

MODELING OF THE DYNAMICS OF THE CHANGE IN THE INDEX OF REFRACTION DURING RESONANCE INTERACTION OF RADIATION WITH VIBRATIONAL-ROTATIONAL TRANSITIONS

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It is well known that resonance absorption of radiation by a gas can lead to excitation of molecular internal degrees of freedom, and this determines, to a significant degree, the nonlinear response of the medium. The dielectric permittivity of the medium has both imaginary and real parts. The imaginary part is associated with the absorption coefficient k , and the real part is associated with the index of refraction n . A change of n in the beam channel causes the light rays to be deflected from the initial direction and determines, to a significant degree, the character of laser propagation in a nonlinear medium [1]. This is why there are so many works on the mechanisms responsible for the change in the index of refraction under the action of resonance radiation. Special attention is devoted to the analysis of the mechanism of the change in n during propagation of an IR pulse (radiation in this region of the spectrum is usually absorbed on vibrational-rotational transitions) [2-7]. This is because it is with IR lasers that the high intensities at which nonlinear effects become very significant are achieved.

It has been shown that the main mechanisms responsible for the change in n are the change in molecular polarizability of the medium due to excitation of molecular vibrations and the change in the density of the medium due to hydrodynamic effects produced by the nonuniform heat transfer from vibrational into translational degrees of freedom. Hydrodynamic effects have been analyzed primarily within the model of a nonviscous thermally nonconducting gas, neglecting the influence of diffusion and heat conduction, which in a vibrationally nonequilibrium gas depends significantly on the degree of excitation and can significantly influence the behavior of the concentrations of the mixture components even over times shorter than the characteristic times of these processes [8]. It is thus of interest to make a comprehensive analysis of the mechanisms of the change in the index of refraction of a mixture of gases, taking into account all processes associated with the excitation of molecular vibrations by resonance radiation. This paper is devoted to such an analysis.

The analysis is performed for a two-component mixture of gases, consisting of molecules of different types, for example A (1) and B (2). The molecules of type A have at least two different types of vibrations k and q with frequencies $\nu_k < \nu_q$, while type-B molecules have vibrations of one type s with frequencies $\nu_s \leq \nu_q$ or $\nu_s \geq \nu_q$. Let the vibrational-translational relaxational time for the mode q be much longer than the vibrational-vibrational exchange times $\nu_q \rightarrow \nu_k$ and $\nu_q \rightarrow \nu_s$, and let the frequency ν_l of the acting radiation be in resonance with the frequency at the line center of the vibrational-rotational transition $m \rightarrow n$, whose upper n and lower m states are vibrations of the types k and q , respectively:

$$\nu_l = (E_{V_n} - E_{V_m} + E_{J_n} - E_{J_m})/h$$

where E_{V_n} and E_{V_m} are the vibrational energies of the excited states n and m of a type-A molecule, E_{J_n} and E_{J_m} are their rotational energies, and h is Planck's constant. This situation is characteristic for many cases of practical interest, for example, absorption of CO_2 -laser radiation in the mixture $\text{CO}_2\text{-N}_2$, employed for both theoretical [9-11] and experimental [12, 13] modeling of different nonlinear processes. We shall consider cases when all molecules are in the ground electronic state and the chemical composition does not change. The index of refraction is then determined by the relations [6, 7]

$$n^2 - 1 = 4\pi \sum_{i=1}^2 N_i \alpha_i, \quad \alpha_i = \alpha_{i0} + \sum_j \alpha_{ij}^V + \alpha_i^R. \quad (1)$$

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Here N_i is the density of i -th molecules; α_{i0} is the nonresonance molecular polarizability of molecules of the i -th component with unexcited internal motion; α_{ij}^V and α_i^R are, respectively, the contribution of molecular vibrations of the j -th type and the contribution of rotation to the nonresonance part of the polarizability of i -th molecules.

We confine our attention to cases when the time of the induced transitions $\tau_1 \gg \tau_{RT}, \tau_{VV}$, where τ_{RT} and τ_{VV} are the characteristic rotational-translational and intramode vibrational-vibrational exchange times. It can thus be assumed that thermodynamic equilibrium exists between the rotational and translational degrees of freedom, and within each j -th mode ($j = k, q, \text{ and } s$) of normal vibrations with frequency ν_j there is a Boltzmann distribution with vibrational temperature T_j . Under these assumptions $\alpha_i^R = \varphi(T)$, and $\alpha_{ij}^V = f(T_j)$. Since for gases $\delta n \ll n_0$, and for $\delta T \ll \delta T_j$ (it is these cases that are studied) $\delta \alpha_i^R \ll \delta \alpha_{ij}^V$ ($\delta \xi = \xi - \xi_0$, $\xi = T, T_j, n, \alpha_i^R, \alpha_{ij}^V$, the index 0 designates unperturbed parameters of the medium at $t = 0$), the change in the index of refraction can be represented, according to Eq. (1), as

$$\delta n = \frac{2\pi}{n_0} \sum_{i=1}^2 (\alpha_{i0} \delta N_i + N_{i0} \sum_j \delta \alpha_{ij}^V). \quad (2)$$

It is evident from Eq. (2) that in order to calculate δn it is necessary to know how N_i and T_j behave. In order to determine the changes in N_i and T_j under the action of resonance radiation on a medium at rest, we shall employ the system of Navier—Stokes equations for a vibrationally nonequilibrium gas. According to [8, 14] this system has the following form:

$$\frac{\partial \rho}{\partial t} + \nabla (\rho \mathbf{u}) = 0; \quad (3)$$

$$\frac{\partial N_i}{\partial t} + \nabla [N_i (\mathbf{u} + \mathbf{V}_i)] = 0; \quad (4)$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \nabla) \mathbf{u} + \nabla p = \sum_{i=1}^2 N_i X_i + \eta \Delta \mathbf{u} + \left(\xi + \frac{2}{3} \right) \nabla (\nabla \mathbf{u}); \quad (5)$$

$$\frac{\partial}{\partial t} \left[\rho \left(E_{RT} + \frac{u^2}{2} \right) \right] + \nabla \left[\rho \mathbf{u} \left(E_{RT} + \frac{p}{\rho} + \frac{u^2}{2} \right) - \mathbf{u}' \sigma' + \mathbf{q}_{RT} \right] = Q_t + \sum_{i=1}^2 N_i X_i (\mathbf{V}_i + \mathbf{u}); \quad (6)$$

$$\frac{\partial \rho e_{\nu}^k}{\partial t} + \nabla (\rho \mathbf{u} e_{\nu}^k) + \nabla q_{\nu}^k = h \nu_k N_1 \left[- \frac{l_k k_{\nu} l}{h \nu_k N_1} - (\epsilon_k - \epsilon_{k0}) W_{k,0} + L_{q,k} r_k W_{q,k} \right]; \quad (7)$$

$$\frac{\partial \rho e_{\nu}^q}{\partial t} + \nabla (\rho \mathbf{u} e_{\nu}^q) + \nabla q_{\nu}^q = h \nu_q N_1 \left[\frac{l_q k_q l}{h \nu_q N_1} - L_{q,k} r_q W_{q,k} - L_{q,s} r_q W_{q,s} N_2 \right]; \quad (8)$$

$$\frac{\partial \rho e_{\nu}^s}{\partial t} + \nabla (\rho \mathbf{u} e_{\nu}^s) + \nabla q_{\nu}^s = h \nu_s N_2 [- (\epsilon_s - \epsilon_{s0}) W_{s,0} + L_{q,s} r_s W_{q,s} N_1], \quad (9)$$

$$\mathbf{q}_{RT} = \rho T \sum_{i=1}^2 C_{RT}^i \mathbf{V}_i - \lambda \nabla T + \frac{KT}{N} \sum_{i=1}^2 \frac{D_i^T N_i}{m_i D_{ij}} (\mathbf{V}_i - \mathbf{V}_j),$$

$$\mathbf{q}_{\nu}^l = \rho e_{\nu}^l \mathbf{V}_i - \lambda_l^{\nu} \nabla T_l + NKT \sum_{j=1}^2 D_{ij}^{\nu} d_j \quad \left(\begin{array}{l} l = k, q \rightarrow l = 1 \\ l = s \rightarrow l = 2 \end{array} \right),$$

$$\mathbf{V}_i = \frac{N^2}{N_i \rho} \sum_{j=1}^2 m_j D_{ij} d_j - \frac{1}{m_i N_i} (D_i^T \nabla \ln T + \delta_{i,1} \sum_{l=k,q} D_l^{\nu} \nabla \ln T_l + \delta_{i,2} D_i^{\nu} \nabla \ln T_s),$$

$$d_j = \nabla \left(\frac{N_j}{N} \right) + \left(\frac{N_j}{N} - \frac{N_j m_j}{\rho} \right) \nabla \ln p + \frac{N_j m_j}{\rho p} \sum_{i=1}^2 N_i X_i - \frac{N_j X_j}{\rho}, \quad j = 1, 2,$$

$$p = \frac{\rho RT}{\mu}, \quad E_{RT} = C_{RT} T, \quad C_{RT} = \sum_{i=1}^2 C_{RT}^i,$$

$$C_{RT}^i = \left(\frac{3}{2} + C_R^i \right) \frac{R}{\mu} \gamma_i, \quad e_{\nu}^l = \frac{h \nu_l R}{K \mu} \gamma_l \epsilon_l,$$

$$\epsilon_{i0} = \epsilon_i(T), \quad \epsilon_i = g_i [\exp(h \nu_i / KT_i) - 1]^{-1},$$

$$W_{q,k} = \sum_i W_{q,k}^i N_{i0}, \quad W_{k,0} = \sum_i W_{k,0}^i N_{i0}, \quad W_{s,0} = \sum_i W_{s,0}^i N_{i0},$$

$$L_{i,m} = \left\{ \varepsilon_i^{\prime\prime} (g_m + \varepsilon_m)^{\prime m} - \varepsilon_m^{\prime\prime} (g_i + \varepsilon_i)^{\prime i} \exp \left[(r_m h\nu_m - r_i h\nu_i) / KT \right] \right\} \frac{1}{g_i^{\prime i} g_m^{\prime m}}, \quad Q_i = k_\nu I (E_j - E_i) / (h\nu_i) + \Phi_\nu,$$

$$\Phi_\nu = h\nu_k N_1 \left[(\varepsilon_k - \varepsilon_{k0}) W_{k,0} + L_{q,k} \left(r_q \frac{\nu_q}{\nu_k} - r_k \right) W_{q,k} \right] +$$

$$+ N_2 h\nu_s \left[(\varepsilon_s - \varepsilon_{s0}) W_{s,0} + L_{q,s} \left(r_q \frac{\nu_q}{\nu_s} - r_s \right) W_{q,s} N_1 \right].$$

Here ρ , p , and T are the density, pressure, and temperature of the gas; R is the universal gas constant; K is Boltzmann's constant; \mathbf{u} is the velocity of the medium; $\mu = \sum \mu_i \gamma_i$; μ_i and γ_i are the molecular mass of the i -th component and the molar fraction of this component in the mixture; N is the total number of molecules per unit volume; g_i is the degree of degeneracy of the i -th vibration; \mathbf{X}_i is a nonlinear force acting on the i -th component in an electromagnetic field; k_ν is the absorption coefficient; I is the intensity of the acting radiation; l_j is the number of vibrational quanta acquired by the mode j via induced transitions; $C_R^i = 1$ for linear molecules and $C_R^i = 1.5$ for nonlinear molecules; m_i is the molecular mass of the i -th component; λ is the thermal conductivity; λ_i^V is the vibrational conductivity of the i -th component; D_i^T and D_{ij} are the thermal and multicomponent diffusion coefficients for the i -th component; D_{ij}^V is the vibrational diffusion coefficient between the i -th and j -th oscillators; D_j^V is the vibrational thermal diffusion coefficient for the j -th mode; $W_{k,0}^i$ and $W_{q,k}^i$ are, respectively, the VT-exchange rate constant in the k -th oscillator and the intramolecular VV'-exchange rate constant between oscillators q and k in a collision with an i -th partner; $W_{q,s}$ is the intermolecular VV'-exchange rate constant in the case of a collision of molecules of type A (q) and B (s); r_j is the number of vibrational quanta lost by the j -th mode in VV' exchange; ξ and η are the coefficients of viscosity; $(\mathbf{u}'\sigma')$ is a vector with the components $u_j \sigma_{jk}'$; and, σ_{jk}' is the viscous-stress tensor.

It follows from the linear dependence of Eq. (3) and two equations of the form (4) (ρ , N_1 and N_2 are related by the relation $\rho = m_1 N_1$ and $m_2 N_2$) that, together with the standard relations between the multicomponent diffusion and thermodiffusion coefficients $D_{ij} = D_{ji}$ and $D_1^T = -D_2^T$, the following equality should also hold:

$$\sum_{j=k,q,s} D_j^V \nabla \ln T_j = 0, \quad (10)$$

i.e., the vibrational thermodiffusion coefficients for the modes k , q , and s are not independent. We shall consider axisymmetric beams with a Gaussian radial intensity distribution $I(r, t) = I_0(t) \times \exp(-r^2/R_a^2)$ for $R_a \ll k_\nu^{-1}$ (R_a is the characteristic radius of the beam), and $I_0(t) = I_0$ ($0 \leq t \leq \tau_p$) and $I_0(t) = 0$ ($t > \tau_p$), where τ_p is the duration of the acting radiation pulse. Introducing the dimensionless coordinates $r' = r/R_a$ and $t' = t/\tau_p$ and switching to the dimensionless variables $\tilde{N}_i = N_i/N_{i0}$, $\tilde{u} = \mathbf{u}\tau_p/R_a$, $\tilde{p} = p/\rho_0$, $\tilde{p} = p/(N_0KT_0)$, $\tilde{T} = T/T_0$, $\tilde{V}_j = V_j\tau_p/R_a$, $\tilde{T}_j = T_j/T_0$, $\tilde{k}_\nu = k_\nu/k_\nu^0$, $\tilde{I} = I/I_0$, the system (3)-(9) can be represented, using the fact that $\tilde{E}_{RT} = E_{RT}/C_{RT}^0 T_0$, in the following form (tildes and primes are dropped):

$$\partial \rho / \partial t = -\nabla (\rho \mathbf{u}); \quad (11)$$

$$\frac{\partial N_i}{\partial t} = -\nabla \left\{ N_i \left[\mathbf{u} - \frac{\tau_p}{\tau_{Ti}} \frac{\nabla \ln T}{N_i} - \frac{\tau_p}{N_i} \left(\delta_{i,1} \sum_{l=k,q} \frac{\nabla \ln T_l}{\tau_{Dl}} + \delta_{i,2} \frac{\nabla \ln T_s}{\tau_{Ds}} \right) + \frac{\tau_p}{\tau_D} \sum_{j=1}^2 d_j \frac{P_m^{2-j} (1 + P_N)^2 N^2}{(P_m + P_N) P_n^{-1} N_i \rho} \right] \right\}; \quad (12)$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \nabla) \mathbf{u} = - \left(\frac{\tau_p}{\tau_a} \right)^2 \frac{\nabla p}{\kappa} + \left(\frac{\tau_p}{\tau_k} \right) \left[\Delta \mathbf{u} + \left(\frac{1}{3} + \frac{\xi}{\eta} \right) \nabla (\nabla \mathbf{u}) \right] + \left(\frac{\tau_p}{\tau_F} \right)^2 \sum_{i=1}^2 N_i X_i \gamma_{i0}; \quad (13)$$

$$\rho \frac{\partial E_{RT}}{\partial t} + \rho (\mathbf{u} \nabla) E_{RT} = -p \nabla \mathbf{u} (\kappa - 1) + \kappa (\kappa - 1) \left[\left(\frac{\tau_a}{\tau_F} \right)^2 \sum_{i=1}^2 N_i X_i V_i \gamma_{i0} + \left(\frac{\tau_a}{\tau_{pk}} \right)^2 \nabla (\mathbf{u}'\sigma') \right] + \frac{\xi \tau_p}{\tau_V} \gamma_{i0} k_\nu I + (\kappa - 1) \left[\sum_{l=k,s} \frac{\tau_p}{\tau_{Vl}} \theta_l N_l (\varepsilon_l - \varepsilon_{l0}) \gamma_{l0} + \frac{\tau_p}{\tau_{qk}} L_{q,k} (r_q \theta_q - r_k \theta_k) N_1 \gamma_{l0} + \frac{\tau_p}{\tau_{qs}} L_{q,s} (r_q \theta_q - r_s \theta_s) N_1 N_2 \right]; \quad (14)$$

$$\begin{aligned}
& - \nabla \left[\frac{\rho T}{C_{RT}^0} \sum_{i=1}^2 C_{RT}^i V_i - \frac{\tau P}{\tau_\lambda} \nabla T + (\kappa - 1) \frac{T}{N} \sum_{i \neq j} \frac{\tau_D}{\tau_{Ti}} N_j \gamma_{i0} \gamma_{j0} (V_i - V_j) \right]; \\
\rho \frac{\partial e_i^k}{\partial t} + \rho (\mathbf{u} \nabla) e_i^k &= \frac{\theta_k}{C_{k0}^V} \left[-l_k k_v J \frac{\tau P}{\tau_i} - \frac{\tau P}{\tau_k^{V'}} N_1 (\epsilon_k - \epsilon_{k0}) + \frac{\tau P}{\tau_{qk}^{V'}} N_1 L_{q,k} r_k \right] - \\
& - \nabla \left[\rho e_i^k V_k - \frac{\tau P}{\tau_k} \nabla T_k + \frac{NT}{C_{k0}^V \gamma_{10}} \sum_{j=1}^2 \frac{\tau P}{\tau_{kj}^V} d_j \right];
\end{aligned} \tag{15}$$

$$\begin{aligned}
\rho \frac{\partial e_l^q}{\partial t} + \rho (\mathbf{u} \nabla) e_l^q &= \frac{\theta_q}{C_{q0}^V} \left[k_v J \frac{l_q \tau P}{\tau_l} - \frac{\tau P}{\tau_{qk}^{V'}} L_{q,k} r_q N_1 - \frac{\tau P}{\tau_{qs}^{V'}} L_{q,s} r_q N_1 N_2 \gamma_{10}^{-1} \right] - \\
& - \nabla \left\{ \rho e_l^q V_q - \frac{\tau P}{\tau_q} \nabla T_q + \frac{NT}{C_{q0}^V \gamma_{10}} \sum_{j=1}^2 \frac{\tau P}{\tau_{qj}^V} d_j \right\};
\end{aligned} \tag{16}$$

$$\rho \frac{\partial e_s^r}{\partial t} + \rho (\mathbf{u} \nabla) e_s^r = \frac{\theta_s}{C_{s0}^V} \left[-\frac{\tau P}{\tau_s} N_2 (\epsilon_s - \epsilon_{s0}) + \frac{\tau P}{\tau_{sr}^{V'}} L_{q,s} r_s N_1 N_2 \gamma_{20}^{-1} \right] - \nabla \left\{ \rho e_s^r V_s - \frac{\tau P}{\tau_s} \nabla T_s + \frac{NT}{C_{s0}^V \gamma_{20}} \sum_{j=1}^2 \frac{\tau P}{\tau_{sj}^V} d_j \right\}, \tag{17}$$

$$V_i = -\frac{\tau P}{\tau_{Ti}} \frac{\nabla \ln T}{N_i} - \frac{\tau P}{N_i} \left(\delta_{i,1} \sum_{l=k,q} \frac{\nabla \ln T_l}{\tau_{Dl}^V} + \delta_{i,2} \frac{\nabla \ln T_s}{\tau_{Ds}^V} \right) + \frac{\tau P}{\tau_D} \sum_{j=1}^2 d_j \frac{N^2}{N_i P} \frac{P_m^{2-j} (1 + P_N)^2}{(P_m + P_N) P_N^{j-1}},$$

$$d_j = \gamma_{j0} \nabla \left(\frac{N_j}{N} \right) + \gamma_{j0} \left(\frac{N_j}{N} - \frac{N_j P_m^{2-j}}{\rho (P_m + P_N) \gamma_{10}} \right) \nabla \ln p +$$

$$+ \frac{\kappa \gamma_{j0} \tau_a^2}{\rho \tau_F^2} \left[\frac{N_j P_m^{2-j} (1 + P_N)}{\rho (P_m + P_N)} \sum_i \frac{P_N^{i-1}}{1 + P_N} N_i X_i - N_j X_j \right],$$

$$C_{i0}^V = \frac{\theta_i \exp(\theta_i)}{[\exp(\theta_i) - 1]^2}, \quad \theta_i = \frac{h\nu_i}{KT_0}, \quad \gamma_{i0} = \frac{P_N^{i-1}}{1 + P_N},$$

$$\kappa = 1 + \left(e_{RT}^0 \frac{\mu_0}{R} \right)^{-1}, \quad \xi = \frac{E_j - E_i}{KT_0}, \quad C_{RT}^0 = \sum_{i=1}^2 C_{RT}^i \frac{\mu_{i0} N}{\mu_0 N_i},$$

$$P_N = \gamma_{20} / \gamma_{10}, \quad P_m = m_1 / m_2.$$

Here $\tau_a = R_a / \sqrt{\kappa p_0 / \rho_0}$ is the sound propagation time across the beam; $\tau_D = R_a^2 / D_{ij}$, $\tau_{Ti} = R_a^2 m_i N_{i0} / D_i^T$, $\tau_{Di}^V = R_a^2 m_i N_{i0} / D_i^V$, and $\tau_{ij}^V = R_a^2 / D_{ij}^V$ are, respectively, the multicomponent diffusion time, the thermal diffusion time of the i -th component, the diffusion time of the vibrational energy of the i -th oscillator belonging to molecule of type i , and the vibrational diffusion time between the i -th and j -th oscillators; $\tau_\lambda = \rho R_a^2 C_{RT}^0 / \lambda$ is the thermal conduction time; $\tau_1^V = R_a^2 C_{i0}^V N_{i0} K / \lambda_i^V$

is the vibrational thermal conduction time for the i -th oscillator; $\tau_1^{VT} = \left(\sum_{k=1}^2 W_{i0}^* N_{k0} \right)^{-1}$ is the VT-relaxation time for the i -th

oscillator; $\tau_{q,s}^{VV'} = \{W_{q,s} \gamma_{10} \gamma_{20} N_{0i}\}^{-1}$ and $\tau_{ij}^{VV'} = \left\{ \sum_{k=1}^2 W_{i,j}^* N_{k0} \right\}^{-1}$ are, respectively, the intermolecular and intramolecular VV'-

exchange times; $\tau_i = N_{i0} h \nu_i / k_v^0 J_{i0}$; $\tau_F = \sqrt{\frac{\rho_0 R_a}{\chi_0 N_0}}$ is the time over which the state of the medium changes under the action of

the external forces \mathbf{X}_0 ($\tau_F = \tau_g$ for $\mathbf{X}_0 = \mathbf{m}\mathbf{g}$, where \mathbf{g} is the acceleration of gravity, m is the characteristic molecular mass, and $\tau_F = \tau_{NL}$ with $\mathbf{X}_0 = \mathbf{f}_{NL}$, \mathbf{f}_{NL} is the force acting on a particle in the electromagnetic field); and, $\tau_\kappa = R_0^2 \rho_0 / \eta$ is the convection time due to viscosity.

A specific analysis was performed for the example of resonance absorption of CO₂-laser radiation with $\nu_1 = 944.2 \text{ cm}^{-1}$ (the line P20 [00⁰1 \rightarrow 10⁰0]) in the mixture of gases CO₂-N₂, when τ_p and τ_1 are significantly longer than the VV'-exchange times between the symmetric ν_1 and bending ν_2 -vibrations of CO₂. Here the relaxation of the energies in the modes ν_1 and ν_2 can be combined, making the assumption that the 10⁰0 and 02⁰0 states of the CO₂ molecule are in exact resonance ($h\nu_1 = 2h\nu_2$). In our investigation this combined mode corresponds to ν_k , the asymmetric vibrations of CO₂ (ν_3) correspond to ν_q , and the vibrations N₂ (ν_4) correspond to ν_s . We note that the form of the right-hand side of Eq. (7) changes somewhat due to the fact that the ν_1 and ν_2 modes in CO₂ are combined [15]. The rate constant of VT and VV' processes and the molecular

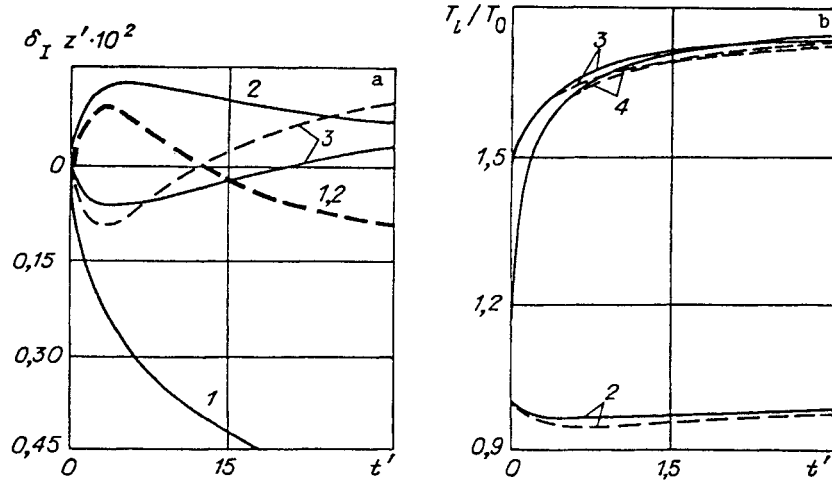


Fig. 1

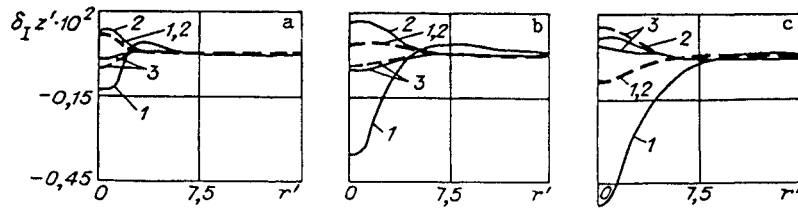


Fig. 2

constants required for the calculations were taken to be the same as in [11, 16]. The coefficients D_{12} and D_i^T and the thermal conductivity λ were calculated from [17] ($D_{12} = 1.4 \cdot 10^{-3}$ m²/sec, $\lambda = 1.1 \cdot 10^{-5}$ J/(m·sec·K), and $D_1^T = 4.8 \cdot 10^{-8}$ kg/(m·sec)). The values of D_{ij}^V and D_j^V for the mixture CO₂–N₂ were not found, either experimentally or theoretically. However, the relations between the self-diffusion coefficients of the vibrationally excited CO₂ molecules and (D_{ii}^V) and ordinary diffusion were determined in [18–20]. These relations have the form $D_{ii}^V = K_j^V D_{ii}$, where $K_j^V = \text{const}$ and K_j^V depends on the type of vibration. At $T_0 = 300$ K $K_1^V = K_2^V = 1$ for the bending and symmetric vibrations; $K_3^V = 0.6$ for asymmetric vibrations and $K_4^V = 0.4$ for excited nitrogen.

Assuming, as in [8], that the relations presented also hold for the diffusion coefficients in a binary gas, we obtain

$$D_{14}^V = D_{24}^V = D_{12}, \quad D_{34}^V = 0,6 D_{12}, \quad D_1^V = D_2^V = D_1^T, \quad D_3^V = 0,6 D_1^T.$$

The quantity D_4^V was calculated in accordance with Eq. (10) in the form

$$D_4^V = -D_2^V \frac{2\nabla \ln T_2 + 0,6 \nabla \ln T_3}{\nabla \ln T_4}. \quad (18)$$

The vibrational thermal conductivities λ_i^V were determined from the relation

$$\lambda_i^V = D_{ij}^V C_i^V N_i K, \quad C_i^V = \frac{\theta_{vi}^2 \exp(\theta_{vi})}{[\exp(\theta_{vi}) - 1]^2}, \quad \theta_{vi} = \frac{h\nu_i}{KT_i}.$$

We now estimate the characteristic times for the medium CO₂–N₂ = 0.1 : 0.9 under typical experimental conditions: $R_a = 0.1$ – 1 cm, $I_0 = 0.1$ – 10 kW/cm², $p_0 = 1$ kPa, and $T_0 = 300$ K. The hierarchy of times determines, to a significant degree, the extent to which the different transport processes affect the change in the N_i and T_j . Under the indicated conditions $\tau_a = 2.9 \cdot 10^{-6}$ – $2.9 \cdot 10^{-5}$ sec, $\tau_D = 7 \cdot 10^{-4}$ – $7 \cdot 10^{-2}$ sec, $\tau_{T1} = 3.7 \cdot 10^{-2}$ – 3.7 sec, $\tau_{D2}^V = 3.7 \cdot 10^{-2}$ – 3.7 sec, $\tau_{D3}^V = 6.1 \cdot 10^{-2}$ – 6.1 sec, $\tau_{24}^V = \tau_D$, $\tau_{34}^V = 1.7 \tau_D$, $\tau_\lambda = 9.7 \cdot 10^{-4}$ – $9.7 \cdot 10^{-2}$ sec, $\tau_2^V = 3.5 \cdot 10^{-4}$ – $3.5 \cdot 10^{-2}$ sec, $\tau_3^V = 1.67 \tau_2^V$, $\tau_4^V = 1.5 \cdot 10^{-4}$ – $1.5 \cdot 10^{-2}$ sec, $\tau_k = 5 \cdot 10^{-2}$ – 5 sec, $\tau_{NL} = 3$ – 10 sec, $\tau_g = 0.1$ – 0.3 sec, $\tau_1 = 1.3 \cdot 10^{-2}$ – $1.3 \cdot 10^{-4}$ sec, $\tau_2^{VT} = 1 \cdot 10^{-3}$ sec, $\tau_{32}^{VV'} = 1.1 \cdot 10^{-3}$ sec, $\tau_{34}^{VV'} = 1.1 \cdot 10^{-4}$ sec, $\tau_4^{VT} = 3.9$ sec. Thus the following hierarchy of times holds: $\tau_a < \tau_{34}^{VV'} < \tau_D = \tau_2^V = \tau_3^V \sim \tau_1 \sim \tau_2^{VT} \sim \tau_{32}^{VV'} \sim \tau_{24}^V \sim \tau_{34}^V \sim \tau_\lambda < \tau_k \sim \tau_{D2}^V < \tau_{D3}^V < \tau_g < \tau_{NL} \sim \tau_4^{VT}$. We

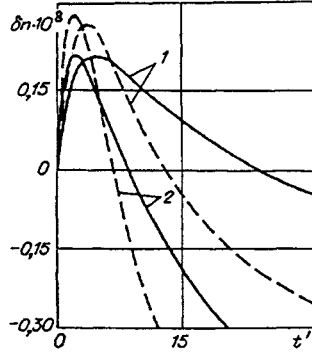


Fig. 3

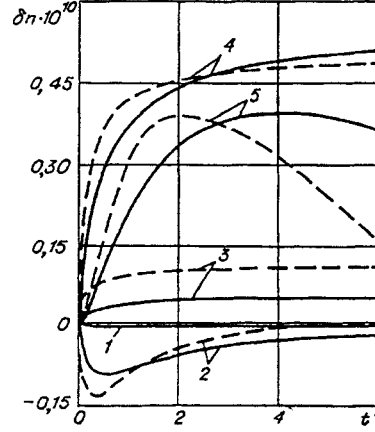


Fig. 4

consider pulses with $\tau_p \ll \tau_g, \tau_{NL}$, and τ_4^{VT} . Moreover, in experiments performed under the indicated conditions the inequality $\delta_1 \ll 1$ is always satisfied,

$$\delta_i = k_i^0 I_0 \tau_p / \rho_0 E_{RT}.$$

In this case the terms containing the ratios of times $(\tau_p/\tau_F)^2$, $(\tau_a/\tau_F)^2$, and τ_p/τ_s^{VT} in Eqs. (13), (14), and (17) can be neglected and Eqs. (11)-(14) can be linearized, representing ρ , N_i , T , \mathbf{u} , \mathbf{V}_i , and \mathbf{d}_i in the form $z = 1 + \delta_1 z'$, where $z = \rho$, N_i , T , and $\mathbf{V}_i = \delta_1 \mathbf{V}_i'$, $\mathbf{d}_i = \delta_1 \mathbf{d}_i'$, $\mathbf{u} = \delta_1 \mathbf{u}'$.

The system of linearized equations (11)-(14) together with the equations of the form (15)-(17) describing the vibrational kinetics for the mixture $\text{CO}_2\text{-N}_2$ was solved numerically by the method developed in [8]. The nonresonance part of the polarizability α_{ij}^V was calculated for the CO_2 molecule ($i = 1, j = 1-3$) using the formulas of [6] and for the N_2 molecule ($i = 2, j = 4$) using the formulas of [21].

We consider first the change in the concentration of the components $N_1'(t)$ and $N_2'(t)$ on the beam axis in the presence of diffusion and heat conduction processes, associated with excitation of molecular vibrations (the characteristic times τ_{D2}^V , τ_{D3}^V , τ_{D4}^V , τ_{24}^V , τ_{34}^V , τ_i^V ($i = 2-4$ are finite), and in the absence of these processes (these times are infinite).

Figures 1a and b display the functions $\delta_1 z'(t')$ ($z' = N_1', N_2', T'$ (lines 1-3), $t' = t/\tau_D$) and $T_i(t')$ ($i = 2-4$ — lines 2-4) on the beam axis ($r' = 0$), and Figs. 2a-c display the distributions N_1', N_2', T' (lines 1-3) over r' at $t' = 1, 8$, and 30 ($\delta_1 = 0.01$), respectively, obtained for these two cases (solid and dashed lines) in calculating the action of radiation with $I_0 = 0.1 \text{ kW/cm}^2$ and $\nu_1 = 944.2 \text{ cm}^{-1}$, $R_a = 0.1 \text{ cm}$ for the gas mixture $\text{CO}_2\text{-N}_2 = 0.1:0.9$ with $T_0 = 300 \text{ K}$ and $p_0 = 1 \text{ kPa}$. It is evident from the distributions presented that the diffusion processes associated with excitation of vibrational degrees of freedom of CO_2 and N_2 molecules (analysis shows that vibrational thermal diffusion, owing to significant gradient of the vibrational temperatures T_2, T_3 , and T_4 over r , dominates), significantly influence the change in N_1' and T' even for $t \ll \tau_{D1}^V$. Thus, if in the model with $\tau_{ij}^V = \tau_{Dj}^V = \tau_{Dj}^V = \tau_j^V = \infty$ $N_1' = N_2'$ for any t , then when these times are finite, $N_1'(t) \neq N_2'(t')$. Since $\tau_a \ll \tau_D$, at $t \sim \tau_D$ in the case $\tau_{ij}^V = \tau_{Dj}^V$, $\tau_i^V = \infty$ the distributions N_1', N_2' and N' as a function of r are identical to the distribution $\rho'(r)$, and $\rho' = -T'$. When τ_{D1}^V and τ_i^V are finite, vibrational thermal diffusion processes strongly influence the character of the distributions $N_1'(r)$. The behavior of $N_1'(r)$ is determined by competition between two diffusion fluxes, oriented in opposite directions. The first flux is determined by the gradient T_2 (for short $t \nabla T_2 > 0$) and, since $D_2^V > 0$, it is directed from the periphery to the center of the beam. The second flux is determined by the gradient of T_3 ($\nabla T_3 < 0$), and since $D_3^V > 0$, the gradient is oriented from the center toward the periphery. The interaction of these two fluxes results in a quite complicated distribution $N_1'(r)$, which is characterized by the existence of a minimum in some section with $r \neq 0$ (Fig. 2a), whose distance from beam center increases with i_0 . This section shifts with time toward the beam axis owing to the decrease in ∇T_2 . The diffusion flux for $N_2'(r)$ is determined by the magnitude and sign of D_4^V and depends on $\nabla T_2, \nabla T_3$ and ∇T_4 . For this reason, according to Eq. (18), the behavior of $N_2'(r)$ is similar to the behavior of $N_1'(r)$ with the opposite sign. We note that diffusion processes owing to excitation of vibrational degrees of freedom result in expansion of the region with $N_1' \neq 0$. Thus, if $N_1' = 0$ for $\tau_{ij}^V = \tau_{D1}^V = \tau_i^V = \infty$ even at $r' \approx 6$, then in the case when these times are finite $N_1' = 0$ only at $r' \approx 15$.

Since δn is determined, to a significant degree, by the change in the concentrations N_1' and N_2' , it is obvious that the behavior of $\delta n(t)$ should be significantly influenced by diffusion processes associated with the excitation of molecular vibrations. This influence is illustrated in Fig. 3, where the functions $\delta n(t')$ at $r = 0$ are displayed for the mixture $\text{CO}_2\text{--N}_2 = 0.1:0.9$ and $0.2:0.8$ (lines 1 and 2) with $T_0 = 300$ K, $p_0 = 1$ kPa, and $I_0 = 0.1$ kW/cm² for the case when $\tau_{ij}^V = \tau_{Di}^V = \tau_i^V = \infty$ and when these times are finite (dashed and solid lines, respectively). It is evident that the influence of the vibrational thermal diffusion on δn weakens with increasing CO_2 concentration. Figure 4 illustrates the relative role of the concentration component δn and the contributions of nonresonance parts of the polarizability, which are caused by excitation of separate modes of CO_2 and N_2 molecules, to δn . Here the lines 1-4 refer to the functions $\delta n(t)$, owing to the changes CO_2 and N_2 (the scale for the concentration component δn is reduced by a factor of 50). The dashed and solid lines, just as in Fig. 3, refer to mixtures with different content of the components. It is evident that under these conditions the change in the CO_2 and N_2 concentrations has the determining influence. The change in n owing to the change in polarizability can compete with the concentration part δn only for short times t .

The change in the temperature of the medium under the action of resonance radiation is often determined from the change in the index of refraction (in particular, the degree of kinetic cooling is judged [13]). It follows from the results presented above that this method is inapplicable in most cases of practical interest. Even when the change in the nonresonance part of the polarizability owing to excitation of molecular vibrations is small, δn is not related by a simple relation to the change in the temperature T ($\delta n = -(n_0 - 1)\delta T/T_0$), but rather it depends on the change in the concentrations of the mixture components, which is determined significantly by the vibrational thermal diffusion processes.

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