Theory of light-induced drift

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A critical analysis of the theory of light-induced drift (LID) is attempted. The need for this analysis is indicated by the experimentally established absence of this effect in a mixture of SF_6 with He. It is shown that for any central scattering potential one can calculate the lighter-component flux induced in a mixture with a heavy buffer gas by an arbitrary anisotropic perturbation of the distribution function. This possibility is used to calculate the LID line. It is established that the LID line shape is sensitive to the scattering potential, that the field-induced deformation of the line may be due to homogeneous saturation and is not due to broadening of the Bennett hole, and that the diffusion coefficient changes in a strong field and this change must be taken into account in the calculation of the signals due to the LID. It is shown that in molecules with rotational-vibrational transitions the LID may be decreased by the small ratio of the diffusive collision frequency to the rotational-relaxation rate.

1. INTRODUCTION

A number of experimental searches have been made for the suggested[1,2] effect of selective diffusion[1] or light-induced drift (LID).[2] Diffusion of SF_6 in He excited by CO_2-laser radiation was investigated in Ref. 3. It was established that the change of the SF_6 density is due mainly to laser thermodiffusion, and no LID is produced in this system.

The $\lambda = 10\ \mu$m transition in SF_6 satisfies all the LID-theory requirements for multilevel sytems. Indeed, it can be seen from the experimental data cited in Ref. 3 that the relative difference betwen the relaxation characteristics of the upper and lower working levels can be close to $5\cdot10^{-2}$. These data are for SF_6 and not for the SF_6–He mixture. This, however, is of no fundamental significance. The parameters of various collisional relaxation processes have by now been spectroscopically measured and are as a rule of the same order. Thus, the dipole-moment relaxation rates in SF_6–SF_6 and SF_6–He collisions differ by a factor of 1.5 (Ref. 4), and the cross sections for SF_6–SF_6 and SF_6–He elastic scattering differ by a factor of two.[5] It is natural to expect the same for the difference between the relaxation characteristics. It was, however, established in Ref. 3 that according to existing LID theory the upper bound for this relative difference is (3–6) $\cdot 10^{-4}$. In light of the foregoing statements, such a small value seems unlikely.

The absence of LID in a system such as SF_6 points to the need for a critical theoretical analysis of this effect, and this is the purpose of the present paper. We present the main results, needed to verify the experimental data, of the LID theory that has become in a certain sense "canonized" in a set of papers by Shagalin and Gel'mukhanov.[6–10]

A flux J is produced in a gas of atoms that are resonantly excited by radiation and are mixed with a buffer gas. This produces in the gas-filled cell a density drop ΔN. The theory states that there exist combinations of experimentally measurable parameters that depend only on the frequency detuning Ω, on the field intensity, and on the transition width Γ. These combinations are of the form

$$\varphi(\Omega)=J(\gamma+\nu_2)/(Npv_0\Delta\bar{\nu}/\nu_1), \tag{1}$$

$$\varphi_1(\Omega)=\Delta N\hbar\omega v_0(\gamma+\nu_2)/(2\Delta S\bar{\nu}\Delta\nu/\nu_1), \tag{2}$$

where γ is the rate of relaxational decay from the upper level 2 to the lower 1, ν_i is the collision frequency on the ith level, $\Delta\nu=\nu_1-\nu_2$, ω is the field frequency, N is the resonant-gas density, v_0 is the thermal velocity, p is probability, averaged over the velocities, of atom excitation per unit time, ΔS is the absorbed power density, $\bar{\nu}$ is some "intermediate" frequency between ν_1 and ν_2, the functions $\varphi(\Omega)$ and $\varphi_1(\Omega)$ coincide and are equal to

$$\varphi(\Omega)=\varphi_1(\Omega)=\mathrm{Re}\,(zw(z))/\mathrm{Re}\,w(z), \tag{3}$$

where

$$z=x+iy,\quad x=\Omega/kv_0,\quad y=\Gamma_B/kv_0,\quad \Gamma_B=\Gamma(1+\varkappa')^{1/2},$$

k is the wave vector, $\varkappa'$ is the saturation parameter, and

$$w(z)=\exp(-z^2)\left[1+2i\pi^{-1/2}\int_0^z dt\exp(t^2)\right].$$

In particular, in the Doppler limiting case $y\ll1$ we have

$$\varphi(\Omega)=\varphi_1(\Omega)=\Omega/kv_0. \tag{4}$$

The functions φ and φ_1 will be referred to as the LID line shapes.

It has been asserted[6–8] that Eqs. (1) and (2) are universal (in these papers a direct connection between the experimentally measured parameters is established, and it is proposed to determine $\Delta\nu/\nu_1$ by measuring the LID), and that the LID line shape is not sensitive to singularities of the relaxation processes.

These are very strong assertions. The formalism for the description of the LID is based on the Boltzmann kinetic equation. Well-known difficulties (see, e.g., Ref. 11) are encountered in solving this equation in the theory of transport coefficients, where fluxes induced by distribution-function perturbations that are smooth as functions of velocity and are anisotropic are calculated. In the LID case the perturbation is selective with respect to the degrees of freedom and, in the Doppler limiting case, also with respect to velocity. It

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follows[1)] from Eq. (2) for ΔN (see §3 below) that no new singularities whatever arise for selective perturbations. In a weak field this holds true in those cases when the collision integral multiplied by the velocity and integrated over the velocities yields an expression that is proportional to the particle flux, i.e., in the strong collision model,[6,10,12,13] as well as in the familiar Maxwell molecule case, when the scattering potential U is proportional to r^{-4}, and also for perturbations of heavy particles, when the diffusion approximation can be used for the collision integral.

We consider in this paper the case when the mass m of the resonant-gas particles is smaller than the buffer-particle mass M:

$$m/M \ll 1. \tag{5}$$

Besides providing the ability to check the final results,[6-8] this case is natural for further development of the LID theory, since we obtain here quantitative information on the singularities that arise in selective perturbation. Thus, whereas for a smooth perturbation and scattering, in the hard-sphere model, the expressions for the particle flux at small and large values of the parameter m/M differ by only 12% (cf. the exercise in §12 of Ref. 16), in the case of the selective perturbation corresponding to the LID the expressions for ΔN under the same conditions differ near the line center by a factor 2.35.

Specifically, Eqs. (1) and (2) do not account for the following circumstances.

1. Only nonequilibrium increments to the population levels contribute to the expressions of Ref. 8 for the collision frequencies. Therefore the ν_i depend, for example, on the field frequency ω. Only by determining the character of the dependence (or the absence of this dependence) can we regard the LID line as definitely known. The procedure proposed below for the LID calculation can be used to determine this dependence explicitly. It becomes clear in this case that the collision frequencies do not remain constant when ω is varied within the limits of the Doppler profile, but can vary by a factor of 4. We shall therefore not use such quantities below, We note, however that the fact that ν_i depends on ω and on other parameters makes it impossible to measure the relative frequency difference, since the latter can change together with ν_i when the experimental conditions are varied.

2. It follows from (1) and (2) that the only effect of the field on the LID line is the broadening of the Bennett hole. It is known that at not too small values of Γ/kv_0 and at a sufficiently high collision frequency the homogeneous saturation of the populations plays an important role. The influence of these processes on the CO_2 lasing line was observed and explained in Ref. 17, and their theory is given in Ref. 18. From the strong-collision model it follows[6-8] that they do not affect the LID line shape. This result, however, is not general. We consider below a case when homogeneous saturation alters both the absorption line and the LID line.

3. In the strong-collision model, Eq. (2) must be corrected. It takes no account of the obvious field-induced change of the gas diffusion coefficient. We present for it an expression that is valid in this model in the case of a two-level system at $\nu_i \gg \gamma$:

$$D = \frac{v_0^2}{2\nu_1}\left(1 + \frac{\nu_1 - \nu_2}{\nu_2}\frac{p}{\gamma}\right). \tag{6}$$

Since p is a function of the detuning Ω, when account is taken of the field-induced increments to D the obtained field dependence of ΔN on Ω is different from (2).

2. APPROXIMATE ANALYSIS

We determine approximately how the flux depends on the detuning. If (5) is satisfied the collisions cause the direction of the light-particle velocity to rotate, but leave its absolute value v constant. The angular velocity of this rotation is of the order of the collision frequency ν_i. At those instants when the velocity projection on the wave-propagation direction (the z axis) is equal (to within the width $\Delta v_B = \Gamma/k$ of the Bennett hole) to Ω/k the particle is in resonance with the field, excitation sets in, adds to the populations $n_i(v)$ and produces on the levels $J_i(v) \sim (\Omega/k)n_i(v)$ fluxes along z, while for $\nu_1 \neq \nu_2$ the total flux is $J(v) = J_1(v) + J_2(v)$. Thus, at high collision frequency ($\nu_i \gg \gamma$) all the atoms brought by collisions to within the confines of the Bennet hole will contribute to the flux. Obviously, in the limiting Doppler case ($\Delta v_B \ll v$) contributions are made only by those atoms with $v \geqslant |\Omega|/k$. The field increments $n_i(v)$ are proportional to the number of particles whose absolute velocity is in an interval dv close to the given v, i.e., $dvv^2 \cdot \exp(-v^2/v_0^2)$, and to the time of interaction of the i-level particles with the field. The field is on the order of the ratio of the angle interval $\Delta\theta$ in which the excitation takes place to the rotation rate ν_i. It can be seen from Fig. 1 that $\Delta\theta \sim \Gamma/kv$. Summing the contributions of all velocities, we thus get

$$J \propto \Omega \int_{|\Omega|/k}^{\infty} dv \frac{v}{\nu_i} \exp\left(-\frac{v^2}{v_0^2}\right).$$

Since the absorption line in a weak field has a Doppler profile, $p \propto \exp[-(\Omega/kv_0)^2]$, we obtain for

$$\varphi(\Omega) \propto \Omega \exp[\Omega^2/(kv_0)^2] \int_{|\Omega|/k}^{\infty} dv \frac{v}{\nu_i} \exp\left(-\frac{v^2}{v_0^2}\right).$$

This line coincides with (4) only if ν_i is independent of veloc-

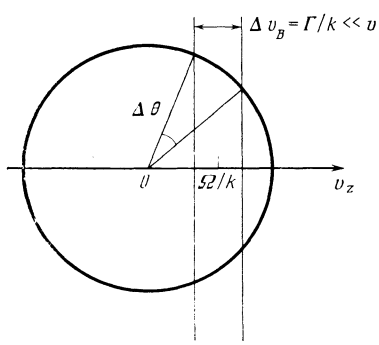

FIG. 1. Illustrating the approximate determination of the LID line shape.

ity. It will be shown below that if condition (5) is met the collision frequencies can be expressed in terms of the transport cross sections. Their velocity dependence is determined by the scattering potential, so that the LID line is sensitive to this potential.

3. LIGHT-INDUCED DRIFT OF A RESONANT LIGHT GAS

The kinetic equations for a gas of two-level atoms in a resonant traveling-wave field

$$E(\mathbf{r}, t)=E\exp(-i\omega t+i\mathbf{kr})+\text{c.c.}$$

where E, ω, and $\mathbf{k}$ are the amplitude, frequency, and wave vector of the field, are of the form

$$\begin{aligned}\gamma\rho_2(\mathbf{v})-\mathrm{St}(\rho_2(\mathbf{v}))&=p(\mathbf{v}),\\ -\gamma\rho_2(\mathbf{v})-\mathrm{St}(\rho_1(\mathbf{v}))&=-p(\mathbf{v}),\end{aligned}\tag{7}$$

where $\mathbf{v}$ is the atom velocity, $\rho_i(\mathbf{v})$ is the particle level distribution function normalized to

$$\int d\mathbf{v}(\rho_1(\mathbf{v})+\rho_2(\mathbf{v}))=1,$$

γ is the radiative-decay rate of level 2, $\mathrm{St}(\rho_i)$ is the integral of the i-level particle elastic collisions with the buffer-gas atom,

$$p(\mathbf{v})=\frac{2|G|^2\Gamma}{\Gamma^2+(\Omega-\mathbf{kv})^2}[\rho_1(\mathbf{v})-\rho_2(\mathbf{v})]\tag{8}$$

is the probability of atom excitation by the field per unit time, $G=dE/\hbar$, where d is the dipole matrix element of the 2–1 transition, Γ is the homogeneous line width, and $\Omega=\omega-\omega_{21}$ is the detuning of the field frequency from the transition frequency ω_{21}.

To calculate the collision frequencies ν_i introduced in Refs. 8 and 9 at an arbitrary mass ratio, we must solve the kinetic equation. It can be shown, however that if the field is weak at $\nu_i\gg\tau$ and the differential cross sections $d\sigma_i$ for scattering on the levels have a constant ratio

$$d\sigma_2/d\sigma_1=c=\text{const}\tag{9}$$

the ratio of these frequencies is also constant. If we assume also that $|1-c|\ll 1$, then $\nu_2\approx\nu_1$ and hence $\bar{\nu}=\nu_2$. At the end we obtain from (2)

$$\varphi_1(\Omega)=\Delta N\hbar\omega v_0/2\Delta S(1-c).\tag{10}$$

We adopt Eqs. (1) and (10) as the definitions of the functions φ and φ_1. We shall consider the function φ_1 only under the conditions listed above, and set the collision frequencies in (1) equal to $\nu_i=\nu_i(v_0)$, where

$$\nu_i(v)=N_6 v\sigma_{tr,i},$$

$\sigma_{tr,i}$ is the transport cross section for particle scattering on level i, and N_b is the buffer-gas density.

Taking (5) into account we have in a weak field (Ref. 16, §11)

$$\mathrm{St}(\rho_i(\mathbf{n}))=N_6 v\int d\mathbf{n}'F_i[\rho_i(\mathbf{n}')-\rho_i(\mathbf{n})],\tag{11}$$

where $\mathbf{n}=\mathbf{v}/v$, and $F_i=d\sigma_i/d\mathbf{n}'$ for a central scattering potential depends only on the scalar product $\mathbf{n}\cdot\mathbf{n}'$.

We introduce the particle flux on the ith level in the space of the velocity modulus:

$$J_i(v)=\int d\mathbf{n}\mathbf{n}\rho_i(\mathbf{n}).$$

The total flux is

$$J=N\int_0^\infty dvv^3J(v),\tag{12}$$

where $J(v)=J_1(v)+J_2(v)$ and N is the density of the resonant component of the mixture. From (7) and the collision integrals (11) we can obtain algebraic equations for $J_1(\mathbf{v})$. Indeed, multiplying the integral terms by $\mathbf{n}$ and integrating over the angles, we get

$$\int d\mathbf{n}\mathbf{n}\,\mathrm{St}(\rho_i(\mathbf{n}))=-\nu_i(v)J_i(v).$$

We have used here an equation that is valid for scattering by a central potential

$$\int d\mathbf{n}'(\mathbf{n}-\mathbf{n}')F_i=\mathbf{n}\sigma_{tr,i}.$$

We ultimately get

$$J(v)=\frac{1-c(v)}{\gamma+\nu_2(v)}\int d\mathbf{n}\mathbf{n}p(\mathbf{v}),\quad c(v)=\frac{\nu_2(v)}{\nu_1(v)}.\tag{13}$$

Our calculation method is similar to that for obtaining the familiar Maxwell expression for the diffusion coefficient (see, e.g., Ref. 19). Whereas, however, in the standard method of obtaining Maxwell's results we get, without solving the equations, expressions for the flux as a whole at an arbitrary mass ratio, but only with a potential $U\propto r^{-4}$, in our case for $m\ll M$ we calculate the flux density, so that we can determine the total flux for an arbitrarily weak anisotropic perturbation of the distribution function and with an arbitrary central scattering potential.

If the field is weak, Eq. (7) can be solved by iterating with respect to the right-hand side of (8), putting

$$\rho_2(\mathbf{v})=0,\quad \rho_1(\mathbf{v})=(4\pi)^{-1}f(v),$$

where $f(v)=4\pi^{-1/2}v_0^{-3}\exp(-v^2/v_0^2)$ is the Maxwellian atomic velocity distribution function. When

$$c(v)=c=\text{const}\tag{14}$$

we then obtain for the flux

$$\mathbf{J}=\mathbf{n}_k N(1-c)\frac{|G|^2\Gamma}{k^2}\int_0^\infty dvvf(v)\frac{a(v)}{\gamma+\nu_2(v)},\tag{15}$$

where $\mathbf{n}_k=\mathbf{k}/k$, $k=|\mathbf{k}|$,

$$\begin{aligned}a(v)&=\frac{\Omega}{\Gamma}\Phi(v)+\frac{1}{2}\ln\left[\frac{\Gamma^2+(\Omega-kv)^2}{\Gamma^2+(\Omega+kv)^2}\right],\\ \Phi(v)&=\mathrm{arctg}\,[(kv-\Omega)/\Gamma]+\mathrm{arctg}\,[(kv+\Omega)/\Gamma].\end{aligned}\tag{16}$$

Hence, using an equation that is valid in a weak field[6]

$$p=(2|G|^2/kv_0)\pi^{1/2}\,\mathrm{Re}\,w,$$

we obtain for the function defined in (1)

$$\varphi(\Omega)=\frac{\Gamma}{2k\pi^{1/2}\,\mathrm{Re}\,w}\int_0^\infty dvvf(v)a(v)\frac{\gamma+\nu_2}{\gamma+\nu_2(v)}. \tag{17}$$

We consider the Doppler limiting case

$$\Gamma/kv_0\ll 1. \tag{18}$$

Here

$$a(v)=(\Omega/\Gamma)\Phi(v),\quad \Phi(v)=\pi\theta(v-|\Omega|/k), \tag{19}$$

where $\theta(x)$ is the Heaviside step function. Let the $\nu_i(v)$ be proportional to powers of the velocity

$$\nu_i(v)=\nu_i(v/v_0)^s. \tag{20}$$

We consider below the following cases: $s=1$, which appears in the hard-sphere model; $s=1/3$, which corresponds to a Van der Waals interaction with a potential $U\propto r^{-6}$; $s=0$, which corresponds to the Maxwell case; $s=3$, which appears[2)] in the Born approximation (Ref. 20, §126).

At $\nu_i\gg\tau$ we obtain then

$$\varphi(\Omega)=2x\exp(x^2)F_{1-s}(|x|), \tag{21}$$

where $x=\Omega/kv_0$,

$$F_i(x)=\int_x^\infty dvv^i\exp(-v^2)=1/2\Gamma((i+1)/2,x^2), \tag{22}$$

and Γ is the Γ function.

We proceed to calculate N. In a sealed cell the density drop produced by the LID in the absorbing gas is

$$\Delta N=\int dzJ/D, \tag{23}$$

where $J=J_z$. For a transparent medium ($\Delta S\gg S$, where S is the Poynting vector of the field), using the formula[6] $S=N\hbar\omega pL$, where L is the cell length, we obtain for the function defined in (10)

$$\varphi_1=(v_0^2/2\nu_1D)\varphi.$$

In a weak field, the gas diffusion coefficient is $D=D_1$, where

$$D_i=(2/3\pi^{1/2})\Gamma((5-s)/2)\,(v_0^2/\nu_i) \tag{24}$$

is the diffusion coefficient of the light particle on the ith level in the heavy buffer gas (Refs. 16, 11) and $\Gamma(x)$ is a Γ function. From this we get

$$\varphi_1(\Omega)=\frac{3\pi^{1/2}}{2\Gamma((5-s)/2)}x\exp(x^2)F_{1-s}(|x|). \tag{25}$$

Near the line center Ω/kv_0 we obtain

$$\varphi_1(\Omega)=\frac{3\pi^{1/2}\Gamma(1-s/2)}{4\Gamma((5-s)/2)}\frac{\Omega}{kv_0}; \tag{26}$$

in the asymptotic approximation[3)] $\Omega\gg kv_0$ we have

$$\varphi_1(\Omega)=\frac{3\pi^{1/2}}{4\Gamma((5-s)/2)}\,\mathrm{sign}(\Omega)\,|\Omega/kv_0|^{1-s}. \tag{27}$$

Figure 2 shows a plot of the function $\varphi_1(\Omega)$.

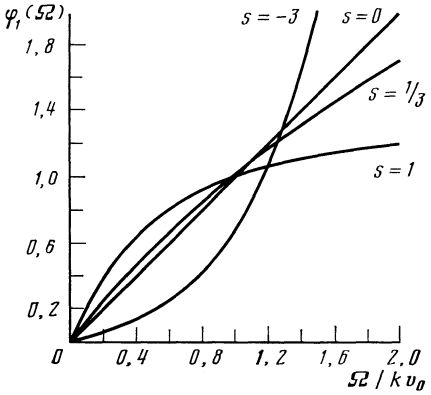

FIG. 2. LID line shape in a weak field for different scattering potentials.

4. FIELD EFFECTS

When a light gas collides with a heavy one, the relaxation in angle is known (Ref. 16, §22) to be M/m times faster than relaxation in the modulus of the velocity. The distribution function can therefore be sought in the form

$$\rho_i(\mathbf{v})=(4\pi)^{-1}\rho_i(v)+\rho_i(\mathbf{n}),\quad \int d\mathbf{n}\rho_i(\mathbf{n})=0 \tag{28}$$

and to consider the anisotropic parts of $\rho_i(\mathbf{n})$ as small additions. Then by omitting $\rho_i(\mathbf{n})$ in Eq. (8), we obtain

$$\int d\mathbf{n}p(\mathbf{v})=\gamma\varkappa(v)\,[\rho_1(v)-\rho_2(v)],$$

where the saturation parameter, which depends on the velocity modulus, is

$$\varkappa(v)=\varkappa(v_0/v)\Phi(v), \tag{29}$$

and $\varkappa=|G|^2/(\gamma kv_0)$ is the characteristic homogeneous-saturation parameter.

The equations for the isotropic part are

$$\begin{aligned}&\gamma\rho_2(v)-S(\rho_2(v))=\gamma\varkappa(v)\,[\rho_1(v)-\rho_2(v)],\\ &-\gamma\rho_2(v)-S(\rho_1(v))=-\gamma\varkappa(v)\,[\rho_1(v)-\rho_2(v)].\end{aligned} \tag{30}$$

The explicit form of the collision integral $S(\rho_i(v))$ is given in (Ref. 16, §22). Its distinctive feature is that it is of order $\nu_i(m/M)\rho_i(v)$. Therefore if the condition

$$\gamma\gg\nu_i m/M \tag{31}$$

is satisfied in (14) along with $\nu_i\gg\gamma$, we obtain from (30), in analogy with Ref. 15,

$$\begin{aligned}&\rho_1(v)+c\rho_2(v)=Af(v),\\ &\rho_2(v)/\rho_1(v)=\varkappa(v)/(1+\varkappa(v)),\end{aligned} \tag{32}$$

where A is determined from the normalization condition. We note that the condition (14) is of fundamental importance only in the strong-field case and is weaker than the condition (9) used in Ref. 15.

In contrast to Ref. 15, where the case $\gamma\gg\nu_i$ is used, we assume that the particle lifetime in the excited state is long enough for rapid relaxation to the equilibrium distribution

function in angle on each individual level, but is short compared with the kinetic-energy relaxation time. Our saturation parameters depend therefore on the modulus of the velocity and not on v_z.

Solving (32) for the LID line shape, we get

$$\varphi(\Omega)=\frac{\Gamma}{kv_0}\frac{\int_0^\infty dvvf(v)a(v)[\nu_2/\nu_2(v)][1+(1+c)\varkappa(v)]^{-1}}{\int_0^\infty dvvf(v)\Phi(v)[1+(1+c)\varkappa(v)]^{-1}}. \tag{33}$$

We consider now limiting cases. We assume as before that the Doppler broadening is large. If

$$1\ll\varkappa\ll kv_0/\Gamma, \tag{34}$$

only atoms with velocities $v>|\Omega|/k$ are strongly saturated. Then

$$\varphi(\Omega)=xF_{2-s}(|x|)/F_2(|x|). \tag{35}$$

At $\Omega\ll kv_0$ and $\Omega\gg kv_0$ this function is given respectively by

$$\varphi(\Omega)=2\pi^{-1/2}\Gamma((3-s)/2)\Omega/kv_0, \tag{36}$$

$$\varphi(\Omega)=\operatorname{sign}(\Omega)|\Omega/kv_0|^{1-s}. \tag{37}$$

Now let

$$\varkappa\gg kv_0/\Gamma. \tag{38}$$

In this case the populations of all the atoms become saturated. The denominator in (33) does not depend on the detuning Ω. The term proportional to $\Phi(v)$ in $a(v)$ yields a term linear in Ω, while the logarithmic term [see Eq. (16)] need be taken into account only at $v<|\Omega|/k$, where $\Phi(v)$ is small. Indeed, for these velocities, the parameter

$$\varkappa(v)=2\varkappa\Gamma kv_0[\Omega^2-(kv)^2]^{-1}$$

is large if condition (38) is satisfied, and enters in the denominator of the integrand. In the final analysis, the contribution from the logarithmic term is comparable at $v<|\Omega|/k$ with the other terms, and at so large a saturation it must be retained. We obtain then

$$\varphi(\Omega)=2\pi^{-1/2}\left[\Gamma((3-s)/2)x-\int_0^x dvv^{1-s}\exp(-v^2)(x^2-v^2)\times\ln\left(\frac{x+v}{x-v}\right)\right]. \tag{39}$$

At small Ω and $s<3$ Eq. (39) coincides with (36), and at kv_0 we obtain

$$\varphi(\Omega)=(4/3)\pi^{-1/2}\Gamma((5-s)/2)kv_0/\Omega. \tag{40}$$

Figures 3 and 4 show the LID line shape calculated fom (21), (35), and (39) for different scattering potentials.

We present also expressions for the absorption probability and for the gas diffusion coefficient in a strong field

$$p=\gamma A\int_0^\infty dvv^2\varkappa(v)f(v)[1+(1+c)\varkappa(v)]^{-1}, \tag{41}$$

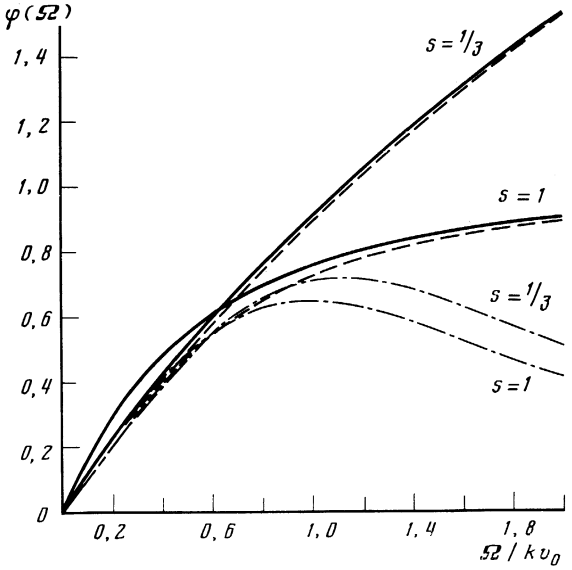

FIG. 3. LID line shape in scattering by a Van der Waals potential and in the hard-sphere model in various ranges of the saturation parameter: $\varkappa\ll 1$ (solid line), $1\ll\varkappa\ll kv_0/\Gamma$ (dashed curves), and $kv_0/\Gamma\ll\varkappa$ (dash-dot).

$$D=\frac{A}{3}\int_0^\infty dv\left(\frac{v^4}{\nu_2(v)}\right)f(v)[\varkappa(v)+c(1+\varkappa(v))]\times[1+(1+c)\varkappa(v)]^{-1}, \tag{42}$$

$$A^{-1}=\int_0^\infty dvv^2f(v)\frac{1+2\varkappa(v)}{1+(1+c)\varkappa(v)}.$$

To obtain (42) it is necessary to introduce into the right-hand sides of (7) the terms $-\mathbf{v}\nabla\ln(N)\rho_i(v)$, where $\rho_i(v)$ are the solutions (32). Assuming the latter to be small, we calculate in analogy with §2 that part of the flux which is proportional to ∇N. It is assumed here that in the zeroth approximation in ∇N the level populations are $n_i(\mathbf{r},\mathbf{v})=N(\mathbf{r})\rho_i(\mathbf{v})$, where ρ_i is independent of the coordinates. For this assumption to be valid it is necessary, as usual, that the mean free path be less than $|\nabla\ln(N)|^{-1}$. Using Eq. (2), which is of the correct order

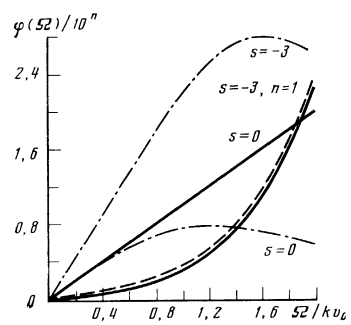

FIG. 4. The same as Fig. 3, but for scattering in the Born approximation and by a Maxwellian potential. Except for the case $n=0$ indicated in the figure, the solid, dashed, and dash-dot curves are for $\varkappa\ll 1$, $1\ll\varkappa\ll kv_0/\Gamma$, and $kv_0/\Gamma\ll\varkappa$.

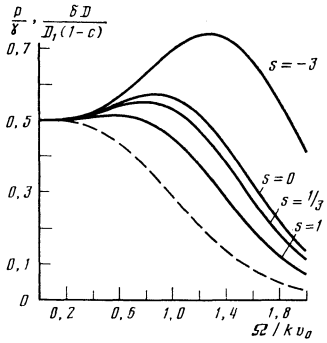

FIG. 5. Diffusion-coefficient line shape for different scattering potentials (solid curves) and absorption line shape (dashed) for $1 \ll \varkappa \ll kv_0/\Gamma$.

of magnitude, as well as the formula for ΔS (Ref. 6), we find that at $p \lesssim \gamma$ this condition is equivalent to (21).

For $\varkappa$ as bounded in (34) we obtain

$$p=4\gamma\pi^{-1/2}F_2(|x|)\,[1+c+(1-c)4\pi^{-1/2}F_2(|x|)]^{-1}, \tag{43}$$

$$D=\left[D_1+\frac{4(1-c)v_0^2}{3\pi^{1/2}\nu_2}F_{4-s}(|x|)\right] \times\left[1+\frac{1-c}{1+c}4\pi^{-1/2}F_2(|x|)\right]^{-1}. \tag{44}$$

Figure 5 shows the absorption lines and the increments δD to the diffusion coefficient at $|1-c| \ll 1$. When $\Omega = 0$ and $\Omega \gg kv_0$ we obtain

$$p=\gamma/2, \quad D=(D_1+D_2)/2; \tag{45}$$

$$p=\frac{2\gamma}{\pi^{1/2}(1+c)}|x|\exp(-x^2),$$

$$D=D_1+\frac{2(1-c)v_0^2}{3\pi^{1/2}\nu_2}|x|^{3-s}\exp(-x^2). \tag{46}$$

Equations (45) are valid for $\varkappa$ as bounded in (38). This result has an obvious meaning: if the atoms are strongly saturated at all velocities, equal distribution functions close to Maxwellian are established on both levels. The absorption probability reaches then the maximum value $\gamma/2$ and the gas diffusion coefficient is the average of the diffusion coefficients on the levels.

Equations (33), (41), and (42) can be used to calculate the gas-density changes. For a transparent medium we obtain

$$\Delta N=[(1-c)v_0\Delta S/\hbar\omega\nu_2 D]\varphi(\Omega). \tag{47}$$

5. LIGHT-INDUCED DRIFT IN MOLECULAR SYSTEMS[4)]

Multilevel molecular systems can undergo several relaxation processes that differ both in their rates and in their influences on the translational degrees of freedom. Thus, the fastest in SF_6 is rotational relaxation, and its rate $R = 3 \cdot 10^7$ $s^{-1} \cdot Torr^{-1}$ (Ref. 4) exceeds both the vibrational relaxation rate and the quantity $\bar{\nu} = v_0^2/2D$ introduced in Ref. 7, which we shall call the diffusional collision frequency. This relation between the parameters is typical of molecules. Allowing for it can alter, compared with (2), not only the density-variation line shape but also the order of magnitude of the estimate of this signal.

The diffusion coefficient in an SF_6–He mixture at 1 Torr is $D = 300$ cm^2/s (Ref. 21), whence

$$\bar{\nu}/R \approx 2\cdot 10^{-2}. \tag{48}$$

The model considered in Ref. 6, from which it follows that $\bar{\nu} \sim R$, is thus inapplicable. We present estimates that show that the same can hold also for the model[13] in which it is assumed that the rotational-relaxation rate does not change at all, so that the translational relaxation is due only to elastic collisions. But in that case it is they which will cause the diffusion. Assuming in accordance with Ref. 5 that the elastic cross section σ_e and the cross section for rotational relaxation are equal, and using the expressions for D (Ref. 16, §12) and σ_e (Ref. 20, §127), we find that with a scattering potential[5)] $U = \alpha r^6$ we have $U = \alpha/r^6$, $\bar{\nu}/R = 0.6(M/m)\theta^{1/3}$, where m and M are the masses of SF_6 and He, $\theta = (\hbar/Mv_0')$ $\times(\alpha/\hbar v_0')^{-1/5}$ is the elastic-scattering angle, and v_0' is the thermal velocity of He. For SF_6-SF_6 collisions, we have $\theta = 6.4\cdot 10^{-3}$ (Ref. 22). Assuming that in SF_6-He collisions, where there are no exchange processes, θ does not exceed this value, we obtain $\bar{\nu}/R \approx 3\cdot 10^{-3}$, which is 6.6 times smaller than (48). This difference shows that both in the case of diffusion and in the case of LID the translational degrees of freedom can be mainly affected by collisions with changes of the rotational quantum number. Retaining in the kinetic equation only the contribution from these collisions, we obtain, say for the distribution function on the lower vibrational term,

$$R_j(v)\rho_j(\mathbf{v}) - \sum_{j'}\int d\mathbf{v}' R_{jj'}(\mathbf{v},\mathbf{v}')\rho_{j'}(\mathbf{v}') = A_j(\mathbf{v}), \tag{49}$$

$$A_j(\mathbf{v}) = -p(\mathbf{v})\delta_{jj_1}, \tag{50}$$

where j_1 is the lower working sublevel. We proceed now to the equations for the fluxes and populations

$$J_j = \int d\mathbf{v}(\mathbf{n}_k\mathbf{v})\rho_j(\mathbf{v}), \quad \rho_j = \int d\mathbf{v}\rho_j(\mathbf{v}),$$

the forms of which are

$$\sum_{j'} R^N_{jj'}\rho_{j'} = -p\delta_{jj_1}, \quad \sum_{j'} R^c_{jj'}J_{j'} = -pv_0\varphi(\Omega)\delta_{jj_1}, \tag{51}$$

where $\varphi(\Omega)$ coincides with the value given in Refs. 6–8. We have formally obtained algebraic rather than integral equations, but their coefficients are expressed in terms of the solutions (49). Thus, for example,

$$R^N_{jj'} = \rho_{j'}^{-1}\int d\mathbf{v}\left[\delta_{jj'}R_j(v)\rho_j(\mathbf{v}) - \int d\mathbf{v}' R_{jj'}(\mathbf{v},\mathbf{v}')\rho_{j'}(\mathbf{v}')\right].$$

Transformation from (49) to (51) therefore yields nothing. Although such an approach is used in the LID theory[9] and is basic for the derivation of Eqs. (1) and (2),[8] the kinetic equation cannot be solved by this method. We, on the other hand, need the system (51) only for a definite qualitative derivation.

In the absence of vibrational relaxation, the field increments to the populations increase without limit in absolute value, i.e., $\det|R^N| = 0$. But it does not follow from this at all that the same is valid also for R^c. The equations for the

fluxes can perfectly well be linearly independent.

In the calculation of the diffusion coefficient we must put in (49)

$$A_j(\mathbf{v}) = -\mathbf{v}\nabla \ln (N)\rho_j^0(\mathbf{v}), \tag{52}$$

where $\rho_j^0(\mathbf{v})$ is the distribution function in the absence of the field. Let R^d be the matrix of equations for the flux corresponding to (52). It follows from (48) that the $\det|R^d/R| \ll 1$. At the same time $\det|R^c/R|$ can be ~ 1. In fact, however, the right-hand sides of (50) and (52) differ significantly: Eq. (50) is selective with respect to all degrees of freedom, and (52) only with respect to the vibrational quantum number. The solutions (49) are consequently also substantially different, and with them the matrices R^d and R^c. It must be emphasized here that in a multilevel system even a small difference R^i is sufficient to cause $\det R^i/R$ to become of order of unity.

If $\det|R^c/R| \sim 1$, the flux due to the LID is $J_i \sim pv_0/R$ on each of the vibrational terms. There is no LID if the rotational relaxation processes on the terms coincide. Consequently, if the difference between them is small the total flux is $J \sim (\Delta R/R)J_i$, where $\Delta R/R$ is the characteristic relative difference between the relaxation properties on the terms [the analog of $\Delta\nu/\nu_1$ in (1) and (2)]. Collecting all the factors, we obtain for ΔN an estimate that contains the small factor (48) besides the factors taken into acocunt in (2).

We present now estimates for SF_6. If we assume in accordance with Ref. 3 that the relative difference between the relaxational characteristics on the terms is of order $5 \cdot 10^{-2}$, the upper bound obtained in Ref. 3 for the LID is smaller by two orders of magnitude than predicted by Eq. (2). To explain this difference it suffices to take into account the decrease of the signal by the factor (48). However, even if this decrease is not fully effective, the onset in the medium of temperature and intensity gradients and of laser power and frequency fluctuations can additionally decrease the LID.[23] The reason here is the dependence of the collision frequencies on the rotational quantum number.

6. CONCLUSIONS

Let us compare the end results of our paper with the results of previous work. Although direct comparison is difficult, there are two cases in which Eqs. (3) and (4) of Refs. 6–8 should be valid for the functions φ and φ_1 we have calculated.

1. If the right-hand sides of (2) and (10) are equal (see §3 for the necessary conditions), the lines (25) and (4) should also coincide. We emphasize that in Refs. 6–8 it is proposed to calculate the experimental data by using Eq. (2) with only the right-hand side, which coincides at $\nu_2 \gg \gamma$ with the right-hand side of (10) in which $1 - c = \Delta\nu/\nu_1$, and with a function $\varphi_1(\Omega)$ equal to Eq. (3) or in Doppler limit to (4). Yet the line (4) agrees with (25) only for a Maxwell scattering potential. In other cases the slope of the $\varphi_1(\Omega)$ plot at the line center changes according to (26) from 2.35 $(kv_0)^{-1}$ in the hard-sphere model to 0.29 $(kv_0)^{-1}$ in the Born approximation. At large Ω, within the limits of the Doppler profile (see footnote 3) this function increases like Ω^4 and $\Omega^{2/3}$ in the Born approximation and for an α/r^6 potential, while in the hard-sphere model it tends to a constant value. The cause of the difference is that the LID-induced flux in (1) contains the collision frequency that depends on Ω, whereas the collision frequency contained in the diffusion coefficient has no such dependence [see Eq. (24)].

2. In the case of a Maxwell scattering potential the collision frequencies are independent of the nonequilibrium increments to the level populations, and hence of the field parameters. The dependence of the flux on the detuning is determined here by (33), in which we must put $\nu_2(v) = \nu_2$. It can be shown that it is precisely this expression, and not Eq. (3), which follows from the definition given in Refs. 6–8 for $\varphi(\Omega)$. The difference between (3) and (33) is connected with the peculiarities of the homogeneous saturation of the Doppler-broadened line. Its value can be assessed by comparing the dash-dot and solid curves of Fig. 4 at $s = 0$. At larger Ω Eqs. (39) and (40) yield, within the limits of the Doppler contour, not the linear law (4) but to the exact opposite $\varphi(\Omega) = kv_0/\Omega$. For (39) to be valid we must have $\varkappa \gg kv_0/\Omega$, but here the inhomogeneous saturation can be neglected only if $M/m \gg (kv_0/\Gamma)^2$. It is important to us nonetheless that by solving analytically the kinetic equation we have obtained here an example that confirms the following conclusion: to determine the dependence of the flux on the detuning in a strong field it is necessary, at any scattering potential, to obtain an exact or an approximate expression for the gas distribution function.

We note also that if $\Delta\nu/\nu_1$ is not small the field dependence of the diffusion coefficient makes it impossible, as can be seen from (47), to obtain a combination of the experimentally measured parameters that is linear in ΔN and is equal to the relative difference of the collision frequencies.

As for multilevel systems, it can be seen from the qualitative treatment in §5 that the LID-induced signals can change not only in shape but also in order of magnitude. The reason here can be the small value of the parameter $\bar{\nu}/R$ as well as the gradients and fluctuations of the system parameters. We assume that these factors can be of importance, to one degree or another, not only in SF_6 but also in other molecules. From this viewpoint the LID in molecules can hardly be used to measure $\Delta\nu/\nu_1$. We doubt therefore that the parameter measured in Ref. 24 is directly conencted with this quantity.

To sum up, the statement that Eqs. (1) and (2) are universal is not a rigorous consequence of the kinetic equation and is not reliably confirmed by experiments known to us. Deviations of the LID line shape from (4) can be quite finite in value. But this is not all that matters. The universality premise, if accepted, leaves an isolated line with only one "degree of freedom" with which to explain the experiment, namely the parameter $\Delta\nu/\nu_1$. This is confirmed by the analysis[13] of the situation in SF_6, which was reduced in effect to the statement that $\Delta\nu/\nu_1$ is less than $4 \cdot 10^{-4}$ in absolute value. We however, regard other factors as physically more plausible causes of the absence of the effect. These, however, do not agree with the postulated universality.

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ratory staff, and B. M. Smirnov for numerous and helpful discussions.

[1)]We note apropos of Eq. (1) that it relates the flux to the parameters that have been measured to date if the decay rate is high, $\gamma \gg \nu_i$, and either[14] the diffusion approximation for the collision integral is valid, or else[15] the cross sections for particle scattering by levels are similar, since $\Delta\nu/\nu_1$ is constant in these cases.

[2)]It is interesting to note that the same law $\nu_i \propto v^{-3}$ is valid in all the known cases when consideration of small-angle scattering suffices to calculate the transport cross section. The equations for σ_{tr} coincide in the Born, eikonal (Ref. 20, §131), and classical approximations.

[3)]The asymptotic relations (27) and others (see (37), (40), and (46) below) can be used only if a detuning region exists in which the use of the limiting Doppler case is still justified. Analysis shows that at $\Omega/kv_0 \sim 2$ the accuracy of the asymptotic form is $\lesssim 10\%$. The Doppler contour can be used in this region if $\Gamma/kv_0 \lesssim 10^{-2}$.

[4)]I use in this section data supplied by N. N. Rubtsova and I. M. Beterov, to whom I am grateful.

[5)]The calculation of D for this scattering potential gives rise to an integral $\int_0^\infty d\rho\,\rho(1+\cos+2\varphi)$, where $\varphi = \int_0^{x_0} dx[1-x^2-(x/\rho)^6]^{-1/2}$ and x_0 is the point where the radicand vanishes. The value of the integral is 0.556.

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