

## INTRODUCTION

The creation of powerful electrical discharge and gas dynamic lasers with large volumes of the active medium and transportation of the resonance IR radiation through the vibrationally nonequilibrium molecular medium posed new problems including the problem of propagation of optical perturbations in a nonequilibrium gas. A vibrationally nonequilibrium gas can differ noticeably from an equilibrium gas in its optical properties. This difference is associated primarily with the different values of the mean polarizability of the molecules in the equilibrium and nonequilibrium states.

Vibrational excitation of molecules, realizable, say, during optical or electronic pumping, results in a small change in the geometric structure of the molecules. Thus, as the vibrational energy grows, the mean spacing between the vibrating atoms generally grows. The reason for this is the anharmonicity of the molecular vibrations. A change in the mean linear dimensions of molecules and their mean volume affects the electrical characteristics, the dipole moment, the polarizability, and the hyperpolarizability. Indeed, all the characteristics listed depend on the mean dimension of the molecules: the dipole moment contains the length to the first degree, the polarizability has the dimensionality of a volume, etc.

A change in the molecule electrical characteristics results in a change in the optical properties of the medium. Thus, in conformity with the Lorenz-Lorentz law

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi N \alpha. \quad (1)$$

If  $\alpha_n$  denotes the polarizability of a molecule in the  $n$ -th vibrational state, then  $\alpha = \sum_n y_n \alpha_n$ , where  $y_n$  is the population of the  $n$ -th level.

It is seen from (1) that by changing the mean polarizability of molecules, nonequilibrium vibrational excitation changes the refractive index of a gas. Therefore, nonequilibrium excitation of the molecule vibrational degrees of freedom can be a reason for the change in the refractive index, and this, in turn, results in the appearance of new effects. Let us examine two of them that must be taken into account in the interferometry of a nonequilibrium gas and in the description of resonance IR radiation propagation therein.

The ordinary method of determining the density by an interferometric method is based on utilizing the dependence between the shift of the interference fringes (the change in the refractive index) and the change in density. It is taken into account that  $n \approx 1$  for a gas, then the Lorenz-Lorentz formula (1) can be rewritten in the form

$$\frac{n - 1}{\rho} = K, \quad (2)$$

where  $K = 2\pi(N_{AV}/\mu)\alpha$ . Formula (2) is known as the Gladstone-Dale formula. It is seen from (2) that

$$\Delta n = K \Delta \rho. \quad (3)$$

If the dependence of the Gladstone-Dale constant on the vibrational excitation is taken into account (for instance, the vibrational temperature  $T_v$  as is indicated in the monograph [1]), then we should write in place of (3)

$$\Delta n = K\Delta\rho + \Delta K\rho, \quad (4)$$

where  $\Delta K = (\partial K/\partial T_V)_\rho \Delta T_V$ .

It follows from (4) that the shift of the interferometer fringes in a nonequilibrium gas is due to two effects, the change in density and vibrational excitation. The role of the second component can here be quite significant, for instance, during pulse excitation of vibrational degrees of freedom occurring under conditions of a "frozen" constant density, the change in the refractive index does not characterize the change in density but is determined just by the vibrational excitation. This effect is not ordinarily taken into account.

The change in the refractive index during vibrational excitation results in still another physical effect, laser beam focusing or self-focusing. If laser radiation is propagated in a channel with a refractive index elevated as compared with the environment, then the focusing effect is possible. The refractive index can change both because of an external effect, under the influence of an electronic beam, say, and under the effect of vibrational excitation initiated by the intrinsic laser radiation field. In this latter case the self-focusing effect is observed.

The necessity to take account of molecular vibrations in computing the optical properties of molecules was mentioned sufficiently long ago [2]. The influence of vibrational excitation on the self-focusing effect was first discussed in [3]. A detailed theoretical examination of the influence of vibrational excitation on the refractive index and also specific computations of the refractive index of a nonequilibrium gas and the effect of self-focusing induced by vibrational excitation are executed in [4-8]. The influence of the degree of vibrational excitation of an active medium on sweeping of the radiation frequency of a single frequency atmospheric pressure CO<sub>2</sub> laser that generates at practically the center of the line is investigated theoretically in [9].

It should be noted that vibrational excitation also changes other molecular characteristics (see [10-12], say). Let us emphasize that all the effects listed remain valid during excitation of any internal degrees of freedom and not only of molecular vibrations. For example, the influence of translational nonequilibrium on the optical characteristics of active media of lasers was analyzed by R. I. Soloukhin, et al. [13]. The contribution to the refractive index of vibrational-rotational transitions for CO molecules is investigated theoretically in [14].

The aim of the present paper is a survey elucidating the physical bases and general regularities of the change in the optical properties of a gas subjected to a nonequilibrium vibrational excitation of molecules.

### 1. Dipole Moment, Polarizability, and Hyperpolarizability of Vibrationally Excited Molecules

The dipole moment  $\mu$ , the polarizability  $\alpha$ , and the hyperpolarizability  $\beta$  of a molecule are determined from the expression for the molecule energy  $W_e$  in the presence of an external electrical field of intensity  $E$

$$W_e = W_0 - \mu(Q)E - \frac{1}{2}\alpha(Q)E^2 - \frac{1}{6}\beta(Q)E^3 + O(E^4). \quad (5)$$

In the general case,  $\mu$  is a vector and  $\alpha$  and  $\beta$  are tensors of different dimensionality. For simplicity in the exposition, we shall later consider the quantities  $\mu$  and  $\alpha$  to be averaged over all possible molecule orientations, while the field  $E$  is directed along the  $Z$  axis.

In such a case the standard procedure [15] is utilized to determine  $\mu$ ,  $\alpha$ , and  $\beta$ . The Hamiltonian of the molecule is expanded in a series in the normal coordinates while the molecule energy in the external field is found by second-order perturbation theory. In this case, within the framework of the harmonic oscillator model the following expressions [4] are obtained for vibrational contributions to the dipole moment  $\mu_V$ , the polarizability  $\alpha_V$  and the hyperpolarizability  $\beta_V$

$$\begin{aligned} \mu_v &= \sum_j g\{v_j\} \frac{2v_j + 1}{4a_j^2} \left( \frac{\partial^2 \mu}{\partial Q_j^2} \right)_0, \\ \alpha_v &= \sum_j g\{v_j\} \left\{ \frac{1}{\hbar\omega_j a_j^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0^2 + \frac{2v_j + 1}{4a_j^2} \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0 + \frac{(v_j + 1)(v_j + 2)}{16\hbar\omega_j a_j^4} \left( \frac{\partial^2 \mu}{\partial Q_j^2} \right)_0^2 \right\}, \end{aligned} \quad (6)$$

$$\beta_v = \sum_j g \{v_j\} \left\{ \frac{2v_j + 1}{4a_j^2} \left( \frac{\partial^2 \beta}{\partial Q_j^2} \right)_0 + \frac{3}{\hbar \omega_j a_j^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0 \left( \frac{\partial \alpha}{\partial Q_j} \right)_0 + \frac{3(v_j + 1)(v_j + 2)}{8\hbar \omega_j a_j^4} \left( \frac{\partial^2 \mu}{\partial Q_j^2} \right)_0 \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0 \right\}, \quad (6)$$

summation here is over all modes  $j$ .

The expressions (6) are obtained to the accuracy of second order terms in the expansion of the molecular Hamiltonian in an electric field in normal coordinates. Taking account of the higher derivatives, i.e., the next terms of the electrooptical anharmonicity, as well as corrections to the mechanical anharmonicity associated with replacement of a harmonic by an anharmonic oscillator, is executed in [5, 8]. It is shown in [8] that the contribution of terms due to the electrooptical anharmonicity to the polarizability  $\alpha_v'$  and hyperpolarizability  $\beta_v'$  is small, as a rule, and is of the magnitude of 3-5% of  $\alpha_v$  and  $\beta_v$  for the CO molecule, say. The influence of the mechanical anharmonicity also turns out to be small. According to estimates [5, 8], they can be neglected if the following conditions are satisfied

$$\bar{v}^2 x_e \ll \bar{v}, \quad \bar{v}^3 x_e \ll \bar{v}^2. \quad (7)$$

The  $\bar{v}$  in (7) is the mean value of the vibrational quantum number and averaging is performed over vibrational energy distribution functions. Since  $x_e \sim 10^{-2}$ , then conditions (7) are satisfied for all real distribution functions. The single correction to the mechanical anharmonicity, that should be introduced into (7) for  $\alpha_v$ , is  $2\xi_j/D_j(\partial\alpha/\partial Q_j)_0$ , where  $D_j$  and  $\xi_j$  are constants in the Morse potential  $U(Q_j) = 2D_j[\exp(-2\xi_j Q_j) - 2\exp(-\xi_j Q_j)]$ .

Therefore, the following expression can be used in practical computations for the vibrational addition to molecule polarizability that takes account of mechanical anharmonicity

$$\alpha_v = \sum_j g \{v_j\} \left\{ \frac{1}{\hbar \omega_j a_j^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0^2 + \frac{2v_j + 1}{4a_j^2} \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0 + \frac{(v_j + 1)(v_j + 2)}{16\hbar \omega_j a_j^4} \left( \frac{\partial^2 \mu}{\partial Q_j^2} \right)_0^2 + \frac{2\xi_j}{D_j} \left( \frac{\partial \alpha}{\partial Q_j} \right)_0 \right\}. \quad (8)$$

The derivatives of  $\mu$  and  $\alpha$  with respect to the normal coordinates must be known for specific computations of the vibrational computations to the dipole moment, polarizability and hyperpolarizability. These derivatives are either computed by quantum mechanics methods (see [15], say) or are determined from spectrum line intensities [16]. Values of the vibrational additions to molecule polarizability that are utilized extensively in the physics of lasers and in laser chemistry are presented in Table 1.

## 2. Interferometry of a Nonequilibrium Gas

One of the most widespread methods of determining the density and gas temperature in gas flow investigations is the interferometric method that is utilized extensively in the study of kinetic effects, for example, the kinetic cooling effect.

The phase difference of two beams (the shift of interference fringes) by which a change in the refractive index  $\Delta n(t)$  is easily computed because of the perturbation induced in the gas, is measured in the interferometric experiment. In the general case a change in the refractive index of a vibrationally excited gas is written in the form

$$\Delta n = \frac{\partial n}{\partial \rho} \Delta \rho + \frac{\partial n}{\partial T} \Delta T + \sum_j \frac{\partial n}{\partial T_{v_j}} \Delta T_{v_j}, \quad (9)$$

where  $T_{v_j}$  is the vibrational temperature and summation is over all normal vibration modes. It is considered that its Boltzmann distribution with the vibrational temperature  $T_{v_j}$  is successfully built up in each mode.

The last term in (9) is neglected in traditional computations of the density by means of the change in the refractive index, resulting in a number of cases in an incorrect interpretation of the results of interferometric investigations of laser and beam channels, and errors in the determination of the characteristic relaxation times, etc. For instance, the equality [1]  $\Delta n = \lambda \delta/d$ , supplemented by the Gladstone-Dale relationship

TABLE 1. Values of the Vibrational Contributions to Molecule Polarizability (in the atomic system of units)

Molecule	$\omega, \text{cm}^{-1}$	$\alpha_v^i$	$\alpha_v$	$\alpha_0$
CO	2143		0,843	11,2
HBr	2559		0,080	23,8
HCl	2886		0,299	16,4
HF	3962		0,312	5,6
HI	2230		0,001	35,3
NO	1876		0,506	11,5
CO <sub>2</sub>	667	1,344		
	2349	1,586	2,930	17,5
H <sub>2</sub> O	3657	0,014		
	1595	1,543		
	3756	0,186	1,743	9,8
N <sub>2</sub> O	1285	2,231		
	589	1,487		
	2224	3,718	7,436	
O <sub>3</sub>	1103	0,123		
	701	0,558		
	1042	5,019	5,700	
BCl <sub>3</sub>	455	0,446		
	956	15,800		
	249	0,799	17,045	
CCl <sub>4</sub>	793	31,600		
	310	0,130	31,730	68,8
CH <sub>4</sub>	3019	0,446		
	1311	1,152	1,598	17,3
C <sub>2</sub> H <sub>4</sub>	949	5,576		
	3105	0,162		
	810	0,019		
	2989	0,095		
	1443	0,297	6,149	
SF <sub>6</sub>	948	5,018		
	615	0,454	5,472	30,2

$$\frac{n-1}{\rho} = K. \quad (10)$$

was used in computing the density behind a shock front. Large errors are possible [4] in such a method of determining  $\Delta\rho$  because of neglect of the last term in (9).

We use the Lorenz-Lorentz formula to estimate the vibrational contribution to the refractive index, by representing it in the form

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} \sum_v y_v \langle \alpha(v) \rangle, \quad (11)$$

where  $y_v$  is the density of the number of molecules in the vibrational state  $\{v\}$ , and  $\langle \alpha(v) \rangle$  is the value of the polarizability of one molecule in the state  $\{v\}$  averaged over different orientations. For an isotropic medium

$$\langle \alpha(v) \rangle = \frac{1}{3} [\alpha_{xx}(v) + \alpha_{yy}(v) + \alpha_{zz}(v)].$$

Moreover, the form of the vibrational distribution function must be known to compute the refractive index of a vibrationally excited gas. If the molecule is modelled by a set of harmonic oscillators and it is considered that the fast V-V-exchange results in formation of a quasistationary Boltzmann distribution with vibrational temperature  $T_{vj}$  in each mode, then we can write for  $y_v$  [17]

$$y_v = \frac{N}{\Theta_1 \dots \Theta_n} \prod_j^n g\{v_j\} \exp\left(-\frac{\hbar\omega_j v_j}{kT_{vj}}\right), \quad (12)$$

TABLE 2. Values of the Temperature Coefficient  $\chi$ 

Molecule	CO	CO <sub>2</sub>	SF <sub>6</sub>	H <sub>2</sub> O
$\omega$ , cm <sup>-1</sup>	2170	2349	948	1595
$\chi$ , K <sup>-1</sup>	4.53 · 10 <sup>-5</sup>	1.16 · 10 <sup>-5</sup>	4.37 · 10 <sup>-5</sup>	3.86 · 10 <sup>-5</sup>
$\chi \exp K^{-1}$	—	1.50 · 10 <sup>-5</sup>	—	—

where  $\Theta_i = \left[ 1 - \exp\left(-\frac{\hbar \omega_i}{kT_{v_i}}\right) \right]^{-r_i}$  is the statistical sum corresponding to the  $r_i$ -tuply degenerated  $i$ -th mode.

Taking (12) into account and that  $\bar{v}_j = r_j \exp(-\theta_j)/(1 - \exp(-\theta_j))$ ,  $\overline{(v_j+1)(v_j+2)} = \frac{\exp(-2\theta_j)(r_j^2 - 3r_j + 2) + 4 \exp(-\theta_j)(r_j - 1) + 2}{[1 - \exp(-\theta_j)]^2}$ ,  $\theta_j = \hbar \omega_j/(kT_{v_j})$ , we can write

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N \left\{ \alpha_0 + \sum_j g\{v_j\} \left[ \frac{1}{\hbar \omega_j a_j^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0^2 + \frac{1 + \exp(-\theta_j)(2r_j - 1)}{4a_j^2 [1 - \exp(-\theta_j)]} \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0 + \frac{2 + 4 \exp(-\theta_j)(r_j - 1) + \exp(-2\theta_j)(r_j^2 - 3r_j + 2)}{16 \hbar \omega_j a_j^4 [1 - \exp(-\theta_j)]^2} \left( \frac{\partial^2 \mu}{\partial Q_j^2} \right)_0^2 \right] \right\}, \quad (13)$$

here  $\alpha_0$  is the polarizability of nonvibrating molecules.

If  $r_j = 1$  is considered for simplicity while  $n \approx 1$  for rarefied gases,

$$n = 1 + 2\pi N \left\{ \alpha_0 + \sum_j \left[ \frac{1}{\hbar \omega_j a_j^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0^2 + \frac{1 + \exp(-\theta_j)}{4a_j^2 [1 - \exp(-\theta_j)]} \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0 + \frac{1}{8 \hbar \omega_j a_j^4 [1 - \exp(-\theta_j)]^2} \left( \frac{\partial^2 \mu}{\partial Q_j^2} \right)_0^2 \right] \right\}. \quad (14)$$

In the limit case of high vibrational excitation ( $\hbar \omega_j \ll kT_{v_j}$ ), formula (14) can be represented in the form

$$n - 1 = 2\pi N \alpha_0 \left( 1 + \sum_j A_j T_{v_j} \right), \quad (15)$$

where  $A_j = \frac{k}{\alpha_0 (a_j \hbar \omega_j)^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0^2 + \frac{k}{2\alpha_0 \hbar \omega_j a_j^2} \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0$ ; and (15) does not take account of the third component in the right side of (14), which is small in the majority of cases.

The expression (15) is a generalized Gladstone-Dale relationship that takes the following form in the case of a single-mode molecule

$$\frac{n - 1}{\rho} = K(1 + \chi T_v), \quad (16)$$

where

$$\chi = \frac{k}{\alpha_0} \sum_j \left[ \frac{1}{(\hbar \omega_j a_j)^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0^2 + \frac{1}{2 \hbar \omega_j a_j^2} \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0 \right]. \quad (17)$$

The expression (16) is valid for polyatomic molecules in case the vibrational temperatures of the excited modes are equal. It was first written without deviation in [18], and the value  $1.0 \cdot 10^{-5} \text{ deg}^{-1}$  for  $\chi$  found experimentally is presented there for the CO<sub>2</sub> gas. Values of the temperature coefficient  $\chi$  are indicated in Table 2 for a number of molecules that have been obtained by using the relationship (17).

Let us emphasize that the linear dependence of the Gladstone-Dale constant on the vibrational temperature should be observed only for high vibrational excitation.

As has already been remarked, the Gladstone-Dale relationship is used extensively to determine the density or gas temperature by means of the change in refractive index. Taking

account of a nonequilibrium vibrational contribution to the Gladstone-Dale constant results in corrections to the determination of the magnitude of the density. Indeed, values of  $\rho$  determined from the usual Gladstone-Dale relationship

$$\frac{n-1}{\rho} = K \left( 1 + \frac{\overline{\alpha_v(T)}}{\alpha_0} \right),$$

are associated with the true values  $\rho^*$  that are calculated with the nonequilibrium vibrational contribution to the Gladstone-Dale constant

$$\frac{n-1}{\rho} = K \left( 1 + \frac{\overline{\alpha_v(T_v)}}{\alpha_0} \right),$$

taken into account as follows

$$\rho^*/\rho = \left( 1 + \frac{\overline{\alpha_v(T)}}{\alpha_0} \right) / \left( 1 + \frac{\overline{\alpha_v(T_v)}}{\alpha_0} \right). \quad (18)$$

According to estimates [4], the correction to  $\rho$  is approximately 15% ( $\rho^*/\rho \approx 0.85$ ) for CO with  $T = 300$  K and  $T_v = 5000$  K.

If we go over from the density to the gas temperature, then replacement of  $\rho$  by  $\rho^*$  will result in a change in  $T$ . This effect must be taken into account, say, in the determination of the depth of kinetic cooling and the conversion of experimental data into characteristic relaxation times [19].

Let us note that taking the average over a Trinorov distribution with a plateau, as is realized for intensive laser or electronic pumping, say, results in a still greater correction to  $T$  (see [4], say).

### 3. Refractive Index for a Cascade Mechanism of Molecular Vibration Excitation

As already noted [8], the form of the distribution function over the vibrational states exerts substantial influence on the refractive index of a molecular gas. One means for effectively populating highly excited vibrational levels is cascade excitation by laser radiation according to the scheme  $v-1 \rightleftharpoons v$ , where  $v = 1, 2, 3, \dots$ . This mechanism can be utilized extensively in laser chemistry, in the creation of ionized conduction channels, etc. It was investigated theoretically in [20-25], where the analysis was carried out on both the basis of the balance equations for the vibrational level populations [20, 23] and within the framework of the diffusion model [24, 25].

The model of a cut-off harmonic oscillator can be used to estimate the upper bound of refractive index variation during cascade excitation. Without taking account of dissociation the molecule distribution function over vibrational energy levels under powerful laser pumping is approximated well by a step distribution of the form

$$y_v = \Phi^v y_0, \quad 1 \leq v \leq v'; \quad y_v = y_{v'} \exp \left[ - (v - v') \frac{\hbar \omega}{kT_v} \right], \quad v \geq v' + 1, \quad (19)$$

where

$$\Phi = \frac{P_{10} \exp \left( - \frac{\hbar \omega}{kT_v} \right) + \varepsilon Q_{10} + W_{10}}{P_{10} + (1 + \varepsilon) Q_{10} + W_{10}},$$

$P_{10}$  and  $Q_{10}$  have their usual meaning of probabilities of vibrational-translational and vibrational-vibrational exchanges (see [7], say), and  $T_v$  is the effective vibrational temperature determined by the vibrational energy reserve. Under saturation conditions ( $W_{10} \gg P_{10}$ ,  $Q_{10}$ )  $\Phi \approx 1$  and the distribution function (19) goes over into

$$y_v = y_0, \quad 1 \leq v \leq v', \quad y_v = y_{v'} \exp \left[ - (v - v') \frac{\hbar \omega}{kT_v} \right], \quad v \geq v' + 1. \quad (20)$$

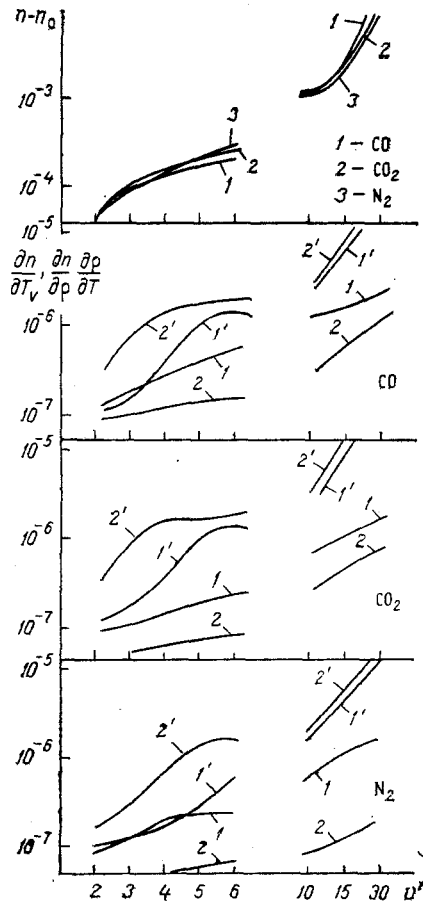


Fig. 1

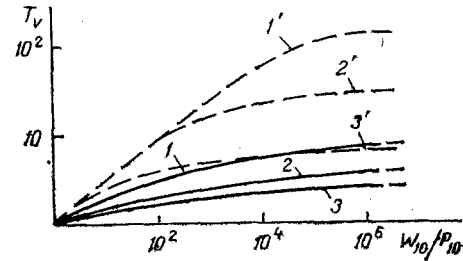


Fig. 2

Fig. 1. Values of  $n - n_0$  as well as magnitudes of the derivatives  $\partial n / \partial T_V$  (curves 1 and 1') and  $(\partial n / \partial \rho)(\partial \rho / \partial T)$  (curves 2 and 2') as a function of  $v'$  for the gases CO, the  $v_3$ -mode of CO<sub>2</sub> and N<sub>2</sub> computed with (curves 1 and 2) and without (curves 1' and 2') taking account of the dissociation process, at a  $p = 9.81 \cdot 10^4$  Pa pressure and  $T = 300$  K gas temperature.  $\partial n / \partial T_V$ ,  $(\partial n / \partial \rho)(\partial \rho / \partial T)$ , deg<sup>-1</sup>.

Fig. 2. Dependences of the vibrational temperature  $T_V$  on the dimensionless probability of optical pumping  $W_{10} / P_{10}$  computed with (curves 1, 2, 3) and without (curves 1', 2', 3') taking account of the dissociation process: 1, 1')  $Q_{10} / P_{10} = 10$ ; 2, 2')  $10^2$ ; 3, 3')  $10^3$ ;  $m = 15$ .  $T_V$ ,  $h\omega/k$ .

Taking account of the first two components in the right side of (8) and the distribution function (20), the change in the refractive index is written as follows

$$\begin{aligned}
 n - n_0 = & \sum_j g\{v_j\} \left[ 1 + \frac{y_0}{N} \left( \frac{1}{2} + \beta_V \exp(-\theta_V) \right) + \beta_V (v' + 1) \times \right. \\
 & \times \exp[-\theta_V (v' + 1)] - \beta_V^2 \exp(-\theta_V) (1 - \exp(-\theta_V v')) \left. \right] \frac{1}{\hbar \omega_j a_j^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0^2 + \\
 & + \sum_j g\{v_j\} \left[ \frac{1}{2} + \frac{y_0}{N} ((v' + 1)^2 - (1 + 2\beta_V \exp(-2\theta_V)) \beta_V + \right. \\
 & \left. + 2\beta_V \exp(-\theta_V (v' + 1))) (v' + \beta_V + 1) \frac{1}{2a_j} \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0 \right],
 \end{aligned} \tag{21}$$

where  $N = y_0 [v' + \beta_V \exp(-\theta_V (v' + 1))]$  is the number of molecules per unit volume, and  $\beta_V = [1 - \exp(-\theta_V)]^{-1}$  is the statistical sum of the harmonic oscillator. The dependences  $(n - n_0)$

as well as the derivatives  $\partial n/\partial T_V$  and  $(\partial n/\partial \rho)(\partial \rho/\partial T)$  as functions of  $v'$  for the gases CO, the  $v_3$ -mode of CO<sub>2</sub> and N<sub>2</sub> are presented in Fig. 1 for a  $p = 1$  atm pressure and  $T = 300$  K gas temperature.

The numerical computations performed [8] and the analysis of the results obtained permit making a deduction about the governing role of the vibrational contribution to the change in the refractive index in the case of cascade excitation, especially in the initial stage of relaxational processes when a noticeable separation exists between the mean vibrational energy of the molecules and the equilibrium value determined by the gas temperature.

However, a correct description of the change in the refractive index is impossible in a number of cases without taking account of the dissociation process. It is shown in [26, 17] that dissociation results in a substantial deviation of the distribution function from the equilibrium function for a group of levels lying in an energy domain of the order of  $kT$  from the dissociation boundary. A nonequilibrium distribution function over the vibrational levels that takes account of the laser pumping and dissociation effects is obtained in [20] for the cut-off harmonic oscillator model.

$$y_n = \Phi^n y_0 - \frac{K_d}{P_{10} + (1 + \varepsilon) Q_{10} + W_{10}} \sum_{i=1}^n i^{-1} \Phi^{n-i} \quad (1 \leq n \leq k),$$

$$y_n = - \frac{K_d}{P_{10} + (1 + \varepsilon) Q_{10}} \sum_{i=k+1}^n i^{-1} \exp[-(n-i)\theta_V] + y_k \exp[-(n-k)\theta_V] \quad (k+1 \leq n \leq l), \quad (22)$$

$$y_n = y_l \exp[-(n-l)\theta_V] - \frac{K_d}{P_{10} + (1 + \varepsilon) Q_{10}} \sum_{i=l+1}^n i^{-1} \exp[-(n-i)\theta_V] \quad (l+1 \leq n \leq m).$$

Here  $K_d$  is the collision dissociation constant, the value of the vibrational level  $k$  prior to which cascade excitation of molecules occurs is determined by both the excitation conditions and the relationship between the laser radiation and oscillator vibrations frequencies, and the dissociation process carries the molecule over into a continuous spectrum from a certain vibrational level  $l > k$ .

Under saturation conditions ( $W_{10} \gg P_{10}, Q_{10}$ ) the following expression is obtained for the refractive index of a vibrationally excited molecular gas

$$n = 1 + 2\pi N \left\{ \alpha_0 + \sum_j g\{v_j\} \left[ 1 + \frac{y_0}{N} \left( \frac{1}{2} + \beta_V \exp(-\theta_V) \right) + \beta_V (v' + 1) \exp(-\theta_V (v' + 1)) - \beta_V^2 \exp(-\theta_V) (1 - \exp(-\theta_V v')) - \frac{K_d}{2W_{10}} \beta_V v' (v' + 1) \left( C + \ln v' + \frac{1}{2v'} - \sum_{k=2}^{\infty} \frac{F_k}{v' (v' + 1) \dots (v' + k + 1)} \right) \right] \right\} \times$$

$$\times \frac{1}{\hbar \omega_j a_j^2} \left( \frac{\partial \mu}{\partial Q_j} \right)_0^2 + \sum_j g\{v_j\} \left[ \frac{1}{2} + \frac{y_0}{N} ((v' + 1)^2 - \beta_V (2\beta_V \exp(-2\theta_V) + 1)) + 2\beta_V \exp(-\theta_V (v' + 1)) (v' + \beta_V + 1) - \frac{K_d}{W_{10}} \beta_V (v' + 1)^2 \left( C + \ln v' + \frac{1}{2v'} - \sum_{k=2}^{\infty} \frac{F_k}{v' (v' + 1) \dots (v' + k - 1)} \right) \right] \frac{1}{2a_j^2} \left( \frac{\partial^2 \alpha}{\partial Q_j^2} \right)_0 \Bigg\}, \quad (23)$$

where  $C$  is the Euler constant, and  $F_k = \frac{1}{k} \int_0^1 x(1-x)(2-x)\dots(k-1-x) dx$ , in particular  $F_2 = 1/12$ ,  $F_3 = 1/12$ ,  $F_4 = 19/80$ ,  $F_5 = 9/20$ , etc. The following expression is used for  $K_d$

$$K_d = P_{md} y_0 \exp[-(m-v')\theta_V] \left[ 1 + \exp(-m\theta_V) \frac{P_{md}}{P_{10} + (1 + \varepsilon) Q_{10}} L(\theta_V, W_{10}, m) \right]^{-1}, \quad (24)$$



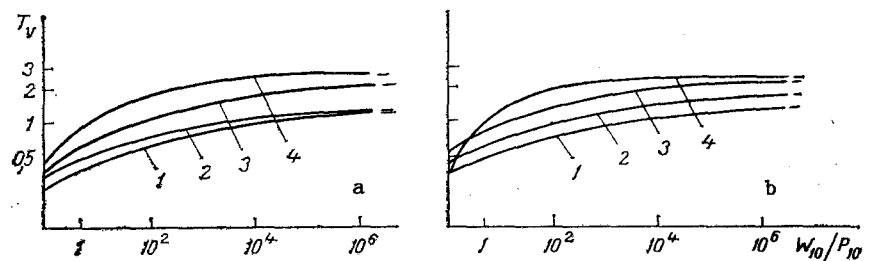


Fig. 3. Dependences of the vibrational temperature  $T_v$  on the dimensionless magnitude of the optical pumping  $W_{10}/P_{10}$  computed with the dissociation process taken into account for the molecules CO (a) and CO<sub>2</sub> (b): 1)  $Q_{10}/P_{10} = 10^6$ ; 2)  $10^4$ ; 3)  $10^2$ ; 4) 10;  $m = 10$ .

where

$$L(\theta_v, W_{10}, m) \approx \frac{[P_{10} + (1 + \epsilon) Q_{10}] \exp(-v'\theta_v)}{W_{10}} \left( C + \ln v' + \frac{1}{2v'} - \sum_{k=2}^{\infty} \frac{F_k}{v'(v'+1)\dots(v'+k-1)} \right) + \frac{\exp(m\theta_v) - 1}{\exp(\theta_v) - 1}.$$

It is seen from Fig. 2 that the dissociation process has substantial influence on the magnitude of the oscillator vibrational temperature governing the change in the refractive index. Analogous dependences are shown in Fig. 3 for the molecules CO and the  $\nu_3$ -vibrations CO<sub>2</sub>.

Figure 4 illustrates the behavior of magnitudes of the nonequilibrium contribution  $n - n_0$  to the refractive index as well as of the derivatives  $\partial n/\partial T_v$  and  $(\partial n/\partial \rho)(\partial \rho/\partial T)$  for gases obtained by using the relationship (23).

Let us note that the nonequilibrium vibrational contribution to the change in the refractive index is not always an addition. Thus, in kinetic investigations of a nonequilibrium gas with pulse excitation of the vibrational degrees of freedom, the change in the refractive index in the initial instants follows from the energy redistribution within and between the vibrational modes and only with the lapse of time of the V-T exchange (or the time of the nonresonance V-V'-exchange) do gas heating processes start to induce a contribution to the change in the refractive index. This circumstance can be used for the experimental determination of the characteristic relaxation times.

#### 4. Self-Focusing of Laser Radiation Induced by Nonequilibrium Vibrational Excitation of Molecules

Among the large group of phenomena occurring during interaction of powerful laser radiation with a molecular gas, the self-action of the light beams is important in practice and can be used in laser technology, communications, laser location, etc.

As is known, resonance interaction between radiation and a molecular gas occurs with the participation of a small number of degrees of freedom and the state of the remaining degrees of freedom of the molecular gas changes during relaxation. As a rule, a molecular gas with a high vibrational excitation level is considered in laser radiation self-action problems, where the translational temperature remains practically unchanged at the initial time after the selective laser action, and then after a lapse of time on the order of the characteristic relaxation time, equilibrium of the mean reserve of translational and vibrational energy occurs and a single temperature results. The processes accompanying laser radiation absorption at the vibrational-rotational transitions and the subsequent relaxation of the excess energy are here determined by a whole set of characteristic times (the rotational  $\tau_{R-T}$  and vibrational  $\tau_{V-V}$ ,  $\tau_{V-T}$  relaxation times, the pulse duration, etc.).

Thermal defocusing occurs under the action of laser radiation on a molecular gas because of the heating due to radiation absorption and the temperature and refractive index gradients occurring here. However, in addition to the obvious fact of heating of the medium, in a number of cases absorption of resonance laser radiation can be accompanied by gas cooling. By using a highly selective laser action on a molecular gas, such a deviation from equilibrium

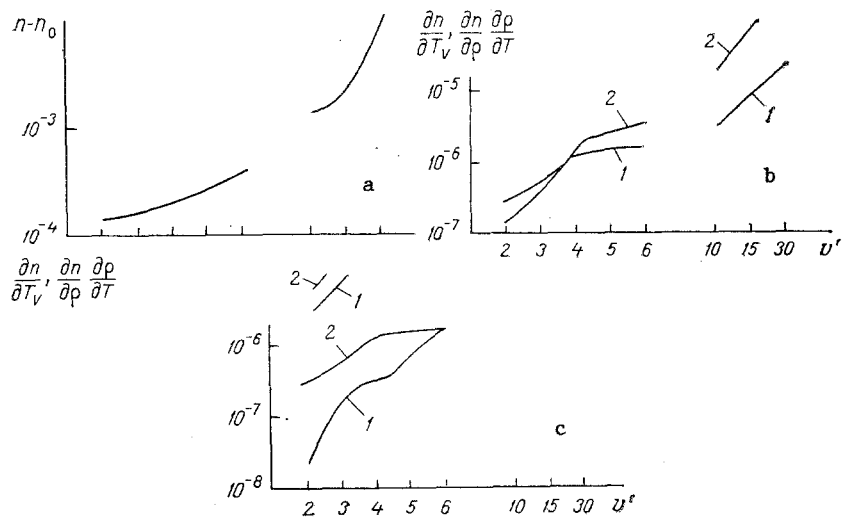


Fig. 4. The quantities  $n - n_0$  (a),  $\partial n / \partial T_v$  (curves 1), and  $(\partial n / \partial \rho)(\partial \rho / \partial T)$  (curves 2) for the CO molecules, computed for two values of the effective temperature of the first vibrational level 1000 K (b) and 3000 K (c).

can be produced for which the energy flux from the molecule internal degrees of freedom to the translational will be less than the reverse flux during relaxation. A similar pattern is observed during excitation of a vibrational mode with small quanta. The exchange of vibrational energy with a mode possessing large quanta results in cooling since the resonance defect will be covered because of the energy of the translational degrees of freedom. Although the degree of cooling is comparatively low, the density growth associated with it in the domain of ray propagation can result in self-focusing. Thus, the problem of interaction between CO<sub>2</sub>-laser radiation and a mixture of carbon dioxide and nitrogen is solved numerically in [28] and conditions are clarified for which self-focusing because of kinetic cooling can be determined in the experiment. Model computations in [29] showed that kinetic cooling results in a significant growth of radiation intensity in a beam at temperatures on the order of 500 K in a nitrogen mixture containing 5% carbon dioxide gas (for instance, self-focusing can result in an almost 7 times growth in intensity at distances on the order of 10 m).

The kinetic cooling effect is not the single reason that can cause self-focusing. An increase in the optical polarizability of the molecule, and therefore, the refractive index, because of excitation of the vibrational degrees of freedom during interaction with resonance IR radiation can result in focusing. Indeed, a medium with nonequilibrium vibrational excitation of molecules, i.e., with an elevated refractive index, is formed during powerful laser radiation propagation in a laser ray channel, which is a reason for self-focusing.

To estimate the efficiency of different self-focusing mechanisms we use the known expression for its length

$$R_f = \frac{r_0}{2} \sqrt{\frac{n}{\delta n}}, \quad (25)$$

where  $n$  is the refractive index of the medium prior to the arrival of the laser radiation.

Let us compare the focal lengths during kinetic cooling  $R_f(\Delta T)$  and during resonance excitation  $R_f(\Delta T_v)$ . It follows from the Gladstone-Dale relationship (16) that for  $\rho = \text{const}$

$$\delta n_v = \rho K \chi \Delta T_v, \quad (26)$$

while for  $T_v = \text{const}$

$$\delta n_p = \rho K (\Delta T / T). \quad (27)$$

Thus we have

$$\frac{R_f(\Delta T)}{R_f(\Delta T_v)} = \sqrt{\frac{\delta n(\Delta T_v)}{\delta n(\Delta T)}} = \sqrt{\frac{\chi \Delta T_v}{\Delta T / T}}. \quad (28)$$

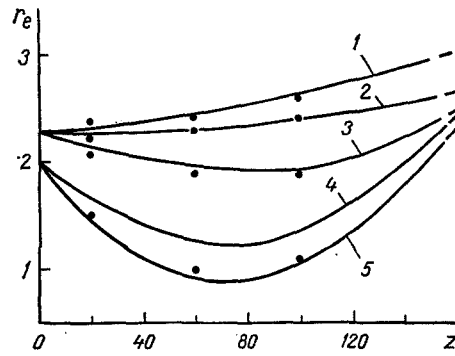


Fig. 5

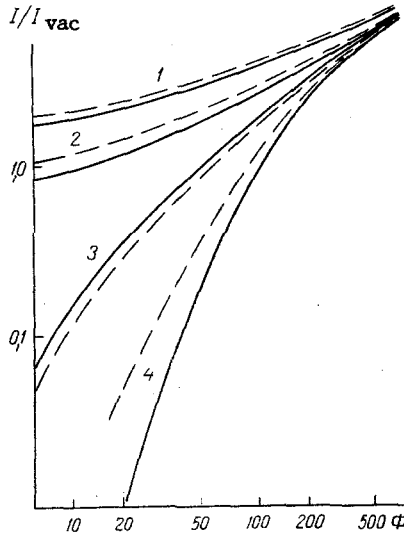


Fig. 6

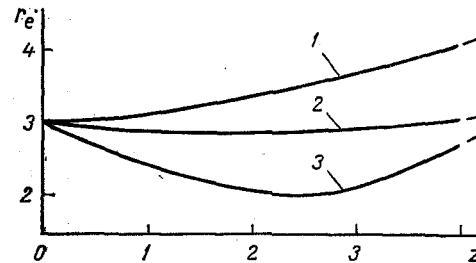


Fig. 7

Fig. 5. Dependences of the light beam radius on the distance in a cuvette with the gas  $\text{SF}_6$  for different values of the laser radiation intensity: 1) vacuum; 2)  $10 \text{ mJ/cm}^2$ ; 3)  $100$ ; 4)  $300$ ; 5)  $1 \text{ J/cm}^2$ ; points are data of an experiment [32],  $r_e$ , mm;  $z$ , cm.

Fig. 6. Self-focusing in an  $\text{SF}_6$ -He mixture for a  $0.4 \text{ torr SF}_6$  pressure and He pressures  $0$  (1),  $50$  (2),  $200$  (3), and  $1030$  (4) torr; dashed curves are results from [32].  $\Phi$ ,  $\text{mJ/cm}^2$ .

Fig. 7. Focusing a light beam of radius  $r_e$  in a nonequilibrium channel produced by electrons: 1) outside the focusing channel; 2, 3) in the channel (1 and  $50 \text{ A/cm}^2$  current density, respectively),  $z$ , m.

According to estimates [30] (see [31] also), the degree of kinetic cooling  $\Delta T$  is  $10^{-1}$ - $10^{-2}$  K for a  $\text{CO}_2$ - $\text{N}_2$  mixture at  $T = 300 \text{ K}$ . Under the conditions considered in [28]  $\delta n(\Delta T) \approx 1.3 \cdot 10^{-7}$ , while  $\delta n(\Delta T_V) \approx 7 \cdot 10^{-7}$ . Therefore, self-focusing because of vibrational excitation will be more effective than because of kinetic cooling.

Let us also note that self-focusing because of kinetic cooling occurs after the vibrational exchange time  $\tau_{V-V}$  when a change in the translational temperature will occur. Self-focusing because of vibrational excitation starts practically without delay since photoexcitation is a fast process not associated with molecular collisions. Moreover, self-focusing because of the formation of a vibrationally excited waveguide is a universal property, it occurs even in the absence of kinetic cooling. The lifetime of such a waveguide is determined by the characteristic relaxation time  $\tau_{V-T}$  if there is no additional pumping of vibrational energy.

A detailed examination of self-focusing induced by vibrational excitation of molecules is presented in [6] in the "quasioptics" approximation, i.e., on the basis of a parabolic equation for the complex electrical field amplitude.

It is seen in Fig. 5, taken from [6], that taking account of the induced polarizability narrows the beam, where this narrowing increases as the laser radiation intensity grows.

Results of numerical computations of self-focusing in a SF<sub>6</sub>-He mixture are presented in Fig. 6 as a function of the radiation flux  $\Phi$  ( $I_{\text{vac}}$  is the laser radiation intensity on the beam axis in a vacuum) for different helium concentrations at a 108 cm distance from the cuvette wall. It is seen from Fig. 6 that for small  $\Phi$  the V-T-exchange accelerated because of the presence of He results in a noticeable reduction in the self-focusing efficiency (because of the faster drop in the vibrational energy). The defocusing influence of He weakens at high laser radiation intensities since the V-T-exchange cannot already compete with the pumping.

Computations performed in [8] showed the importance of not only the polarizability of the vibrationally excited states for self-focusing but also of the form of the distribution function over the vibrational levels.

Formation of a zone with an elevated refractive index is possible not only because of the action of the laser beam itself. Still another method of creating a focusing channel is excitation of molecular media during electron-molecular collision. In general, such focusing can be observed experimentally if a laser beam is transmitted behind an electron beam with a delay not exceeding the characteristic V-T-exchange time. The focusing action of an electron beam can be estimated by computing the distribution function over the vibrational levels with the V-V and V-T-exchange processes as well as electron pumping taken into account. Such estimates are executed in [8].

Dependences of the light beam radius on  $z$  ( $z$  is the distance from the element injecting the charged particles) inside and outside the focusing channel are presented in Fig. 7. It is seen from the figure that quite effective radiation focusing takes place resulting in a growth in radiation intensity on the beam axis and additional heating of the molecule vibrational degrees of freedom. Let us note that numerical computations were performed with the dependence of the absorption coefficient on the level of vibrational excitation of the molecules taken into account.

#### CONCLUSION

The study of the optical properties of vibrationally excited gas is part of the general problem of studying the physicochemical properties of a nonequilibrium gas. A nonequilibrium gas is a new state of a substance with extraordinary properties. Since stationary nonequilibrium is maintained by external pumping, then by changing the external conditions the properties of a nonequilibrium gas can be altered within quite broad limits. The presence of an excess reserve of internal (vibrational) energy transforms the medium into a nonlinear one. The characteristics of the medium start to depend on factors disturbing the nonequilibrium. On the other hand the disturbing factors themselves, say, the optical or gasdynamic disturbance, the charged particle fluxes, etc., will depend in turn on the nonequilibrium that they produce. Such self-consistency makes solution of the problem difficult but then it results in new phenomena such as self-focusing.

#### NOTATION

$N_{\text{Av}}$ , Avogadro number;  $\rho$ , density;  $n$ , refractive index;  $N$ , density of the number of molecules;  $\alpha$ , their mean polarizability;  $Q_j$ , set of normal coordinates;  $W_0$ , energy of a molecule without a field;  $g\{v_j\}$ , statistical weight of the vibrational state  $\{v_j\}$  with normal coordinate  $Q_j$ ;  $a_j = (m_j\omega_j/\hbar)^{1/2}$ ;  $m_j$ , reduced mass;  $\omega_j$ , frequency of the  $j$ -th mode;  $x_e$ , anharmonicity constant of the molecule;  $\lambda$ , probing radiation wavelength;  $\delta$ , shift of the interference fringe;  $d$ , length of the interferometer "arm";  $r_0$ , initial light beam radius.

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