[1)]In the calculation of the integrals (3a), (4a), and (5a) we used certain integral identities employed in Ref. 19. In the subsequent formulas we have omitted the arguments of the functions $\alpha(z, \tau)$ and $\delta(z, \tau)$, which should cause no confusion in respect of the notation for the critical indices used in the published literature.

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Theory of drift motion of molecules in the field of resonant infrared radiation

A. M. Dykhne and A. N. Starostin

The distinguishing features of the effect of molecule drift in the field of resonant infrared radiation are discussed. The kinetics and hydrodynamics of the drift streams in a multicomponent gas mixture, which take place at a constant summary gas pressure, are formulated with account taken of the collision quenching of the excited molecules and of the rotational relaxation. The stationary distribution of the concentrations of the resonant molecules and of the buffer-gas particles are obtained for a closed cuvette as well as in the case of drift of the gas-mixture components from one vessel to another. Instability of the two-stream flow in a mixture of neutral gases, reminiscent of two-stream instability in a plasma, is predicted.

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Gel'mukhanov and Shalagin[1] have predicted theoretically the existence of a very interesting phenomenon—the onset, under the influence of a traveling resonant wave, of macroscopic atom streams directed along or against the light flux. These streams appear only in the presence of an extraneous buffer gas, which moves in this case opposite to the resonant particles, so that the summary matter flux is zero. A similar phenomenon was apparently observed in the experiment of Ashkin and co-workers,[2] but the cause of the effect remained unexplained. In a recent experiment[3] performed under conditions close to those of Ref. 2, a partial separation of a mixture of sodium vapor and a noble gas (He, Ne)

was observed,[1)] and the direction of the effect was in agreement with the predictions of the theory[1] and with the observations.[2] At the optimal choice of the mixture parameters and of the radiation, the equivalent force acting on the resonant atoms can exceed the force of the spontaneous light pressure by six orders of magnitude. It is therefore of interest to investigate various aspects of this phenomenon in greater detail.

Particularly urgent is the assessment of the possibility of obtaining molecule streams in an infrared (IR) resonant field. First, sources of infrared radiation are available, such as tunable CO_2 lasers,[4] with average

power and efficiency greatly exceeding the sources in the visible and ultraviolet bands. Second, the amount of energy needed when IR radiation sources are used is smaller by a factor M/m than in the optical band (M is the mass of the atom or molecule, m is the mass of the electron). Third, when molecules with high elastic vapor pressure are used the densities of the gas mixtures exceed by many orders of magnitude the densities of the atoms at the same temperatures. Fourth, the complex character of the vibrational-rotational spectrum of polyatomic molecules imposes much less stringent requirements on the widths of the spectrum and on the tuning of the source frequency. Finally, the use of molecules would greatly extend the range of possible applications of this effect, particularly because it is more convenient to work at lower temperatures, and this would uncover prospects of ecological applications.

A direct application of the results of the Ref. 1 to molecular gases and infrared radiation leads, however, to pessimistic estimates. In fact, for a resonant-atom flow velocity u, Ref. 1 cites the qualitative estimate

$$u \sim \frac{\nu_1 - \nu_2}{\nu_1} \frac{\gamma_r}{\nu_2} v_T. \tag{1}$$

Here $\nu_i (i = 1, 2)$ are the transport frequencies of the collisions of the resonant atoms with the buffer gas in the lower (1) and upper (2) states, γ_r^{-1} is the radiative lifetime of the excited particle, and v_T is the thermal velocity. Estimates quoted in Ref. 1 for a mixture of Na with He yield $u \sim (0.1 - 0.002) v_T$, which is quite appreciable. For the case of molecules in an IR field, there are a number of physical factors that make velocity calculated from (1) low. The radiative lifetime of the molecules for vibrational transitions is usually smaller by more than five orders of magnitude than for optical transitions in atoms. As will be shown below, for molecules it is necessary to use in place of the radiation frequency γ_r the frequency of the quenching collisions ν_T ($V-T$ relaxation), but even this frequency is low compared with ν_2. For most molecules $\nu_T/\nu_2 \sim 10^{-2} - 10^{-4}$. Whereas for atoms almost all the particles can enter into resonance, on going from a nondegenerate ground state, for molecules irradiated with monochromatic IR only one or several rotational sublevels of the vibrational band, in which a small fraction ($\leqslant 0.1 - 0.01$) of the particles is concentrated, enters into resonance.

Measurements of ν_1 and ν_2 have been made for atoms[5] and have yielded a value $|(\nu_1 - \nu_2)/\nu_1| \sim 1$. Practically no such measurements have been made for molecules, and arguments are advanced in the literature[6] that this quantity is generally speaking small. Thus, the overall loss in the effect on going from atom to molecules seems at first glance to exceed 3–6 orders of magnitude.

It must be noted that in a molecular gas the production of streams of resonant particles by IR radiation is accompanied by a much larger number of processes than in an atomic gas. These include the processes of $V-T$ relaxation, rotational relaxation, $V-V$ exchange, cascade excitation of various vibrational states in addition to processes common to both cases, such, as excitation of resonant particles by the field and collisions

with change of momentum. Thus, the phenomenon as a whole is more greatly varied in a molecular gas. As shown in our earlier paper,[7] if a number of conditions are satisfied the drift velocity of the resonant molecules can reach values comparable with their thermal velocity. The present paper constitutes further development of Ref. 7 and contains a more detailed investigation of the kinetics and the two-fluid hydrodynamics that describes the internal flows in a gas mixture. The stability of the streams of resonant particles in the field of a wave is considered.

1. QUALITATIVE DESCRIPTION OF THE EFFECT

For a qualitative explanation of the effect, we shall trace the fate of a single resonant molecule in an IR field. Let the radiation frequency ω be tuned away from the center ω_0 of the absorption line of the given vibrational transition by an amount $\Delta = \omega - \omega_0 \sim k v_T$; $k = \omega/c$. The molecule will absorb most effectively this radiation if the projection of the molecule velocity on the direction of the wave satisfies the Doppler condition

$$\Delta = k v_{\parallel}, \tag{2}$$

and the molecule rotational states corresponds to the resonant state (j_0). After a number of collisions, a particle having initially an arbitrary velocity and an arbitrary number j becomes resonant. This takes place after a time

$$t_1 \sim \max \left(\frac{k v_T}{\Gamma} \tau_{el}; \ \frac{1}{k_{j_0}} \tau_R \right).$$

Here Γ is the collision width of the resonance and is determined by the time of loss of phase matching of the state (in the general case $\Gamma \gtrsim \tau_{el}^{-1}$), τ_{el} is the momentum relaxation time, k_j is the Boltzmann weight of the j-th rotational state, and τ_R is the rotational relaxation time. The particle is then excited after a time τ_{ex} that depends on the electric field intensity E and on the excitation mechanism (coherent $\mu_{12}E/\hbar\Gamma > 1$ or incoherent $\mu_{12}E/\hbar\Gamma < 1$; μ_{12} is the dipole moment of the transition).

The transport mean free paths of the molecule in the excited (l_2) and unexcited (l_1) states, in collisions with the buffer gas, are generally speaking different. Consequently the molecule, which executes random walks prior to the excitation, acquires a directional displacement amounting to $\delta l = l_1 - l_2$, collinear with the wave vector of the radiation. The sign of this displacement is determined by the sign of $\Delta \delta l$. The subsequently colliding particle, after the lapse of the characteristic time τ_{el}^B of momentum relaxation on the buffer-gas particle, will again execute random walks with a new mean free path. This collision, in contrast to all others, must be precisely with a buffer-gas particle, otherwise the total displacement of the two colliding particles is equal to zero.[2] In order for the molecule to be displaced once more in the same direction, it must be returned to the initial state by the quenching, after a time $\sim \tau_T \ll \gamma_r^{-1}$. The cycle so described is completed within a time t_m on the order of the longest of the times listed above, and is accompanied by a displacement δl of the resonant molecule. Multiple repetitions of this cycle lead to a drift[3] of the resonant particles with average velocity

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$$u \sim \delta l / t_m; \qquad (3)$$

here

$$t_m = \max \left(\frac{k v_T}{\Gamma} \tau_{el}; \ \frac{1}{k_j} \tau_R; \ \tau_{ex}; \ \tau_{el}{}^B; \ \tau_T \right). \qquad (4)$$

2. ESTIMATES OF THE MAGNITUDE OF THE EFFECT. EXAMPLES

In order for the velocity u to be as large as possible, it is desirable, first, to have $\delta l \sim l$, and second, the time t_m must be minimized. This is easiest to do by making all the times in (4) of the same order. Inasmuch as a large number of processes of different kinds come into play and are determined by different physical mechanisms, one can hope to satisfy these requirements by choosing, generally speaking, a multicomponent mixture in which each component performs various functions (quenching, rotational relaxation, momentum relaxation) that are different for different vibrational states.

The foregoing processes, which are needed to realize a cyclic displacement of the resonant molecule, compete with the "harmful" collisions that lengthen the time of the cycle and decrease the fraction of particles involved in the flow. Such processes are elastic collisions of the excited particle with molecules of its own gas, and $V-V$ exchange. If the amount of buffer gas is small, then the first process decreases the velocity u in a ratio $\sim \nu_B / (\nu + \nu_B)$, where ν_B is the frequency of the collision with the buffer-gas particle and ν is the frequency of the collision of the resonant particles with one another. If the $V-V$ exchange is the fastest process, the fraction of the resonant particles decreases because of the particle flow to the upper vibrational levels. However, as will be shown below, in the optimal regime the radiation power should be of the order of the power of saturation of the resonant vibrational band (in this case $\tau_{ex} \sim \tau_T$ and the fraction of the resonant particles is ~ 1).

We note that $V-V$ exchange processes can increase the drift velocity in certain cases (e.g., when the resonant radiation is applied in pulses) and assume the role of quenching collisions. If the width of the vibrational band is comparable with the anharmonic change of the frequency on the higher vibrational transitions, then the upper vibrational-rotational states can enter into resonance with the radiation field, on account of the $V-V$ exchange, and thus participate in the total drift of the molecules. We present estimates of the characteristic times that determine the duration of the cycle. For the SF_6 molecule[8] we have $p\tau_R \sim 40$ nsec-Torr, $p\tau_{VV} \sim 1$ μsec-Torr, $p\tau_{VT} \sim 160$ μsec-Torr, $p\tau_{el} \ 1$ μsec-Torr, and $\mu_{12} \sim 0.3$ D. When the vibrations are quenched by buffer-gas particles, it is possible to obtain $\tau_T \gtrsim \tau_{el}$ by selecting the proper pressure and mixture composition (e.g., $p\tau_{VT} \sim 30$ μsec-Torr when SF_6 is quenched by CH_3F molecules[9]), etc.

It should be noted that the quenching rate can increase with decreasing gas temperature.[9] The decrease of the temperature is helpful also from the point of view of increasing the fraction of particles on the lower resonant vibrational-rotational level. It is seen thus that by op-

timizing the conditions it is possible in principle to attain equality of the times in (4), so that $t_m \sim \tau_{el}$.

To increase the drift velocity of a resonant particle it is necessary that the difference between the mean free paths of the excited and unexcited molecules not be small. The difference in the cross sections of elastic scattering of particles in states 1 and 2 can be the result of van der Waals attraction of the molecule to the particles of the buffer gas. The van der Waals potential of the interaction of the molecule in the vibrational state v with an atom can be represented in the form

$$U_v(R) = -\frac{\langle v | \hat{\mu}_v^2 | v \rangle}{R^6} \alpha - \frac{C}{R^6}. \qquad (5)$$

Here R is the distance between the particles, α is the polarizability of the atom in the ground state, and C is given by

$$C = \sum_{n,m} \frac{| \langle m_0 | \hat{\mu}_M | m \rangle |^2 | \langle n_0 | \hat{\mu}_A | n \rangle |^2}{E_m + E_n - E_{m_0} - E_{n_0}}. \qquad (6)$$

In (6), m and n are the electronic states of the molecule and the atom, $\hat{\mu}_M$ and $\hat{\mu}_A$ are the dipole-moment operators, and E_m and E_n are the energies of the corresponding states. The contribution from the vibrational states, which is determined by the first term of (5), differs by a factor of 3 in the states 1 ($V=0$) and 2 ($V=1$). At the same time, it can be much smaller than the contribution from the interaction via electronic states, since the dipole moment of the vibrational transition for a number of molecules is commensurate with the electronic transitions. (Thus, $\mu_{12} \sim 0.3$ D for the SF_6 molecule.) It should be noted that over dimensions of the order of the gas-kinetic radius of the molecule, the energy of the van der Waals interaction is comparable with the thermal energy of the relative motion, and consequently its contribution to the scattering cross section is comparable with the contribution from the short-range repulsion potential.

We now estimate the influence of the short-range potential. The characteristic dimension ξ of the molecule vibration amplitude is $\sim (m/\mu)^{1/4} R_0$ (here m is the electron, μ is the reduced mass of the vibration, R_0 is the equilibrium dimension of the molecule) and is commensurate with the radius ~ 0.2 Å of the short-range potential.[10] For this reason the relative difference between the scattering cross sections in states 1 and 2, due to the repulsion potential, can also amount to $\leqslant 1$. Thus, by choosing a molecule with a large transition dipole moment, and a buffer gas with high polarizability, one can expect the case $\delta l \leqslant l$ to be realistic in the molecular gas. It is known from experiment,[6] for example, that the diffusion coefficient of vibrationally excited CO_2 [in the state $(0,0,1)$] differs noticeably from the corresponding coefficient in the ground state.

The foregoing arguments show that the drift velocity of molecules acted upon by resonant IR radiation can reach under optimum conditions values $u \lesssim 0.1 \ v_T$. Of course, the realization of these conditions depends essentially on a large number of parameters and calls for experimental research.

3. KINETIC PROCESSES IN A MOLECULAR GAS IN THE PRESENCE OF RESONANT RADIATION

A quantitative description of the drifts of molecules under the influence of resonant IR radiation requires that a large number of processes be taken into account and is in the general case extremely unwieldy. We consider a model that reflects the main features of the phenomenon and makes it possible to determine the dependence of the drift velocity of the resonant particles on different parameters, and also to describe the ensuing flow of various components of the mixture and to investigate the stability of this flow. To simplify the notation, we consider first the case when the rotational relaxation processes need not be written out explicitly in the kinetic equations for the resonant gas. This can be done if the rates of the corresponding processes are low or, conversely, large compared with the rates of the quenching processes (with frequency ν_T) and with the momentum relaxation (with frequencies ν_1 and ν_2 for the lower and upper states).[4] A more general case is considered in the Appendix. The velocity distribution functions of the resonant particles in states 1 and 2 satisfy the system of equations[5]

$$-\frac{\partial f_2}{\partial t}-(v,\nabla)f_2+\frac{I\sigma}{\hbar\omega}(f_1-f_2)-\nu_T f_2-\nu_2 f_2+\nu_2 W_M(v)n_2=0, \qquad (7)$$

$$-\frac{\partial f_1}{\partial t}-(v,\nabla)f_1-\frac{I\sigma}{\hbar\omega}(f_1-f_2)+\nu_T f_2-\nu_1 f_1+\nu_1 W_M(v)n_1=0. \qquad (8)$$

Here I is the radiation intensity, σ is the cross section of its resonant absorption,

$$\sigma=\frac{\lambda^2}{4}\frac{A\Gamma/2\pi}{(\Delta-kv_{\parallel})^2+\Gamma^2/4} \qquad (9)$$

(λ is the wavelength and A is the probability of the spontaneous emission).[6] In the model considered, strong collisions[12] of the resonant particles with the buffer gas are assumed, so that the particle relaxes from a state with any initial velocity to a Maxwellian distribution $W_M(v)$ (if the buffer gas moves, then the argument of the function W_M is shifted by an amount equal to the buffer gas velocity). This model is valid if the density n of the resonant particles is small compared with the density n_B of the buffer particles, and the change of the velocity in each collision is of the order of the velocity itself, e.g., if the particles are light and the buffer is heavy. The collision frequencies ν_1 and ν_2 in Eqs. (7) and (8) are proportional to μ/M, where μ is the reduced mass of the resonant and buffer particles and M is the mass of the resonant molecules. We note that it is correct to express the processes of excitation of the molecules by resonant radiation in the form $I\sigma$ in the case of monochromatic radiation. In the more general case this quantity must be averaged over the pump spectrum. The quantities n_1 and n_2 in (7) and (8) are equal to the populations in the states 1 and 2:

$$n_i=\int f_i dv \quad (i=1,2). \qquad (10)$$

The homogeneous stationary solution of the system (7) and (8) takes the following form (the dependence on the transverse velocities v is determined by the Maxwellian function W_M)

$$f_1^{(0)}(v)=W_M n_1+\frac{\nu_2}{\nu_1}W_M n_2-\frac{\nu_2}{\nu_1}f_2^{(0)}(v), \qquad (11)$$

$$f_2^{(0)}(v)=W_M\left(\nu_2 n_2+\frac{I\sigma}{\hbar\omega}\left(\frac{\nu_2}{\nu_1}n_2+n_1\right)\right)\Big/ D. \qquad (12)$$

Here $D=\nu_2+\nu_T+(I\sigma/\hbar\omega)(1+\nu_2/\nu_1)$. Integrating (12) with respect to the velocities and using the condition $n_1+n_2=n_0$, we obtain

$$n_2=\frac{n_0}{B}\int\frac{W_M}{D}\frac{I\sigma}{\hbar\omega}dv; \quad B=\int\frac{W_M}{D}\left(\nu_T+\frac{2I\sigma}{\hbar\omega}\right)dv. \qquad (13)$$

The quantity n_0 is equal to the sum of the populations in the states 1 and 2. It follows from (13) that the population on the upper level saturates at a radiation power $I \sim I_s \sim \hbar\omega\nu_T/2\langle\sigma\rangle$, where $\langle\sigma\rangle=\int\sigma W_M dv$. The summary average velocity of all the resonant particles is given by

$$u=\int v(f_1^{(0)}+f_2^{(0)})dv/n. \qquad (14)$$

From (11) and (14) we have

$$nu=v_x^B\left(n_1+\frac{\nu_2}{\nu_1}n_2\right)+\left(1-\frac{\nu_2}{\nu_1}\right)\int f_2^{(0)}v\,dv. \qquad (15)$$

Here v_x^B is the velocity of the buffer-gas particles in the laboratory frame. The quantities u and v_x^B are connected by the condition that there be no macroscopic flow

$$nu+n_B v_x^B=0. \qquad (16)$$

In the model considered we have $|v_x^B| \ll u$. It follows from (15) that the motion of the resonant particles relative to the buffer gas sets in only at $\nu_1 \neq \nu_2$. The distribution function $f_2^{(0)}(v)$ is not in equilibrium in the presence of resonant irradiation; in the region of the resonant velocity $v_r=\Delta/k$, a peak appears in the velocity distribution. Using (9), (12) and (15) we obtain (at $v_x^B \ll u$)

$$u=\left(1-\frac{\nu_2}{\nu_1}\right)\frac{\Gamma\Gamma}{2\pi}\int_{-\infty}^{\infty}\frac{W_M v}{(\Delta-kv)^2+\Gamma_{abs}^2/4}dv; \qquad (17)$$

here

$$\Gamma=\frac{\pi\Gamma}{2}\frac{I\sigma_r}{\hbar\omega}\frac{[\nu_1\nu_2(n_1-n_2)/n+\nu_T(\nu_2 n_2/n+\nu_1 n_1/n)]}{\nu_1(\nu_2+\nu_T)^2}, \qquad (18)$$

$\sigma_r=\lambda^2 A/2\pi\Gamma$ is the absorption cross section at resonance,

$$\Gamma_{abs}=\Gamma\left(1+\frac{I\sigma_r}{\hbar\omega}\frac{1+\nu_2/\nu_1}{\nu_2+\nu_T}\right)^{1/2}. \qquad (19)$$

From (17) we can obtain

$$u=\left(1-\frac{\nu_2}{\nu_1}\right)\frac{\Gamma\Gamma}{\pi\Gamma_{abs}kv_T}\frac{\Delta}{k}\Psi(a,y). \qquad (20)$$

Here $a=\Gamma_{abs}/2kv_T$ and $y=\Delta/kv_T$. The function $\Psi(a,y)$ is determined in terms of the Voigt profile of the absorption line[13]

$$H(a,y)=\int_0^{\infty}e^{-at-t^2/4}\cos yt\,dt$$

and the function

$$L(a,y)=\int_0^{\infty}e^{-at-t^2/4}\sin yt\,dt$$

by the relation

$$\Psi(a,y)=H(a,y)-\frac{a}{y}L(a,y). \qquad (21)$$

Asymptotically, at large and small values of a, we have

$$\Psi(a,y)\approx\pi^{1/2}\exp(-y^2)+a/y^4+\ldots,\quad a\ll 1;$$
$$\Psi(a,y)\approx a/(y^2+a^2)^2+\ldots,\quad a\gg 1.$$

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The quantity $\langle\sigma\rangle$ is determined with the aid of $H(a,y)$:
$\langle\sigma\rangle=\sigma_r a'H(a',y)$, where $a'=\Gamma/2kv_T$.

The direction of the velocity relative to the x axis along $\mathbf{k}$ depends on the sign of $(1-v_2/v_1)\Delta$. At $v_1, v_2 \gg v_T$ and $I < I_s v_2/v_T$ we have

$$\Gamma = \frac{\pi I \sigma_r v_T n_0}{2\hbar\omega v_2 (v_T + 2I\langle\sigma\rangle/\hbar\omega)n}$$

$$u = \left(1-\frac{v_2}{v_1}\right)\frac{\Delta}{k}\frac{n_0}{n}\frac{v_T}{v_2}\frac{I\sigma_r}{\hbar\omega}\frac{\Gamma^2}{\Gamma_{abs}kv_T}\Psi(a,y) \Big/ \left(v_T + \frac{2I\langle\sigma\rangle}{\hbar\omega}\right). \quad (22)$$

If $\mu_{12}E/\hbar\Gamma \ll 1$ and $a < y$ (incoherent case), then $\Gamma_{abs} \approx \Gamma$ and

$$u = \left(1-\frac{v_2}{v_1}\right)\frac{\Delta}{k}\frac{n_0}{n}\frac{v_T}{v_2}\frac{I\langle\sigma\rangle}{\hbar\omega} \Big/ \left(v_T + \frac{2I\langle\sigma\rangle}{\hbar\omega}\right). \quad (23)$$

The optimal rate corresponds to the saturation power and is given by [cf. (1)]

$$u \approx \left(1-\frac{v_2}{v_1}\right)\frac{\Delta}{k}\frac{v_T}{v_2}.$$

At $\mu_{12}E/\hbar\Gamma \gg 1$ ($I > I_s v_2/v_T$) we have $\Gamma_{abs} \gg \Gamma$ and the velocity decreases with increasing power:

$$u = 2\frac{v_1-v_2}{v_1+v_2}\frac{\Delta}{k}\frac{n_0}{n}\frac{\hbar\omega v_T}{I\sigma_r}\left(\frac{kv_T}{\Gamma}\right)^2. \quad (24)$$

We investigate now the dependence of the velocity on the detuning Δ (at $I \lesssim I_s$). If $a \ll 1$, then the velocity reaches a maximum at $\Delta = kv_T/\sqrt{2}/$ At $a \gg 1$, on the other hand[7] the maximum velocity corresponds to a value $\Delta = \Gamma/\sqrt{3}$ (in this case the velocity decreases like a^{-3}). If the buffer-gas velocity is not low ($|v_x^B| \lesssim u$), then expressions (15) and (16) become the equations for the velocity of the resonant particles, and if there is no buffer gas, then there is no motion of the resonant particles, and the kernel of the Maxwellian distribution shifts into the region of the velocities whose sign is opposite to the sign of the detuning from resonance.

In the case when the resonant particles serve as a small admixture to the gas that absorbs the incident radiation on the line wing, a situation can arise in which the total number of the "usefully" excited particles is small compared with the number of excited buffer-gas particles. The latter will then slow down the motion of the resonant particles, but this deceleration is determined by the ratio of the cross sections $\langle\sigma\rangle$ for particles far from resonance for and the useful ones:

$$u = u_0\left(1-\frac{\Delta_B}{\Delta}\frac{\langle\sigma\rangle_B}{\langle\sigma\rangle}\right) = u_0\left(1-\frac{1}{S}\right). \quad (25)$$

Since $\langle\sigma\rangle \sim \exp(-y^2)$, it is relatively easy to ensure a selectivity $S \gtrsim 2$, thereby weakening the harmful effect due to excitation of the buffer particles on the velocity of the resonant molecule.

By adding to the mixture of nonresonant gases a small admixture of resonant molecules, it is possible to separate the mixture, since under resonant irradiation the magnitudes and the directions of the velocities of the different mixture components can be different.

4. HYDRODYNAMICS OF INTERNAL FLOWS

In the absence of motion of the medium as a whole, the inner flows due to the drift of the resonant particles lead to a peculiar picture of hydrodynamic flow. A study of such flows is of independent interest regardless of the possible applications of the described effect. In the simplest mixture consisting of a resonant gas and a buffer gas, two-stream flow sets in, in which an effective force is present and acts from opposite sides on the resonant and buffer particles. This situation recalls plasma hydrodynamics, in which the role of the force acting from opposite sides on the electrons and ions is played by the electric field. The expression for the volume force F can be obtained by rewriting the condition (15) in the form

$$F - \mu n_s n k_1 (u - v_B) = 0, \quad (15a)$$

where $F = M(v_1 - v_2)n_2(u_2 - v_B)$ and k_1 is the elastic-scattering rate constant. Here $n_2 u_2 = \int f_2^{(0)}v\,dv$. The quantity u_2 depends on the buffer-gas velocity. Expression (15a) coincides with the condition that the force acting on the resonant molecules be equal to the friction force between the resonant and buffer particles.

The hydrodynamic equations of resonant particles can be derived from the system of kinetic equations (7) and (8), using as the initial approximation the homogeneous solutions for the quantities $f_1^{(0)}$ and $f_2^{(0)}$. These solutions are not in equilibrium and describe already the drift of the resonant particles under the influence of the radiation force. The distribution functions $f_i^{(0)}$ depend on the parameters n, I, T, and others. Therefore the hydrodynamics equations reduce in this case to a system of equations for the balance of the particles with the drift, diffusion (proportional to ∇n), thermal diffusion (∇T) fluxes as well as fluxes proportional to the gradients of the intensity and other parameters on which the locally homogeneous solutions $f_i^{(0)}$ depend. It is necessary to add to these equations the condition (16) that the medium as a whole remain immobile, and also the equation for the radiation intensity.

We consider for simplicity one-dimensional flow. We seek the solutions of the inhomogeneous system (7), (8) in the form of a series in the parameter l/X, where X is the characteristic scale of the inhomogeneity. Substituting the solution in the form

$$f_i = f_i^{(0)} + f_i^{(1)} + \ldots$$

in Eqs. (7), and (8), we obtain the quantities $f_i^{(1)} \sim (v/\nu)\partial f_i^{(0)}/\partial x$. Adding Eqs. (7) and (8) and integrating with respect to their velocities, we obtain

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}un + \frac{\partial}{\partial x}j_1 = 0. \quad (26)$$

Here u is the drift velocity of the resonant particles (14) or (17), and $j_\|$ is the "diffusion" flux, equal to

$$j_\| = -\int_{-\infty}^{\infty}\frac{v_{x2}}{v_1}\frac{\partial f_0}{\partial x}dv - \left(1-\frac{v_2}{v_1}\right)\left\{\frac{A}{B}\int_{-\infty}^{\infty}\frac{v_x}{D}\left(\frac{\partial f_2^{(0)}}{\partial x} + \frac{I\sigma}{\hbar\omega v_1}\frac{\partial f_0}{\partial x}\right)dv_x \right.$$

$$\left. + \int_{-\infty}^{\infty}\frac{v_x^2}{D}\left(\frac{\partial f_2^{(0)}}{\partial x} + \frac{I\sigma}{\hbar\omega v_1}\frac{\partial f_0}{\partial x}\right)dv_x\right\}. \quad (27)$$

Here $f_0 = f_1^{(0)} + f_2^{(0)}$.

$$A = \int_{-\infty}^{\infty}\frac{v_x W_x v_2}{D}\left[1-\frac{I\sigma}{\hbar\omega v_2}\left(1-\frac{v_2}{v_1}\right)\right]dv_x.$$

The quantities B and D were defined above [see (12) and (13)]. At $v_1 = v_2 = v$ the flux $j_\|$ describes the diffusion

$(\sim\nabla n)$ and the thermal diffusion $(\sim\nabla T)$. In the case $\nu_1 \neq \nu_2$ of interest to us, an additional flux arises and is proportional to the intensity gradient. It is possible to derive similarly an expression for the transverse "diffusion" flux $j_\perp$:

$$j_\perp = -\int_{-\infty}^{\infty} \frac{v_y^2}{\nu_1}\frac{\partial f_0}{\partial y}\,dv_y - \left(1-\frac{\nu_2}{\nu_1}\right)\int_{-\infty}^{\infty}\frac{v_y^2}{D}\left(\frac{\partial f_2^{(0)}}{\partial y} + \frac{I\sigma}{\hbar\omega\nu_1}\frac{\partial f_0}{\partial y}\right)dv_y. \quad (28)$$

If $I\sigma \ll \hbar\omega\nu$, then the total "diffusion" flux can be reduced to the form

$$j_D = -D_1\nabla n_0 - \left(1-\frac{\nu_2}{\nu_1}\right)D_2\nabla n_2.$$

$$D_i = \int\frac{v^2}{\nu_i}W_u\,dv. \quad (29)$$

Introducing the population difference $m = n_1 - n_2$, it is convenient to rewrite (29) in the form

$$j_D = -\nabla n_0\langle D\rangle - \nabla m\langle \Delta D\rangle. \quad (30)$$

The quantities $\langle D\rangle$ and $\langle \Delta D\rangle$ are defined as follows:

$$\langle D\rangle = (D_1+D_2)/2, \quad \langle\Delta D\rangle = (D_1-D_2)/2.$$

Expression (30) describes the effect of drawing in the resonant particles into the beam and expelling them, respectively (at $\nu_1 \neq \nu_2$), an effect observed in Ref. 14 for the case of an intensity distribution that is inhomogeneous in the transverse direction. It follows from (13) that absorption gives rise to an analogous effect also for the longitudinal diffusion (along the beam). In the more general case $(I\sigma/\hbar\omega \sim \nu)$ the diffusion remains anisotropic.

In pulsed excitation of resonant particles, an additional flux is produced and is proportional to the rate of change of the intensity with time. This flux adds up with $j_\parallel$ and takes at $I\sigma/\hbar\omega \ll \nu$; $v_x^B \ll u$ the form

$$j_i = -\left(\frac{1}{\nu_1}+\frac{1}{\nu_2}\right)\frac{\partial}{\partial t}nu. \quad (31)$$

Expression (31) is valid at $\nu\tau > 1$, where τ is the characteristic time scale of the intensity variation. The equation for the radiation intensity is

$$\frac{\partial I}{\partial x} = -I\int\sigma(f_1-f_2)\,dv = -I\varkappa(n,I). \quad (32)$$

In (32), f_i can be replaced by the homogeneous solution $f_i^{(0)}$ (if l/X and $\varkappa_0 l \ll 1$).

To close the system of two-fluid hydrodynamics equations we must add to (16), (32), and (32) the condition that the total pressure be constant:

$$n_B T + M\int_{-\infty}^{\infty} v_x^2 f_0\,dv_x = \text{const}. \quad (33)$$

In the case $v_T/v < 1$ the condition (33) can be written in the form

$$n_B + n - n_x = \text{const}. \quad (34)$$

5. EXAMPLES OF HYDRODYNAMIC FLOWS

Interest attaches to problems involving the distribution of the concentrations of the resonant and buffer particles in a closed cell, internal flow of gas in a tube from one vessel to another, and other problems.

We consider the first problem, neglecting the variation of the radiation intensity over the cell length $(\varkappa L$

$\ll 1$, L is the cell length). From the particle-conservation condition we have the boundary conditions on the walls (u is along the x axis)

$$un|_{0,L} = D_\parallel\frac{\partial n}{\partial x}\bigg|_{0,L}. \quad (35)$$

If the condition $n(x) \ll n_C$ is satisfied, then the problem reduces to a solution of the linear equations (26) with boundary conditions (35). After a characteristic time

$$\tau \sim \frac{2L}{u}\left(\frac{4\pi^2}{\text{Pe}^2}+1\right)^{-1}$$

(at Pe > 1, where Pe $= uL/D_\parallel$ is the Peclet number), a stationary distribution is established:

$$n(x) = n_0\,\text{Pe}\exp\left(\frac{x\,\text{Pe}}{L}\right)(e^{\text{Pe}}-1)^{-1}; \quad (36)$$

here n_0 is the initial concentration of the resonant particles. If $n(x) \sim n_C$, then the expressions for the velocity u and for the diffusion coefficient $D_\parallel$ no longer hold, inasmuch as the model described above neglects the collisions of the resonant particles with one another. A qualitative solution of the problem can be obtained by taking into account the relations $u = u_0\nu_B/\nu_C$; $D_\parallel = \langle v^2\rangle/\nu_C$ (u_0 is obtained from the solution of the problem of a small admixture of resonant particles). As a result we get

$$n(x) = n_x(1+e^{(x_0-x)/d})^{-1}, \quad (37)$$

where $x_0 = L(1-\beta)$, $d = D_\parallel/u_0 = L/\text{Pe}$; β is the initial fraction of the resonant particles. At $\beta\,\text{Pe} > 1$ the degree of separation of the gases becomes exponentially large. Thus, the fraction of the resonant particle at $x = 0$ is $n(0)/n_C \infty\, e^{-\text{Pe}(1-\beta)}$, and the fraction of the buffer particles at $x = L$ is $n_B(L)/n \infty\, e^{-\beta\text{Pe}}$.

It is easily seen that in such a flow the boundary layer near the wall has a constant thickness h of the order of the mean free path l. Depending on the difference between the degrees of diffusion reflection for the excited and unexcited particles, as well as between the accommodation coefficients of the vibrationally excited molecules, the flow velocity in the boundary layer can be either larger or smaller than the velocity of the main flow.[8] When this velocity decreases, the characteristic dimension over which a radical change takes place in the particle density is determined by the expression $d = D_\parallel/\langle u_0\rangle$, where $\langle u_0\rangle$ is determined by the mean value $u_0(y)$ over the cross section. A particle located in the boundary layer will leave this layer after a diffusion time $\sim\tau_{el}$ and will be carried away by the stream. The return motion will bring it back into the boundary layer, resulting in an effective decrease of the velocity by an amount $\Delta u/u \sim -h/(D_\perp t)^{1/2}$, with the time t taken to be $(L/u_0, R^2/D_\perp)$. Here R is the cell radius. As a result we obtain for the relative decrease of the velocity

$$\frac{\Delta u}{u} \sim -\max\left\{\left(\frac{lu_0}{Lv_T}\right)^{1/2}, \frac{l}{R}\right\}.$$

This decrease has practically no effect on the conclusion that the gas becomes highly purified.

We consider now the distribution of the density of the resonant particles with account taken of the radiation absorption.[9] We confine ourselves to the case $n \ll n_C$ and $I < I_s$. At $I < I_s$ we have $u \sim I$ and $\varkappa = \sigma n$, and the

problem reduces to an investigation of the solutions of the equation

$$\frac{\partial \Phi}{\partial t} + u_0 e^{-\sigma\Phi}\frac{\partial \Phi}{\partial x} = D\frac{\partial^2 \Phi}{\partial x^2}. \qquad (38)$$

Here $\Phi = \int_0^x n(x)dx$; u_0 is the velocity at $x = 0$. The stationary distribution of the density in a closed cell is given by

$$n = \frac{\partial \Phi_0}{\partial x} = \frac{n_0(1+\varepsilon)e^{\xi}}{e^{\xi}+\varepsilon}. \qquad (39)$$

Here $\xi = x\sigma n_0(1+\varepsilon)$; $\varepsilon = u_0/\sigma D n_0$; the quantity ε is connected with the initial density $\langle n \rangle$ and with n_0 by the relation

$$\varepsilon = \left(\exp\left(Pe\frac{1+\varepsilon}{\varepsilon}\right) - \exp(\sigma\langle n \rangle L)\right)(\exp(\sigma\langle n \rangle L) - 1)^{-1}.$$

Under the condition $D\sigma\langle n \rangle/u < 1$, $\xi > 1$ we obtain[10] $\varepsilon \approx \exp(Pe - \sigma\langle n \rangle L)$. Let us check the obtained distribution for stability. Linearizing Eq. (38) for perturbations of the type $e^{-\Gamma t}u(\xi)(\varepsilon e^{-\xi}+1)^{-1/2}$, we obtain

$$u'' + u\left[\lambda + \frac{2\varepsilon e^{-\xi} - \varepsilon^2 e^{-2\xi}}{4(\varepsilon e^{-\xi}+1)^2}\right] = 0. \qquad (40)$$

Here $\lambda = \Gamma/D[\sigma n_0(1+\varepsilon)]^2$; $0 \le \xi \le \sigma n_0 L(1+\varepsilon) \equiv L'$; the boundary conditions for Eq. (40) are of the form $u(0) = u(L') = 0$. It is easy to show that the value $\lambda = 0$ lies below the ground state of Eq. (40), since it is impossible to construct from the solutions of the equation at $\lambda = 0$

$$u_{01} = (\varepsilon e^{-\xi}+1)^{-1/2}; \quad u_{02} = (\varepsilon+\xi-\varepsilon e^{-\xi})/(\varepsilon e^{-\xi}+1)^{1/2}$$

a combination that satisfies the boundary condition on one of the ends and reverses sign in the interval $(0, L')$. The obtained distribution is thus stable.

For gas flowing through a tube from one vessel to another, we must seek solutions of the system (26) and (32) with the flux j. We then have in place of (35)

$$un = D\partial n/\partial x + j.$$

As a result of the solution we get

$$y(\xi) = 1 - \eta\xi\frac{\varepsilon}{1+\varepsilon} + \varepsilon(1-a(\xi))\cdot \qquad (41)$$

Here $y(\xi) = n(\xi)/n_0$; $\eta = j/n_0 u_0$;

$$u = u_0 b(\xi)\left(1 - \frac{\varepsilon}{1+\varepsilon}\int_0^{\xi} b(\xi)d\xi\right)^{-1} \equiv u_0 a(\xi), \qquad (42)$$

where

$$b(\xi) = \exp\left(-\xi + \frac{\eta}{2}\xi^2\frac{\varepsilon}{(1+\varepsilon)^2}\right). \qquad (43)$$

At $\eta = 0$ expressions (41) and (43) go over into the solution of the problem of the distributions of n and u in a closed cell. If the densities of the resonant particles at $\xi = 0(n_0)$ and $\xi = L'(n_1)$ are given, we can obtain from expression (41) at $\xi = L'$ the reduced value of the flux η. The flux reverses sign upon reversal of the sign of

$$\frac{1+\varepsilon}{1+\varepsilon e^{-L'}} - y_1.$$

At a fixed flux $(\eta > 0)$, y vanishes on a finite length $\xi_{cr} \sim (1+\varepsilon)^2/\varepsilon\eta$ (at $\varepsilon > 1$ and $L' > 1$). This means that the flow becomes nonstationary in this situation.

Neglecting diffusion, we can find for the problem (26), (32) a nonstationary solution that reduces in this case to

the equation

$$\frac{\partial \Phi}{\partial t} - \frac{u_0(t)}{\sigma}\frac{\partial}{\partial x}e^{-\sigma\Phi} = j(t) = n_0(t)u_0(t). \qquad (44)$$

Changing over to new variables $\Psi = \Phi - \int_0^t j(t)dt$, $v = e^{-\sigma\Psi}$, and

$$\tau = \int_0^t u_0(t)\exp\left(-\sigma\int_0^t j(t')dt'\right)dt = \tau(t).$$

We reduce (44) to the form

$$\partial v/\partial\tau + v\partial v/\partial x = 0. \qquad (45)$$

Equation (45) has solutions of the type[15]

$$v = F(\tau - x/v); \quad F(\tau) = \exp\left[\sigma\int_0^{t(\tau)} j(t)dt\right],$$

where $t(\tau)$ is the inverse of $\tau(t)$. Solutions of this type can be subject to discontinuities of $v(x,\tau)$. This means that the particle density

$$n = -\frac{1}{\sigma}\left(\frac{\partial \ln v}{\partial x}\right)_{\tau}$$

becomes infinite over a finite length after a finite time. Thus, if $u(0, t) = u_0 = $ const and $n(0, t) = n_0(1 + \sigma n_0 u_0 t)^{-1}$ are specified at $x = 0$, then a singularity at $x > l_\kappa/e$ appears for the times $t > t_k = (ex - l_\kappa)/u_0$, $l_\kappa = \sigma n_0)^{-1}$. When diffusion is taken into account, the singularity vanishes, but the obtained solutions point to instability the flow.

Considering perturbation of the type $e^{-i\omega t + ikx}$ with wave vector satisfying the conditions $\kappa_0 \ll k \ll (\kappa_0 u/D)^{1/2}$, we obtain from the system (26) (32)

$$\omega(k) = \omega^*(k) + i\Gamma.$$

Here

$$\omega^*(k) = ku, \quad \Gamma = 2\kappa_0 u.$$

The instability $(\Gamma > 0)$ arises when the resonant particles move in the direction of propagation of the wave (along k) and is due to the fact that the fluctuation perturbation δn of the density (e.g., its increase, accompanied by a decrease of the velocity by virtue of the continuity of the flow) leads to a change in the radiation intensity that determines the drift velocity (in this case the intensity decreases and the velocity of the perturbed section slows down even more). The instability is of the drift type, and during the time that the particles drift out over a length L the perturbations increase by a factor $e^{2\kappa_0 L}$. The instability is not dangerous if $\kappa_0 L \le 1$. In addition, it is convenient to work in the $I > I_s$ regime, where the velocity depends little on the intensity.

APPENDIX

1. We consider the question of the velocity of the resonant particles with account taken of the finite time of rotational relaxation. In the homogeneous case, the system of equations [which generalizes (7) and (8)] is of the form

$$\delta_{j,k}\frac{I\sigma_j}{\hbar\omega}(f_{1j} - f_{2j}) - \nu_{R_k}(f_{2j} - k_j f_2) - \nu_T f_{2j} - \nu_2 f_{2j} + \nu_2 W_{M_r}n_{2j} = 0, \qquad (A.1)$$

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$$-\delta_{j,j_0}\frac{I\sigma_j}{\hbar\omega}(f_{1j}-f_{2j})+\nu_T f_{2j}-\nu_{R_1}(f_{1j}-k_j f_1)-\nu_1 f_{1j}+\nu_1 W_\varkappa n_{1j}=0. \qquad (A.2)$$

Here j_0 is the rotational quantum number of the resonant transition, ν_{R_i} are the frequencies of the rotational relaxation in the i-th vibrational state,

$$f_1=\sum_j f_{1j}; \quad f_2=\sum_j f_{2j}.$$

The quantities n_{1j} and n_{2j}, which are equal to the populations on the rotational sublevels, are determined by the relations

$$n_{(i)j}=\int f_{(i)j}\,dv, \quad i=1,2.$$

The populations on the vibrational levels n_i are connected with $n_{(i)j}$:

$$n_i=\sum_j n_{(i)j}.$$

The drift velocity is determined by the expression

$$nu=\left(1-\frac{\nu_2}{\nu_1}\right)\int vf_2\,dv.$$

Solving the system (A.1) and (A.2), we get

$$f_2(v)=W_\varkappa\left(\nu_2 n_2+\frac{I\sigma}{n\omega}D_1\right)\Big/D_2. \qquad (A.3)$$

Here

$$D_1=k_{j_0}n_0+\frac{n_2}{\nu_1+\nu_{R_1}}\left[\nu_2\frac{\nu_T+k_{j_0}\nu_{R_1}}{\nu_T+\nu_{R_1}}-\nu_1\left(k_{j_0}+\frac{\nu_{R_1}}{\nu_{R_1}}\frac{\nu_T(1-k_{j_0})}{\nu_T+\nu_{R_1}}\right)\right.$$
$$-k_{j_0}\nu_{R_1}\left(1-\frac{\nu_2}{\nu_1}\right)+\frac{\nu_2\nu_{R_1}(1-k_{j_0})(\nu_1+\nu_2+\nu_{R_1}+\nu_{R_1})}{(\nu_T+\nu_{R_1})(\nu_1+\nu_T+\nu_{R_1})}\right], \qquad (A.4)$$

$$D_2=\nu_2+\nu_T+\frac{I\sigma}{\hbar\omega(\nu_1+\nu_{R_1})}\left[\frac{(\nu_1+\nu_T+k_{j_0}\nu_{R_1})}{\nu_1+\nu_T+\nu_{R_1}}(\nu_1+\nu_2+\nu_{R_1}+\nu_{R_1})\right.$$
$$-k_{j_0}\left(\nu_{R_1}-\frac{\nu_2}{\nu_1}\nu_{R_1}\right)\Big]. \qquad (A.5)$$

For n_2 we have

$$\frac{n_2}{n_0}=k_{j_0}\int\frac{I\sigma}{\hbar\omega D_2}W_\varkappa\,dv\left[\int\frac{W_\varkappa}{D_2}\left[\nu_T+\frac{I\sigma}{\hbar\omega(\nu_1+\nu_{R_1})}D_1\right]dv\right]^{-1}. \qquad (A.6)$$

The quantity D_3 is defined by the expression

$$D_3=\frac{\nu_2+\nu_T+k_{j_0}\nu_{R_1}}{\nu_2+\nu_T+\nu_{R_1}}(\nu_1+\nu_2+\nu_{R_1}+\nu_{R_1})-k_{j_0}(\nu_{R_1}-\nu_{R_1})$$
$$-\nu_2\frac{\nu_T+k_{j_0}\nu_{R_1}}{\nu_T+\nu_{R_1}}+\nu_1\left(k_{j_0}+\frac{\nu_{R_1}}{\nu_{R_1}}\frac{\nu_T(1-k_{j_0})}{\nu_T+\nu_{R_1}}\right)$$
$$-\frac{\nu_2\nu_{R_1}(1-k_{j_0})(\nu_1+\nu_2+\nu_{R_1}+\nu_{R_1})}{(\nu_T+\nu_{R_1})(\nu_2+\nu_T+\nu_{R_1})}. \qquad (A.7)$$

To simplify the results, we put $\nu_{R_1}=\nu_{R_2}=\nu_R$ and $\nu_1=\nu_2=\nu$ in the expressions for D_1, D_2 and D_3. In this case we obtain for the velocity u

$$u=\left(1-\frac{\nu_2}{\nu_1}\right)\int_{-\infty}^{\infty}vW_\varkappa\left\{\nu_2\frac{n_2}{n}+\frac{I\sigma}{\hbar\omega}\left[k_{j_0}+\frac{2n_1}{n}(1-k_{j_0})\frac{\nu\nu_R}{(\nu_T+\nu_R)(\nu+\nu_T+\nu_R)}\right]\right\}$$
$$\times\left\{\nu+\nu_T+\frac{2I\sigma}{\hbar\omega}\frac{\nu+\nu_T+k_{j_0}\nu_R}{\nu+\nu_T+\nu_R}\right\}^{-1}dv. \qquad (A.8)$$

If $\nu>\nu_T+2I\sigma/\hbar\omega$, we get from (A.8)

$$u=\frac{(1-\nu_2/\nu_1)}{\nu}\int_{-\infty}^{\infty}W_\varkappa vk_{j_0}\nu_T\frac{I\sigma}{\hbar\omega}\left\{\nu_T+2\frac{I\sigma}{\hbar\omega}\frac{\nu_T+k_{j_0}\nu_R}{\nu_T+\nu_R}\right\}^{-1}dv. \qquad (A.9)$$

In the case of slow rotational relaxation $\nu_R\ll\nu_T$ we obtain from (A.9) the old result (18), and the drift velocity is proportional to k_{j_0}—the fraction of the resonant particles of the rotational sublevel.

If $\nu_R\gg\nu_T$ but $\nu_T\gg k_{j_0}\nu_R$, we obtain from (A.9) $(I\sim I_s^{(1)})$

$$u\sim\left(1-\frac{\nu_2}{\nu_1}\right)\frac{k_{j_0}\nu_R}{2\nu}\nu_T,$$

The saturation power being $I^{(1)}\sim\hbar\omega\nu_R/2\langle\sigma\rangle$. For the case of rapid rotational relaxation $k_{j_0}\nu_R\gg\nu_T$ we have for the drift velocity $(I\sim I_s^{(2)})$

$$u\sim\left(1-\frac{\nu_2}{\nu_1}\right)\frac{\nu_T}{2\nu}\nu_T.$$

The saturation power is determined in this case by the expression

$$I_s^{(2)}\sim\hbar\omega\nu_T/2\langle\sigma\rangle k_{j_0},$$

i.e., it is larger by $1/k_{j_0}$ times than in the case of slow rotational relaxation.

In the case when the width Δ_L of the source spectrum exceeds the distance between the components of the vibrational-rotational absorption spectrum (which is split for polyatomic molecules), it is necessary to retain in (A.1) and (A.2) the terms that take into account transitions from many rotational states. In the limit $k_j\nu_R\gg\nu_T$ it turns out that the drift velocity is determined by expressions (14), (11), and (12), in which $I\sigma$ should be replaced by

$$\sum_n k_n I\int\varphi\left(\frac{\Delta}{\Delta_L}\right)\frac{\sigma_{pn}\Gamma^2}{(\Delta_0-kv-\delta_n-\Delta)^2+\Gamma^2/4}\frac{d\Delta}{\Delta_L}.$$

The summation extends here over all the components of the absorption spectrum, k_n is the fraction of particles on the n-th sublevel, the function $\varphi(\Delta/\Delta_L)$ (normalized to unity) describes the line contour of the incident radiation, Δ_0 is the detuning of the centers of the line contours of the source and of the rotational-vibrational band, δ_n is the distance from the center of the band to the position of the n-th component of the absorption spectrum (in the case of a diatomic molecule $n=j$ and $\delta_n=2Bj$, and B is the rotational constant; the summation is from $-\infty$ to $+\infty$). In the limit $kv_T\ll\Delta_0-\delta_n$, $(\Gamma,\ \delta_n)<\Delta_L<\Delta_0$ it can be found that the direction of the drift velocity is given by

$$-\frac{\nu_1-\nu_2}{\nu_1}\left(\frac{\partial k_n\sigma_{pn}}{\partial n}\right)_{n_0},$$

where n_0 is obtained from the condition $\delta_{n_0}\approx\Delta_0$. Thus, in the case of a broad source spectrum the direction of the drift velocity is determined by the derivative of the envelopes of the absorption spectrum $(k_n\sigma_{pn})$.

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[1] As noted by the authors of Ref. 1, this phenomenon can be used for laser separation of the isotopes of one element.
[2] Actually the particle can be excited after many collisions, at which case it acquires the same directional displacement after a time $\sim\tau_{ex}$.
[3] The authors of Ref. 1, in our opinion, have inappropriately named the effect predicted by them "light-induced diffusion." Obviously, the diffusion can only decrease the magnitude of the effect (see Sec. 5).
[4] Since the wave functions of states 1 and 2 are intermixed in a resonant field, in the general case the quantities ν_1 and ν_2 are determined by the scattering cross sections σ_i of the buffer particles by these states in the absence of a field (see, e.g., Ref. 11); in this case $\Delta\nu/\nu\sim(\sigma_1-\sigma_2)/(\sigma_1+\sigma_2)$.
[5] The two-level approximation (or the more general case, described in the Appendix, of two rotational bands) is, of course, an idealization. The theory becomes much more complicated when account is taken of the excitation of many vibrational-rotational states.
[6] To simplify the derivations, the arrival term due to the

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quenching is written in Eq. (8) in model form. Correct allow-
ance for the quenching would lead to an additional difference
between the transport frequencies of the collisions in the ex-
cited and the unexcited states, which can only enhance the
considered effect.

[7] It is precisely this case which is considered in Ref. 1, but
in the numerical example formula (4) of Ref. 1 was used at
$a \approx 1/6$.

[8] In a number of cases it may turn out to be convenient to use
Knudsen flow through a capillary, if the indicated difference
in the degree of diffuse reflection is not small, and the
quenching of the vibrational excitation is produced by colli-
sion with the wall.

[9] If the source has a broad spectrum that overlaps several
vibrational-rotational transitions, it is necessary to take
into account in the hydrodynamic equations the evolution of
the spectral distribution of the intensity. In this case a
self-consistent problem arises, in which the velocity depends
on the spectral distribution of the radiation (see the Appen-
dix), and this distribution changes in the course of absorption
in the medium in which the drift fluxes are excited.

[10] If the velocity u_0 is directed opposite to the wave vector of
the radiation (against the beam), then it is necessary to make
in (39) the substitutions $\varepsilon \to -\varepsilon$, $\text{Pe} \to -\text{Pe}$. We have then ε
$\sim \text{Pe}/(\text{Pe} + \langle n \rangle \sigma L) \sim 1(\text{Pe} > \sigma \langle n \rangle L)$; $n_0 \sim u_0/\sigma D \gg n(L) \propto \langle n \rangle$.

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Rotational relaxation of isotope-substituted molecules and excited complexes produced in muon catalysis

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The cross sections of electron-rotatonal transitions produced in collisions of isotope-substituted molecules
with atomic particles are expressed within the framework of the adiabatic approximation in terms of the cross
sections of the transitions in the corresponding homonuclear reactions. The general formulas are used to
calculate the rates of rotational relaxation of the excited complexes produced in muon catalysis of nuclear
reactions. The relaxation rate is determined mainly by transitions with odd change of the rotational quantum
number, which are forbidden in homonuclear molecules. It is shown that under experimental conditions the
relaxation de-excitation of the complexes is much faster than their breakup into the initial products, thus
producing favorable conditions for the nuclear fusion reaction.

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1. INTRODUCTION

Replacement of one of the nuclei in a homonuclear
molecule by its isotope leads to a number of new ef-
fects. The appearance of a dipole moment and of a vi-
brational-rotational emission spectrum has been fre-
quently investigated (for homonuclear molecules, the
corresponding transitions are forbidden by the selec-
tion rules in the dipole approximation). For the HD
molecule such a spectrum was observed experimen-
tally,[1] calculated theoretically,[2] and used to register
HD molecules in planetary atmospheres and in inter-
stellar medium.[3]

An analogous effect is present in the physics of atom-
ic collisions, namely rotational transitions with odd
change of the rotational quantum number, which are
strictly forbidden in a homonuclear molecule (if we
disregard the low-probability processes accompanied
by a change of the nuclear spin of the molecule). Col-

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