Optically induced drift of single-component gas in capillaries

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(Submitted 18 November 1992)
Zh. Eksp. Teor. Fiz. **103**, 1571–1583 (May 1993)

We investigate theoretically the drift of a single-component gas acted upon in a capillary by resonant optical radiation. We analyze the surface mechanism and so-called collisional mechanisms which are governed respectively by the difference between the accommodation coefficients and the collision cross sections of the excited and unexcited particles. An optically induced pressure difference in a closed cell is considered. The results are the dependences of the kinetic coefficients on the Knudsen number. A possibility, previously observed in experiment, of changing the drift direction in an intermediate regime is described. The theory and experiment are compared.

INTRODUCTION

Optically induced drift (OID), predicted in Ref. 1, consists of the onset of a directed macroscopic flow of a gas that absorbs optical radiation selectively in accord with the molecule velocities and is mixed with a buffer gas. The existence of a *bulk* OID requires in principle the presence of a buffer gas whose molecules interact differently with the excited and unexcited particles of the absorbing gas.

The feasibility of OID of a single-component gas in a capillary was demonstrated by Ghiner *et al.*[2] for a free-molecular regime, when the molecule mean free path exceeds greatly the capillary radius. The role of the buffer gas is assumed here by the surface of the capillary, with which the excited and unexcited particles interact differently. This is *surface* OID. The same mechanism was used[3] to estimate the OID of a single-component gas in a capillary under hydrodynamic conditions, with the molecule mean free path much shorter than the capillary radius. OID of a single-component gas was experimentally obtained in Ref. 4.

The pressure dependence of OID was investigated[5] in the gases $^{13}CH_3F$ and $^{12}CH_3F$ in a resonant infrared field. It was established that this dependence is nonmonotonic. Moreover, at intermediate pressures the OID reverses direction in the case of the $R(4,3)$ vibrational-rotational transition.

Analysis[2,3] of the theoretical results show that the experiments of Ref. 5 cannot be attributed to the OID surface mechanism.

Optically induced slip of a one-component gas along a plane surface was investigated in Refs. 6 and 7. A new so-called *collision* OID mechanism has been predicted, so named because it is due to the difference between the collision cross sections of the excited and unexcited particles and it exists independently of the character of the interaction between the gas and the surface. The collision OID mechanism, however, unlike the bulk mechanism,[1] is possible only in a confined gas. In some respect this is similar to diffuse slippage of an isotopic gas mixture.

The aim of the present paper is a theoretical study of the OID of a one-component gas in capillary, with account taken, in the description of the data of Ref. 5, of the collision and surface mechanisms, for arbitrary gas pressure from hydrodynamic to free-molecular. This can be done only by a rigorous solution of the Boltzmann gaskinetic equation or of its models.

BASIC ASSUMPTIONS AND EQUATIONS

Consider a single-component gas in a capillary of length L much larger than its radius r_0, so that the end-point distortions of the gas-stream profile can be neglected. A traveling light wave propagating along the capillary axis Z is absorbed by the gas particle via an electronic or a vibrational-rotational transition from the ground state n into the excited m. The frequency ω of the monochromatic radiation deviates from the center ω_{mn} of the absorption line by an amount $\Omega=(\omega-\omega_{mn})\ll\omega,\omega_{mn}$. Owing to the Doppler effect, the radiation interacts only with particles whose projection of the velocity $\mathbf{v}$ on the direction of the wave vector $\mathbf{k}$ are close to the resonant $\mathbf{kv}=\Omega$. The radiation-absorbing particles acquire new transport properties, particularly collision cross sections. The resultant resonant gas can be simulated in a two-level approximation by a binary gas mixture in which the particles have equal masses but different interaction cross sections. Particle exchange between the components is made possible here by radiative decay of the excited level and of the collisional and induced transitions.

The distributions f_m and f_n of the excited and unexcited particles in velocity have near the resonance values $v_z=\Omega/k$ a peak and a Bennett hole.[8] If $\Omega\neq0$, these distributions are asymmetric about $v_z=0$. There are therefore no macroscopic fluxes J_m and J_n of excited and unexcited particles oppositely directed along the capillary. If the different interaction with the surface and the different mean free paths cause the probabilities of flow of excited and unexcited capillaries through the capillary to differ, a resultant flux $J=J_m+J_n$, the OID, is produced.

Under stationary conditions, the distribution functions f_m and f_n satisfy in the two-level approximation the following system of kinetic equations:[8]

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$$\mathbf{v}\nabla f_m = \tfrac{1}{2}\varkappa(\mathbf{v})\Gamma_m(f_n - f_m) - \Gamma_m f_m + S_m,$$

$$\mathbf{v}\nabla f_n = -\tfrac{1}{2}\varkappa(\mathbf{v})\Gamma_m(f_n - f_m) + \Gamma_m f_m + S_n, \tag{1}$$

where

$$\varkappa(\mathbf{v}) = \frac{4|G_{mn}|^2\Gamma}{\Gamma_m[\Gamma^2 + (\Omega - \mathbf{kv})^2]}, \quad G_{mn} = \frac{Ed_{mn}}{2\hbar};$$

Γ_m is the radiative-decay constant; Γ is the homogeneous half-width of the absorption line; S_m and S_n are the Boltzmann collision integrals; E is the electric-field amplitude; d_{mn} is the dipole moment of the $m-n$ transition; $\hbar$ is the Planck constant; the saturation parameter $\varkappa(\mathbf{v})$ indicative of the probability of induced transitions is proportional to the emission intensity I.

Let the capillary and the gas have the same coordinate-independent temperature T. We assume also that the collisions of the molecules with the capillary surface are elastic and can be approximated by the specularly-diffuse Maxwell model, according to which the fraction ε_i of particles in a state i after collision with the surface is diffusely scattered with a Maxwellian velocity distribution, while the fraction $(1-\varepsilon_i)$ is specularly reflected. The boundary conditions for Eq. (1) take then the form

$$f_i^+(\mathbf{v}) = \varepsilon_i f_i^s(\mathbf{v}) + (1-\varepsilon_i) f_i^-[\mathbf{v} - 2(\mathbf{vn})\mathbf{n}], \quad \mathbf{vn} > 0; \tag{2}$$

$$f_i^s = n_i^s \left(\frac{m_0}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m_0 v^2}{2k_B T}\right); \quad i = m,n; \tag{3}$$

n is the inward normal to the capillary surface; the superscripts $+$, s, and $-$ label respectively the particles that are reflected, diffusely emitted, and incident on the surface; n_i^s is the numerical density of the diffusely emitted particles in the ith state; m_0 is the particle mass; k_B is Boltzmann's constant.

Consider the case of low values of the saturation parameter $\varkappa(\mathbf{v}) \ll 1$, which limits the radiation intensity I. The gas is then in a weak equilibrium and can be described by a distribution function that differs insignificantly from the equilibrium Maxwellians

$$f_i(\mathbf{r},\mathbf{v}) = f_{i0}[1 + h_i(\mathbf{r},\mathbf{v})], \tag{4}$$

where

$$f_{i0} = n_{i0}\left(\frac{m_0}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m_0 v^2}{2k_B T}\right), \quad i = m,n;$$

n_{i0} is the equilibrium numerical density of the particles in the ith state.

Further simplification is obtained by assuming that the interparticle collisions are elastic, and their frequencies are $\gamma_i = \gamma_{ii} + \gamma_{ij}$ (γ_{ii} and γ_{ij} are the collisions of the ith particles with one another and with the jth particles, respectively) is much larger than the radiative-decay constant Γ_m, i.e., $\Gamma_{mi} = \Gamma_m/\gamma_i \ll 1$.

The intensity change ΔI over the capillary length in an optically thin medium is small, and one can neglect in the first approximation the dependence of the perturbation function h_i on the longitudinal coordinate Z. We assume in addition that the emission intensity is uniform over the capillary cross section. The saturation parameter $\varkappa(\mathbf{v})$ is therefore independent of the radial coordinate r.

Under the above assumptions, the kinetic equation (1), linearized with respect to the perturbation functions h_i and the parameters Γ_{mi} and made nondimensional, takes when second-order approximating parameters[9] are used the form:

$$c_\perp \frac{\partial h_i}{\partial \mathbf{R}} + \delta_i h_i = \delta_i \Gamma_{mi} \frac{1}{2} \varkappa(\mathbf{v}) \left(\frac{n_{j0}}{n_{i0}} - 1\right) + 2\delta_i c_z [u_i - (u_i - u_j)\varphi_{ij}^{(1)}] + 4c_r c_z \delta_i [(1 - \varphi_{ii}^{(3)} + \varphi_{ii}^{(4)} - \varphi_{ij}^{(3)})\pi_{irz} + \varphi_{ij}^{(4)}\pi_{jrz}], \tag{5}$$

where

$$c = \frac{\mathbf{v}}{\bar{v}}, \quad \bar{v} = \left(\frac{2k_B T}{m_0}\right)^{1/2}, \quad c_\perp^2 = c_r^2 + c_\varphi^2,$$

$$\mathbf{R} = \frac{r}{r_0}, \quad \delta_i = \frac{\gamma_i}{\bar{v}} r_0, \quad \varphi_{ij}^{(n)} = \frac{\nu_{ij}^{(n)}}{\gamma_i}, \quad \varphi_{ii}^{(n)} = \frac{\nu_{ii}^{(n)}}{\gamma_i},$$

$$u_i = \frac{U_i}{\bar{v}} = \int c_z E h_i dc, \quad \pi_{irz} = \frac{P_{irz}}{2P_i} = \int c_r c_z E h_i dc,$$

$$\mathbf{E} = \pi^{-3/2} \exp(-c^2), \quad (i,j) = m,n, \quad i \neq j; \tag{6}$$

U_i, P_{irz}, and P_i are the partial velocity, stress tensor and pressure of the jth component of the mixture; δ_i is the rarefaction parameter and is inversely proportional to the Knudsen number (Kn, the ratio of the particle mean free path to the capillary radius); expressions for the frequencies $\nu_{ij}(n)$ in terms of the Chapman–Cowling integrals that depend on the form of the intermolecular-interaction potential are given in Ref. 9.

It can be shown that owing to the momentum-conservation law the complete tensor of the tangential stresses is zero, while the relation between the partial quantities is $n_m \pi_{mrz} = -n_n \pi_{nrz}$.

The boundary conditions for the perturbation functions h_i follow from expressions (2) and (4):

$$h_i^+(\mathbf{R}_0,\mathbf{c}) = (1-\varepsilon_i) h_i^-(\mathbf{R}_0,\mathbf{c}) + \varepsilon_i \frac{n_i^s - n_{i0}}{n_{i0}},$$

$$\mathbf{R}_0 = \frac{r_0}{r_0}, \quad |\mathbf{R}_0| = 1, \quad i = m,n. \tag{7}$$

The second term in the right-hand side of (7) is independent of the molecular velocities and therefore does not contribute to the macroscopic velocity and to the stress tensor (6). It will therefore be omitted hereafter.

Equations (5)–(7) make it possible to determine the function $h_i(\mathbf{R},\mathbf{c})$ uniquely. In final analysis, however, practical interest attaches to a determination of the resultant particle flux (OID) averaged over the capillary cross section

$$J = J_m + J_n = 2\bar{v} \int_0^1 (n_n u_n + n_m u_m) R dR. \tag{8}$$

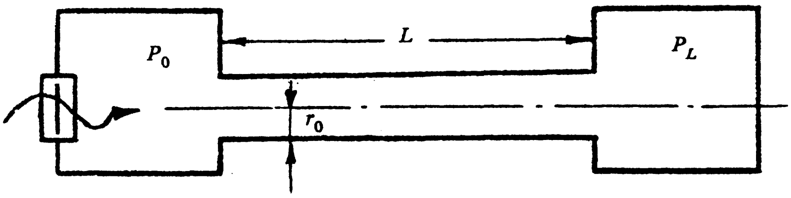

FIG. 1. Optically induced pressure difference in a closed cell.

For numerical calculations it is convenient to change to a dimensionless quantity G whose connection with the flux J is

$$J=\frac{nr_0\Gamma_m}{2\pi^{1/2}}\varkappa G, \tag{9}$$

where

$$\varkappa=\int_{-\infty}^{+\infty} c_z\exp(-c_z^2)\varkappa(\mathbf{v})dc_z. \tag{10}$$

OPTICALLY INDUCED PRESSURE DIFFERENCE

Consider a gas in a closed cell comprising two volumes joined by a narrow capillary (Fig. 1). The gas pressure in the cell is initially uniform. Application of resonant optical emission along the capillary produces OID. The result is a redistribution of the gas pressure in the system. The light-induced pressure difference (LPD) in the volumes will increase until a stationary regime is established in which the OID is fully offset by a Poiseuille flow J_p, i.e.,

$$J+J_p=0. \tag{11}$$

The dynamic equilibrium described by (11) means that the resultant particle flux in any cross section of the capillary is zero. This pertains, of course, only to flows averaged over the channel cross sections. Relation (11) does not hold in general for local flows under stationary conditions.

Poiseuille flow at arbitrary values of the Kn number and of the specularly-diffuse reflection coefficient ε can be expressed as[10]

$$J_P=-\bar{v}r_0G_p\frac{dn}{dz}, \tag{12}$$

where the function G_p (Kn,ε) has a simple form if Kn$\ll$1 and Kn$\ll$1, and was calculated numerically for intermediate Kn values.[10]

It follows from (9), (11), and (12) that

$$\frac{dn}{dz}=\frac{\Gamma_m\varkappa n}{2\pi^{1/2}\bar{v}}\hslash, \quad \hslash=\frac{G}{G_p}. \tag{13}$$

If W is the absorption per unit time, averaged over the particle velocities, the continuity equation for the radiation intensity is:[11]

$$\frac{dI}{dz}=-n\hbar\omega W, \quad n=n_n+n_m. \tag{14}$$

Integrating (13), with allowance for (14), along the capillary over the gas pressure from p_0 to p_L and over the intensity from I_0 to I_L (where p_0 and p_L are the pressures in the volumes and I_0 and I_L are the intensities at the beginning and the end of the capillary), we obtain

$$\frac{\Delta P}{P}=\frac{\Delta I\varphi(\Omega)}{n\hbar\omega\bar{v}}\hslash, \quad \Delta p=p_L-p_0,$$

$$\Delta I=I_0-I_L, \quad \varphi(\Omega)=\frac{\Gamma_m^\kappa}{2\pi^{1/2}W}; \tag{15}$$

p is the average gas pressure in the system; $\varphi(\Omega)$ is an antisymmetric function of the detuning Ω, depends on the parameters $\Omega/k\bar{v}$ and $\Gamma/k\bar{v}$. In the general case φ is expressed in terms of the plasma function,[11] but in the case of inhomogeneous broadening ($\Gamma\ll k\bar{v}$) we have $\varphi(\Omega)\simeq\Omega/k\bar{v}$.

SOLUTION OF KINETIC EQUATIONS

We use an integral-moment method based on the transformation of the integrodifferential kinetic equation for the distribution system into a system equations for its moments.

We integrate the kinetic equation (5), with allowance for the boundary condition (7), along the direction of the velocity vector $\mathbf{c}_\perp$ (Fig. 2).[10] Using the resultant expression for the perturbation function h_i and the definitions (6) for the macroscopic quantities, we obtain the following system of integral equations for the dimensionless velocity and for the stress tensor of the ith component of the gas mixture:

$$u_i=\frac{\delta_i}{\pi}\int_{(\Sigma)}\left[A_i\left(\frac{T_0}{|\mathbf{R}-\mathbf{R}'|}-\frac{K_0}{|\mathbf{R}_N-\mathbf{R}'|}\right)+[u_i-(u_i\right.$$

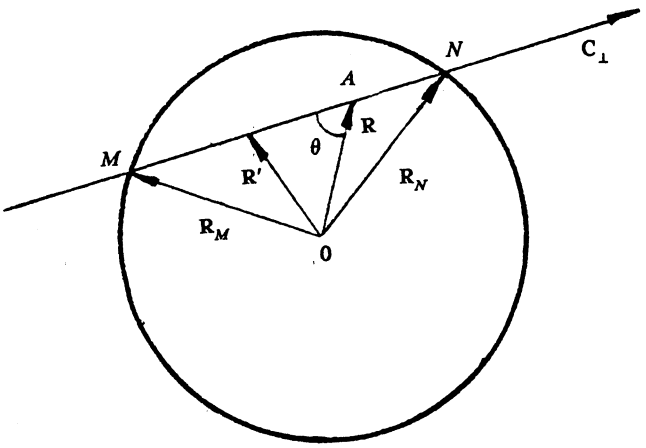

FIG. 2. Scheme of integration along the c_1 direction.

$$-u_j)\varphi_{ij}^{(1)}]\left(\frac{T_0}{|\mathbf{R}-\mathbf{R}'|}-\frac{K_0}{|\mathbf{R}_N-\mathbf{R}'|}\right)+2[(1$$

$$-\varphi_{ii}^{(3)}+\varphi_{ii}^{(4)}-\varphi_{ij}^{(3)})\pi_{irz}+\varphi_{ij}^{(4)}\pi_{jrz}]\left(\frac{T_1}{|\mathbf{R}-\mathbf{R}'|}\mathbf{e}\right.$$

$$\left.-\frac{K_1}{|\mathbf{R}_N-\mathbf{R}'|}\mathbf{e}_0\right)\frac{\mathbf{R}'}{R'}\Bigg]d\mathbf{R}', \tag{16}$$

$$\pi_{irz}=\frac{\delta_i}{\pi}\int_{(\Sigma)}\left[A_i\left(\frac{T_1}{|\mathbf{R}-\mathbf{R}'|}-\frac{K_1}{|\mathbf{R}_N-\mathbf{R}'|}\right)+[u_i-(u_i\right.$$

$$-u_j)\varphi_{ij}^{(1)}]\left(\frac{T_1}{|\mathbf{R}-\mathbf{R}'|}-\frac{K_1}{|\mathbf{R}_N-\mathbf{R}'|}\right)+2[(1$$

$$-\varphi_{ii}^{(3)}+\varphi_{ii}^{(4)}-\varphi_{ij}^{(3)})\pi_{irz}+\varphi_{ij}^{(4)}\pi_{jrz}]$$

$$\left.\times\left(\frac{T_2}{|\mathbf{R}-\mathbf{R}'|}e-\frac{K_2}{|\mathbf{R}_N-\mathbf{R}'|}e_0\right)\frac{\mathbf{R}'}{R'}\right]\frac{\mathbf{eR}}{R}d\mathbf{R}', \tag{17}$$

where

$$e=\frac{\mathbf{R}-\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|},\quad e_0=\frac{\mathbf{R}_N-\mathbf{R}'}{|\mathbf{R}_N-\mathbf{R}'|},$$

$$A_i=\frac{\Gamma_{mi}\varkappa}{2\pi^{1/2}}\left(\frac{n_{0j}}{n_{0i}}-1\right),$$

$$T_p(t)=\int_0^\infty x^P\exp(-x^2-t/x)dx,$$

$$(i,j)=m,n,\quad i\neq j,$$

$$K_P=\frac{\mathbf{R}_M\mathbf{R}}{R^2}\sum_{k=0}^{\infty}(1-\varepsilon_i)^k T_P[\delta_i((k-1)|\mathbf{R}_N-\mathbf{R}_M|+|\mathbf{R}$$

$$-\mathbf{R}_M|+|\mathbf{R}_N-\mathbf{R}'|)];$$

the argument of the functions T_P in (16) and (17) is $t=\delta_i|\mathbf{R}-\mathbf{R}'|$; the integration in (16) and (17) is over the cross-section area Σ of the capillary.

Equations (16) and (17) are Fredholm integral equations of the second kind. To solve them it is convenient to use the Bubnov–Galerkin method[12] which is effective because it permits calculation, with any prescribed accuracy, the fluxes J_i averaged over the coordinates without calculating the velocity and stress profiles u_i and π_{irz}. The convergence of the method depends on the proper choice of the trial functions for u_i and π_{irz}. Experience shows that an approximation of the form

$$\tilde{u}_i=\alpha_{1i}+\alpha_{2i}R^2,\quad \tilde{\pi}_{irz}=\alpha_{3i}R \tag{18}$$

ensures accurate enough results (maximum error not higher than $\approx 3\%$) for the partial fluxes J_m and J_n of the excited and unexcited particles in the entire range of the Kn values.[10]

Substituting relations (18) in the integral equations (16) and (17) and stipulating orthogonality of the resultant expression to each of the basic functions [1 and R^2 for (16) and R for (17)], we obtain a system of algebraic equations for the unknown constants $\alpha_{1i},\alpha_{2i},\alpha_{3i}$. The orthognality condition for the two arbitrary function f and g takes here the form

$$(f,g)=2\pi\int_0^1 f(R)g(R)RdR=0.$$

We choose the effective collision frequency in the form[10] $\gamma_n=p/\eta$ (η is the dynamic viscosity coefficient and p is the pressure). We simulate the gas particles by hard elastic spheres with diameters σ_m and σ_n for excited and unexcited particles, respectively. The connection between the rarefaction coefficient δ_n and the Knudsen number is then[10]

$$\delta\equiv\delta_n=\frac{\pi^{1/2}}{2}\mathrm{Kn}^{-1},\quad \mathrm{Kn}=\frac{l}{r_0}. \tag{19}$$

To decrease the number of variable parameters and simplify the numerical calculations we confine ourselves to a small difference between the diameters of the excited and unexcited particles, and assume also that the particle scattering from the capillary surface is almost diffuse. The theory acquires thus the two small parameters

$$\frac{|\Delta\sigma|}{\sigma_n}\ll 1,\quad (1-\varepsilon_i)\ll 1,\quad \Delta\sigma=\sigma_m-\sigma_n,\quad i=m,n. \tag{20}$$

After linearizing expressions (9) and (15) we obtain for the OID flux and for the LPD

$$J=\frac{nr_0\Gamma_m\varkappa}{2\pi^{1/2}}\left(G_1\Delta\varepsilon+G_2\frac{\Delta\sigma}{\sigma_n}\right),\quad \Delta\varepsilon=\varepsilon_n-\varepsilon_m, \tag{21}$$

$$\frac{\Delta P}{P}=\frac{\Delta I\varphi(\Omega)}{\hbar\omega n\bar{v}}\left(\not{h}_1\Delta\varepsilon+\not{h}_2\frac{\Delta\sigma}{\sigma_n}\right),\quad \not{h}_1=\frac{G_1}{G_p},\quad \not{h}_2=\frac{G_2}{G_p}. \tag{22}$$

The kinetic coefficients G_1 and G_2 indicative of the contributions made to the OID by the surface and collision mechanisms, respectively, depend only on the rarefaction parameter δ.

RESULTS AND COMPARISON WITH EXPERIMENT

Analytic expressions for the kinetic coefficients G_1, G_2, $\not{h}_1$, and $\not{h}_2$ can be obtained only for large and small values of the Kn number.

1. Almost free-molecule regime ($\mathrm{Kn}\gg 1$)

$$G_1=\frac{16}{3\pi^{1/2}}+6\delta\ln\delta,\quad \not{h}_1=4+\frac{9\pi^{1/2}}{2}\delta\ln\delta,$$

$$G_2=\delta\ln\delta,\quad \not{h}_2=\frac{3\pi^{1/2}}{4}\delta\ln\delta. \tag{23}$$

2. Hydrodynamic regime with slip ($\mathrm{Kn}=1$)

$$G_1=\frac{6}{5\delta},\quad \not{h}_1=\frac{48}{5\delta^2},\quad G_2=\frac{9}{20\delta},\quad \not{h}_2=\frac{18}{5\delta^2}. \tag{24}$$

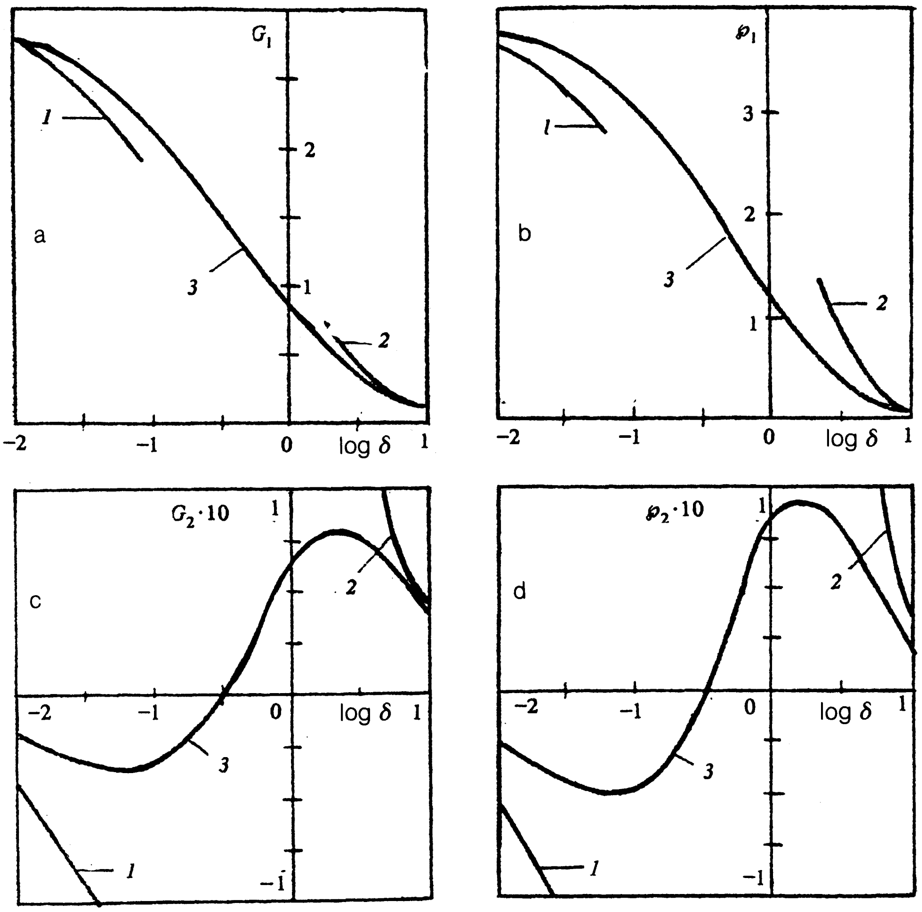

FIG. 3. Dependence of kinetic coefficients G_1 (a), $\wp_1$ (b), G_2 and $\wp_2$ on the rarefaction parameter δ; *1*—Eqs. (23), *2*—Eqs. (24), *3*—Numerical calculation.

The OID velocity $U=J/n$ can be estimated for typical values of the defining parameters. If $\Gamma\simeq\Omega\simeq 10^9$ Hz, $|G_{mn}|\simeq 10^8$ Hz, $I\simeq 1$ W/cm^2, $\omega\simeq 3\times 10^9$ MHz, $\bar{v}\simeq 10^3$ m/s, $\gamma_n\simeq 10^8$ Hz, we have

$$U=\frac{J}{n}\simeq\left(4\Delta\varepsilon+1.5\frac{\Delta\sigma}{\sigma_n}\right)\frac{M}{c}.$$

The numerical results for intermediate Kn numbers are shown in Fig. 3. Evidently, on going from the hydrodynamic to the Knudsen regime (with decrease of the rarefaction parameter δ) the values of G_1 and $\wp_1$ increase monotonically from the values given by (24) to the constant values of Eqs. (23). This behavior of the coefficients G_1 and $\wp_1$ indicative of the surface OID and LPD) is obvious. When the gas rarefaction parameter increases the relative number of particles colliding with the channel walls decreases. The role of the walls as a buffer weakens and the value of the optically induced gas flow therefore decreases and with it the pressure drop in the closed cell.

The direction of the surface component of the OID is

TABLE I. Experimental parameters for CH_3F molecules.

Branch	$\Omega/2\pi$, MHz line CO_2	$\varphi(\Omega)$	$\varphi(\Omega)\Delta\varepsilon$, 10^{-4}	$\varphi(\Omega)\Delta\sigma/\sigma_n$, 10^{-4}	$\Delta\varepsilon$, 10^{-3}	$\Delta\sigma/\sigma_n$, 10^{-3}
$R(4,3)$ $^{13}CH_3F$	25,8 $9P(32)$	0,49	−7,5	2,47	−1,53	5,05
$R(31,9)$ $^{13}CH_3F$	121 $9R(6)$	0,31 ÷ 0,39	−15,8	−201	−(4,05 ÷ 5,1)	−(51,5 ÷ 64,8)
$Q(12,3)$ $^{12}CH_3F$	−201 $9P(20)$	−(0,18 ÷ 0,19)	−3,07	201	(16,2 ÷ 17,1)	−(106 ÷ 112)
$P(24,13)$ $^{13}CH_3F$	−52 $10R(30)$	−(0,49 ÷ 0,75)	31,4	474	−(4,19 ÷ 6,41)	−(63,2 ÷ 96,7)

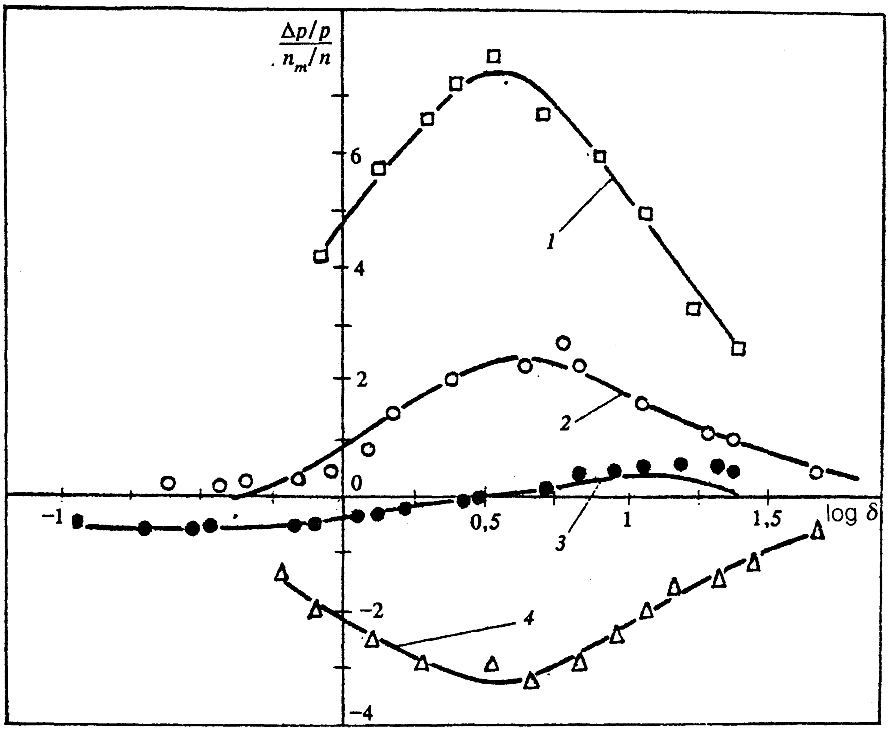

FIG. 4. Comparison of theory (solid lines) with experiment;[5] *1* (□)—Branch $P(24,13)$, *2* (○)—$Q(12,3)$, *3* (●)—$R(4,3)$, *4* (△)—$R(31,9)$.

determined by the signs of the of the differences $\Delta\varepsilon=\varepsilon_n-\varepsilon_m$ between the accommodation coefficients of the unexcited and excited particles and by the deviation $\Omega=\omega-\omega_{mn}$ of the emission frequency from the absorption line center. If $\Delta\varepsilon>0$, the surface component of the OID has the radiation direction for $\Omega>0$ and the opposite direction for $\Omega<0$.

The dependences of the kinetic coefficients G_2 and $\hbar_2$, which are indicative of the collisional OID and LPD, on the rarefaction parameter δ is nonmonotonic, having a maximum at $\delta\simeq2.7$ and a minimum at $\delta\simeq0.07$. At $\delta\simeq0.32$ the coefficients G_2 and $\hbar_2$ reverse sign. This means that the direction of the collisional component of the OID is determined not only by the sign of the deviation Ω of the radiation frequency from the absorption-line center, but also by the gas pressure in the capillary.

The possible cause of this dependence of the function $G_2=G_{2m}+G_{2n}$ on the Kn number is the following. It has been established that the components G_{2m} and G_{2n} for excited and unexcited particles are constant-sign functions of the Kn number, with $G_{2m}<0$ and $G_{2n}>0$. In the hydrodynamic regime ($\mathrm{Kn}\ll1$) the values of G_{2m} and G_{2n} are determined by kinetic processes in the Knudsen layer next to the wall. The effective thickness of the Knudsen layer for particles with smaller collision cross section (long-range particles), for example those in the ground n-state, is larger. The capillary is therefore less resistant to the flux J_n and $|G_{2n}|>|G_{2m}|$. When the pressure is lowered the Knudsen layer becomes thicker. The capillary resistance is therefore decreased and the quantities $|G_{2n}|$ and $|G_{2m}|$ increase and reach maxima in the intermediate regime ($\mathrm{Kn}\approx1$). A nonlinear decrease of the pressure at $\mathrm{Kn}\geqslant1$ weakens the proper collision mechanism of the OID, i.e., lowers the values of $|G_{2n}|$ and $|G_{2m}|$. In the Knudsen limit as $\mathrm{Kn}\to\infty$ we have $|G_{2m}|=0$ and $|G_{2n}|=0$. It is obvious, however, that if $\mathrm{Kn}\geqslant1$ and increases, the macroscopic flow of long-range particles decreases more rapidly. At $\mathrm{Kn}\approx2.8$ it turns out that $|G_{2m}|\approx|G_{2n}|$, while in the region $\mathrm{Kn}>2.8$ we have $|G_{2n}|<|G_{2m}|$. The function $G_2=G_{2m}+G_{2n}$, thus reverses sign at the point $\mathrm{Kn}\approx2.8$ (or $\delta\approx0.32$).

The LPD effect in CH_3F molecules was investigated experimentally in Ref. 5. Resonant infrared CO_2- laser radiation passed along a quartz capillary with radius $r_0\simeq0.75$ mm and length $L\simeq300$ mm. The gas pressure in the cell was varied in the range from $\simeq0.7$ to $\simeq280$ Pa, corresponding to rarefaction parameters $\delta\simeq0.1-47$.

The nonmonotonic dependence of the LPD of the pressure, observed in Ref. 5, and even the reversal of the sign of Δp in the case of an $R(4,3)$ transition, is in fact an experimental confirmation that the existence of a collisional OID mechanism due to the difference between the collision cross sections of the excited and unexcited particles. For best agreement in a quantitative comparison of theory with experiment we determined initially the unknown parameters $\Delta\varepsilon$ and $\Delta\sigma/\sigma_n$. The results are shown in Table I. Here we present the values of Ω and $\varphi(\Omega)$. The uncertainty of the values of $\varphi(\Omega)$ is due to the fact that this function depends on an unknown function Γ, which is the homogeneous half-width of the absorption line.[11]

The measurement results are given in Ref. 5 for the quantity $(\Delta p/p)/(n_m/n)$, where

$$\frac{n_m}{n}=\frac{\Delta I}{\hbar\omega nL}\left(\frac{\bar{v}}{2r_0}+\gamma_n\right)^{-1},$$

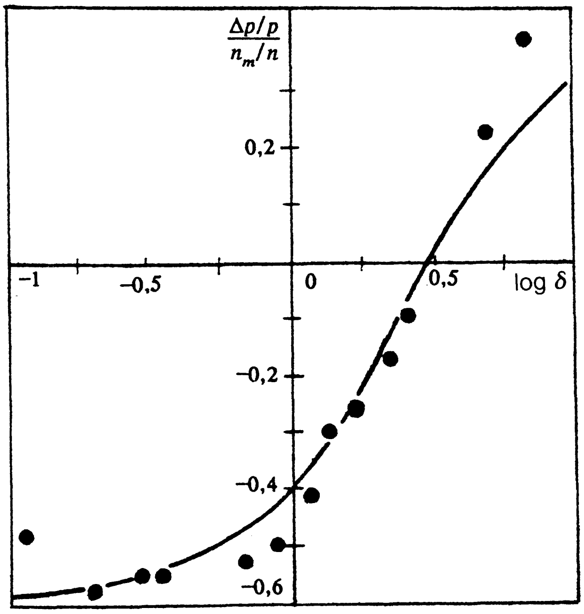

FIG. 5. Comparison of theory with experiment[5] for the $R(4,3)$ transition at low pressures.

where

$$\frac{\Delta p/p}{n_m/n}=\frac{L}{r_0}\varphi(\Omega)\left(\frac{1}{2}+\delta\right)\left(\not{k}_1\Delta\varepsilon+\not{k}_2\frac{\Delta\sigma}{\sigma_n}\right). \tag{25}$$

Figures 4 and 5 show a comparison of the theory with experiment. The theoretical curves corresponding to Eq. (25) with the parameters $\Delta\varepsilon$ and $\Delta\sigma/\sigma_n$ describe adequately the experimental data in the entire range of pressures. It must be noted, however, that the theoretical model does not reflect adequately enough the experimental conditions. This pertains first of all to the two-level approximation, which can be used only conditionally in the case of vibrational-rotational transitions.[13] In addition, in experiment we have $\varkappa(\mathbf{v}) > 1$, and the radiation intensity is not uniform over the capillary cross section. Allowance for these factors would apparently alter the parameters $\Delta\varepsilon$ and $\Delta\sigma/\sigma_n$. One can expect at the same time that allowance for the many levels of the particles and for the radial inhomogeneities of the radiation intensity would not influence substantially the obtained functional dependence of the kinetic coefficients G_1, G_2, $\not{k}_1$, and $\not{k}_2$ on the Kn number.

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Translated by J. G. Adashko