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Kinetic theory of light-induced drift of particles with degenerate energy levels

F Kh Gel'mukhanov, L V Il'ichov and A M Shalagin
Institute of Automation and Electrometry, Novosibirsk, 630090, USSR

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Abstract. The theory of light-induced drift of particles with degenerate levels is proposed. Kinetic equations which are semiclassical with respect to rotational degrees of freedom and with a phase memory accounting are obtained. The drift velocity dependence on radiation polarisation is predicted. Numerical calculation, which has been made in a strong collision model, shows that the accounting of level degeneracy leads to a velocity change of up to 10-20% under some conditions.

1. Introduction

In 1979 a new kinetic gas phenomenon in a laser radiation field, light-induced drift (LID), was predicted theoretically by Gel'mukhanov and Shalagin (1979, 1980a). Numerous theoretical works (Gel'mukhanov and Shalagin 1980a, b, Mironenko and Shalagin 1981, Dykhne and Starostin 1980, Gel'mukhanov and Telegin 1981, Popov *et al* 1981, 1982, Gel'mukhanov 1982, Gel'mukhanov and Il'ichov 1984) and experimental works (Antsigin *et al* 1979, Atutov *et al* 1982, Folin and Chapovsky 1983, Krasnoperov *et al* 1984, Riegler *et al* 1983, Panfilov *et al* 1981, 1983, Werij *et al* 1984) which have been made during recent years allow us to speak about the appearance of a new direction in the physics of radiated media, and more specifically about the kinetic gas in a laser radiation field.

Let us recall the physics of the LID phenomenon. We consider the interaction of a plane-running monochromatic light wave with an ensemble of absorptive particles in a mixture with a buffer gas. Radiation is absorbed at a transition n-m from the ground state n. The absorptive line is broadened by the Doppler effect. Under these conditions, only those particles whose velocity projection on the wavevector $\boldsymbol{k}$ is close to the 'resonant' one, i.e. which corresponds to the condition $\boldsymbol{kv} = \Omega \equiv \omega - \omega_{mn}$, interact with the radiation (ω is the radiation frequency, ω_{mn} is the frequency of the transition n-m). If $\Omega \neq 0$ the excited particles appear with a non-zero velocity projection on the wavevector, i.e. there is a flow of the excited particles $\boldsymbol{j}_m$ which is collinear to $\boldsymbol{k}$. In the ground state the opposite flow $\boldsymbol{j}_n$ occurs due to the decrease of unexcited particles in the interval of resonant velocities.

Until collisions have manifested themselves the radiation initiates the flows $\boldsymbol{j}_m$ and $\boldsymbol{j}_n$ with equal intensities and opposite directions (if the light pressure phenomenon, which can usually be neglected in the LID theory, is not taken into account). In the presence of a buffer gas each flow $\boldsymbol{j}_i$ is impeded, and the friction force density $\boldsymbol{F}_i$ is

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equal to

$$\boldsymbol{F}_i = -m_a \nu_i \boldsymbol{j}_i$$

where m_a is the mass of an absorptive particle, ν_i is the transport collisional frequency, $i = m, n$. In general the interaction laws for excited and unexcited particles are different, so the transport frequencies are different as well ($\nu_m \neq \nu_n$). As a consequence of this a total non-zero force density $\boldsymbol{F} = \boldsymbol{F}_m + \boldsymbol{F}_n$ arises, which affects the gas and sets it in motion. This is the physical basis of the LID phenomenon.

The drift direction depends on the sign of the difference $\nu_m - \nu_n$ and changes with the change of sign of the detuning Ω. For example, if $\nu_m > \nu_n$ and $\Omega > 0$, the particles drift against the wavevector $\boldsymbol{k}$. The momentum conservation law causes the buffer gas to move in the opposite direction.

The same effect as LID is also produced qualitatively by spontaneous light pressure, i.e. it produces flows of absorbing particles in the gas, and leads to spatial redistribution of the density. We compare now the degrees of manifestation of LID and of spontaneous light pressure. Let us consider a gas in a cell with closed ends. In this case $\boldsymbol{j} = \boldsymbol{j}_m + \boldsymbol{j}_n = 0$ and therefore $\boldsymbol{F} = -(\nu_m - \nu_n)\boldsymbol{j}_m$. If $\Omega = k\bar{v}$, we obtain the following rough estimate for the friction force density:

$$F \sim m_a(\nu_n - \nu_m)\bar{v}\rho_m$$

where $\bar{v}$ is the mean thermal velocity and ρ_m is the excited particle density. We compare this force with the spontaneous light pressure force, whose density $\boldsymbol{F}_L$ is approximately equal to $\hbar k \gamma_m \rho_m$. Here, γ_m is the decay constant of the excited state. For $\gamma_m \sim \nu_m$ we obtain

$$\frac{F}{F_L} \sim \frac{m_a \bar{v}}{\hbar k}\left(\frac{\nu_n - \nu_m}{\nu_m}\right).$$

The principal factor that determines this relation is $m_a\bar{v}/\hbar k$—the ratio of the thermal momentum of the particle to the photon momentum. For the optical region of the spectrum and at room temperature $m_a\bar{v}/\hbar k \sim 10^4$. Thus, the force density F causing LID can exceed the force density of the spontaneous light pressure by three or four orders of magnitude.

Unlike the light pressure and other effects LID is not connected with the direct force action exerted by the radiation on the individual particles. In this respect LID occupies a special position. The energy of the directional motion of the particles, produced in the case of LID, is drawn from the thermal energy of the gas. This decreases, of course, the entropy of the gas mixture, but this decrease is offset by the entropy of the radiation produced when it is scattered in the gas.

In the earliest publications (see Gel'mukhanov and Shalagin 1979, 1980a) and in almost all subsequent theoretical works on LID a model of absorptive particles with non-degenerate energy levels was used. The first step in the calculation of the multilevel structure of real objects has been made by Gel'mukhanov and Shalagin (1980b), Dykhne and Starostin (1980) and Mironenko and Shalagin (1981) who investigated LID at the vibrational-rotational transition of molecules. But the degeneracy of the energy levels of absorptive particles has not been taken into account in these works. This degeneracy has been considered by Gel'mukhanov (1982), and the kinetic equation for the density matrix of the two-level system has been solved in the linear radiation intensity approximation and in the limit of the homogeneously broadening absorption line. In this statement the drift velocity does not depend on the radiation polarisation, as has been shown.

Widely available experimental data were treated using non-degenerate levels in the LID phenomenon theory. On the other hand, the precision and reliability of available experimental results, especially for molecular objects, give rise to the indispensability of a modification of the theoretical description. A new formalism must describe the LID phenomenon taking into account the level degeneracy under arbitrary radiation intensity conditions with regard to collisional transitions between rotational levels and magnetic sublevels.

This problem is not solvable in the general case. But for molecules the situation of having large rotational quantum numbers J_m and J_n is typical ($J_m, J_n \gg 1$). In this limit a semiclassical description of rotational motion is effective.

The main aim of the present paper is to investigate the influence of the level degeneracy and radiation polarisation in the translational non-equilibrium state which is induced by light (the LID phenomenon).

The basic idea of our work is as follows. The main Ω dependence of the LID effect is described by a so-called φ function (see below). From the LID theory of particles with non-degenerate levels it is known that in the general case the φ function depends on the light intensity and on a dipole matrix element of transition n-m (Mironenko and Shalagin 1981). However, the degeneracy of the magnetic M sublevels takes place in the real atoms and molecules. The M distribution of particles influence the φ function due to the M dependence of the dipole matrix element of a transition. But the M distribution of particles depends on the light polarisation. Hence the φ function must also depend on the light polarisation.

2. Kinetic equations in the semiclassical description of rotational motion

The interaction of particles with a running monochromatic wave $\boldsymbol{E}\exp(-\mathrm{i}\omega t+\mathrm{i}\boldsymbol{kr})$, which is resonant to the vibrational-rotational transition nJ_0-mJ_0', is described by the following system of kinetic equations for the density matrix (see Rautian *et al* 1979) ($\mathrm{d}/\mathrm{d}t=\partial/\partial t+\boldsymbol{v}\nabla$):

$$
\begin{aligned}
&(\mathrm{d}/\mathrm{d}t)\boldsymbol{\rho}_m(J\boldsymbol{v}) = \boldsymbol{S}_m(J\boldsymbol{v})+\mathrm{i}\delta_{JJ_0'}[\boldsymbol{\rho}_{mn}(\boldsymbol{v})\boldsymbol{V}_{nm}-\boldsymbol{V}_{mn}\boldsymbol{\rho}_{nm}(\boldsymbol{v})]\\
&(\mathrm{d}/\mathrm{d}t)\boldsymbol{\rho}_n(J\boldsymbol{v}) = \boldsymbol{S}_n(J\boldsymbol{v})+\mathrm{i}\delta_{JJ_0}[\boldsymbol{\rho}_{nm}(\boldsymbol{v})\boldsymbol{V}_{mn}-\boldsymbol{V}_{nm}\boldsymbol{\rho}_{mn}(\boldsymbol{v})] \qquad (2.1)\\
&[(\mathrm{d}/\mathrm{d}t)+\Gamma-\mathrm{i}(\Omega-\boldsymbol{kv})]\boldsymbol{\rho}_{mn}(\boldsymbol{v}) = S_{mn}(\boldsymbol{v})+\mathrm{i}[\boldsymbol{\rho}_m(J_0'\boldsymbol{v})\boldsymbol{V}_{mn}-\boldsymbol{V}_{mn}\boldsymbol{\rho}_n(J_0\boldsymbol{v})].
\end{aligned}
$$

Matrices $\boldsymbol{\rho}_i(J\boldsymbol{v})$ ($i=m, n$), $\boldsymbol{\rho}_{mn}(\boldsymbol{v})$ with the corresponding elements $\rho_i(JM|JM'\boldsymbol{v})$, $\rho_{mn}(J_0'M'|J_0M\boldsymbol{v})$ are presented here; M, M' enumerate the magnetic sublevels, $\boldsymbol{V}_{mn}$ is the intersection matrix with the elements $V_{mn}(J_0'M'|J_0M)$ and Γ is the homogeneous linewidth of the absorption line. The collisional integral $\boldsymbol{S}_i(J\boldsymbol{v})$ for particles with degenerate levels was first investigated by Waldman (1957, 1958) and Snider (1960, 1964). The collisional relaxation of the off-diagonal element of the density matrix is described by the collisional integral $\boldsymbol{S}_{mn}(\boldsymbol{v})$ whose structure has been investigated by Andreeva *et al* (1973).

The solution of the system (2.1) under conditions of arbitrary radiation intensity and J is a very complicated problem. We shall consider this system in the semiclassical limit $J \gg 1$, which allows us to simplify its solution considerably. This approach has been made by Ducloy (1975, 1976) and Nasyrov and Shalagin (1981). Following the latter work we transform equation (2.1) from the JM representation to the new one

with transformation of the density matrix elements and the interaction Hamiltonian

$$\rho_i(sJv) = \frac{J}{2\pi}\sum_{\mu}\exp(-i\mu\varphi)\rho_i(J\bar{M}+\mu/2|\bar{J}M-\mu/2, v)$$

$$\rho_{mn}(sv) = \frac{\bar{J}}{2\pi}\sum_{\mu}\exp(-i\mu\varphi)\rho_{mn}(J_0'\bar{M}+\mu/2|J_0\bar{M}-\mu/2, v) \qquad (2.2)$$

$$V_{mn}(s) = \sum_{\mu}\exp(-i\mu\varphi)V_{mn}(J_0'\bar{M}+\mu/2|J_0\bar{M}-\mu/2).$$

Here s is a unit vector of the direction of semiclassical angular momentum; s is characterised by the polar (θ) and azimuthal (φ) angles, and

$$\cos\theta = \bar{M}/J \qquad \text{or} \qquad \cos\theta = \bar{M}/\bar{J} \qquad \bar{J} = \tfrac{1}{2}(J_0+J_0').$$

Transformation (2.2) is analogous to the Wigner transformation for translational degrees of freedom (see Landau and Lifshitz 1976, Rautian *et al* 1979).

In the new representation when $J \gg 1$ equations (2.1) have the following form:

$$\begin{aligned}
&(d/dt)\rho_m(sJv) = S_m(sJv) + \delta_{JJ_0'}\rho p(sv)\\
&(d/dt)\rho_n(sJv) = S_n(sJv) - \delta_{JJ_0}\rho p(sv)\\
&[(d/dt)+\Gamma - i(\Omega - kv)]\rho_{mn}(sv) = S_{mn}(sv) + i\,V_{mn}(s)[\rho_m(sJ_0'v) - \rho_n(sJ_0v)]\\
&p(sv) = (2/\rho)\,\mathrm{Re}[i(V_{mn}^*(s)\rho_{mn}(sv)].
\end{aligned} \qquad (2.3)$$

In these equations neither an exchange of angular momentum between a photon and a molecule nor a momentum exchange are taken into account. The differential terms presented in the paper of Nasyrov and Shalagin (1981) are responsible for the angular momentum exchange (these terms vanish when $J \gg 1$).

In this paper the collisional relaxation of the absorptive particles has been described within the limits of the model of relaxation constants. It seems to be natural to introduce the semiclassical representation of angular momentum in exact collisional integrals.

We proceed from the collisional integrals in the JM representation which have been adduced in the book by Rautian *et al* (1979). Using some calculations and the optical theorem we obtain

$$\begin{aligned}
S_i(sJv) = \sum_{jJ'}\int\,&[A_{ij}(sJv|s'J'v')\rho_j(s'J'v')\\
&- A_{ji}(s'J'v'|sJv)\rho_i(sJv)]\,ds'\,dv' \qquad (i,j=m,n).
\end{aligned} \qquad (2.4)$$

A semiclassical limit form (2.4) for the collisional integral has been proposed by some authors. A review of these works can be found in the paper by Kuščer *et al* (1981), where the connection between classical and quantum mechanical Boltzmann equations is considered. The collisional integral kernels in (2.4) have the following connection with characteristics of a collisional elementary act:

$$\begin{aligned}
A_{ij}(sJv|s'J'v') = 2\sum_{J_bJ_b'}\int\,&ds_b\,ds_b'\,du\,du'\,\delta[v-v'-(u-u')m/m_a]\\
&\times\delta(u^2-u'^2+2\Delta E/m)\rho_b(s_b'J_b'v'-u')\sigma_{ij}(sJs_bJ_bu|s'J's_b'J_b'u')\\
&\Delta E = E_i(J)-E_j(J')+E(J_b)-E(J_b')
\end{aligned} \qquad (2.5)$$

where

$$\sigma_{ij}(sJs_bJ_bu|s'J's'_bJ'_bu') = (2\pi)^{-2}JJ_b \sum_{\mu\mu'} \sum_{\mu_B\mu'_B} \exp[i(\mu'\varphi' - \mu\varphi + \mu'_b\varphi'_b - \mu_b\varphi_b)]$$
$$\times f_{ij}(J, \bar{M}+\mu/2, J_b, \bar{M}_b+\mu_b/2, u|J', \bar{M}'+\mu'/2, J'_b, \bar{M}'_b+\mu'_b/2, u')$$
$$\times f_{ij}(J, \bar{M}-\mu/2, J_b, \bar{M}_b-\mu_b/2, u|J', \bar{M}'-\mu'/2, J'_b, \bar{M}'_b-\mu'_b/2, u')$$

is the collisional cross section which is expressed in scattering amplitudes $f_{ij}(JMJ_bM_bu|J'M'J'_bM'_bu')$, $m = m_am_b/(m_a+m_b)$ is the reduced mass of colliding particles (m_a and m_b are masses of absorptive and buffer particles, respectively), u and u' are relative velocities of particles before and after a collision and the δ functions in (2.5) represent the momentum and energy conservation laws.

In the collisional integrals $S_m(sJv)$ and $S_n(sJv)$ in (2.4) a collisional exchange between rotational levels in m and n states and a collisional decay of the excited vibrational state m are taken into account. In the kernel of a collisional integral only the collisions of the absorptive particles with buffer particles are taken into account. This assumption is true if the buffer particle density ρ_B is great in comparison with the density ρ of the absorptive particles. Below we assume that $\rho_B \gg \rho$.

Analogous calculations for the collisional integral $S_{mn}(sv) = -S^{(1)}_{mn}(sv) + S^{(2)}_{mn}(sv)$ in the equation for the off-diagonal element $\rho_{mn}(sv)$ lead to the extinction term

$$S^{(1)}_{mn}(sv) = \frac{2\pi\hbar}{im} \sum_{J_B} \int ds_b\, du\, \rho_b(s_bJ_bv - u)[f_{mm}(sJ'_0s_bJ_bu) - f_{nn}(sJ_0s_bJ_bu)]\rho_{mn}(sv) \tag{2.6}$$

where the scattering amplitudes in the $\theta\varphi$ representation take place:

$$f_{ij}(sJs_bJ_bu) = \sum_{\mu\mu_B} \exp[-i(\mu\varphi + \mu_b\varphi_b)]$$
$$\times f_{ij}(J, \bar{M}+\mu/2, J_b, \bar{M}_b+\mu_b/2, u|J, \bar{M}-\mu/2, J_B, \bar{M}_B-\mu_B/2, u).$$

For $S^{(2)}_{mn}(sv)$ we have

$$S^{(2)}_{mn}(sv) = \int ds'\, dv'\, A(sv|s'v')\rho_{mn}(s'v'). \tag{2.7}$$

In the kernel

$$A(sv|s'v') = \sum_{J_B} \int ds_b\, ds'_b\, du\, d\hat{u}'\, u\delta[v - v' - (u-u')m/m_a]\rho_b(s'_bJ_bv' - u')\sigma(ss_bu|s's'_bu') \tag{2.8}$$

only elastic collisions ($u = u'$) make a contribution; $d\hat{u}'$ is the differential of angle coordinates u'

$$\sigma(ss_bu|s's'_bu') = (2\pi)^{-2}\bar{J}J_b \sum_{\mu\mu'} \sum_{\mu_B\mu'_B} \exp[i(\mu'\varphi' - \mu\varphi + \mu'_b\varphi'_b - \mu_b\varphi_b)]$$
$$\times f_{mm}(J'_0, \bar{M}+\mu/2, J_b, \bar{M}_b+\mu_b/2, u|J'_0, \bar{M}'+\mu'/2, J_b, \bar{M}'_b+\mu'_b/2, u')$$
$$\times f_{nn}(J_0, \bar{M}-\mu/2, J_b, \bar{M}_b-\mu_b/2, u|J_0, \bar{M}'-\mu'/2, J_b, \bar{M}'_b-\mu'_b/2, u').$$

In contrast to $S_i(sJv)$ from (2.4) the use of the optical theorem does not reduce $S_{mn}(sv)$ to a more compact form.

We shall find the expressions for the LID velocity. Multiplying both parts of (2.3) by $m_a \boldsymbol{v}$, integrating over $\boldsymbol{v}$, $\boldsymbol{s}$ and summing over J we obtain a gas dynamical equation for flows of the absorption particles

$$\boldsymbol{j}_i = \sum_J \int \mathrm{d}\boldsymbol{s}\, \mathrm{d}\boldsymbol{v}\, \boldsymbol{v}\rho_i(\boldsymbol{sJv}).$$

The integrals

$$m_a \sum_J \int \mathrm{d}\boldsymbol{s}\, \mathrm{d}\boldsymbol{v}\, \boldsymbol{v}S_i(\boldsymbol{sJv})$$

on the right-hand sides of these equations define the friction force density $\boldsymbol{F}_i$ which acts on the flow $\boldsymbol{j}_i$ from the side of the buffer particles. For the total force density acting on the absorptive gas we can obtain

$$\boldsymbol{F} = \boldsymbol{F}_m + \boldsymbol{F}_n = -m_a \sum_J \int \mathrm{d}\boldsymbol{s}\, \mathrm{d}\boldsymbol{v}\, \boldsymbol{v}[\nu_m(\boldsymbol{sJv})\rho_m(\boldsymbol{sJv}) + \nu_n(\boldsymbol{sJv})\rho_n(\boldsymbol{sJv})] \tag{2.9}$$

with the transport collisional frequencies

$$\begin{aligned} &\nu_m(\boldsymbol{sJv}) = \nu_{mm}(\boldsymbol{sJv}) + \nu_{nm}(\boldsymbol{sJv}) \qquad \nu_n(\boldsymbol{sJv}) = \nu_{nn}(\boldsymbol{sJv}) \\ &\nu_{ij}(\boldsymbol{sJv}) = \sum_{J'} \int \mathrm{d}\boldsymbol{v}'\, \mathrm{d}\boldsymbol{s}'(1 - \boldsymbol{vv}'/v^2) A_{ij}(\boldsymbol{s'J'v'}|\boldsymbol{sJv}). \end{aligned} \tag{2.10}$$

For the transport collisional frequencies $\nu_{ii}(\boldsymbol{sJv})$ the processes of velocity change, J–J exchange and change of the angular momentum direction $\boldsymbol{s}$ for the particles in the vibrational state i are taken into account; $\nu_{nm}(\boldsymbol{sJv})$ is the transport frequency of the collisional decay of the state m.

In this work we neglect some weak effects of the influence of light-induced multipole moments on the absorptive particle drift (see Gel'mukhanov and Il'ichov 1985) and so the total friction force density $\boldsymbol{F}$ is collinear to the flows $\boldsymbol{j}_m$ and $\boldsymbol{j}_n$ and can be represented as

$$\boldsymbol{F} = -m_a(\nu_m \boldsymbol{j}_m + \nu_n \boldsymbol{j}_n) \qquad \nu_m = \nu_{mm} + \nu_{nm} \qquad \nu_n = \nu_{nn}. \tag{2.11}$$

Introduced here are the coefficients ν_{ij} defined by the following integral equations:

$$\nu_{ij}\boldsymbol{j}_j \equiv \sum_J \int \mathrm{d}\boldsymbol{s}\, \mathrm{d}\boldsymbol{v}\, \nu_{ij}\boldsymbol{v}\rho_j(\boldsymbol{sJv}) = \sum_J \int \mathrm{d}\boldsymbol{s}\, \mathrm{d}\boldsymbol{v}\, \nu_{ij}(\boldsymbol{sJv})\boldsymbol{v}\rho_j(\boldsymbol{sJv}). \tag{2.12}$$

As is evident from these equations, the quantities ν_{ij} depend in the general case on a distribution function form and, consequently, on radiation characteristics (intensity, spectrum, polarisation). The degree of this dependence is determined by the dependence of collisional frequencies on $\boldsymbol{s}$, J and $\boldsymbol{v}$.

Thus the quantities ν_{ij}, as is clear from (2.12), are the transport frequencies $\nu_{ij}(\boldsymbol{sJv})$ averaged in a definite manner. If the dependence of $\nu_{ij}(\boldsymbol{sJv})$ on $\boldsymbol{s}$, J and $\boldsymbol{v}$ can be neglected, ν_{ij} and $\nu_{ij}(\boldsymbol{sJv})$ are undistinguished. In particular a velocity dependence of collisional frequencies which corresponds to the total cross section has been analysed in some works on non-linear spectroscopy (see for example Rautian *et al* 1979). As has been shown, collisional frequency depends weakly on velocity in some cases. It is to be noted that the dependence of collisional frequencies on velocity is neglected in the majority of papers on non-linear spectroscopy.

Let us define a drift velocity $\boldsymbol{U}$ of the absorptive particles. Under spatially homogeneous conditions the total friction force $\boldsymbol{F}$ is absent. So from (2.11) we have

$$\boldsymbol{U} = \frac{\boldsymbol{j}_m + \boldsymbol{j}_n}{\rho} = \boldsymbol{j}_m \left(\frac{\nu_n - \nu_m}{\rho \nu_n} \right). \tag{2.13}$$

The flow of excited particles can be determined from (2.3) by multiplying it by $\boldsymbol{v}$, integrating it over $\boldsymbol{v}$ and $\boldsymbol{s}$ and summing over J:

$$(\nu_{mm} + \tilde{\nu}_{nm}) \boldsymbol{j}_m = (\boldsymbol{k}/k) \bar{v} p \rho \varphi(\Omega) \tag{2.14}$$

$$p = \int p(\boldsymbol{sv}) \, \mathrm{d}\boldsymbol{s} \, \mathrm{d}\boldsymbol{v} \qquad \varphi(\Omega) = (k\bar{v}p)^{-1} \int \boldsymbol{kv} p(\boldsymbol{sv}) \, \mathrm{d}\boldsymbol{s} \, \mathrm{d}\boldsymbol{v} \tag{2.15}$$

where p is the absorptive probability for a unit time, $\varphi(\Omega)$ is a function which gives the dependence of LID on the frequency detuning Ω (Gel'mukhanov and Shalagin 1980b, Mironenko and Shalagin 1981) and the quantity $\tilde{\nu}_{nm}$ is the collisional decay frequency for the m state, which is defined by the following equation:

$$\tilde{\nu}_{nm} \boldsymbol{j}_m \equiv \sum_J \int \mathrm{d}\boldsymbol{s} \, \mathrm{d}\boldsymbol{v} \, \tilde{\nu}_{nm} \boldsymbol{v} \rho_m(\boldsymbol{sJv}) = \sum_J \int \mathrm{d}\boldsymbol{s} \, \mathrm{d}\boldsymbol{v} \, \tilde{\nu}_{nm}(\boldsymbol{sJv}) \boldsymbol{v} \rho_m(\boldsymbol{sJv}) \tag{2.16}$$

where

$$\tilde{\nu}_{nm}(\boldsymbol{sJv}) = \sum_{J'} \int \mathrm{d}\boldsymbol{s}' \, \mathrm{d}\boldsymbol{v}' \, A_{nm}(\boldsymbol{s'J'v'} | \boldsymbol{sJv}).$$

The expression for LID velocity follows directly from (2.13) and (2.14):

$$\boldsymbol{U} = \frac{\boldsymbol{k}}{k} \frac{(\nu_n - \nu_m) \bar{v} p \varphi(\Omega)}{\nu_n (\nu_{mm} + \tilde{\nu}_{nm})}. \tag{2.17}$$

From the experimental viewpoint the LID phenomenon can be conveniently detected from the measurement of the change of one-component concentration or partial pressure over the length of an absorptive cell.

It can be shown that the partial pressure overfall δP_a over the cell length is

$$\delta P_a = \frac{(\nu_m - \nu_n) m_a \bar{v} \varphi(\Omega)}{(\nu_{mm} + \nu_{nm}) \hbar \omega} \delta S \tag{2.18}$$

where δS is the absorbed radiation power density.

The expression (2.18) is convenient for the treatment of LID experimental results, because it relates the change of the partial pressure (or concentration) of the absorptive particles to an experimentally easily measurable quantity δS—the change of radiation intensity due to its absorption in the cell. The function $\varphi(\Omega)$ and the relative difference of the collisional frequencies constitute the specific character of the LID phenomenon. Here, as has been mentioned above, the main specific dependence on the frequency detuning is given by $\varphi(\Omega)$. An additional and generally weak dependence on Ω can be contained in the factor $(\nu_n - \nu_m)/(\nu_{mm} + \nu_{nm})$ due to the velocity dependence of collisional frequencies.

When the radiative intensity is weak an explicit expression for $\varphi(\Omega)$ can be obtained. Let us make an ordinary assumption about the absence of phase memory in collisions. It means neglecting the collisional integral S_{mn} in (2.3) for the off-diagonal element

ρ_{mn} and simultaneous renormalisation of the constant Γ (now Γ is a homogeneous linewidth). In the case of a running monochromatic wave

$$p(\boldsymbol{sv}) = \frac{\Gamma|G(\boldsymbol{s})|^2 \rho W(\boldsymbol{v}) W_B(J_0)}{2\pi[\Gamma^2 + (\Omega - \boldsymbol{kv})^2]} \qquad V_{mn}(\boldsymbol{s}) = -G(\boldsymbol{s}) \tag{2.19}$$

where $W(\boldsymbol{v})$ is the Maxwellian velocity distribution and $W_B(J)$ is the Boltzmann distribution for rotational levels. In accordance with the definition (2.15) we obtain the following expression for $\varphi(\Omega)$:

$$\varphi(\Omega) = \frac{\mathrm{Re}[zw(z)]}{\mathrm{Re}[w(z)]} \qquad z = \frac{\Omega + \mathrm{i}\Gamma}{k\bar{v}}$$
$$w(z) = \exp(-z^2)\left(1 + 2\pi^{-1/2}\mathrm{i}\int_0^z \exp(t^2)\,\mathrm{d}t\right). \tag{2.20}$$

In the case of a higher radiation intensity the expression for $\varphi(\Omega)$ becomes dependent on a concrete collisional mechanism and on the degeneracy of energy levels.

The collisional mechanism has been analysed in some aspects in early theoretical works on LID for the model of non-degenerate levels. Our theory permits us, in addition, to consider the degree of the influence of this degeneracy on $\varphi(\Omega)$. To make the analysis easier and to discover the degeneracy effects in 'pure' form we shall simplify as much as possible the collisional part of the problem, i.e. we shall exploit the model of strong collisions.

3. The model of strong collisions

In the model of strong collisions the equations for $\rho_m(\boldsymbol{sJv})$ and $\rho_n(\boldsymbol{sJv})$ under stationary spatially homogeneous conditions have the following form:

$$(\gamma_m + \nu_m)\rho_m(\boldsymbol{sJv}) = \nu_{m\mathrm{T}}\rho_m(\boldsymbol{sJ})\,W(\boldsymbol{v}) + \nu_{m\mathrm{R}}\rho_m W(\boldsymbol{v})\,W_B(J)/4\pi + \rho p(\boldsymbol{sv})\delta_{JJ_0'}$$
$$\nu_n\rho_n(\boldsymbol{sJv}) = \nu_{n\mathrm{T}}\rho_n(\boldsymbol{sJ})\,W(\boldsymbol{v}) + \nu_{n\mathrm{R}}\rho_n W(\boldsymbol{v})\,W_B(J)/4\pi \tag{3.1}$$
$$+ \nu_{m\mathrm{V}}\rho_m W(\boldsymbol{v})\,W_B(J)/4\pi + \gamma_m\rho_m(\boldsymbol{sJv}) - \rho p(\boldsymbol{sv})\delta_{JJ_0}$$

where

$$\nu_m = \nu_{m\mathrm{T}} + \nu_{m\mathrm{R}} + \nu_{m\mathrm{V}} \qquad \nu_n = \nu_{n\mathrm{T}} + \nu_{n\mathrm{R}}$$
$$\rho_i(\boldsymbol{sJ}) = \int \rho_i(\boldsymbol{sJv})\,\mathrm{d}\boldsymbol{v} \qquad \rho_i = \sum_J \int \rho_i(\boldsymbol{sJ})\,\mathrm{d}\boldsymbol{s}.$$

In these equations collisional processes of the following four types are taken into account: with a strong velocity change but without a change of rotational and oscillational state (frequencies $\nu_{i\mathrm{T}}$), the collisions establishing the equilibrium distribution $W(\boldsymbol{v})\,W_B(J)/4\pi$ according to rotational and translational degrees of freedom (frequencies $\nu_{i\mathrm{R}}$), the collisions which initiate the downward transition $m \to n$ and establish a simultaneous equilibrium distribution over $\boldsymbol{s}$, J and $\boldsymbol{v}$ (frequency $\nu_{m\mathrm{V}}$) and, finally, the decay of the m state without a change of $\boldsymbol{v}$, J and $\boldsymbol{s}$ (frequency γ_m). In (3.1) the

field term $\rho p(\boldsymbol{sv})$ is used, which gives the number of light-induced transitions $(nJ_0\boldsymbol{sv}) \to (mJ_0'\boldsymbol{sv})$ for unit time. In the absence of a phase memory we have

$$\rho p(\boldsymbol{sv}) = \frac{2\Gamma|G(\boldsymbol{s})|^2}{\Gamma^2 + (\Omega - \boldsymbol{kv})^2}[\rho_n(\boldsymbol{sJ}_0\boldsymbol{v}) - \rho_m(\boldsymbol{sJ}_0'\boldsymbol{v})]. \tag{3.2}$$

The distribution functions $\rho_m(\boldsymbol{sJv})$ and $\rho_n(\boldsymbol{sJv})$ can be presented as

$$\begin{aligned}\rho_m(\boldsymbol{sJv}) &= \rho[\tau_{1m}p(\boldsymbol{sv})\delta_{JJ_0'} + \tau_{2m}p(\boldsymbol{s})W(\boldsymbol{v})\delta_{JJ_0'} + \tau_{3m}pW(\boldsymbol{v})W_B(J)/4\pi] \\ \rho_n(\boldsymbol{sJv}) &= \rho[W(\boldsymbol{v})W_B(J)/4\pi - (\tau_{1n}\delta_{JJ_0} - \tau_{1n}'\delta_{JJ_0'})p(\boldsymbol{sv}) \\ &\quad - (\tau_{2n}\delta_{JJ_0} - \tau_{2n}'\delta_{JJ_0'})p(\boldsymbol{s})W(\boldsymbol{v}) - \tau_{3n}pW(\boldsymbol{v})W_B(J)/4\pi]\end{aligned} \tag{3.3}$$

where

$$\begin{aligned}&p(\boldsymbol{s}) = \int p(\boldsymbol{sv})\,\mathrm{d}\boldsymbol{v} \qquad p = \int p(\boldsymbol{s})\,\mathrm{d}\boldsymbol{s} \\ &\tau_{1m} = (\gamma_m + \nu_m)^{-1} \qquad \tau_{1m} + \tau_{2m} = (\gamma_m + \nu_{m\mathrm{R}} + \nu_{m\mathrm{V}})^{-1} \\ &\tau_{1n} = \nu_n^{-1} \qquad \tau_{1n} + \tau_{2n} = \nu_{n\mathrm{R}}^{-1} \\ &\tau_{1n}' = \frac{\gamma_m/\nu_n}{\gamma_m + \nu_m} \qquad \tau_{1n}' + \tau_{2n}' = \frac{\gamma_m/\nu_{n\mathrm{R}}}{\gamma_m + \nu_{m\mathrm{R}} + \nu_{m\mathrm{V}}} \\ &\tau_{1m} + \tau_{2m} + \tau_{3m} = \tau_{1n} - \tau_{1n}' + \tau_{2n} - \tau_{2n}' + \tau_{3n} = (\gamma_m + \nu_{m\mathrm{V}})^{-1}.\end{aligned}$$

From (3.2) and (3.3) we obtain the following expression for the field term, which gives the velocity non-equilibrium terms in $\rho_i(\boldsymbol{sJv})$:

$$\rho p(\boldsymbol{sv}) = \frac{\rho W_B(J_0)X(\Omega\boldsymbol{sv})}{1 + \tau_3 X(\Omega)}. \tag{3.4}$$

The following notation is introduced here:

$$\begin{aligned}&X(\Omega\boldsymbol{sv}) = \frac{|G(\boldsymbol{s})|^2 Y(\Omega\boldsymbol{sv})(2\pi\Gamma)^{-1}}{1 + 2\tau_2|G(\boldsymbol{s})|^2 Y(\Omega\boldsymbol{s})\Gamma^{-1}} \\ &Y(\Omega\boldsymbol{sv}) = \frac{\Gamma^2 W(v)}{\Gamma^2(1 + 2\tau_1|G(\boldsymbol{s})|^2\Gamma^{-1}) + (\Omega - \boldsymbol{kv})^2} \\ &X(\Omega) = \int X(\Omega\boldsymbol{sv})\,\mathrm{d}\boldsymbol{s}\,\mathrm{d}\boldsymbol{v} \qquad Y(\Omega\boldsymbol{s}) = \int Y(\Omega\boldsymbol{sv})\,\mathrm{d}\boldsymbol{v} \\ &\tau_1 = \tau_{1n} + \tau_{1m} - \tau_{1n}'\delta_{J_0J_0'} \qquad \tau_2 = \tau_{2n} + \tau_{2m} - \tau_{2n}'\delta_{J_0J_0'} \\ &\tau_3 = \tau_{3n}W_B(J_0) + \tau_{3m}W_B(J_0').\end{aligned} \tag{3.5}$$

For the drift velocity

$$\boldsymbol{U} = \rho^{-1}\sum_J \int \boldsymbol{v}[\rho_m(\boldsymbol{sJv}) + \rho_n(\boldsymbol{sJv})]\,\mathrm{d}\boldsymbol{s}\,\mathrm{d}\boldsymbol{v}$$

we obtain, using (3.3), the expression

$$\boldsymbol{U} = \frac{\boldsymbol{k}}{k}\frac{(\nu_n - \nu_m)\bar{v}p\varphi(\Omega)}{\nu_n(\gamma_m + \nu_m)} \tag{3.6}$$

which coincides with (2.17). The frequencies of strong collisions play the role of transport frequencies. Taking into account the structure of the field term, the function

$\varphi(\Omega)$ can be given by the following expression:

$$\varphi(\Omega)=\frac{\int \boldsymbol{kv}X(\Omega \boldsymbol{sv})\,\mathrm{d}\boldsymbol{s}\,\mathrm{d}\boldsymbol{v}}{k\bar{v}X(\Omega)}. \tag{3.7}$$

Let us assume the molecule lifetime in vibrational-rotational levels mJ_0' and nJ_0 with velocity equilibrium small, so that

$$\tau_2^{-1} \gg \max \Gamma^{-1}|G(\boldsymbol{s})|^2 Y(\Omega \boldsymbol{s}).$$

In this case the expression for $\varphi(\Omega)$ can be simplified considerably and it takes the form

$$\varphi(\Omega)=\frac{\int \boldsymbol{kv}|G(\boldsymbol{s})|^2 Y(\Omega \boldsymbol{sv})\,\mathrm{d}\boldsymbol{s}\,\mathrm{d}\boldsymbol{v}}{k\bar{v}\int |G(\boldsymbol{s})|^2 Y(\Omega \boldsymbol{sv})\,\mathrm{d}\boldsymbol{s}\,\mathrm{d}\boldsymbol{v}}. \tag{3.8}$$

The general form for $G(\boldsymbol{s})$ under electric dipole interaction is (Nasyrov and Shalagin 1981)

$$G(\boldsymbol{s})=\sum_{\sigma} G^{\sigma} D^{(1)*}_{\sigma\Delta}(\varphi\theta 0) \qquad \Delta = J_0' - J_0.$$

Here $G^{\sigma}=E^{\sigma}d_{mn}/2\hbar(2\bar{J})^{1/2}$, E^{σ} are circular contravariant components of the electric field ($\sigma=-1,0,1$), d_{mn} is the matrix element of the reduced dipole moment and $D^{(1)}_{\sigma\Delta}(\alpha\beta\gamma)$ are the Wigner functions. When $J_0=J_0'$ (Q branch) $G(\boldsymbol{s})=\boldsymbol{G}\boldsymbol{s}$.

We shall calculate $\varphi(\Omega)$ for linear and circular polarisations. The result of $\boldsymbol{s}$ integration in (3.8) is expressed through elementary functions

$$\varphi_{0,1}(\Omega)=\int_{-\infty}^{\infty} x\exp(-x^2)f_{0,1}(x)\,\mathrm{d}x\left(\int_{-\infty}^{\infty}\exp(-x^2)f_{0,1}(\tilde{x})\,\mathrm{d}x\right)^{-1} \qquad x=\boldsymbol{kv}/k\bar{v}. \tag{3.9}$$

The indices 0 and 1 correspond to linear and circular polarisations, respectively. In the case of a linear polarisation we have

$$f_0(x)=1-\zeta\tan^{-1}(\zeta^{-1}) \qquad \zeta=\zeta(x)=(\varkappa^{-1}\{1+[(xk\bar{v}-\Omega)/\Gamma]^2\})^{1/2} \tag{3.10}$$

and for a circular polarisation

$$f_1(x)=1-2^{-1/2}\zeta\ln\left(\frac{(1+2\zeta^2)^{1/2}+1}{(1+2\zeta^2)^{1/2}-1}\right). \tag{3.11}$$

The saturation parameter $\varkappa=2\tau_1|G|^2/\Gamma$ is introduced here.

In the model of non-degenerate levels and strong collisions the function of detuning (we shall designate it $\tilde{\varphi}(\Omega)$) is given by (3.9) where $f_{0,1}(x)$ are replaced by $f(x)=[\varkappa(1+\zeta^2)]^{-1}$. By integrating (3.9) with $f(x)$ over x we obtain (2.20) with $z=[\Omega+\mathrm{i}\Gamma(1+\varkappa)^{1/2}]/k\bar{v}$.

In the present paper the functions $\varphi_0(\Omega)$, $\varphi_1(\Omega)$ and $\tilde{\varphi}(\Omega)$ are calculated for different ratios $k\bar{v}/\Gamma$ and $\Gamma_B/k\bar{v}$, where Γ_B/k is a half-width of the Bennet structure in a velocity distribution of molecules. $\Gamma_B/k\bar{v}$ is determined by a half-width of $f_0(x)$, $f_1(x)$ and $\tilde{f}(x)$. The corresponding graphs are represented in figure 1. In the case of R and P branches (transitions $J_0\to J_0\pm 1$) the expressions for $\varphi_0(\Omega)$ and $\varphi_1(\Omega)$ coincide with $\varphi_1(\Omega)$ and $\varphi_0(\Omega)$ for the Q branch (transition $J_0\to J_0$) respectively.

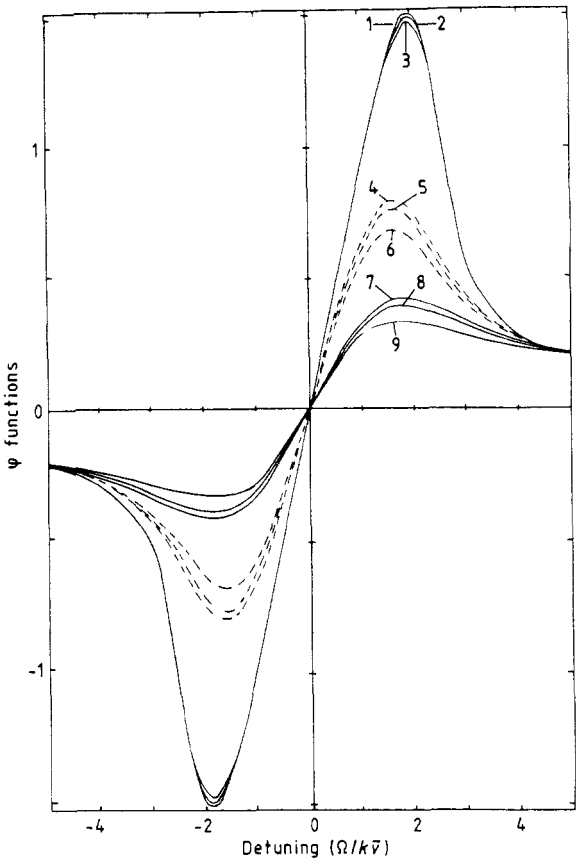

Figure 1. Functions $\tilde{\varphi}$, φ_1 and φ_0. (*a*) $k\bar{v}/\Gamma = 100$, $\Gamma_B/\Gamma = 3$ (1: $\tilde{\varphi}$, 2: φ_1, 3: φ_0) (*b*) $k\bar{v}/\Gamma = 30$, $\Gamma_B/\Gamma = 10$ (4: $\tilde{\varphi}$, 5: φ_1, 6: φ_0) (*c*) $k\bar{v}/\Gamma = 10$, $\Gamma_B/\Gamma = 10$ (7: $\tilde{\varphi}$, 8: φ_1, 9: φ_0).

4. Discussion

Hitherto the function $\tilde{\varphi}(\Omega)$, which corresponds to the model of non-degenerate levels, has being used for the analysis of experimental material for the LID of molecules. The question concerning the correctness of this use is natural.

To answer this question we compare $\varphi_0(\Omega)$ and $\varphi_1(\Omega)$ with $\varphi(\Omega)$. It seems to be natural to compare these functions for the same ratio $\Gamma/k\bar{v}$ of homogeneous and Doppler width and for an equal width of the Bennet structure Γ_B/k which is created by radiation in the velocity distribution of molecules. This width can be measured in an independent experiment.

The graphs in figure 1 have been constructed for three pairs of the ratios $\Gamma/k\bar{v}$ and $\Gamma_B/k\bar{v}$. We recall that $\Gamma_B/k\bar{v}$ is equal to the half-width of $f_0(x)$, $f_1(x)$ and $\tilde{f}(x)$, as it has been defined. The saturation parameter $\varkappa$ from the expressions for $f_0(x)$, $f_1(x)$ and $\tilde{f}(x)$ has been determined numerically for each function, so that the given half-width Γ_B/kv can be realised. The difference between $\varphi_0(\Omega)$ and $\varphi_1(\Omega)$ for the given ratios $\Gamma/k\bar{v}$ and Γ_B/kv is conditioned by the dependence of the non-equilibrium part of the velocity distribution on the radiation polarisation.

When $\Gamma_B/k\bar{v} \sim 1$, calculation of level degeneracy and radiation polarisation does not greatly change $\varphi_0(\Omega)$ and $\varphi_1(\Omega)$ in comparison with $\tilde{\varphi}(\Omega)$. When $\Gamma/k\bar{v} \sim 1$ the difference of $\varphi_0(\Omega)$, $\varphi_1(\Omega)$ and $\tilde{\varphi}(\Omega)$, as is evident from figure 1, can attain 10–20%, and this is realised for a sufficiently high radiation intensity ($\varkappa \gg 1$).

For weak intensity ($\varkappa \ll 1$), when

$$f_0(x) \simeq f_1(x) \simeq \tfrac{1}{3}\zeta^{-2}$$

all three functions $\varphi_0(\Omega)$, $\varphi_1(\Omega)$ and $\tilde{\varphi}(\Omega)$ coincide and are described by (2.20).

When $|\Omega| \gg kv$, Γ_B the behaviour of $\varphi_0(\Omega)$, $\varphi_1(\Omega)$ and $\tilde{\varphi}(\Omega)$ is also universal and does not depend on the radiation intensity and ratio $\Gamma/k\bar{v}$. Under these conditions the wings of $f_0(x)$, $f_1(x)$ and $\tilde{f}(x)$ in the area important for integration (near $|x| \leqslant 1$) have the same behaviour $\sim\zeta^{-2}$. Using the asymptote for $w(z)$ for $|z| \gg 1$

$$w(z) \simeq i\pi^{-1/2}[z - (1/2z)]^{-1}$$

and we have $\varphi_0(\Omega) \simeq \varphi_1(\Omega) \simeq \tilde{\varphi}(\Omega) \simeq k\bar{v}/\Omega$.

A promising use of the LID phenomenon for measurements of the collisional frequency ν_m or diffusion coefficient $D_m = v^2/2\nu_m$ of the excited molecules has been pointed out in the first papers on LID.

A diffusional coefficient for CH_3F in the excited vibrational state has been measured in this way (Panfilov *et al* 1983). It follows from the formula for the drift velocity or pressure change that the accuracy of $(\nu_n - \nu_m)/\nu_n$ measurements depends on the known precision of $\varphi(\Omega)$. The present paper shows that the difference between functions $\varphi_0(\Omega)$, $\varphi_1(\Omega)$ and $\tilde{\varphi}(\Omega)$, which corresponds to the model of non-degenerate levels is about 10–20%. Changing intensity and buffer gas pressure in the experiment we can work in the area of parameters $\Omega/k\bar{v}$, Γ/kv, $\Gamma_B/k\bar{v}$ where this difference is less than 1%.

Thus the use of the simple model of non-degenerate levels for an analysis of LID experimental results has proved to be correct in most cases. On the other hand a deviation from the model of strong collisions and the role of radiation polarisation can be detected in experiments with sufficiently high accuracy of measurement. For this aim, as it follows from the present paper, one has to choose the conditions

$$|\Omega| \sim \Gamma_B \sim k\bar{v} \qquad \varkappa \geqslant 1.$$

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