0^{b^*} db_2 \\ &\times \int_{-\infty}^{\infty} dv_2\, P_0(t, t_2)\, P(t_2, v_2, b_2) \\ &\times \exp\{i\chi(b_2, v_2)\}\, P_0(t_2, t_1)\, P(t_1, v_1, b_1) \\ &\times \exp\{i\chi(b_1, v_1)\}\, P_0(t_1, t') + \cdots,\end{aligned} \tag{82}$$

where $P_0(t, t')$ is the probability that there was no collision in the interval (t', t) with $b<b^*$; $P(t, v, b)$ is the probability density per unit time that a collision occurred with an impact parameter $b(b<b^*)$ and a relative speed v at time t. Each term in Eq. (82) should be thought of as a sum of terms of the kind

$$P_0(t, t_1)\, P(t_1, v, b) \exp\{i\chi(v, b)\}\, P_0(t_1, t')\, dt_1, \tag{83}$$

which represents a particular history, i.e., there was no collision in the intervals (t', t_1), (t_1+dt_1, t) and a collision with b and v occurred at the time t_1 in dt_1.

The probability $P_0(t, t')$ may be evaluated as the solution of a simple differential equation. The probability for one collision of a specified type in a short time dt is $2\pi b db\, |v|\, W(v)\, dv \rho dt$, where ρ is the number density of the perturbers and $W(v)$ is their velocity distribution. In a sufficiently short time the probability $P_0(t, t')$ can decrease only because of the occurrence of one collision, consequently

$$dP_0(t, t')/dt = -\rho\sigma\bar{v} P_0(t, t'), \tag{84}$$

where σ is the cross section

$$\sigma = 2\pi \int_0^{b^*} b db = \pi b^{*2}, \tag{85}$$

and $\bar{v}$ the average speed

$$\bar{v} = 2 \int_0^{\infty} dv\, |v|\, W(v), \tag{86}$$

and we have tacitly assumed that the perturbers are uniformly distributed in space. The solution of this differential equation subject to the initial condition $P_0(t', t') = 1$ is

$$P_0(t, t') = \exp\{-\rho\sigma\bar{v}(t-t')\} \tag{87}$$

and the characteristic function $\Gamma_c^+(t', t)$ now takes the form

$$\begin{aligned}\Gamma_c^+(t-t') = P_0(t-t') \Bigg[1 &+ \int_{t'}^{t} dt_1 \int_0^{b^*} db_1 \int_{-\infty}^{\infty} dv_1 \\ &\times P(t_1, v_1, b_1) \exp\{+i\chi(v_1, b_1)\} \\ &+ \int_{t'}^{t} dt_2 \int_{t'}^{t_2} dt_1 \int_0^{b^*} db_1 \int_{-\infty}^{\infty} dv_1 \int_0^{b^*} db_2 \\ &\times \int_{-\infty}^{\infty} dv_2\, P(t_2, v_2, b_2) \exp\{+i\chi(b_2, v_2)\} \\ &\times P(t_1, v_1, b_1) \exp\{+i\chi(b_1, v_1)\} + \cdots \Bigg].\end{aligned} \tag{88}$$

By changing the limits of the time integrations the above Eq. (88) may be written as

$$\begin{aligned}\Gamma_c^+(t-t') &= P_0(t-t') \sum_{n=0}^{\infty} (n!)^{-1} \left[\int_0^{b^*} db \int_{-\infty}^{\infty} dv \int_{t'}^{t} d\hat{t} \times P(\hat{t}, v, b) \exp\{i\chi(v, b)\}\right]^n \\ &= P_0(t-t') \exp\left\{\int_0^{b^*} db \int_{-\infty}^{\infty} dv \int_{t'}^{t} d\hat{t} \times P(\hat{t}, v, b) \exp\{i\chi(v, b)\}\right\}.\end{aligned} \tag{89}$$

In order to normalize this average we may note that the average of unity is

$$\langle 1 \rangle = P_0(t-t') \exp\left\{\int_0^{b^*} db \int_{-\infty}^{\infty} dv \int_{t'}^{t} d\hat{t}\, P(t, v, b)\right\}, \tag{90}$$

and hence write the characteristic function in the familiar Foley form[4,7]

$$\begin{aligned}\Gamma_c^{\pm}(t-t') &= \exp\left\{\int_0^{b^*} db \int_{-\infty}^{\infty} dv \int_{t'}^{t} d\hat{t}\, P(\hat{t}, v, b) \times [\exp\{\pm i\chi(b, v)\} - 1]\right\} \\ &= \exp\{-(\delta \mp i\Delta)(t-t')\}.\end{aligned} \tag{91}$$

[7] H. M. Foley, Phys. Rev. 69, 616 (1946).

Since it was assumed that

$$P(t,v,b)\,db\,dv=2\pi\rho b db\,|\,v\,|\,W(v)\,dv, \tag{92a}$$

we have

$$\delta=2\pi\rho\int_0^{b^*}db\int_{-\infty}^{\infty}dv\,b\,|\,v\,|\,W(v)[1-\cos\chi(b,v)], \tag{92b}$$

$$\Delta=2\pi\rho\int_0^{b^*}db\int_{-\infty}^{\infty}dv\,b\,|\,v\,|\,W(v)\,\sin\chi(b,v). \tag{92c}$$

Because of our assumption that the phase shifts $\chi(v,b)$ are independent, we can now trivially calculate the other relevant characteristic functions (18) as follows:

$$\begin{aligned}\Gamma_c^{\pm}(t''',t'',t',t)&=\left\langle\exp\left\{-i\int_{t'}^{t}d\hat{t}\times\Delta\omega(\hat{t})\pm i\int_{t'''}^{t''}d\hat{t}\,\Delta\omega(\hat{t})\right\}\right\rangle\\&=\left\langle\exp\left\{-i\int_{t'}^{t}d\hat{t}\,\Delta\omega(\hat{t})\right\}\right\rangle\times\left\langle\exp\left\{\pm i\int_{t'''}^{t''}d\hat{t}\,\Delta\omega(\hat{t})\right\}\right\rangle\\&=\Gamma_c^{-}(t',t)\,\Gamma_c^{\pm}(t''',t'').\end{aligned} \tag{93}$$

As we shall see later, δ is an additive term to the decay constant γ_{ab}, while Δ is a shift in the transition frequency ω.

(c) *Statistical Theory Limit*

In this section we shall consider the effects of the distant collisions whose duration is long compared to T.[8] We assume here that all of the perturbers are stationary with respect to the radiating atom for times comparable to $1/\gamma_{ab}$ and, instead of averaging

$$\exp\left\{\pm i\int_{t'}^{t}d\hat{t}\,\Delta\omega(\hat{t})\right\}$$

over time histories, perform an ensemble average over all possible static configurations of the perturbers. For a particular configuration the effect of the perturbers on the transition frequency is

$$\Delta\omega=\sum_{j=1}^{N}Br_j^{-6}, \tag{94}$$

where N is the total number of perturbers in a large volume V and r_j is the distance of the jth perturber from the radiating atom. For a nearly ideal gas, the atomic positions are uncorrelated, and the ensemble average in the definition of the characteristic functions for distant collisions $\Gamma_d^{\pm}(t',t)$ reduces to an average over a single-particle phase space in the following manner:

$$\begin{aligned}\Gamma_d^{\pm}(\tau')&=\langle\exp\{\pm i\tau'\sum_{j=1}^{N}Br_j^{-6}\}\rangle=\langle\prod_{j=1}^{N}\exp\{\pm i\tau'Br_j^{-6}\}\rangle\\&=\prod_{j=1}^{N}\langle\exp\{\pm i\tau'Br_j^{-6}\}\rangle\\&=(1-\langle1-\exp\{\pm i\tau'Br^{-6}\}\rangle)^N.\end{aligned} \tag{95}$$

By defining the quantity

$$Y^{\pm}(\tau')=\int_{b*}^{r_{\max}}dr\,r^2(1-\exp\{\pm iBr^{-6}\tau'\}), \tag{96}$$

the characteristic function can be written in the form

$$\Gamma_d^{\pm}(\tau')=[1-V^{-1}(4\pi Y^{\pm}(\tau'))]^N. \tag{97}$$

Let us now consider the limit where the volume of the cavity V and the number of perturbers N go to infinity, but the density $\rho=N/V$ remains finite, and write

$$\begin{aligned}\Gamma_d^{\pm}(\tau')&=\lim_{N\to\infty}[1-4\pi\rho Y^{\pm}(\tau')N^{-1}]^N\\&=\exp\{-4\pi\rho Y^{\pm}(\tau')\},\end{aligned} \tag{98}$$

where $Y^{+}(\tau')$ may be evaluated as

$$\begin{aligned}Y^{+}(\tau')&=\int_0^{\infty}dr\,r^2(1-\exp\{+i\tau'Br^{-6}\})\\&=+\tfrac{1}{3}(B\tau')^{1/2}\int_0^{\infty}dx\,(x^{-1/2}\sin x-ix^{-1/2}\cos x)\\&=\tfrac{1}{6}(2\pi B\tau')^{1/2}(1-i)\end{aligned} \tag{99}$$

and $Y^{-}(\tau')$ may be obtained from $Y^{-}(\tau')=(Y^{+}(\tau'))^*$. To avoid ambiguities, we have assumed $B>0$ and $\tau'>0$. By taking the lower limit of the r integration to be zero and not b^* we have included some configurations which have already been treated in the interruption theory limit. Let us defer the discussion of this approximation for the time being, and write the single time characteristic function for the distant collisions in the form

$$\Gamma_d^{+}(\tau')=\exp\{-\tfrac{2}{3}\pi\rho(2\pi B\tau')^{1/2}(1-i)\},\qquad\tau'>0. \tag{100}$$

As opposed to the case encountered in the interruption theory limit where the changes of the phase at different times were statistically independent and we could factor the three-time characteristic function, we must now regard the phase changes at two different times as absolutely correlated because of our assumption of stationary perturbers and write $\Gamma_d^{\pm}(\tau''',\tau'',\tau')$ in

[8] This treatment is adapted from P. W. Anderson and J. D. Talman, Bell Telephone System, Tech. Publ., Monographs **3117**.

the form

$$\Gamma_d^{\pm}(\tau''',\tau'',\tau')=\left\langle \exp\left\{-i\int_0^{\tau'} d\hat{t}\,\Delta\omega(\hat{t}) \pm i\int_0^{\tau'''} d\hat{t}\,\Delta\omega(\hat{t})\right\}\right\rangle$$
$$=\langle\exp\{-i\Delta\omega(\tau'\mp\tau''')\}\rangle$$
$$=\Gamma_d^{-}(\tau'''\mp\tau'). \quad (101)$$

VI. CALCULATION OF THE INTENSITY PROFILE

To sum up the discussion we now turn to the calculation of the intensity profile $I(\omega-\nu)$ from Eq. (30), taking into account both the variations of atomic velocity and the modulation of the transition frequency. For that purpose, we must evaluate the following integrals:

$$\mathfrak{J}(\mu)=iKu\int_0^\infty d\tau'\exp\{-\mu\tau'\}\Delta(\tau')\Gamma_c^{-}(\tau')\Gamma_d^{-}(\tau'), \quad (102)$$

$$\mathfrak{J}^{\pm}(\mu_1,\mu_2)=iKu\gamma_a\gamma_b\sum_{\alpha=a,b}\int_0^\infty d\tau'\int_0^\infty d\tau''\int_0^\infty d\tau''' \times\exp\{-\mu_1\tau'-\gamma_\alpha\tau''-\mu_2\tau'''\} \times\Delta(\tau''',\tau'',\tau')\Gamma_c^{\pm}(\tau''',\tau'',\tau') \times\Gamma_d^{\pm}(\tau''',\tau'',\tau'). \quad (103)$$

It is useful to make a Fourier analysis of the characteristic function $\Gamma_d^{+}(\tau')$ in the form

$$\Gamma_d^{+}(\tau')=\int_{-\infty}^{\infty} d\Delta\omega\exp\{i\Delta\omega\tau'\}P(\Delta\omega) \quad (104)$$

with Fourier transform

$$P(\Delta\omega)=(2\pi)^{-1}\int_{-\infty}^{\infty} d\tau'\exp\{-i\Delta\omega\tau'\}\Gamma_d^{+}(\tau'), \quad (105)$$

where $\Gamma_d^{+}(-\tau')=(\Gamma_d^{+}(+\tau'))^*$ for $\tau'>0$. By making use of Eqs. (101) and (104), Eqs. (102) and (103) may be rewritten as

$$\mathfrak{J}(\mu)=\int_{-\infty}^{\infty} d\Delta\omega\,\mathfrak{J}_d(\mu+i\Delta\omega)P(\Delta\omega), \quad (106)$$

$$\mathfrak{J}^{\pm}(\mu_1,\mu_2)=\int_{-\infty}^{\infty} d\Delta\omega\,\mathfrak{J}_d^{\pm}(\mu_1+i\Delta\omega,\mu_2\mp i\Delta\omega)P(\Delta\omega), \quad (107)$$

where $\mathfrak{J}_d(\mu)$ and $\mathfrak{J}_d^{\pm}(\mu_1,\mu_2)$ are defined by the equations

$$\mathfrak{J}_d(\mu)=iKu\int_0^\infty d\tau'\exp\{-\mu\tau'\}\Delta(\tau')\Gamma_c^{-}(\tau'), \quad (108)$$

$$\mathfrak{J}_d^{\pm}(\mu_1,\mu_2)=iKu\gamma_a\gamma_b\sum_{\alpha=a,b}\int_0^\infty d\tau'\int_0^\infty d\tau''\int_0^\infty d\tau''' \times\exp\{-\mu_1\tau'-\gamma_\alpha\tau''-\mu_2\tau'''\} \times\Delta(\tau''',\tau'',\tau')\Gamma_c^{\pm}(\tau''',\tau'',\tau'). \quad (109)$$

Since $P(\Delta\omega)$ is the Fourier transform of a characteristic function, it is a probability distribution and hence Eqs. (106) and (107) may be interpreted as averaging the functions $\mathfrak{J}_d(\mu)$, $\mathfrak{J}_d^{\pm}(\mu_1,\mu_2)$ over changes in the transition frequency according to the distribution $P(\Delta\omega)$.

With the help of Eqs. (91) and (93) we now rewrite $\mathfrak{J}_d(\mu)$ and $\mathfrak{J}_d^{\pm}(\mu_1,\mu_2)$ in the forms

$$\mathfrak{J}_d(\mu)=iKu\int_0^\infty d\tau'\exp\{-\bar{\mu}\tau'\}\Delta(\tau'), \quad (110)$$

$$\mathfrak{J}_d^{\pm}(\mu_1,\mu_2)=iKu\gamma_a\gamma_b\sum_{\alpha=a,b}\int_0^\infty d\tau'\int_0^\infty d\tau''\int_0^\infty d\tau''' \times\exp\{-\bar{\mu}_1\tau'-\gamma_\alpha\tau''-\bar{\mu}_2^{\pm}\tau'''\} \times\Delta(\tau''',\tau'',\tau'), \quad (111)$$

where

$$\bar{\mu}=\mu+\delta+i\Delta=\gamma_{ab}+\delta+i(\omega-\nu+\Delta),$$
$$\bar{\mu}_1=\mu_1+\delta+i\Delta,$$
$$\bar{\mu}_2^{\pm}=\mu_2+\delta\mp i\Delta. \quad (112)$$

We note that the $\mathfrak{J}_d$ functions (110) and (111) can very easily be calculated by repeating the derivation in Sec. IV(*b*) with μ replaced by $\bar{\mu}$, μ_1 by $\bar{\mu}_1$, and μ_2 by $\bar{\mu}_2^{\pm}$. Then, with the approximations made in the derivation of Eq. (74),

$$\mathrm{Im}\mathfrak{J}_d(\mu+i\Delta\omega)=\pi^{1/2}[\exp\{-(\omega-\nu+\Delta+\Delta\omega)^2/(Ku)^2\}+\pi^{1/2}\epsilon], \quad (113)$$

$$\mathrm{Im}\mathfrak{J}_d^{-}(\mu+i\Delta\omega,\mu+i\Delta\omega)$$
$$=2\pi^{1/2}[(\gamma_{ab}'\gamma_a\gamma_b)/(\bar{\gamma}_{ab}'\gamma_a'\gamma_b')]\{\mathfrak{L}_1(\omega-\nu+\Delta+\Delta\omega) \times[\exp\{-(\omega-\nu+\Delta+\Delta\omega)^2/(Ku)^2\}+2\pi^{1/2}\epsilon] +\pi^{1/2}(\bar{\gamma}_{ab}'/Ku)[(\gamma_{ab}\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)-1]\}, \quad (114)$$

$$\mathrm{Im}\mathfrak{J}_d^{+}(\mu+i\Delta\omega,\mu^*-i\Delta\omega)$$
$$=2\pi^{1/2}[(\gamma_{ab}'\gamma_a\gamma_b)/(\bar{\gamma}_{ab}'\gamma_a'\gamma_b')] \times\{[\exp\{-(\omega-\nu+\Delta+\Delta\omega)^2/(Ku)^2\}+2\pi^{1/2}\epsilon] +\pi^{1/2}(\bar{\gamma}_{ab}'/Ku)[(\gamma_{ab}\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)-1]\}, \quad (115)$$

where γ_a', γ_b', and γ_{ab}' are given by Eq. (72),

$$\bar{\gamma}_{ab}'=\gamma_{ab}+\delta+T^{-1}, \quad (116)$$

and

$$\mathfrak{L}_1(\omega-\nu+\Delta+\Delta\omega)$$
$$=(\bar{\gamma}_{ab}')^2[(\bar{\gamma}_{ab}')^2+(\omega-\nu+\Delta+\Delta\omega)^2]^{-1}. \quad (117)$$

The intensity profile (30) can be written approximately as

$$I(\omega-\nu)=\bar{A}\exp\{(\omega-\nu+\Delta)^2/(Ku)^2\}\int_{-\infty}^{\infty}d\Delta\omega\, P(\Delta\omega)$$
$$\times[\exp\{-(\omega-\nu+\Delta+\Delta\omega)^2/(Ku)^2\}-\mathfrak{N}^{-1}]$$
$$\times\Bigg[\int_{-\infty}^{\infty}d\Delta\omega\, P(\Delta\omega)\{1+\mathfrak{L}_1(\omega-\nu+\Delta+\Delta\omega)$$
$$+2\pi^{1/2}(\bar{\gamma}_{ab}'/Ku)$$
$$\times[(\gamma_{ab}\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)-1]\}\Bigg]^{-1}, \quad (118)$$

where

$$\bar{A}=8[(\bar{\gamma}_{ab}\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)](1+2\pi^{1/2}\epsilon). \quad (119)$$

To complete the discussion we must evaluate the distribution $P(\Delta\omega)$. By taking the Fourier transform of Eq. (100) we are led to the expression

$$P(\Delta\omega)=(2\pi)^{-1/2}\Gamma(\Delta\omega)^{-3/2}\exp\{-\tfrac{1}{2}\Gamma^2/\Delta\omega\}, \quad \text{for } \Delta\omega>0$$
$$=0, \quad \text{for } \Delta\omega<0 \quad (120)$$

where

$$\Gamma=\tfrac{2}{3}\pi\rho(2\pi B)^{1/2}. \quad (120')$$

The maximum of this unsymmetric distribution is at

$$(\Delta\omega_m)=\tfrac{1}{3}\Gamma^2=(8/27)\pi^3\rho^2B. \quad (121)$$

We note that $\hbar\rho^2B$ is just the interaction energy of the radiating atom with a nearest neighbor whose separation is $\rho^{-1/3}$. Hence, the most likely configuration is that whose total effect may be replaced by the interaction of a single atom at a distance slightly less than $\rho^{1/3}$. Since a typical value of ρ^2B at the pressures usually encountered in experiments (1 or 2 Torr) is about 10 kHz (much less than γ_{ab}) we are assured that the integration over $\Delta\omega$ in Eq. (118) will change the function $I(\omega-\nu)$ only slightly. In fact the smallness of $\Delta\omega_m/\gamma_{ab}$ warrants the expansion[9] of the integrals

$$i_1(a,Ku)=\int_{-\infty}^{\infty}d\Delta\omega\, P(\Delta\omega)\exp\{-(a+\Delta\omega)^2/(Ku)^2\}, \quad (122)$$

$$i_2(a,\gamma_{ab})=\int_{-\infty}^{\infty}d\Delta\omega\, P(\Delta\omega)\mathfrak{L}(a+\Delta\omega) \quad (123)$$

in powers of $(\Gamma)/(\gamma_{ab})^{1/2}$ and $(\Gamma)/(Ku)^{1/2}$, respectively. We find

$$i_1(a,Ku)=\exp\{-a^2/(Ku)^2\}$$
$$-(1.23)(2)^{1/2}(\pi)^{-1/2}(\Gamma^2/Ku)^{1/2}$$
$$\times[1+1.479(a/Ku)] \quad (122')$$

[9] A method for carrying out such an expansion is given in Appendix III.

and

$$i_2(a,\gamma)=\gamma^2(\gamma^2+a^2)^{-1}-\tfrac{1}{2}\pi^{1/2}(\Gamma^2/\gamma)^{1/2}$$
$$\times\text{Re}[(1-i)\{\gamma(\gamma-ia)^{-1}\}^{3/2}]. \quad (123')$$

Then

$$I(\omega-\nu)=\bar{A}\exp\{(\omega-\nu+\Delta)^2\}[i_1(\omega-\nu+\Delta,Ku)-\mathfrak{N}^{-1}]$$
$$\times[1+i_2(\omega-\nu+\Delta,\bar{\gamma}_{ab}')+2\pi^{1/2}(\bar{\gamma}_{ab}'/Ku)$$
$$\times\{(\gamma_{ab}\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)-1\}]^{-1}. \quad (124)$$

It is clear that the "dip" shape is a function of pressure because it depends on the pressure-dependent parameters T^{-1}, δ, Δ, and Γ. An attempt to compare Eq. (124) with experiment will be made in the next section.

VII. COMPARISON WITH EXPERIMENTS

Experimental studies of a pressure-dependent intensity profile for the case of single-mode oscillation have been carried out by Szöke and Javan,[3] Smith,[10] and Cordover.[11] Similar observations for two-mode oscillation have been made by Fork and Pollack,[12] but our theory has not yet been developed to handle this case, and we will therefore discuss only the case of single-mode operation.

The intensity curves of Szöke and Javan and of Cordover show some signs of asymmetry. However, the asymmetry is small, and they have fitted their experimental tracings with a nearly symmetric intensity function $I(\omega-\nu)$. In our theory, an asymmetry can only come from the effects of distant collisions, and accordingly we dispense with averaging over the asymmetric distribution $P(\Delta\omega)$ in Eq. (118). This approximation not only simplifies our expression for the intensity profile but also corresponds to the fact that these effects are indeed small as we shall show later. The intensity function $I(\omega-\nu)$ can be written in a form equivalent to that used first by Szöke and Javan,

$$I(\omega-\nu)=A_1[1-\mathfrak{N}^{-1}\exp\{(\omega-\nu+\Delta)^2/(Ku)^2\}]$$
$$\times[1+(\gamma_2/\gamma_1)\mathfrak{L}_1(\omega-\nu+\Delta)]^{-1}, \quad (125)$$

where

$$A_1=8[(\bar{\gamma}_{ab}'\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)](\gamma_2/\gamma_1)(1+2\pi^{1/2}\epsilon)^{-1}, \quad (126)$$

$$\gamma_1=\bar{\gamma}_{ab}'=\gamma_{ab}+G_{ab}P+T^{-1}+\delta, \quad (127)$$

$$\gamma_2=\bar{\gamma}_{ab}'(1+\theta)^{-1}, \quad (128a)$$

where

$$\theta=2\pi^{1/2}(\bar{\gamma}_{ab}'/Ku)\{[(\gamma_{ab}\gamma_a'\gamma_b')/(\gamma_{ab}'\gamma_a\gamma_b)]-1\}^{-1}, \quad (128b)$$

[10] P. W. Smith, J. Appl. Phys. **37**, 2089 (1966).
[11] R. H. Cordover, thesis, M.I.T., 1967 (unpublished). We are indebted to Dr. Cordover and Professor Javan for making this material available to us before publication.
[12] R. L. Fork and M. A. Pollack, Phys. Rev. **139**, A1408 (1965).

with

$$\mathcal{L}_1(\omega-\nu+\Delta)=\gamma_1^2[\gamma_1^2+(\omega-\nu+\Delta)^2]^{-1}, \quad (129)$$

and

$$\gamma_a'=\gamma_a+G_aP+T^{-1},$$
$$\gamma_b'=\gamma_b+G_bP+T^{-1},$$
$$\gamma_{ab}'=\gamma_{ab}+G_{ab}P+T^{-1}. \quad (130)$$

The parameters δ, Δ, T are defined by Eqs. (92b) and (92c) and Eq. (55), and the constants G_a, G_b, G_{ab} are introduced for reasons mentioned in Sec. II.

Equation (125) for the intensity profile looks very similar to that obtained in the collisionless theory [see Eq. (34)]. Apart from a different multiplicative factor A_1 (which would be very hard to detect experimentally) there are three main differences: (1) The curve $I(\omega-\nu)$ is shifted in frequency by an amount Δ associated with the phase shifting (close) collisions of Sec. IV; (2) the Lorentzian term in the denominator has an increased width parameter γ_1; and (3) the size of the Lorentzian term is reduced through multiplication by a factor (γ_2/γ_1). The immediately noticable consequence of changes (2) and (3) is that the central tuning dip becomes less pronounced.

It is interesting to consider the condition under which $\mathrm{I}(\omega-\nu)$ should have a central tuning dip. By expanding (125) in a Taylor series in powers of $(\omega-\nu+\Delta)$ we obtain the condition on the relative excitation

$$\mathfrak{N}>1+(\gamma_1/Ku)^2[1+(\gamma_1/\gamma_2)], \quad (131)$$

in contrast to the prediction of the collisionless theory which gives

$$\mathfrak{N}>1+2(\gamma_{ab}/Ku)^2. \quad (132)$$

Since γ_1 and γ_2 are increasing functions of pressure, we see that as the pressure increases the dip will be found only at higher excitation.

Szöke and Javan and Cordover analyzed their data by a semiempirical equation of the same form as Eq. (125) and $\Delta=0$. They have taken the damping constants γ_1 and γ_2 to be linear functions of pressure, writing in effect

$$\gamma_1=\gamma_{ab}+h+s, \quad (133)$$

$$\gamma_2=\gamma_{ab}+h, \quad (134)$$

where h and s are supposed to describe "hard" and "soft" collisions, respectively. In their terminology the "soft" collisions are the ones which give the radiating atom a zig-zag path due to a number of small-angle collisions, and "hard" collisions result in a sudden and complete interruption of the radiation process. It can be seen by comparing Eqs. (133), (134) and Eqs. (127), (128) that our theory is more explicit about the expressions for γ_1 and γ_2, and in addition predicts that there could be a nonlinear dependence of γ_2 on pressure, although the importance of the departure from linearity remains to be determined.

By comparing Eqs. (127) and (128) with Eqs. (133) and (134), we see that $h+s$ could be identified with the quantity $\delta+(1/T)$, while the contribution of soft collisions might be taken to be $s=\theta\gamma_2$, where γ_2 and θ are given by (128a) and (128b). In view of the peculiar form and nonlinear pressure dependence of this expression, it does not seem to us that the division of collisions into the hard and soft categories is particularly significant.

Cordover[11] worked with He–Ne lasers at 0.6328μ, $(3s_2-2p_4)$, having a He–Ne mixtures of 8:1 and 5:1. We will only consider the fitting of his data for the 8:1 ratio for which the total pressure P ranged between 0.9 and 2.0 Torr. He found that γ_1 and γ_2 in MHz were given by[13]

$$\gamma_1=13+g_1P, \quad (135)$$

$$\gamma_2=13+g_2P, \quad (136)$$

where $g_1=58$ MHz Torr^{-1} and $g_2=22$ MHz Torr^{-1}.

In order to test our theory we need to have values for such quantities as γ_a, γ_b, γ_{ab}, T, δ, Ku and various G's which enter into Eq. (125). Unfortunately, some of these are not very well known, but as will be seen below we will manage to make a fairly plausible assignment of their values. For the Doppler width parameter we take the value $Ku=855$ MHz which is wavelength scaled from the value 470 MHz used earlier by Szöke and Javan. The radiative decay constants should be determined from measured lifetimes. It appears, however, that the lifetime of the upper laser level has not been measured. Therefore, we take the extrapolated value $\gamma_{ab}=13$ MHz from the experiment of Cordover, and by using Bennett and Kindlmann's measurement[14] of decay rate $\gamma_b=8.30$ MHz for the lower level, we infer that

$$\gamma_a=2\gamma_{ab}-\gamma_b=17.7 \text{ MHz}. \quad (137)$$

We note in passing that the partial decay rate of the $3s_2$ state to one of the $2p$ states is only a small fraction of the total decay rate γ_a obtained above. It seems that the dominant mode of decay from the state $3s_2$ is the optical transition to the ground state. The phenomenon of resonance trapping therefore plays an important role in a measurement of the partial decay rate to the ground state, and would reduce the apparent value of γ_a. However, in our model, if an excited atom A decays to the ground state by emitting radiation (not at the laser frequency), it is discarded. If a distant atom B absorbs this radiation, we consider the process as contributing to the excitation rate of B, and neglect the small correlations between the decay of A and the

[13] It should be remembered that following the convention in Ref. 1, a numerical value stated as $\gamma=10$ MHz really means $\gamma=2\pi\times10^7$ sec^{-1}.

[14] W. R. Bennett, Jr., and P. J. Kindlmann, Phys. Rev. **149**, 38 (1966).

excitation of B. Hence the parameter γ_a which has been determined in (137) should be the decay rate of an isolated atom, which unfortunately has not yet been measured.

As mentioned in Sec. II we are postponing discussion of nonradiative resonant interchanges of excitation which lead to an r^{-3} van der Waals interaction. In some approximation, the effect of these could be described by adding further terms of the form $G_\alpha P$ to each of the decay constants γ_α. We will first try to fit the experimental data of Cordover without including any such terms in our formulas.

We now turn to the determination of the parameters T and δ. Unfortunately, the calculation of their values from first principles would be rather difficult since it would involve the determination of the van der Waals coefficients for the excited states of Ne. It is clear, however, from their definitions, Eqs. (92b) and (55), that δ and $(1/T)$ are linear functions of pressure. Hence, we may attempt to fit the experimental points of Cordover by writing

$$T^{-1}=g_T P_{\mathrm{He}}, \qquad (138)$$

$$\delta=g_\delta P_{\mathrm{He}}. \qquad (139)$$

Since our expression for γ_1 in Eq. (127) is now exactly of the form displayed by Eq. (135) we may conclude that the combination

$$g_\delta+g_T=58.0 \text{ MHz Torr}^{-1}. \qquad (140)$$

We now have to determine T^{-1} and δ separately from the knowledge of γ_2. However, unless Eq. (128) can be linearized in the pressure region where the experimental points are taken, a direct comparison between Eq. (128) and Eq. (136) is not possible. On the other hand one may try to fit experimental points to Eq. (128). In doing that, we determine T by demanding that Eq. (128) give an approximate fit to experimentally observed values of γ_2 at pressures near 2 Torr. Accordingly, we find

$$g_T=17.0 \text{ MHz Torr}^{-1},$$

$$g_\delta=41.0 \text{ MHz Torr}^{-1}. \qquad (141)$$

Plots of γ_1 and γ_2 as functions of pressure are shown in Fig. 1. Within the limits of experimental errors, our nonlinear expression Eq. (128) fits the experimental points as well as a straight line. Clearly, more experiments with wider ranges of pressure would be helpful in an attempt to observe the more strongly nonlinear portions of the γ_2-versus-pressure curve. It is interesting to note that in the present theory γ_2 depends on the Doppler linewidth Ku, hence experiments on other Ne transitions should be used to further test the theory.

Having obtained δ as a function of pressure, we may now predict a shift for the center of the intensity profile. It has been shown by Foley[7] that for a r^{-6} interaction potential, the ratio of shift Δ to broadening δ is independent of the van der Waals coefficient, and is given by

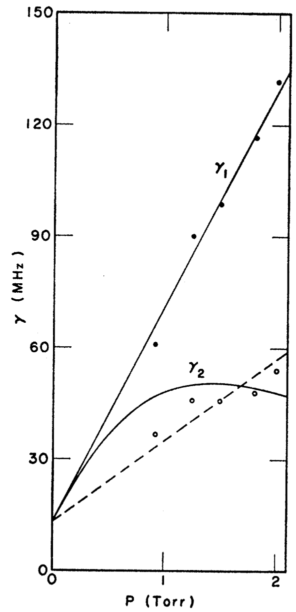

FIG. 1. Plot of damping constants γ_1 and γ_2 against pressure based on Eqs. (127) and (128). The required numerical values of g_T [Eq. (138)] and g_δ [Eq. (139)] are determined from data of Cordover (Ref. 11) for a helium-neon laser operating at 0.63μ. The experimental points are indicated by solid and open circles. Also shown (dashed line) is the linear relation for γ_2 of the Szöke–Javan theory.

$$|\Delta|/\delta=0.726. \qquad (142)$$

Consequently, in an experiment like that of Szöke and Javan one should expect a shift Δ of

$$\Delta/P=29.8 \text{ MHz Torr}^{-1}. \qquad (143)$$

This is a sizeable shift and should be readily detectable.[15] If no shift is found or the observed shift is much less than 29.8 MHz Torr^{-1}, we must conclude that the increase of γ_1 with increasing pressure cannot entirely be caused by collisions which are described by $\delta+(1/T)$, but rather, at least in part, it should be attributed to the inelastic collisions described by the phenomenological constants G_a, G_b, G_{ab}. We can then always assign values to these G's which will reduce the shift to the desired size. A further test of the theory should involve an independent experimental check of the cross sections corresponding to the values of the G's obtained above.

Having decided on a value for δ, one is able to calculate the most likely shift caused by distant collisions. If one carries out the averaging procedure indicated in Eq. (92a), the broadening δ may be written as

$$\delta=4.25(u_{\mathrm{He}})^{3/5}(B)^{2/5}\rho. \qquad (144)$$

[15] Shifts of this order of magnitude have recently been observed [e.g., A. L. Bloom and D. L. Wright, Appl. Opt. **5**, 1528 (1966) and A. D. White, Appl. Phys. Letters **10**, 24 (1967)] but the experimental situation is still somewhat confused. The sign of our frequency shift Δ depends on the unknown sign of the van der Waals coefficient B.

Solving Eq. (144) for the van der Waals coefficient B under the assumptions $\delta=41.0\times(2\pi)\times10^6$ sec^{-1}, $\rho=2.59\times10^{16}$ cm^{-3} (pressure=1 Torr and $T=373°$K), $u_{He}=1.208\times10^5$ cm sec^{-1}, one finds $B=6.32\times10^{-30}$ cm^6 sec^{-1}. The corresponding most probable frequency shift then becomes $\Delta\omega_m=3.89\times10^4$ sec^{-1} or 6.2 kHz in ordinary frequency units. This is the basis for our earlier statement about $\Delta\omega_m$ which led to the expansion (124) of (118) in powers of $(\Gamma/\bar{\gamma}_{ab}^{1/2})$.

As mentioned before, the intensity curves of Cordover do show some asymmetry. The only source of asymmetry in our theory is to be found in the statistical-theory limit of Sec. V(c). One may note that there is a connection between the frequency shift Δ of Sec. V(b) and the asymmetry of Sec. V(c). It is unfortunate that we do not know the value of Δ more directly from the observation of a beat note frequency, as well as the value rather indirectly inferred from the analysis of Eqs. (133) and (136). (Note: Our Δ should not be confused with the Δ symbol used by Cordover.)

With the numerical values for the various parameters as determined in the text, the two peaks of the tuning curve can differ in height by a few percent at pressure 1 Torr. The asymmetry terms vary as the square of the pressure.

The asymmetry effects increase rapidly as one goes into the wings of the atomic response functions α and β. In the studies of Fork and Pollack[12] on the effects of pressure on two-mode operation there was definite evidence for asymmetry, and it is quite possible that an extended theory could fit their data with our value for the van der Waals constant B.

Should a larger asymmetry be found there would be a further indication of the need for an extension of our theory to include resonant interactions.

VIII. DISCUSSION

A general expression for the effect of collisions on the single-mode intensity of a gas laser was given in Eq. (30). A similar general expression for the frequency could easily be written down by working from Eq. (3) instead of Eq. (4). These general expressions were evaluated in an approximate but plausible manner. We took into account two types of interactions (a) short-range nonadiabatic collisions which are described by adding terms $G_\alpha P$ to the radiative damping constants γ_α, and (b) longer-range interactions of van der Waals type. The latter produced three distinct effects which were discussed in Secs. IV–VI. The first of these involved the deflections experienced by an active atom which lead to an irregular amplitude modulation of the optical field seen by it, and eventually caused a modification in the output of the laser. A full discussion of this effect would require the solution of an integral Eq. (48) for a realistic collision kernel. We have contented ourselves with a solution using the simplest form of collision kernel, Eq. (55), which leads to expressions dependent on one parameter T, the collision time.

The second effect of the van der Waals interaction is produced by the frequency modulation $\Delta\omega(t)$ in binary collisions. Here again the general expressions, Eqs. (17) and (18), are available, but we have evaluated them using the approximation that each collision leads to a phase shift $\chi(v, b)$, and that such collisions occur in a random manner. In addition to the collision time T, we find two parameters, δ and Δ, related to each other by Eq. (142), entering the equations. The first leads to a broadening and the second to a displacement in frequency of the intensity curve $I(\omega-\Omega)$.

The third effect of the van der Waals interaction is due to the combined action of many distant atoms and was treated in a static statistical approximation in Sec. VI. Here we found an asymmetrical broadening of the intensity profile which is most noticeable in the wings of the curve.

As an illustration of our theory, in Sec. VII we have analyzed some measurement of Cordover.[11] The agreement was quite satisfactory in view (1) of the simplifying approximations of our theory, (2) the uncertain experimental values for γ_a and γ_b, and (3) the fact that we did not make use of the extra degrees of freedom afforded by the possible terms $G_\alpha P$ which could be added to the radiative decay constants γ_α.

The investigation of pressure effects on laser operation can provide a powerful technique for the study of atomic interactions. In the past, studies of collision-broadened spectral lines could only be carried out at high pressures, where the pressure-dependent distortions were not masked by Doppler broadening, or else one was restricted to the study of line shapes far out in the wings where a Lorentzian dependence prevailed. We hope that this paper will stimulate more experimental work in this interesting and heretofore inaccessible low-pressure range. This would be desirable not only for the increased technical possibilities for laser development but also for the insight which it affords into the interactions of the atoms concerned in the laser action.

In later papers, it is planned to extend the theory of pressure effects by considering the deflecting collisions more realistically and by allowing resonant interactions. The cases of Zeeman and ring lasers, as well as of multimode operations, are also being treated.

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APPENDIX I

A derivation of Eq. (52) is given in this Appendix. It follows from elementary probability theory that the conditional probability density of Eq. (52) obeys the equation

$$P(\mathbf{v}''',\mathbf{r}''',t'''\mid \mathbf{v}'',\mathbf{r}'',t'';\mathbf{v}',\mathbf{r}',t';\mathbf{v},\mathbf{r},t)$$
$$=P(\mathbf{v}''',\mathbf{r}''',t'''\mid \mathbf{v}'',\mathbf{r}'',t'';\mathbf{v}',\mathbf{r}',t')$$
$$\times P(\mathbf{v}''',\mathbf{r}''',t''';\mathbf{v}'',\mathbf{r}'',t'';\mathbf{v}',\mathbf{r}',t'\mid \mathbf{v},\mathbf{r},t),\quad \text{(I1)}$$

using a notation where $P(a\mid b;c;d)$ is the probability that state a implies subsequent states b, c, and d while $P(a;b;c\mid d)$ gives the probability that states a, b, and c taken together imply a later state d. If the scattering process is Markoffian with respect to variables $\mathbf{r}$ and $\mathbf{v}$, it follows that the second P function on the right-hand side of (144) depends only on $\mathbf{v}'$, $\mathbf{r}'$, t' but not on the earlier values $\mathbf{v}'''$, $\mathbf{r}'''$, t''' and $\mathbf{v}''$, $\mathbf{r}''$, t'' and may be written as $P(\mathbf{v}',\mathbf{r}',t'\mid \mathbf{v},\mathbf{r},t)$. Application of similar arguments to the first P function on the right-hand side of (145) gives

$$P(\mathbf{v}''',\mathbf{r}''',t'''\mid \mathbf{v}'',\mathbf{r}'',t'';\mathbf{v}',\mathbf{r}',t')$$
$$=P(\mathbf{v}''',\mathbf{r}''',t'''\mid \mathbf{v}'',\mathbf{r}'',t'')$$
$$\times P(\mathbf{v}''',\mathbf{r}''',t''';\mathbf{v}'',\mathbf{r}'',t''\mid \mathbf{v}',\mathbf{r}',t')$$
$$=P(\mathbf{v}''',\mathbf{r}''',t'''\mid \mathbf{v}'',\mathbf{r}'',t'')\,P(\mathbf{v}'',\mathbf{r}'',t''\mid \mathbf{v}',\mathbf{r}',t').\quad \text{(I2)}$$

The desired result (52) follows by combining (145) and (146).

APPENDIX II

For evaluation of the first term of (68) we must deal with integrals of the form

$$X_{\kappa\kappa'}(v''',v;\tau''',\tau')=\int_{-\infty}^{\infty}dv''\,G_\kappa(v''',0\mid v'',\tau''')G_{\kappa'}(v'',0\mid v,\tau').\quad (69')$$

This can be done most readily using the Boltzmann Eq. (56) which, assuming stationarity, becomes

$$(\partial/\partial\tau')G_{\kappa'}(v'',0\mid v,\tau')=(i\kappa'Kv-T^{-1})G_{\kappa'}(v'',0\mid v,\tau')+(\pi^{1/2}uT)^{-1}\exp\{-(v/u)^2\}\int_{-\infty}^{\infty}d\bar{v}\,G_{\kappa'}(v'',0\mid \bar{v},\tau').\quad \text{(II1)}$$

It follows from this that the τ' dependence of (69′) is determined by the differential equation

$$(\partial/\partial\tau')X_{\kappa\kappa'}(v''',v;\tau''',\tau')=(i\kappa'Kv-T^{-1})X_{\kappa\kappa'}(v''',v;\tau''',\tau')+(\pi^{1/2}uT)^{-1}\exp\{-(v/u)^2\}\int_{-\infty}^{\infty}d\bar{v}\,X_{\kappa\kappa'}(v''',\bar{v};\tau''',\tau').\quad \text{(II2)}$$

We see from (57) that this equation is to be solved subject to the (initial) condition at $\tau'=0$:

$$X_{\kappa\kappa'}(v''',v;\tau''',0)=G_\kappa(v''',0\mid v,\tau''').\quad \text{(II3)}$$

Formal integration of (II2) then gives

$$X_{\kappa\kappa'}(v''',v;\tau''',\tau')=\exp\{(i\kappa'Kv-T^{-1})\tau'\}G_\kappa(v''',0\mid v,\tau''')+(\pi^{1/2}uT)^{-1}\exp\{-(v/u)^2\}\int_0^{\tau'}d\hat{t}\times\exp[(i\kappa'Kv-T^{-1})(\tau'-\hat{t})]\times\int_{-\infty}^{\infty}d\bar{v}\,X_{\kappa\kappa'}(v''',\bar{v};\tau''',\hat{t}).\quad \text{(II4)}$$

Inserting this into (69), we get an equation for $D_{\kappa\kappa'}(\tau''',\tau')$,

$$D_{\kappa\kappa'}(\tau''',\tau')=(\pi^{1/2}u)^{-1}\int_{-\infty}^{\infty}dv''\exp\{-(v'''/u)^2\}\times\int_{-\infty}^{\infty}dv\exp\{(i\kappa'Kv-T^{-1})\tau'\}\times G_\kappa(v''',0\mid v,\tau''')+(1/T)\int_0^{\tau'}d\hat{t}\times\exp\{-\tfrac{1}{4}[\kappa'Ku(\tau'-\hat{t})]^2-(\tau'-\hat{t})T^{-1}\}D_{\kappa\kappa'}(\tau''',\hat{t}).\quad \text{(II5)}$$

We then substitute (57) into (II5) to obtain

$$D_{\kappa\kappa'}(\tau''',\tau')=(\pi^{1/2}u)^{-1}\int_{-\infty}^{\infty}dv'''\exp[-(v'''/u)^2]\times\exp[-(\tau'+\tau''')T^{-1}+iKv'''(\kappa'\tau'+\kappa\tau''')]+(\pi^{1/2}uT)^{-1}\int_0^{\tau'''}d\bar{\tau}\times\int_{-\infty}^{\infty}dv\exp[-(v/u)^2+iKv(\kappa'\tau'+\kappa\tau'''-\kappa\bar{\tau})-(\tau'+\tau'''-\bar{\tau})T^{-1}]\times\left\{(\pi^{1/2}u)^{-1}\int_{-\infty}^{\infty}dv'''\exp[-(v'''/u)^2]\times\int_{-\infty}^{\infty}d\bar{v}\,G_\kappa(v''',0\mid \bar{v},\bar{\tau})\right\}+(1/T)\int_0^{\tau'}d\bar{\tau}\times\exp[-\tfrac{1}{4}\{\kappa'Kv(\tau'-\bar{\tau})\}^2-(\tau'-\bar{\tau})T^{-1}]D_{\kappa\kappa'}(\tau''',\bar{\tau}).\quad \text{(II6)}$$

Noting that from (43) it follows that the expression in the curly brackets in the second term of (II6) may be replaced by the single time correlation function

$\Delta^\kappa(\bar{\tau})$, we obtain an integral equation for $D_{\kappa\kappa'}(\tau''', \tau')$,

$$D_{\kappa\kappa'}(\tau''',\tau')=\exp[-(\tau'+\tau''')T^{-1}-\tfrac{1}{4}(Ku)^2(\kappa'\tau'+\kappa\tau''')^2]+(1/T)\int_0^{\tau'''}d\bar{\tau}\times\exp[-\tfrac{1}{4}(Ku)^2(\kappa'\tau'+\kappa\tau'''-\kappa\bar{\tau})^2-(\tau+\tau'''-\bar{\tau})T^{-1}]\Delta_\kappa(\bar{\tau})+(1/T)\times\int_0^{\tau'}d\hat{t}\exp[-\tfrac{1}{4}(\kappa'Ku)^2(\tau'-\hat{t})^2-(\tau'-\hat{t})T^{-1}]D_{\kappa\kappa'}(\tau''',\hat{t}),\quad\text{(II7)}$$

which is a generalization of (60).

For $\kappa=\kappa'=\pm1$, Eq. (II7) becomes, after a change of integration variable,

$$D_{\pm1\pm1}(\tau''',\tau')=\exp[-(\tau'+\tau''')T^{-1}-\tfrac{1}{4}\{Ku(\tau'+\tau''')\}^2]+(1/T)\int_{\tau'}^{\tau'+\tau'''}d\hat{t}\times\exp[-\tfrac{1}{4}(Ku\hat{t})^2-\hat{t}T^{-1}]\Delta^\pm(\tau'+\tau''-\hat{t})+(1/T)\int_0^{\tau'}d\hat{t}\exp[-\tfrac{1}{4}(Ku\hat{t})^2-\hat{t}T^{-1}]\times D_{\pm1\pm1}(\tau''',\tau'-\hat{t}).\quad\text{(II8)}$$

It follows easily from Eq. (60) that

$$D_{\pm1\pm1}(\tau''',\tau')\equiv\Delta^\pm(\tau'+\tau''')\quad\text{(II9)}$$

is a solution of (II7).

It is more difficult to determine the solution of (II7) when $\kappa=-1$, $\kappa'=+1$. We denote this by

$$D^\mp(\tau''',\tau')\equiv D_{-1+1}(\tau''',\tau')=D_{+1-1}(\tau',\tau''').\quad\text{(II10)}$$

Fortunately, to evaluate (28) we do not need (70″) directly, but rather its double Laplace transform

$$S(\mu_1,\mu_2)=iKu\int_0^\infty d\tau'\int_0^\infty d\tau'''\times\exp\{-\mu_1\tau'-\mu_2\tau'''\}D^\mp(\tau''',\tau').\quad\text{(II11)}$$

Corresponding to the three terms of (II7), we may write (II11) in the form

$$S(\mu_1,\mu_2)=S_{\rm I}+S_{\rm II}+S_{\rm III}.\quad\text{(II12)}$$

We then have

$$S_{\rm I}=iKu\int_0^\infty d\tau'\int_0^\infty d\tau'''\exp[-(\mu_1+T^{-1})\tau'-(\mu_2+T^{-1})\tau'''-\tfrac{1}{4}(Ku)^2(\tau'-\tau''')^2].\quad\text{(II13)}$$

Such integrals can be evaluated by introducing new variables of integration in the τ', τ''' plane, giving

$$S_{\rm I}=[\mu_1'+\mu_2']^{-1}[Z(\mu_1')+Z(\mu_2')],\quad\text{(II14)}$$

where

$$\mu_1'=\mu_1+T^{-1},\qquad \mu_2'=\mu_2+T^{-1}\quad\text{(II15)}$$

as in Eq. (63). The second term is

$$S_{\rm II}=iKuT^{-1}\int_0^\infty d\tau'\int_0^\infty d\tau'''\int_0^{\tau'''}d\hat{t}\times\exp[-\mu_1'\tau'-\mu_2\tau'''-(\tau'''-\hat{t})T^{-1}-\tfrac{1}{4}(Ku)^2(\tau'''-\hat{t}-\tau')^2]\Delta(\hat{t}).\quad\text{(II16)}$$

An interchange of the order of the τ''' and $\hat{t}$ integrations [see Eq. (35) of Ref. 1] and the introduction of a new variable of integration $\bar{\tau}=\tau'''-t$ instead of τ'' gives

$$S_{\rm II}=iKuT^{-1}\int_0^\infty d\hat{t}\,\Delta(\hat{t})\exp[-\mu_2\hat{t}]\int_0^\infty d\tau'\int_0^\infty d\bar{\tau}\times\exp[-\mu_1'\tau'-\mu_2'\bar{\tau}-\tfrac{1}{4}(Ku)^2(\tau'-\bar{\tau})^2],\quad\text{(II17)}$$

and by (27) and (II14) we find

$$S_{\rm II}=(iKuT)^{-1}\mathfrak{Z}(\mu_2)[\mu_1'+\mu_2']^{-1}[Z(\mu_1')+Z(\mu_2')].\quad\text{(II18)}$$

The third integral is

$$S_{\rm III}=iKuT^{-1}\int_0^\infty d\tau'''\int_0^\infty d\tau'\exp[-\mu_1\tau'-\mu_2\tau''']\times\int_0^{\tau'}d\hat{t}\exp[-(\tau'-\hat{t})T^{-1}-\tfrac{1}{4}(Ku)^2\times(\tau'-\hat{t})^2]D^\mp(\tau''',\hat{t}).\quad\text{(II19)}$$

Making an interchange of the τ' and $\hat{t}$ integrations, and replacing the variable τ' by $t=\tau'-t$, we find

$$S_{\rm III}=iKuT^{-1}\int_0^\infty d\tau'''\int_0^\infty d\hat{t}\int_0^\infty dt\times\exp[-\mu_1(t+\hat{t})-\mu_2\tau'''-(t/T)-\tfrac{1}{4}(Kut)^2]D^\mp(\tau''',\hat{t}).\quad\text{(II20)}$$

Using (62) and (II11), this gives

$$S_{\rm III}=(iKuT)^{-1}Z(\mu_1')S(\mu_1,\mu_2).\quad\text{(II21)}$$

In all, the desired quantity $S(\mu_1,\mu_2)$ obeys the equation

$$S(\mu_1,\mu_2)=[\mu_1'+\mu_2']^{-1}[Z(\mu_1')+Z(\mu_2')]\times[1+(iKuT)^{-1}\mathfrak{Z}(\mu_2)]+(iKuT)^{-1}Z(\mu_1')S(\mu_1,\mu_2),\quad\text{(II22)}$$

which may be solved to yield

$$S(\mu_1,\mu_2)=[\mu_1'+\mu_2']^{-1}[Z(\mu_1')+Z(\mu_2')]\times[1+(iKuT)^{-1}\mathfrak{Z}(\mu_2)][1-(iKuT)^{-1}Z(\mu_1')]^{-1}.\quad\text{(II23)}$$

Using Eq. (64) in the form

$$\mathfrak{Z}(\mu_2)=Z(\mu_2')[1-(iKuT)^{-1}Z(\mu_2')]^{-1},\quad\text{(II24)}$$

we find the relation

$$1+(iKuT)^{-1}\mathfrak{Z}(\mu_2)=[1-(iKuT)^{-1}Z(\mu_2')]^{-1}.\quad\text{(II25)}$$

When this is substituted in (II23) we finally obtain the desired expression

$$S(\mu_1, \mu_2) = [\mu_1' + \mu_2']^{-1} \mathfrak{Z}(\mu_1) \mathfrak{Z}(\mu_2) \times \{[Z(\mu_1')]^{-1} + [Z(\mu_2')]^{-1}\} \quad \text{(II26)}$$

as stated in the text.

APPENDIX III

To carry out the expansion leading to Eq. (124) we consider integral representations for the functions $P(\Delta\omega)$, $\mathcal{L}(a+\Delta\omega)$, and $\exp\{-(a+\Delta\omega)^2/(Ku)^2\}$:

$$P(\Delta\omega) = (2\pi)^{-1} \int_0^\infty dt \exp\{-i\Delta\omega t - \Gamma(1-i)t^{1/2}\} + \text{c.c.},$$

$$\mathcal{L}(a+\Delta\omega) = \tfrac{1}{2}\gamma \int_{-\infty}^{\infty} dt \exp\{-\gamma \mid t \mid + i(a+\Delta\omega)t\}, \quad \text{with } \gamma > 0$$

$$\exp\{-(a+\Delta\omega)^2/(Ku)^2\} = \tfrac{1}{2}\pi^{-1/2} Ku \int_{-\infty}^{\infty} dt \times \exp\{+i(a+\Delta\omega)t - \tfrac{1}{4}(Ku)^2 t^2\}.$$

By substituting the above expressions into Eqs. (123) and (124) we obtain

$$i_1(a, Ku) \equiv \int_{-\infty}^{\infty} d\Delta\omega\, P(\Delta\omega) \exp\{-(a+\Delta\omega)^2/(Ku)^2\}$$
$$= \tfrac{1}{2}\pi^{-1/2} Ku \int_0^\infty dt \exp\{-(1-i)\Gamma t^{1/2} + iat - \tfrac{1}{4}(Ku)^2 t^2\} + \text{c.c.},$$

$$i_2(a, \gamma) \equiv \int_{-\infty}^{\infty} d\Delta\omega\, P(\Delta\omega) \mathcal{L}(\Delta\omega) = \tfrac{1}{2}\gamma \int_0^\infty dt \times \exp\{-\gamma \mid t \mid + iat - (1-i)\Gamma t^{1/2}\} + \text{c.c.}$$

We now expand $i_2(a, \gamma)$ to first order in $\Gamma\gamma^{-1/2}$ and obtain

$$i_2(a, \gamma) = \gamma^2(\gamma^2 + a^2)^{-1} - \tfrac{1}{2}\pi^{1/2}(\Gamma^2/\gamma)^{1/2} \times \text{Re}[(1-i)\{\gamma(\gamma - ia)^{-1}\}^{3/2}]. \quad (123')$$

A similar expansion of $i_1(a, Ku)$ under the assumption $(\mid a \mid / Ku) \ll 1$ gives

$$i_1(a, Ku) = \exp\{-a^2/(Ku)^2\} - (1.23)(2)^{1/2}(\pi)^{-1/2}(\Gamma^2/Ku)^{1/2}[1 + 1.479(a/Ku)]. \quad (122')$$

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Paramagnetic Resonance of Fe-Cu, Fe-Ag, and Fe-Li Associates in II–VI Compounds*

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The paramagnetic resonance of the ^6S state of Fe^{3+} has been studied in the monoclinic C_s symmetry which arises from Fe^{3+} associated with a monovalent metal impurity (Cu^+, Ag^+, or Li^+) in ZnS, ZnSe, ZnTe, CdTe, and ZnO. The Fe^{3+} and $\{Cu, Ag, \text{or } Li\}^+$ impurities are substitutional for the metal ions at one of the nearest possible sites. The zero-field splitting due to the crystalline electric fields is frequently large compared to the Zeeman interaction. It is observed that no specific ratio of the two quadratic fine-structure terms in the spin Hamiltonian occurs. This suggests that in many cases the observation of nearly isotropic lines near $g=4.3$ results from a fortuitous set of values for these fine-structure terms, supporting the view that a pure "rhombic" term need not follow from the symmetry of the environment.

I. INTRODUCTION

THE role of copper in the luminescent behavior of the zinc and cadmium chalcogenides has been the subject of considerable investigation for several decades.[1] Recently, the technique of electron paramagnetic resonance (EPR) has been applied to the study of these materials.[1] Although some measure of understanding has been achieved for a variety of impurity centers,

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[1] For an excellent review see *Physics and Chemistry of II–IV Compounds*, edited by A. Aven and J. S. Prener (John Wiley & Sons, Inc., New York, 1967). See Chap. 6 by R. S. Title for spin resonance and Chap. 9 by D. Curie and J. S. Prener for luminescence.