Role of nonequilibrium velocity distributions in the laser excitation of vibrational–rotational transitions of molecules

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(Submitted 28 August 1990; resubmitted 27 November 1990)
Zh. Eksp. Teor. Fiz. **99**, 1088–1102 (April 1991)

Possible deviations from equilibrium velocity distributions are taken into consideration in numerical and analytic solutions of the problem of the laser excitation of vibrational–rotational and vibrational transitions of molecules constituting a small admixture in a buffer gas. Analytic results are derived from a strong-collision model. At low pressures, at which the collisional absorption linewidth is much smaller than the Doppler width, the results are changed not only quantitatively but also qualitatively by incorporating a laser-induced deviation from equilibrium velocity distributions of the molecules. In a strong field, for example, the ratio of the quasisteady probability for a stimulated vibrational–rotational transition to the corresponding probability calculated without consideration of a deviation from an equilibrium velocity distribution is proportional to the ratio of the collisional linewidth to the Doppler width. As a result, the maximum probability for vibrational photoexcitation (the rotational "bottleneck") is reached at significantly higher light intensities. In fields of moderate intensity, the probability for a stimulated vibrational–rotational transition may depend nonlinearly on the light intensity. Various models of the elastic-collision integral are tested by comparison with the results found through a Monte Carlo solution of the Boltzmann equation. Specifically, relaxation-constant models, models of strong and weak collisions, and the Keilson–Störer model are tested. The conditions for the applicability of these models in this particular problem are determined. If the wrong model collision integral is chosen, there may be errors of up to 100% in the calculated distribution functions and absorption coefficient.

INTRODUCTION

The application of laser light to molecular gases may disrupt the equilibrium distributions of the particles with respect to the various degrees of freedom. For molecules in the electronic ground state, it is customary to distinguish a deviation of their vibrational–rotational populations from equilibrium and a deviation of their velocity distributions from equilibrium. The literature on the nonequilibrium vibrational–rotational kinetics of the excitation of multilevel systems in a laser light field is quite diverse and has been the subject of several reviews and monographs (e.g., Refs. 1–4). Distortions of the equilibrium velocity distributions, in contrast, are usually ignored in efforts to solve these problems (see also Refs. 5–7). Effects stemming from a deviation of particle velocity distributions from equilibrium have attracted some interest in problems involving sub-Doppler atomic saturation spectroscopy,[8–10] in particular, the phenomenon of a light-induced drift.[11] Most of the results have been derived analytically for two-level atoms in relaxation-constant models[8,9] or in the limiting cases of strong and weak elastic collisions.[9] Only numerical results have been obtained in intermediate cases,[12] through the use of an approximate description of elastic collisions of atoms in the Keilson–Störer model.[9,13]

In general, the behavior of colliding atoms and molecules in external fields is described by the quantum kinetic equation for the density matrix.[9] Such an equation is exceedingly difficult to solve even by numerical methods. In the simpler case of a classical translational motion of the particles, and if the "phase memory" of these particles is ignored, one can use Boltzmann equations with source terms to derive the velocity distributions of the populations. Solving such equations is no less complicated a problem, particularly if the deviations from equilibrium velocity distributions are pronounced. In this situation, the existing methods of the kinetic theory of gases[14,15] either are inapplicable (this is true of the Chapman–Enskog method) or are of only limited applicability (this is true of the moment methods). This difficulty in solving the quantum kinetic equations and the Boltzmann equations is apparently the reason why distortions of the equilibrium velocity distributions of the molecules either have been ignored altogether (e.g., in problems involving the laser excitation of molecules) or have been dealt with only approximately (e.g., in problems of sub-Doppler saturation spectroscopy).

In the present paper we take up the laser excitation of molecules under collisional conditions, taking account of the distortions of the velocity distributions caused by the light. We focus on (first) deriving and analyzing analytic expressions for the probabilities for stimulated vibrational–rotational and rotational transitions (modified to incorporate the nonequilibrium velocity distributions) and (second) studying the validity of various approximate descriptions of the elastic-collision integral, through a comparison of results calculated on the nonequilibrium velocity distributions of the molecules with results found through a solution of the Boltzmann equations by the Monte Carlo method.

2. FORMULATION OF THE PROBLEM

We consider the absorption of light on the $V \rightarrow V'$ vibrational transition of a small admixture of molecules of an active gas in a medium of a buffer gas. We assume that the vibrational–rotational spectrum of the active gas has a fairly sparse line structure, so that the light effectively interacts

0038-5646/91/040604-09$03.00

with only a single vibrational–rotational transition, $|V,J\rangle$–$|V',J'\rangle$. Under these conditions, the populations of those vibrational–rotational levels which are not in resonance with the light are changed by collisional rotational RT exchange. The time scale of the rotational relaxation, τ_{RT}, at standard temperature is usually several times the time scale between kinetic collisions, τ_0, while the vibrational relaxation time τ_V is several hundred or even thousands of times τ_0. We will be ignoring the effect of collisional vibrational exchange on the populations of the vibrational–rotational levels, under the assumption that these processes are slow in comparison with the optical excitation and the RT relaxation.

The usual kinetic rate equations are valid for the populations of the vibrational–rotational levels $|V,J\rangle$ and $|V',J'\rangle$, which are interacting with the light, over times greater than the phase relaxation time. If we assume that an equilibrium distribution with respect to rotational sublevels is established over the time scale τ_{RT} of the rotational relaxation,[1] then these equations take the following form for each value of the velocity vector **v** of the active molecules in the spatially homogeneous case:

$$\begin{aligned}\frac{df_{V'J'}(\mathbf{v})}{dt}&=W(\mathbf{v})\Big[\frac{g_{V'J'}}{g_{VJ}}f_{VJ}(\mathbf{v})\\&\quad-f_{V'J'}(\mathbf{v})\Big]+\frac{q_{J'}}{\tau_{RT}}N_{V'}{}^{0}\varphi_{V'}(\mathbf{v})\\&\quad-\frac{(1-q_{J'})}{\tau_{RT}}f_{V'J'}(\mathbf{v})+\int[f_{V'J'}(\mathbf{v}')f_B(\mathbf{v}_B{}')\\&\quad-f_{V'J'}(\mathbf{v})f_B(\mathbf{v}_B)]\,|\mathbf{v}-\mathbf{v}_B|\,d\sigma_e\,d\mathbf{v}_B,\end{aligned}\qquad(1)$$

$$\begin{aligned}\frac{df_{VJ}(\mathbf{v})}{dt}&=-W(\mathbf{v})\Big[\frac{g_{V'J'}}{g_{VJ}}f_{VJ}(\mathbf{v})\\&\quad-f_{V'J'}(\mathbf{v})\Big]+\frac{q_{J}}{\tau_{RT}}N_{V}{}^{0}\varphi_{V}(\mathbf{v})\\&\quad-\frac{(1-q_{J})}{\tau_{RT}}f_{VJ}(\mathbf{v})+\int[f_{VJ}(\mathbf{v}')f_B(\mathbf{v}_B{}')\\&\quad-f_{VJ}(\mathbf{v})f_B(\mathbf{v}_B)]\,|\mathbf{v}-\mathbf{v}_B|\,d\sigma_e\,d\mathbf{v}_B,\end{aligned}\qquad(2)$$

$$\frac{dN_{V'}{}^{0}}{dt}=\frac{(1-q_{J'})}{\tau_{RT}}n_{V'J'}-\frac{q_{J'}}{\tau_{RT}}N_{V'}{}^{0}+\left(\frac{dN_{V'}{}^{0}}{dt}\right)_{\text{vibrel}}\qquad(3)$$

$$\frac{dN_{V}{}^{0}}{dt}=\frac{(1-q_{J})}{\tau_{RT}}n_{VJ}-\frac{q_{J}}{\tau_{RT}}N_{V}{}^{0}+\left(\frac{dN_{V}{}^{0}}{dt}\right)_{\text{vibrel}}\qquad(4)$$

$$N_{V'}{}^{0}=\sum_{j'\neq J'}n_{V'j'},\qquad N_{V}{}^{0}=\sum_{j\neq J}n_{Vj},\qquad n_{Vj}=\int f_{Vj}(\mathbf{v})\,d\mathbf{v},$$

$$\varphi_{V'}(\mathbf{v})\approx\varphi_V(\mathbf{v})\approx f_M(\mathbf{v})=\left(\frac{m_A}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m_A\mathbf{v}^2}{2kT}\right).$$

Here $f_{V'J'}(\mathbf{v})$ and $f_{VJ}(\mathbf{v})$ are the velocity distributions of the populations of the active molecules in the vibrational–rotational levels which are in resonance with the light; $N_{V'}=N^0_{V'}+n_{V'J'}$ and $N_V=N^0_V+n_{VJ}$ are the vibrational populations; $(dN^0_{V'}/dt)_{\text{vibrel}}$ and $(dN^0_V/dt)_{\text{vibrel}}$ are vibrational-relaxation terms; $q_{J'}$ and q_J are the equilibrium values of the fraction of molecules in the rotation sublevels which are at resonance with the light; $g_{V'J'}$ and g_{VJ} are the statistical weights of the levels; m_A is the molecular mass of the active gas; k is the Boltzmann constant; T is the temperature of the medium; $f_B(\mathbf{v}_B)$ is the equilibrium velocity distribution of the density of buffer-gas molecules; $d\sigma_e$ is the differential cross section for elastic collisions of the active-gas molecules with the buffer molecules; and $\mathbf{v}'$ and $\mathbf{v}'_B$ are the velocities after a collision. The function $W(\mathbf{v})$, the probability for stimulated emission on the transition $|V,J,\mathbf{v}\rangle$–$|V',J,\mathbf{v}\rangle$ per unit time, is given by

$$W(\mathbf{v})=\frac{\pi c^2A_{VJ}^{V'J'}I}{(\omega_{VJ}^{V'J'})^3\hbar}G[\omega_{\text{las}},\omega_{VJ}^{V'J'}(\mathbf{v})]=\frac{4\pi|d_{VJ}^{V'J'}|^2I}{3c\hbar^2}$$
$$\times G[\omega_{\text{las}},\omega_{VJ}^{V'J'}(\mathbf{v})],\qquad\omega_{VJ}^{V'J'}(\mathbf{v})=\omega_{VJ}^{V'J'}+(\mathbf{kv}),$$
$$G[\omega_{\text{las}},\omega_{VJ}^{V'J'}(\mathbf{v})]=\frac{\Gamma}{\Gamma^2+[\omega_{\text{las}}-\omega_{VJ}^{V'J'}(\mathbf{v})]^2},$$

where c is the velocity of light, $A_{VJ}^{V'J'}$ is the probability for a spontaneous transition per unit time, I is the intensity of the monochromatic light, which we assume remains constant over time, $\omega_{VJ}^{V'J'}$ is the frequency at the center of the $|V,J\rangle$–$|V',J'\rangle$, $|d_{VJ}^{V'J'}|$ is the dipole matrix element of the transition, ω_{las} is the frequency of the laser light, Γ is the collisional half-width of the transition, and **k** is the wave vector of the light.

In the problem formulated in this manner, the distribution functions $\varphi_{V'}(\mathbf{v})$ and $\varphi_V(\mathbf{v})$ can be approximated as Maxwellian, since the change in the resultant populations of the vibrational–rotational levels which are not at resonance with the light, $N^0_{V'}$ and N^0_V, is a relatively slow process, occurring over a time scale τ_{RT}/q_J which satisfies $\tau_{RT}/q_J\gg\tau_0$ [see Eqs. 3 and 4]. The one exception is the case of weak collisions of the molecules in the upper vibrational level, with $N^0_{V'}\sim n_{V'J'}$, in which case the time scale for a change in the population $N^0_{V'}$ becomes the time $\tau_{RT}\gtrsim\tau_0$. In this situation the distribution function $\varphi_{V'}(\mathbf{v})$ may be quite non-Maxwellian, but the incoming term due to rotational exchange in Eq. (1), $q_{J'}N^0_{V'}\varphi_{V'}(\mathbf{v})/\tau_{RT}$ is $O(q_{J'}\ll1)$ and can be completely ignored in comparison with the other terms in the equation.

We have a few words about the model of collisions which are strong in the rotational sense [the model used in writing Eqs. (1)–(4)]. For molecules whose rotational constants are not too large, RT transitions are generally multiquantum transitions.[16] Under these conditions we would expect that a model of collisions which are strong in the rotational sense would work satisfactorily. In particular, it was stated in Refs. 17 and 18 that this model can be used to describe the rotational relaxation of the levels of the $P(20)$ line of the CO_2 molecule, which we will be discussing below, in Sec. 4.

We will be interested primarily in the situation with

$$\Gamma,\ |\omega_{\text{las}}-\omega_{VJ}^{V'J'}|\leqslant{}^1/_2\Delta\omega_D,$$

where

$$\Delta\omega_D=2\omega_{VJ}^{V'J'}\left(\frac{2kT\ln2}{m_A}\right)^{1/2}\frac{1}{c}$$

is the Doppler width of the absorption line. In this case, we know[8-10] that the velocity distributions $f_{VJ}(\mathbf{v})$ and $f_{V'J'}(\mathbf{v})$ may be far from equilibrium (there may be Bennett peaks and dips), so the probabilities for stimulated vibrational–rotational and vibrational transitions may differ from those found without consideration of this deviation from equilibrium). The same is true of the absorption coefficient.

3. EXCITATION PROBABILITIES AND ABSORPTION COEFFICIENT: STRONG-COLLISION MODEL

Integrating Eqs. (1) and (2) over velocity, we find the following expression for the probability for a stimulated transition $|V,J\rangle - |V',J'\rangle$ per unit time:

$$W_{VJ}^{V'J'} = (\Delta n_{VJ}^{V'J'})^{-1} \int W(\mathbf{v}) [f_{VJ}(\mathbf{v}) - f_{V'J'}(\mathbf{v})] d\mathbf{v},$$

$$\Delta n_{VJ}^{V'J'} = n_{VJ} - n_{V'J'}. \tag{5}$$

For simplicity we have assumed $g_{V'J'}/g_{VJ} \approx 1$, as we are always justified in doing for levels with a large rotational number J.

The quantities $n_{VJ}, n_{V'J'}$ and $N_V, N_{V'}$ vary over two quite different time scales. If we are interested in the slow process of the changes in vibrational populations, the populations n_{VJ} and $n_{V'J'}$ can be regarded as quasisteady; i.e., we can set the right sides of Eqs. (1) and (2), integrated over velocity, equal to zero. It then becomes possible to find from Eqs. (3) and (4) expressions for the probability for a stimulated vibrational transition per unit time:[19]

$$W_{V\to V'} = \frac{W_{VJ}^{V'J'} q_J}{1 + 2W_{VJ}^{V'J'} \tau_{RT}}, \quad W_{V'\to V} = \frac{W_{VJ}^{V'J'} q_{J'}}{1 + 2W_{VJ}^{V'J'} \tau_{RT}}. \tag{6}$$

The probability $W_{VJ}^{V'J}$ is generally a function of the time, but all that we need is its quasisteady value for the derivation of (6). If we ignore the deviation of the distributions $f_{VJ}(\mathbf{v})$ and $f_{V'J'}(\mathbf{v})$ from equilibrium in (5) and set $f_{VJ}(\mathbf{v}) = n_{VJ} f_M(\mathbf{v})$ and $f_{V'J'}(\mathbf{v}) = n_{V'J'} f_M(\mathbf{v})$, we find an existing result[1,4-7] for the probability for a stimulated vibrational–rotational transition:

$$(W_{VJ}^{V'J'})_{eq} = \frac{4\pi^2}{3c\hbar^2} |d_{VJ}^{V'J'}|^2 I g_V(a,x). \tag{7}$$

Here $g_V(a,x)$ is a normalized Voigt function with parameters which are independent of the light intensity:

$$g_V(a,x) = \frac{2(\ln 2)^{1/2}}{\pi^{1/2}\Delta\omega_D} \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)}{(x-y)^2 + a^2} dy, \tag{8}$$

$$x = \frac{2(\ln 2)^{1/2} (\omega_{\text{las}} - \omega_{VJ}^{V'J'})}{\Delta\omega_D}, \quad a = \frac{2(\ln 2)^{1/2}\Gamma}{\Delta\omega_D}.$$

Let us determine how the quantity $W_{VJ}^{V'J'}$ and, correspondingly, $W_{V\to V'}$ change when we take the deviation of the distributions $f_{VJ}(\mathbf{v})$ and $f_{V'J'}(\mathbf{v})$ from equilibrium into account.

To derive analytic results, we work from a quasisteady solution of Eqs. (1) and (2). We simplify the collision integrals in (1) and (2), adopting the model of strong elastic collisions. In this model, the active molecules acquire a Maxwellian velocity distribution over the time τ_e between elastic collisions, and the collision integral in (2) becomes

$$\frac{1}{\tau_e} [n_{VJ} f_M(\mathbf{v}) - f_{VJ}(\mathbf{v})]$$

[there is a corresponding expression for (1)]. We will also put the rotational-exchange terms in (1) and (2) in a more convenient form, by setting

$$N_{V'}(\mathbf{v}) = N_{V'} f_M(\mathbf{v}), \quad N_V(\mathbf{v}) = N_V f_M(\mathbf{v}).$$

In doing so we introduce an error $\sim O(q_J \ll 1)$ in (1) and (2) and an error $\sim O(q_J^2)$ in (3) and (4). After some straightforward calculations we find the following expression for the quasisteady value of the probability for a stimulated vibrational–rotational transition $|V',J'\rangle$:

$$W_{VJ}^{V'J'} = \frac{4\pi^2}{3c\hbar^2} \frac{|d_{VJ}^{V'J'}|^2 I g_V(a^*,x)}{(1+\varkappa)^{1/2} - \pi\varkappa\Gamma g_V(a^*,x)},$$

$$\varkappa = \tau_{\text{re}} \frac{8\pi}{3c\hbar^2} |d_{VJ}^{V'J'}|^2 I\Gamma^{-1}, \quad \tau_{\text{re}} = \frac{\tau_{RT}\tau_e}{\tau_{RT}+\tau_e},$$

$$a^* = \frac{(\ln 2)^{1/2}\Delta\omega_L^*}{\Delta\omega_D}, \quad \Delta\omega_L^* = \Delta\omega_L(1+\varkappa)^{1/2}, \quad \Delta\omega_L = 2\Gamma. \tag{9}$$

In the limiting cases of a weak field ($\varkappa \ll 1$) or an "instantaneous" translational relaxation ($\tau_e = 0$), expression (9) for the probability $W_{VJ}^{V'J'}$ becomes expression (7) for the probability $(W_{VJ}^{V'J'})_{\text{eq}}$, which was derived without consideration of the distortions of the velocity distributions.

Just how great is the difference between $W_{VJ}^{V'J'}$ and $(W_{VJ}^{V'J'})_{\text{eq}}$ in other cases? Let us consider the case $\Delta\omega_L^* \gg \Delta\omega_D$. It is not difficult to show that if this condition holds because of a large collisional width $\Delta\omega_L \gg \Delta\omega_D$, for an arbitrary value of the saturation parameter $\varkappa$, the spectral shape of the probability $W_{VJ}^{V'J'}$ is described by a Lorentzian line with a width $\Delta\omega_L$, and we have $W_{VJ}^{V'J'} = (W_{VJ}^{V'J'})_{\text{eq}}$. The most interesting case is the opposite one, with $\Delta\omega_L^* \gg \Delta\omega_D$ (i.e., $\varkappa \gg 1$) but $\Delta\omega_L \ll \Delta\omega_D$. In this case of strong saturation with $|\omega_{\text{las}} - \omega_{VJ}^{V'J'}| \sim \Delta\omega_D$ the difference between $W_{VJ}^{V'J'}$ and $(W_{VJ}^{V'J'})_{\text{eq}}$ is a maximum:

$$\frac{W_{VJ}^{V'J'}}{(W_{VJ}^{V'J'})_{eq}} = \frac{\Delta\omega_L}{\Delta\omega_D} \frac{2\left(\frac{\ln 2}{\pi}\right)^{1/2} \exp\left[4\ln 2 \frac{(\omega_{\text{las}} - \omega_{VJ}^{V'J'})^2}{\Delta\omega_D^2}\right]}{1 + 8\ln 2 \frac{(\omega_{\text{las}} - \omega_{VJ}^{V'J'})^2}{\Delta\omega_D^2}} \ll 1. \tag{10}$$

Since the probabilities $W_{VJ}^{V'J'}$ and $(W_{VJ}^{V'J'})_{\text{eq}}$ in a weak field are the same and are linear functions of the intensity I, and since this linearity persists in a strong field, but with different proportionality factors, according to (10), there exists a region of nonlinearity for the function $W_{VJ}^{V'J'}(I)$. For example, with a Doppler line $W_{VJ}^{V'J'}$, with $\Delta\omega_L^* \ll \Delta\omega_D$ (the field is not too strong, and the condition $\Delta\omega_L \ll \Delta\omega_D$ holds), we have

$$\frac{W_{VJ}^{V'J'}}{(W_{VJ}^{V'J'})_{eq}} = \frac{1}{(1+\varkappa)^{1/2}}. \tag{11}$$

For $\varkappa \gtrsim 1$ this ratio is proportional to $I^{-1/2}$. Figure 1 shows

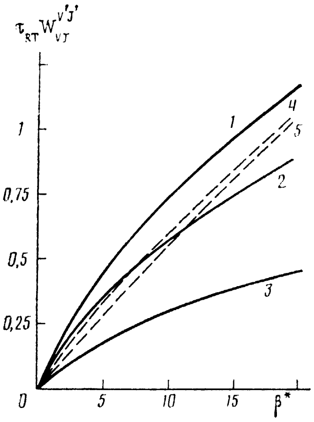

FIG. 1. The quantity $W^{V'J'}_{VJ}\tau_{RT}$ as a function of the parameter $\beta^* = \varkappa\tau_{RT}/2\tau_{re}$ for various values of the normalized detuning and of the collisional absorption linewidth with $\tau_{RT} = 5\tau_e$. ξ,x: 1—0.1, 0; 2—0.1, 0.5; 3—0.1, 1; 4—0.5, 0.5; 5—1, 0.5. The dashed lines show the quantity $W^{V'J'}_{VJ}\tau_{RT}\cdot 0.1/\xi$.

the dimensionless quantity $W^{V'J'}_{VJ}$ as a function of the parameter $\beta^* = \varkappa\tau_{RT}/2\tau_{re} \sim I$ for various values of the detuning (for various values of x) and for various values of the pressure (for various values of the quantity $\xi = \Delta\omega_L/\Delta\omega_D$). These curves illustrate the comments above. We can clearly see a nonlinear region on the plot of $W^{V'J'}_{VJ}(I)$; this nonlinear region gradually fades away with increasing $\Delta\omega_L/\Delta\omega_D$.

Figure 2a shows the change in the vibrational-photoexcitation probability $W_{V\to V'}$ which stems from the change in $W^{V'J'}_{VJ}$. In the case $\Delta\omega_L \gg \Delta\omega_D$ or in the weak-field limit ($\varkappa \ll 1$) we have $W^{V'J'}_{VJ} = (W^{V'J'}_{VJ})_{\text{eq}}$ and thus $W_{V\to V'} = (W_{V\to V'})_{\text{eq}}$. In the strong-field limit ($\varkappa \gg 1$) we have $W^{V'J'}_{VJ} \to \infty$ and $W_{V\to V'} = q_J/2\tau_{RT}$; i.e., there is a rotational "bottleneck,"[19] which does not depend on the translational relaxational rate. On the other hand, we see from Fig. 2a that this effect is manifested at far higher light intensities when the laser-induced deviation from equilibrium velocity distributions is taken into account [see (10)]. In moderate fields ($10 \lesssim \beta^* \lesssim 100$) the differences between $W_{V\to V'}$ and $(W_{V\to V'})_{\text{eq}}$ reach a factor of 1.5 or 2.

An expression for the quasisteady absorption coefficient for monochromatic light on the transition $|V,J\rangle - |V',J'\rangle$ is

$$\alpha^{V'J'}_{VJ} = \frac{\pi\sigma_0 g_V(a^*, x)(1 + 2\tau_{re}W^{V'J'}_{VJ})}{(1+\varkappa)^{1/2}(1 + 2\tau_{RT}W^{V'J'}_{VJ})}(N_V q_J - N_{V'}q_{J'}),$$

$$\sigma_0 = \frac{4\pi|d^{V'J'}_{VJ}|^2}{3c\hbar}\omega^{V'J'}_{VJ}. \qquad (12)$$

Figure 2b shows a plot of this quantity versus the light intensity. It can be seen from this figure that the deviation from equilibrium velocity distributions has only a slight effect on the absorption coefficient in the limits of weak and strong fields, but at intermediate intensities ($2 \lesssim \beta^* \lesssim 40$) the distortions of the Maxwellian distributions change the value of $\alpha^{V'J'}_{VJ}$ by a factor of as much as 1.5 or 2. This point must be kept in mind in analyzing experiments on the propagation of intense laser light in the upper atmosphere[20,21] or in determining the properties of the active media of low-pressure gas lasers by optical methods.[22]

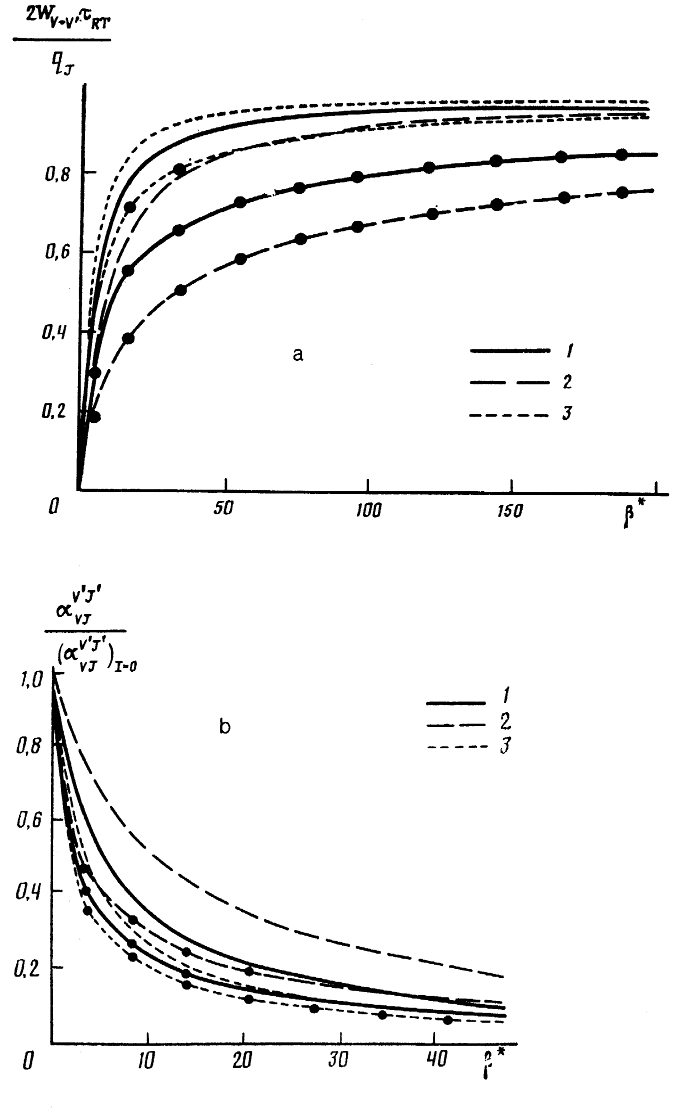

FIG. 2. Plots of (a) the normalized probability for vibrational photoexcitation, $2W_{V\to V'}\tau_{RT}/q_J$, and (b) the normalized absorption coefficient $\alpha^{V'J'}_{VJ}/(\alpha^{V'J'}_{VJ})_{I=0}$ versus the parameter $\beta^* = \varkappa\tau_{RT}/2\tau_{re}$ for various values of ξ and x: 1—$\xi = 0.1$, $x = 0.5$; 2—0.1, 1; 3—0.3, 1. The curves without filled circles were calculated without consideration of the deviation from the equilibrium velocity distributions; those with filled circles reflect these deviations ($\tau_{RT} = 2\tau_e$).

The analytic results derived above for the probability for a stimulated vibrational–rotational transition and for the saturation absorption coefficient are superficially reminiscent of the expressions given in Ref. 8 for the case of the excitation of an atomic transition. However, the latter expressions were derived in a relaxation-constant model, i.e., without consideration of the changes in the particle velocities upon collisions. We would also like to stress that the probability for a stimulated transition which was given in Ref. 8 has a meaning slightly different than that of $W^{V'J'}_{VJ}$ in (5), since $\Delta n^{V'J'}_{VJ}$ in (5) is the instantaneous or running difference between level populations, not the equilibrium difference. The probability $W^{V'J'}_{VJ}$ determined in this manner is required in calculating the probability for vibrational photoexcitation, $W_{V\to V'}$ from expression (6).

4. VALIDITY OF VARIOUS MODELS OF THE ELASTIC-COLLISION INTEGRAL

The results of Sec. 3 show how important it is to consider the distortions of the distributions $f_{VJ}(\mathbf{v})$ and $f_{V'J'}(\mathbf{v})$ in calculating the probability for a stimulated vibrational-rotational transition, the probability for vibrational photoexcitation, and the absorption coefficient. The model of strong elastic collisions which was used in Sec. 3 is obviously of limited applicability. The error of this model is small under the condition $m_B \gg m_A$, where m_B is the mass of the buffer-gas molecule. In the other limit—the case of weak collisions ($m_B \ll m_A$)—the elastic-collision integral can be written as a Fokker–Planck integral. In the limit $m_B/m_A \to 0$, the results of Sec. 3 remain valid if we formally set $\tau_e = \infty$.

In general, the Keilson–Störer model[13,23] is a good approximation of the actual elastic collisions. In that model the collision integral is written in the form

$$\frac{1}{\tau_e}\int_{-\infty}^{\infty} K(v,v_1) f_{VJ}(v_1)\,dv_1 - \frac{1}{\tau_e} f_{VJ}(v),$$

$$K(v,v_1)=\frac{1}{\pi^{1/2}(1-\alpha_{KS}^2)^{1/2}v_0}\exp\left[-\frac{(v-\alpha_{KS}v_1)^2}{(1-\alpha_{KS}^2)\,v_0^2}\right],$$

$$\alpha_{KS}=\frac{m_A}{m_A+m_B}$$

$$+{}^1/_2\frac{m_B}{m_A+m_B}\left[\theta^{-3}(1-2\theta^2)\operatorname{erf}(\theta)-\theta^{-2}\exp(-\theta^2)\right]$$

$$\times\left[\exp(-\theta^2)+(2\theta+\theta^{-1})\operatorname{erf}(\theta)\right]^{-1},$$

$$\theta=\left(\frac{m_B}{m_A}\right)^{1/2},\qquad \operatorname{erf}(\theta)=\int_0^{\theta}\exp(-y^2)\,dy,\qquad v_0=\left(\frac{2kT}{m_A}\right)^{1/2},$$

where α_{KS} is a randomization coefficient. It has a value $\alpha_{KS}=1$ in the case $m_A/m_B \gg 1$ (the weak-collision limit) and a value $\alpha_{KS}=0$ in the case $m_A/m_B \ll 1$ (the strong-collision limit). Here v and v_1 are the projections of the velocity of the molecules onto the direction of the light.

Table I shows values of the coefficient of the Keilson–Störer model, α_{KS}, for certain pairs of colliding molecules (the active molecule and the buffer molecule). The Keilson–Störer integrodifferential equations can be solved only by numerical methods, and the literature reveals extremely few such solutions. A simulation of the Boltzmann equations with a real collision integral is an even more laborious problem from the computational standpoint. An effective method for solving it is the Monte Carlo method whose principles are set forth in Ref. 24. That method makes it possible to simulate collisions of particles with the real interaction potential without any simplification of the collision integral. In this section of the paper, we use that method to analyze how well the models mentioned above correspond to the actual collision integral. Since it is extremely laborious to solve the Boltzmann equations numerically, it is obviously important to know the range of applicability of the simple collision-integral models, particularly in problems involving the interaction of light with multilevel systems. None of the model collision integrals discussed above is valid if the active-gas molecules constitute more than a small admixture in a medium of the buffer gas.

To reduce the time required for the numerical calculations we consider the situation in which a quasisteady state of the transition is reached over a few rotational-relaxation times. In this case the vibrational transition is far from saturation, and the relation $N_{V'}q_{J'} \ll N_V q_J$ holds. Equations (1) and (2) can then be examined without reference to Eqs. (3) and (4), with the rotational-exchange terms in (1) and (2) written in the respective forms

$$-\frac{1}{\tau_{RT}}(1-q_{J'})f_{V'J'}(\mathbf{v})+O(q_{J'}),$$

$$\frac{1}{\tau_{RT}}(1-q_J)\left[n_{VJ}^{\rm init} f_M(\mathbf{v})-f_{VJ}(\mathbf{v})\right]+O(q_J),$$

where $n_{VJ}^{\rm init}$ is the initial equilibrium population of the level $|V,J\rangle$.

To study the models we adopt the example of the excitation of the (10^00)–$(00^01)P(20)$ vibrational–rotational transition of the CO_2 molecule in a medium of N_2 and also in a medium of He. In our formulation of the problem, we can ignore vibrational VV' and VT relaxation. The reason is that the time scale of the fastest VV' exchange in the mixture CO_2–N_2 is[25] $\tau_V \approx 800\tau_0$. In the numerical calculations we adopt the following parameter values for the $P(20)$ line:[1,26]

TABLE I. The coefficient α_{KS} of the Keilson–Störer model for various pairs of colliding molecules.

№	Collision pair	Ratio of molecular masses, m_A/m_B	α_{KS}
1	$CO_2 - N_2$	$^{44}/_{28}$	0,515
2	$CO_2 - He$	$^{44}/_{4}$	0,890
3	$CO_2 - O_2$	$^{44}/_{32}$	0,479
4	$H_2O - N_2$	$^{18}/_{28}$	0,284
5	$HBr - N_2$	$^{81}/_{28}$	0,671
6	$HI - N_2$	$^{128}/_{28}$	0,767
7	$C_2H_2 - N_2$	$^{26}/_{28}$	0,374
8	$HCl - N_2$	$^{36}/_{28}$	0,461
9	$CO - N_2$	$^{28}/_{28}$	0,393
10	$HF - H_2$	$^{20}/_{2}$	0,880
11	$HF - F_2$	$^{20}/_{38}$	0,241
12	$HF - He$	$^{20}/_{4}$	0,783
13	$HF - N_2$	$^{20}/_{28}$	0,308

$$A_{VJ}^{V'J'}=0{,}187\ \mathrm{s}^{-1};\qquad \omega_{VJ}^{V'J'}/2\pi c=944{,}1940\,\mathrm{cm}^{-1};$$
$$q_J\approx q_{J'}\approx 0{,}07;$$

$$g_{VJ}=41,\qquad g_{V'J'}=39;$$

$$\frac{\Gamma(\mathrm{CO_2{-}He})}{2\pi c}=0{,}0615\left(\frac{300\ \mathrm{K}}{T}\right)^{1/2}\mathrm{cm}^{-1}\cdot\mathrm{atm}^{-1},$$
$$\frac{\Gamma(\mathrm{CO_2{-}N_2})}{2\pi c}=0{,}072\left(\frac{296\ \mathrm{K}}{T}\right)^{1/2}\mathrm{cm}^{-1}\cdot\mathrm{atm}^{-1},\qquad T=300\ \mathrm{K}.$$

Apparently the only way to exactly determine the differential elastic cross section $d\sigma_e$ would be to numerically calculate the scattering trajectories of the colliding molecules for a real, spherically asymmetric potential. The complexity of solving that problem is greater than that of solving the kinetic equations (1), (2). However, there is no need to actually solve that problem in order to evaluate the sensitivity of the distribution functions to some model or other for the elastic-collision integral.

Let us assume that the elastic scattering is by a Lennard–Jones (6–12) potential with the parameter values[27,28]

$$\sigma(\mathrm{CO_2{-}CO_2})=4{,}328\ \text{Å};\ \sigma(\mathrm{N_2{-}N_2})=3{,}745\ \text{Å};\ \sigma(\mathrm{He{-}He})=2{,}551\ \text{Å};\ \epsilon(\mathrm{CO_2{-}CO_2})/k=198{,}2\ \mathrm{K};\ \epsilon(\mathrm{N_2{-}N_2})/k=95{,}2\ \mathrm{K};\ \epsilon(\mathrm{He{-}He})/k=10{,}22\ \mathrm{K}.$$

We find the parameters σ_{ij} and ϵ_{ij} for collisions of molecules of species i with molecules of species j by means of the known combinational relations.[15] We take $1/\tau_e$ to be equal to the equilibrium mean transport collision rate $1/\tau_0$:

$$\frac{1}{\tau_e}=\frac{1}{\tau_0}=\frac{2}{\pi^{1/2}}\left(\frac{2kT}{m_r}\right)^{1/2}n_B\pi\sigma_{ij}^2D,$$
$$D=4\int_0^\infty\exp(-c_r'^2)c_r'^3\,dc_r'\int_0^\infty(1-\cos\chi)\,b^*\,db^*,$$

where $c_r'=c_r(m_r/2kT)^{1/2}$, c_r is the relative velocity of the colliding molecules, m_r is their reduced mass, n_B is the number density of the buffer-gas molecules, χ is the scattering angle in the c.m. system, $b^*=b/\sigma_{ij}$, and b is the impact parameter. A change in $1/\tau_0$ by 10–15% has a negligible effect on the calculated results. The relative error of these results is about 0.3% for the populations and about 2% for the distribution functions.

The incoherent approach used in writing Eqs. (1) and (2) (on the one hand) and the classical description of the translational motion (on the other) make it impossible to correctly describe small-angle diffractive scattering, in the course of which the oscillations of the off-diagonal element of the density matrix do not undergo phase relaxation.[29] This is true even for times greater than the mean phase-relaxation time $1/\Gamma$. However, the angular width of the diffractive part of the scattering function is about 3° for CO_2–He collisions and 1° for CO_2–N_2 collisions. In scattering through such small angles the velocity of the molecules and thus their distribution function remain essentially unchanged. In all the numerical calculations we accordingly "truncated" the interaction potential, at a scattering angle $\chi_{\min}=3°$ for CO_2-He and at $\chi_{\min}=1°$ for CO_2-N_2. In other words, we completely ignored the small-angle scattering. Simple estimates show that the error in the distribution functions calculated by this procedure does not exceed the statistical error of the method.

It was not by chance that we selected the gases N_2 and He as buffer media; the choice was dictated by the purpose of this study. When the buffer gas is N_2, the masses of the active molecules (CO_2) and the buffer molecules do not differ greatly, and α_{KS} has a value of 0.515, qualifying CO_2–N_2 collisions as an intermediate case between strong and weak collisions. In this situation, the question of the accuracy of the strong-collision model is particularly interesting.

Figure 3 demonstrates the good agreement between the results calculated on the time evolution of the populations from the Boltzmann equations and from the strong-collision model for various values of the light intensity, the time τ_{RT}, the detuning $\Omega=(\omega_{\mathrm{las}}-\omega_{VJ}^{V'J'})/2\pi c$, and the pressure p of the CO_2-N_2 mixture. The results calculated for the populations in the Keilson–Störer model agree almost perfectly with the results of the solutions of the Boltzmann equations and are thus omitted from Fig. 3. In the cases considered, the calculations demonstrate a good overall agreement in terms of not only the integral populations but also the velocity distributions $f_{VJ}(v)$ and $f_{V'J'}(v)$ of the molecules. This agreement thus extends to the excitation probabilities and the absorption coefficient. As an example, we see from Fig. 4 that the strong-collision model introduces a small error in the region near the absorption resonance and some error on the left-hand tail of the distribution (i.e., on the tail further from the resonance). The Keilson–Störer model accurately reproduces the distribution function in the tails, having a small error only in a narrow region near the resonance.

The situation can change dramatically if a light gas is used as the buffer gas. The results calculated on the populations and velocity distributions (Figs. 5 and 6) agree well with the results of the solution of the Boltzmann equations only in the Keilson–Störer model. Calculations carried out with various values of the mass ratio m_A/m_B lead to the conclusion that the Keilson–Störer model gives a satisfactory description of both strong and weak elastic collisions in

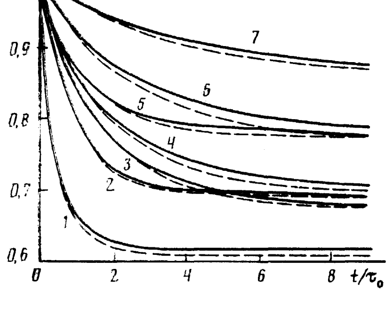

FIG. 3. Time evolution of the population of the $|V,J\rangle$ lower level of the CO_2 molecules. The buffer gas is N_2. 1, 2—$I=10^4$ W/cm²; 3–7—10^3 W/cm². 2—$p=10^{-2}$ atm; other curves—$2\cdot10^{-3}$ atm. 1, 2, 5—$\tau_{RT}=2.5\tau_0$; 3, 4, 6, 7—$5\tau_0$. 1, 2, 4, 5—$\Omega=5\cdot10^{-4}$ cm^{-1}; 3—$2\cdot10^{-4}$ cm^{-1}; 6—10^{-3} cm^{-1}; 7—$1.5\cdot10^{-3}$ cm^{-1}. The solid curves are solutions of the Boltzmann equations, and the dashed curves are calculated from the strong-collision model.

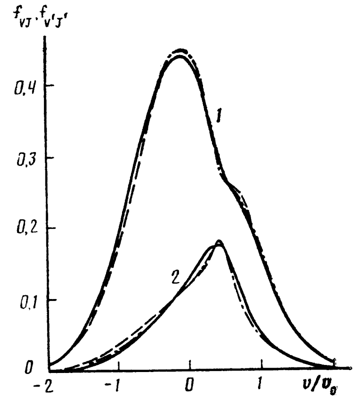

FIG. 4. Velocity distributions of the CO_2 molecules in the quasisteady state. $n_{VJ}^{\text{init}} = 1$, $n_{V'J'}^{\text{init}} = 0$. The buffer gas is N_2. 1—$|V,J\rangle$ lower level; 2—$|V',J'\rangle$ upper level. The curve labels have the same meaning as in Fig. 3. The dot-dashed lines show results calculated from the Keilson–Störer model ($I = 10^3$ W/cm^2, $\Omega = 5\cdot10^{-4}$ cm^{-1}, $p = 2\cdot10^{-3}$ atm, $\tau_{RT} = 2.5\tau_0$).

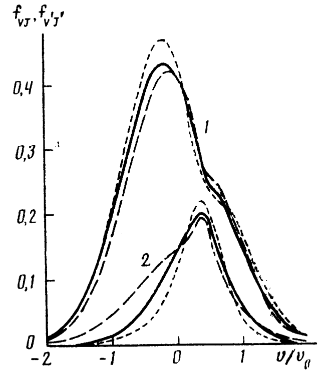

FIG. 6. Velocity distributions of the CO_2 molecules in the quasisteady state. $n_{VJ}^{\text{init}} = 1$, $n_{V'J'}^{\text{init}} = 0$. The buffer gas is He. The solid curves show the solution of the Boltzmann equations and results calculated from the Keilson–Störer model. The curve labels otherwise have the same meaning as in Fig. 5. 1—$|V,J\rangle$ lower level; 2—$|V',J'\rangle$ upper level ($I = 10^3$ W/cm^2, $\Omega = 5\cdot10^{-4}$ cm^{-1}, $p = 2\cdot10^{-3}$ atm, $\tau_{RT} = 5\tau_0$).

our case. In contrast, the models of strong collisions ($\alpha_{\text{KS}} = 0$) and weak collisions ($\alpha_{\text{KS}} = 1$) are both afflicted by significant errors in the determination of the populations and velocity distributions in the CO_2–He case. These errors become particularly obvious in the calculation of the velocity distributions (Fig. 6), where they can reach 100%. These errors lead in turn to equal errors in the absorption coefficient for the given velocity, $\alpha_{VJ}^{V'J'}$ (Fig. 7), and errors in the integral absorption coefficient (the areas under curves 1, 2, and 3 are different).

The errors of the strong- and weak-collision models differ in sign. In addition, for the cases shown in Figs. 6 and 7 the errors of these limiting models are identical in magnitude, although the CO_2–He collisions would appear to be a better approximation of weak collisions ($\alpha_{\text{KS}} = 0.890$). The sensitivity of the velocity distributions of the molecules to the particular model used for the elastic-collision integral obviously depends on the relation between τ_e and τ_{RT}. For $\tau_e > \tau_{RT}$ the model has only a minor effect. In the case $\tau_e \lesssim \tau_{RT}$, as was shown above, the velocity distributions may depend noticeably on the particular model. The calculations show that for $\tau_e \approx \tau_{RT}$ the following assertions are valid: The strong-collision model works at $0 < \alpha_{\text{KS}} < 0.5$. Reliable results can be found at $0.5 < \alpha_{\text{KS}} < 0.85$–$0.9$ only by solving the Boltzmann or Keilson–Störer equation. The Fokker–Planck diffusion equations which follow asymptotically from the Keilson–Störer equations can be used in the interval 0.85–$0.9 < \alpha_{\text{KS}} < 0.95$. For $0.95 < \alpha_{\text{KS}} < 1$ one can completely ignore the effect of elastic collisions on the shape of the velocity distribution functions.

The validity of the strong-collision model was tested by Koura,[30] who solved the problem of the relaxation of an initial perturbation of the distribution function in a process of elastic collisions. However, that study was limited to the particular case $m_A/m_B = 1$, so no general conclusions can be drawn from the good agreement which was found between the model-based results and the Monte Carlo results.

Attempts have been made previously to generalize the strong-collision model to the case of an arbitrary relation

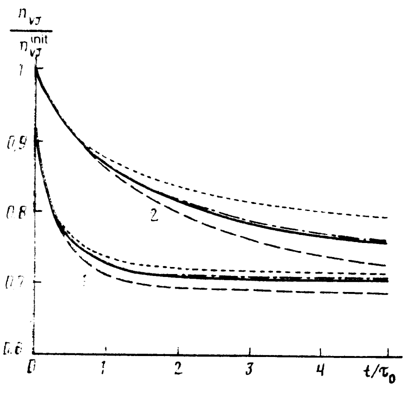

FIG. 5. Time evolution of the population of the $|V,J\rangle$ lower level. The buffer gas is He; $\Omega = 5\cdot10^{-4}$ cm^{-1}; $p = 2\cdot10^{-3}$ atm. 1—$I = 10^4$ W/cm^2, $\tau_{RT} = \tau_0$; 2—10^3 W/cm^2, $5\tau_0$. The curve labels have the same meaning as in Fig. 4. The dashed curves with the shorter dashes show results calculated in the weak-collision limit ($\alpha_{\text{KS}} = 1$).

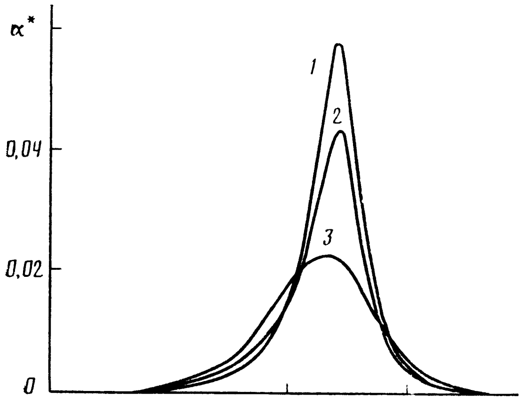

FIG. 7. Normalized absorption coefficient $\alpha^* = \alpha_{VJ}^{V'J'}(v)\cdot v_0\Gamma/(\sigma_0 n_{VJ}^{\text{init}})$ for $I = 10^3$ W/cm^3, $\Omega = 5\cdot10^{-4}$ cm^{-1}, $p = 2\cdot10^{-3}$ atm, and $\tau_{RT} = 5\tau_0$. The buffer gas is He. 1—Strong-collision model; 2—Keilson–Störer model; 3—weak-collision limit ($\alpha_{\text{KS}} = 1$).

between the masses of the molecules, by varying the time τ_e in some manner. For example, Haverkort *et al.*[12] replaced τ_e by an effective time $\tau_{\rm eff} = \tau_e/(1-\alpha)$, where α is a function of m_A/m_B with $\alpha \to 0$ as $m_A/m_B \to 0$ and $\alpha \to 1$ as $m_A/m_B \to \infty$. The physical meaning here is that some of the molecules (a fraction $1-\alpha$) undergo strong collisions, while others (a fraction α) have the same velocity vectors after the collision. If we replace τ_e by $\tau_{\rm eff}$, all the results of Sec. 3 remain in force. The value $\alpha = \alpha_{\rm KS}$ was adopted in Ref. 12 to calculate the velocity of the light-induced drift (i.e., the first moment of the distribution function). That value leads to the best agreement between the expressions for momentum exchange found from this model and from the Keilson–Störer model. However, our own calculations show that the coefficient α should be assigned different values, depending on the particular moment of the distribution function which is being calculated. Consequently, it would be difficult to expect good accuracy in the distribution functions calculated in all applications of this model, and the model itself should be regarded as only semiquantitative.

Finally, we note that in all cases of practical interest in the physics of gas lasers, atmospheric ecology, etc., the ratio of the masses of the colliding molecules is such that we have $0.5 < \alpha_{\rm KS} < 0.85$–$0.9$, so it would not be valid to use simple models of the elastic-collision integral in these cases (see Table I).

5. CONCLUSION

In summary, consideration of the laser-induced deviation of the velocity distributions of the molecules from equilibrium results in substantial changes in the probability for stimulated vibrational–rotational and vibrational transitions and also in the absorption coefficient for the light. Nonequilibrium velocity distributions may depend substantially on the particular model selected for the elastic-collision integral. Here are some more-detailed conclusions.

1. The quasisteady probability $W_{VJ}^{V'J'}$ for the stimulated vibrational-rotational transition is a nonlinear, square-root function of the light intensity I when the collisional absorption linewidth is small in comparison with the Doppler width ($\Delta\omega_L \ll \Delta\omega_D$), and the field is at a moderate level ($\varkappa \gtrsim 1$) [see (11) and Fig. 1].

2. The presence of a nonlinear region on the plot of $W_{VJ}^{V'J'}(I)$ leads to decreases, by a factor up to 1.5 or 2, in the probability for vibrational photoexcitation, $W_{V\to V'}$, and in the optical absorption coefficient $\alpha_{VJ}^{V'J'}$ (in comparison with the values found without consideration of the deviation of the velocity distributions of the molecules from equilibrium) (Fig. 2, a and b).

3. The quasisteady probability for a stimulated vibrational-rotational transition, $W_{VJ}^{V'J'}$, in a strong field ($\varkappa \gg 1$) increases linearly with the light intensity. The ratio of this probability to the probability found without consideration of the deviation of the velocity distributions of the molecules from equilibrium is proportional to $\Delta\omega_L/\Delta\omega_D$ in the case $\Delta\omega_L \ll \Delta\omega_D$ [see (110)]. The slower growth of $W_{VJ}^{V'J'}(I)$ (slower by a factor of tens) has the consequence that the probability for vibrational photoexcitation, $W_{V\to V'} = q_J/2\tau_{RT}$ (the rotational bottleneck), reaches its maximum at substantially higher light intensities (Fig. 2a).

4. An incorrect choice of model for the elastic-collision integral can change the calculated distribution functions by amounts equal to their values. Comparing the results calculated on the basis of models and results of solutions of the Boltzmann equations with the actual collision integral leads to the conclusion that the Keilson–Störer model is quite accurate over the entire range of the parameter $\alpha_{\rm KS}$ (a measure of the ratio of masses of the colliding molecules) in problems of optical excitation and relaxation of a small admixture of absorbing molecules in a medium of a buffer gas. In several cases, simpler approximations are also quite accurate. For example, if the rates of elastic collisions and RT collisions are equal, with $0 < \alpha_{\rm KS} < 0.5$, the model of strong collisions works well, while for $0.85 < \alpha_{\rm KS} < 1$ the model of weak collisions (Fokker–Planck equations) work well. For $0.95 < \alpha_{\rm KS} < 1$ one can completely ignore the effect of collisions on the shape of the nonequilibrium velocity distributions of the molecules. In the interval $0.5 < \alpha_{\rm KS} < 0.85$, the only way to obtain reliable results is to solve the Boltzmann or Keilson–Störer equation.

We wish to thank A. I. Osipov and V. Ya. Panchenko for a useful discussion of this study. We also thank A. A. Makarov for benevolent criticism.

[1] B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, *Kinetic Processes in Gases in Connection with Molecular Lasers*, Nauka, Moscow, 1980.

[2] M. Capitelli (editor), *Nonequilibrium Vibrational Kinetics*, Springer-Verlag, New York, 1986 (Russ. Transl. Mir, Moscow, 1989).

[3] V. S. Letokhov, *Nonlinear Selective Photoprocesses in Atoms and Molecules*, Nauka, Moscow, 1983.

[4] S. V. Ivanov, V. Ya. Panchenko, and A. V. Chugunov, Izv. Akad. Nauk SSSR, Ser. Fiz. **50**, 695 (1986).

[5] M. S. Dzhidzhoev, V. K. Popov, V. T. Platonenko, and A. V. Chugunov, Kvantovaya Elektron. (Moscow) **11**, 1357 (1984) [Sov. J. Quantum Electron. **14**, 917 (1984)].

[6] A. V. Chugunov, M. S. Djidjoev, S. V. Ivanov, and V. Ya. Panchenko, Opt. Lett. **10**, 615 (1985).

[7] S. V. Ivanov and V. Ya. Panchenko, Opt. Atm. **2**, 55 (1989).

[8] V. S. Letokhov and V. P. Chebotaev, *Nonlinear Laser Spectroscopy*, Nauka, Moscow, 1975 (Springer-Verlag, Berlin, 1975).

[9] S. G. Rautian, G. I. Smirnov, and A. M. Shalagin, *Nonlinear Resonances in Atomic and Molecular Spectra*, Nauka (Siberian branch), Novosibirsk, 1979.

[10] W. Demtroder, *Laser Spectroscopy: Basic Concepts and Instrumentation*, Springer-Verlag, New York, 1981 (Russ. Transl. Nauka, Moscow, 1985, p. 95).

[11] F. Kh. Gel'mukhanov and A. M. Shalagin, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 773 (1979) [JETP Lett. **29**, 711 (1979)].

[12] J. E. M. Haverkort, H. G. C. Werij, and J. P. Woerdman, Phys. Rev. A **38**, 4054 (1988).

[13] J. Keilson and J. E. Störer, Quart. Appl. Math. **10**, 243 (1952).

[14] M. N. Kogan, *Rarefied Gas Dynamics*, Nauka, Moscow, 1967 (Plenum, New York, 1969).

[15] J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases*, North-Holland, Amsterdam, 1972 (Russ. Transl. Mir, Moscow, 1976).

[16] A. I. Osipov, Khim. Plazmy **16**, 3 (1990).

[17] R. K. Preston and R. T. Pack, J. Chem. Phys. **69**, 2823 (1978).

[18] W. J. Witteman, *The CO₂ Laser*, Springer-Verlag, New York, 1987 (Russ. Transl. Mir, Moscow, 1990, p. 318).

[19] V. S. Letokhov and A. A. Makarov, Zh. Eksp. Teor. Fiz. **63**, 2064 (1972) [Sov. Phys. JETP **36**, 1091 (1973)].

[20] V. E. Zuev, *Propagation of Laser Light in the Atmosphere*, Radio i svyaz, Moscow, 1981, p. 185.

[21] A. A. Mitsel and Yu. N. Ponomarev, *Optical Models of a Molecular Atmosphere*, Nauka (Siberian branch), Novosibirsk, 1988, p. 57.

[22] V. N. Karnyushin and R. I. Soloukhin, *Macroscopic and Molecular Processes in Gas Lasers*, Atomizdat, Moscow, 1981, p. 195.

[23] M. Borenstein and W. E. Lamb, Phys. Rev. A **5**, 1311 (1972).
[24] G. A. Bird, *Molecular Gas Dynamics*, Oxford Univ., London, 1976 (Russ. Transl. Mir, Moscow, 1981, p. 143).
[25] S. A. Posev, *Gas Dynamic Lasers*, Nauka, Moscow, 1977, p. 110.
[26] L. S. Rothman, Appl. Opt. **20**, 791 (1981).
[27] R. C. Reid and T. K. Sherwood, *Properties of Gases and Liquids*, McGraw-Hill, New York, 1966 (Russ. Transl. Khimiya, Leningrad, 1982).
[28] A. E. Sherwood and J. M. Praushnitz, J. Chem. Phys. **41**, 429 (1964).
[29] R. Shoemaker, in *Laser and Coherence Spectroscopy* (ed. J. I. Steinfeld), Plenum, New York, 1978 (Russ. Transl. Mir, Moscow, 1982).
[30] K. Koura, J. Chem. Phys. **72**, 268 (1980).

Translated by D. Parsons