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KINETICS OF VIBRATIONAL EXCHANGE IN MOLECULES. AMPLIFICATION OF RADIATION IN HYDROGEN HALIDES BY ELECTRIC OR CHEMICAL PUMPING

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An analysis is presented of the relaxation in diatomic molecules with allowance for the anharmonicity, pumping, exchange of vibrational quanta, and mutual transformation of vibrational and translational energy. The obtained molecule-level distributions differ both from Boltzmann's equilibrium distribution and from Treanor's quasistationary distribution[8]. The results are used to analyze amplification in vibrational-rotational transitions in molecular lasers. New lasers are proposed, based on electrically pumped mixtures of the HCl-N_2-He and HI-N_2-He type. A study is made of the kinetics of the processes in a pulsed chemical laser based on the reaction $Cl_2 + H_2$ at different parameters. It is shown that the gain at the upper vibrational levels, resulting from the exchange, can be appreciable, does not depend on the features of the pumping, and is determined by the total reserve of vibrational energy and by the anharmonicity of the molecule.

1. INTRODUCTION

VIBRATIONAL and rotational relaxation in molecules is very extensively used at present in the physics of shock waves, in the study of the atmosphere, in chemical kinetics, in the theory of quantum generators, etc. It is usually assumed that a quasistationary Boltzmann distribution with a vibrational temperature T^{vib} is established in the system of the vibrational levels[1]. It was possible on this basis to explain the operating mechanism and to perform calculations both for a laser operating with gas flow, and for a sealed CO_2 laser in the continuous regime[2] as well as under nonstationary conditions[3,4], and also for a number of other molecules[5]. However, the assumption that the distribution is of the Boltzmann type, which holds in cases[2-5] when the laser transitions lie at the lower levels, turns out to be unsuitable for a number of important applications (at large pump powers and for high levels). It becomes essential therefore to analyze the kinetics of exchange of vibrational quanta. It is necessary to take into account in the calculations the presence of positive and negative sources of vibrational energy (see[6,7]), the transfer of energy to other degrees of freedom, and the anharmonicity of the vibrations[8,9].

The present paper has two purposes. First, a clarification of the principal problems of relaxation and real population distributions arising in vibrational exchange. Second, an analysis of applied problems connected mainly with lasers based on hydrogen halides with electric and chemical pumping. In molecular lasers, an appreciable gain in vibrational-rotational transitions is obtained if the vibrational temperature greatly exceeds the rotational temperature, or if absolute population inversion of the vibrational levels is attained. Such an inversion can be realized in polyatomic molecules in the stationary regime (for example, in a CO_2 laser), and in diatomic molecules only in the pulsed regime and at short time durations (up to the start of the vibrational relaxation)[10]. It was customarily assumed that at large times a quasistationary Boltzmann distribution is established as a result of relaxation in the system of vibrational levels. Actually, however, the real population distribution may greatly differ from a Boltzmann distribution. A clear illustration is the recently attained generation in a stationary electric discharge on rotational vibrational transitions of CO molecules in the CO-N_2-He mixture[11]; this generation, as shown by analysis, cannot be explained by assuming a Boltzmann distribution.

The influence of positive and negative sources of vibrationally-excited molecules on the character of the distribution was considered in[6,7].

Anharmonicity was taken into account in[8,9], and it was shown that in the case when the probability of quantum exchange greatly exceeds the probabilities of the vibrational-translational relaxation, the population distribution over the vibrational levels in an anharmonic oscillator is not of the Boltzmann type. The effective vibrational temperature Θ_{n+1} of the levels $n + 1$ and n for such a distribution is determined from the formula

$$k\Theta_{n+1} = (E_1 - 2n\Delta E) \Big/ \left(\frac{E_1}{k\Theta_1} - \frac{2n\Delta E}{kT}\right) \tag{1}$$

Here E_1 is the energy of the vibrational quantum in the 1–0 transition, Θ_1 is the effective vibrational temperature of the levels 1–0, determined from the total reserve of vibrational energy, ΔE is the anharmonicity of the molecule, and T is the gas temperature.

At the upper levels, where $\Theta_n \gg T$ or even $\Theta_n \ll 0$, the most favorable conditions are produced for obtaining gain. This is precisely why the generation in a stationary CO laser with electric pumping takes place at $7 \leq n \leq 15$.

As seen from (1), the anharmonicity of the oscillation ΔE (as well as the large quantity Θ_1/T) is a favorable factor for obtaining large effective vibrational temperatures at the upper levels. From this point of view, hydrogen halide molecules are quite promising for generation, since they have large anharmonicity. In addition, in these molecules the ratio of the energy of the vibrational quantum to the rotational one is small, and this is also an important factor when it comes to obtaining large gains.

We note, however, that the real distribution of the molecules over the vibrational levels will differ from (1). This is due, first, to the fact that in the derivation of (1)[8,9] no account was taken of the vibrational-translational relaxation, which is significant just at the high levels where the Treanor distribution[8] differs noticeably from the Boltzmann distribution. It is therefore necessary to determine the distribution over the levels with allowance for this relaxation, and also with allowance for the rates of pumping to the individual levels.

2. DISTRIBUTION OF POPULATIONS OVER THE VIBRATIONAL LEVELS IN SYSTEMS OF ANHARMONIC OSCILLATORS

We consider a binary mixture of diatomic molecules X and Y simulated by anharmonic oscillators. The population X_n of the n-th vibrational level of molecule X is described by the equation

$$\begin{aligned}\frac{dX_n}{dt} &= \Big(\sum_i Q^{i-1,\,i}_{n+1,\,n} X_{i-1}\Big) X_{n+1} - \Big(\sum_i Q^{i,\,i-1}_{n,\,n+1} X_i\Big) X_n \qquad (2)\\ &- \Big(\sum_i Q^{i,\,i+1}_{n,\,n-1} X_i\Big) X_n + \Big(\sum_i Q^{i+1,\,i}_{n-1,\,n} X_{i+1}\Big) X_{n-1} + \Big(\sum_i Q^{i-1,\,i}_{n+1,\,n} Y_{i-1}\Big) X_{n+1}\\ &- \Big(\sum_i \tilde{Q}^{i,\,i-1}_{n,\,n+1} Y_i\Big) X_n - \Big(\sum_i \tilde{Q}^{i,\,i+1}_{n,\,n-1} Y_i\Big) X_n + \Big(\sum_i \tilde{Q}^{i+1,\,i}_{n-1,\,n} Y_{i+1}\Big) X_{n-1}\\ &+ R_{n+1,\,n} X_{n+1} - (R_{n,\,n+1} + R_{n,\,n-1}) X_n + R_{n-1,\,n} X_{n-1} + A_{n+1,\,n} X_{n+1}\\ &- A_{n,\,n-1} X_n + B_n - C_n X_n; \qquad n = 0, 1, 2, 3, \ldots\end{aligned}$$

The system of equations for the populations of molecules Y is similar.

The first four terms on the right side of (2) describe exchange of vibrational quanta within the oscillator X with corresponding probabilities Q^{ij}_{mn} (per molecule), the second four terms correspond to exchange of quanta between the oscillators X and Y, with probability Q^{ij}_{mn}, Y_m is the population of the m-th vibrational level of the molecule Y, and the succeeding three terms describe the vibrational-translational relaxation with probabilities R_{mn}; $A_{n+1,n}$ and $A_{n,n-1}$ are the probabilities of the radiative decays of the levels n + 1 and n; B_n and C_n describe respectively the creation and annihilation of the molecules X at the level n. In (2), we neglected the influence of diffusion of the relaxation, something usually justified if the total mixture pressure is $p_\Sigma \lesssim 1$ Torr. In addition, just as in[8,9], we consider only single-quantum exchange. This is valid for not very high levels, at least those for which

$$E_1 - 2n\Delta E \gtrsim {}^1\!/_2 E_1, \text{ i.e., } n \lesssim E_1/4\Delta E.$$

The probabilities for the anharmonic oscillator can be represented in the form

$$Q^{i-1,\,i}_{n+1,\,n} = (n+1)\, i\, Q(i, n, T), \quad R_{n+1,\,n} = (n+1) R(n, T), \qquad (3)$$

where Q(i, n, T) and R(n, T) are determined for a given oscillator and its collision-partner molecule by the interaction potential, by the effective mass of the collision, by the temperature of the gas, and by the energy defect, and consequently depend on i and n. (In the case of a harmonic oscillator Q(i, n, T) = $Q^{01}_{10}(T)$, R(n, T) = $R_{10}(T)$, and do not depend on the numbers i and n.)

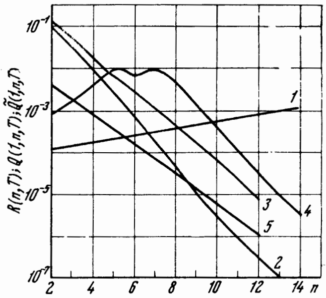

FIG. 1. Dependence of the quantities R(n, T)(curve 1), Q(1, n, T)(curves 2 and 3), and Q(1, n, T)(curves 4 and 5) on the number of the molecule level for different collisions (1, 2—HCl-HCl, 3—HI-HI, 4—HCl-N_2, 5—HI-N_2); T = 410°K.

As will be shown later, the population distribution function for the vibrational levels depends on the relation between Q(i, n, T), Q̃(i, n, T), and R(n, T). In the case of the hydrogen halides HCl and HI, R(n, T) was determined from the most reliable results[12,13] of numerous experiments on the rates of vibrational relaxation of the hydrogen halides, and Q(i, n, T) and Q̃(i, n, T) were calculated by Nikitin's method[14], where account was taken of the contribution of the rotation to the relaxation. An example of such a calculation is shown in Fig. 1, which gives, as functions of the number of the levels n (per collision), the values of Q(1, n, T) and Q̃(1, n, T) for exchange with the lowest quantum (the transition 0, n → 1, n − 1) and of R(n, T) for vibrational-translational relaxation. The figure shows the strong influence of the anharmonicity on the probability. At the upper levels, the principal role is assumed by the vibrational-translational relaxation, which influences the distribution of the molecules among the levels.

Let us find this distribution. We consider first the stationary case, $dX_n/dt = 0$, and also $B_n = C_n = 0$, i.e., there is no direct pumping and there is no loss of molecules at all levels. In this case, nonetheless, the reserve of vibrational energy of the molecules may not correspond to the gas temperature T, and is ensured by exchange of quanta with the molecules Y, in which the direct pumping is realized, i.e., $\tilde{B}_n \neq 0$ and $\tilde{C}_n \neq 0$ for the molecule Y. The system (2) is nonlinear and difficult to analyze. We note, however, that sums of the type $\Sigma_i Q(i, n, T) i X_i$ in (2) are not very sensitive to the form of the distribution of X_i, and are determined principally by the reserve of vibrational energy (thus, for a harmonic oscillator such a sum is directly proportional to the vibrational energy E^{vib}). The system (2) can therefore be linearized by using as the "zeroth" approximation in the evaluation of the sums the Treanor distributions of the molecules X and Y over levels with vibrational energies E^{vib}_X and E^{vib}_y, respectively, Then, substituting (3) in (2) and summing the equations from zero to m, we obtain

$$\begin{aligned}&\Big\{\sum_i i\,[Q(i, m, T) X^0_{i-1} + \tilde{Q}(i, m, T) Y^0_{i-1}]\Big\}(m+1) X_{m+1}\\ &- \Big\{\sum_i i \Big[Q(i, m, T) X_i^0 \exp\Big\{-\frac{2\Delta E_x}{kT}(i-1)\Big\} \qquad (4)\end{aligned}$$

$$+\tilde{Q}(i, m, T)\,Y_i^0 \exp\left\{-\frac{2\Delta E_Y}{kT}(i-1)\right\}\exp\left\{-\frac{E_{1X}-E_{1Y}}{kT}\right\}\Big]\Big\}(m+1)X_m$$
$$\times\exp\left\{\frac{2\Delta E_X}{kT}m\right\}+R(m, T)(m+1)X_{m+1}$$
$$-R(m, T)(m+1)X_m\exp\left\{\frac{2\Delta E_X}{kT}m\right\}\exp\left\{-\frac{E_{1X}}{kT}\right\}+A_{10}(m+1)X_{m+1}=0.$$

Here X_i^0 and Y_i^0 are the Treanor distributions of the molecules X and Y over the levels with vibrational energies E_X^{vib} and E_Y^{vib}.

Thus, we get the recurrence relation

$$X_{m+1}=X_m\exp\left(\frac{2\Delta E_X}{kT}m\right)\exp\left(-\frac{E_{1X}}{k\Theta_1}\right)\varphi_m. \tag{5}$$

From this we obtain for the distribution function of the molecules of the levels

$$X_m=X_0\exp\left\{-m\left[\frac{E_{1X}}{k\Theta_1}-(m-1)\frac{\Delta E_X}{kT}\right]\right\}\prod_{i=1}\varphi_i. \tag{6}$$

In formulas (5) and (6), Θ_1 is the effective vibrational temperature of the levels 1—0 of the molecule X, determined by the total reserve of vibrational energy E_X^{vib}, and

$$\varphi_m=\Big\{\Big[\sum_i Q(i, m, T)\exp\left(-\frac{2\Delta E_X(i-1)}{kT}\right)iX_i^0\Big]$$
$$+\Big[\sum_i\tilde{Q}(i, m, T)\exp\left(-\frac{2\Delta E_Y(i-1)}{kT}\right)iY_i^0\Big]\exp\left(-\frac{E_{1X}-E_{1Y}}{kT}\right)$$
$$+R(m, T)\exp\left(-\frac{E_{1X}}{kT}\right)\Big\}\exp\left(\frac{E_{1X}}{k\Theta_1}\right)\Big\{\Big[\sum_i Q(i, m, T)iX_{i-1}^0\Big]$$
$$+\Big[\sum_i\tilde{Q}(i, m, T)iY_{i-1}\Big]+R(m, T)+A_{10}\Big\}^{-1} \tag{7}$$

with $m \geq 2$ and $\varphi_1 = 1$.

For the effective vibrational temperature Θ_{m+1} of the two levels $m+1$ and m of the molecule X we get from (5)

$$k\Theta_{m+1}=(E_{1X}-2m\Delta E_X)\Big/\left(\frac{E_{1X}}{k\Theta_1}-\frac{2m\Delta E_X}{kT}-\ln\varphi_m\right). \tag{8}$$

Similarly, for the effective vibrational temperature T_{m+1}^{vib} of the levels 0 and $m+1$, characterizing the absolute population of the level $m+1$, we obtain from (6)

$$kT_{m+1}^{\text{vib.}}=(E_{1X}-m\Delta E_X)\Big/\left(\frac{E_{1X}}{k\Theta_1}-\frac{m\Delta E_X}{kT}-\frac{1}{m+1}\sum_{i=1}^{m}\ln\varphi_i\right). \tag{9}$$

The quantity φ_m characterizes the deviation of the distribution of the molecules with the levels from a distribution of the type (1) (see[8,9]), brought about by allowance for the vibrational-translational relaxation. It can be seen from (7) that for the lower levels, where the predominant role is played by exchange of quanta (i.e., terms containing $R(m, T)$ in (7) can be neglected), we have $\varphi_m \approx 1$ and the distribution is close to that obtained in[8,9]. For the upper levels, however, where the vibrational-translational relaxation plays the principal role in the population of the levels, we have, neglecting radiative processes, $\varphi_m \approx \exp(-E_{1X}/kT + E_{1X}/k\Theta_1)$ and consequently $\Theta_{m+1} \approx T$.

The expression obtained for φ_m is particularly lucid in the case when the reserves of vibrational energy E_X^{vib} and E_Y^{vib} are small and are determined by the population of only the first excited state of the molecules. It is then possible to retain in the sums of (10) only the first terms, and we get for φ_m

$$\varphi_m\approx\Big\{Q(1, m, T)X_1+\tilde{Q}(1, m, T)Y_1\exp\left(-\frac{(E_{1X}-E_{1Y})}{kT}\right)$$
$$+R(m, T)\exp\left(-\frac{E_{1X}}{kT}\right)\Big\}\frac{X_0}{X_1}\{Q(1, m, T)X_0+\tilde{Q}(1, m, T)Y_0$$
$$+R(m, T)+A_{10}\}^{-1}. \tag{7'}$$

The solution of the system (2) can be obtained for the stationary case also under the assumption that $B_n \neq 0$ and $C_n \neq 0$ (in order for the stationary case to obtain, it is necessary, however, to satisfy the condition $\Sigma_n B_n = \Sigma_n C_n X_n$). Expressions similar to (5)—(9) are obtained for the case most frequently encountered in practice, when $C_0X_0 \gg \sum_{n=1} C_nX_n$, corresponding to predominant annihilation of the molecules in the ground state.

Under such assumptions, we can obtain for the distribution function the expression

$$X_m=X_0\exp\left\{-m\left[\frac{E_{1X}}{k\Theta_1}-(m-1)\frac{\Delta E_X}{kT}\right]\right\}\prod_{i=1}^{m}\varphi_i$$
$$+\sum_{l=0}^{m-2}\left[\exp\left\{-l\left[\frac{E_{1X}}{k\Theta_1}+\left(\frac{l+1}{2}-m\right)\frac{2\Delta E_X}{kT}\right]\right\}\prod_{i=1}^{l}\varphi_{m-i+1}\psi_{m-l}, \tag{10}$$

where

$$\psi_{m+1}=\frac{1}{m+1}\left(C_0X_0-\sum_{i=0}^{m}B_i\right)\Big\{\Big[\sum_i Q(i, m, T)iX_{i-1}^0\Big]$$
$$+\Big[\sum_i\tilde{Q}(i, m, T)iY_{i-1}^0\Big]+R(m, T)+A_{10}\Big\}^{-1}.$$

Formula (10) generalizes the expressions obtained in[6,7] for the harmonic oscillators in the presence of positive and negative sources.

Let us employ now the results to analyze the amplification of radiation on vibrational-rotational transitions in hydrogen halides.

3. VIBRATIONAL-ROTATIONAL INVERSION IN HYDROGEN HALIDES FOR ELECTRIC PUMPING

Let us consider by way of an example a stationary electric discharge in the gas mixtures HCl-N_2-He and HI-N_2-He. We assume the following simplified model of the relaxation: the electrons excite directly only the vibrational levels of the nitrogen, and then the vibrational energy proceeds to the HCl or HI via exchange of quanta, and finally, the HCl and HI go over from the vibrational degrees of freedom to the translational ones, heating the gas. The vibrational-translational relaxation of N_2, in view of its low rate, can be neglected; the excitation of the molecules HCl and HI by the electrons will likewise be disregarded. Thus, the nitrogen plays the role of the pumping gas, and the helium decreases the diffusion decay of the excited molecules, and owing to its large thermal conductivity it lowers the temperature of the gas. The reserve of vibrational energy E_X^{vib} of the molecules HCl or HI is determined by the rates of the pumping and of the vibrational-translational relaxation. The determination of this energy for an anharmonic oscillator with a non-Boltzmann molecule-level distribution is a complicated problem. In addition, formulas (5)—(10) contain the unknown quantities Θ_1 and X_0, and the unknown parameters of the Treanor distributions of the "zeroth" approximation. All these quantities are func-

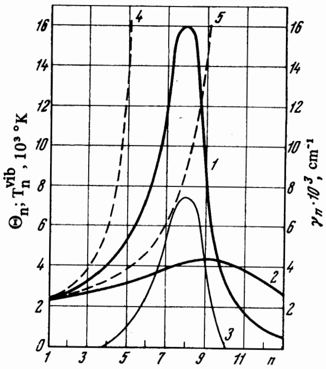

FIG. 2. Effective vibrational temperatures, Θ_n(curve 1) and T_n^{vib}(curve 2) and the gain γ_n (curve 3) vs. the level number for HI in the mixture: 0.5 Torr HI + 5 Torr N_2 + 5 Torr He ($N_e = 3 \times 10^9$ cm^{-3}); T = 380°K. Curves 4, 5—temperatures Θ_n and T_n^{vib} for the Treanor distribution [8].

tions of the energies E_X^{vib} and E_Y^{vib}, and can be determined in principle from the relations for the normalization of X_n^0, X_n, Y_n^0, and Y_n for the total number of particles and the total vibrational energy. Subsequently, however, to simplify the problem of finding this parameter when determining E_X^{vib}, we used the ordinary relaxation equations for the vibrational energy of the harmonic oscillators[11]. From the obtained values of E_X^{vib} and E_Y^{vib} we determined Θ_{1X}, X_0, Θ_{1Y}, and Y_0 in the harmonic approximation, and the vibrational temperatures for the distributions of X_n^0 and Y_n^0 were set equal to Θ_{1X} and Θ_{1Y} (for the molecules HCl (or HI) and N_2, respectively). Such a method is justified if the reserves of the vibrational energies of the molecules X and Y are relatively small and are determined by the populations of several lower levels of the molecules, where the anharmonicity is still weakly felt.

The equations for the vibrational relaxation of the molecules HCl (or HI) and N_2 were solved with a computer together with the thermal-conductivity equation, which determines the gas temperature. The solution was obtained for a cylindrical tube of 1.7 cm radius and wall temperature 300°K. After determining X_i^0 and Y_i^0 and the parameters Θ_1 and from X_0 formulas (5)—(9) we determined the distribution of the molecules HCl or HI over the vibrational levels, the effective vibrational temperatures Θ_{m+1} and T_{m+1}^{vib}, and the gain of the radiation on the vibrational-rotational transitions.

Figure 2 shows a typical plot of the effective vibrational temperatures Θ_n and T_n^{vib} against the level number n. The distributions over the levels are essentially non-Boltzmann (since the effective temperatures depend on the number of the levels), while the distributions and temperatures calculated from formulas (5)—(9) with allowance for the vibrational-translational relaxation differ strongly from the corresponding values obtained without allowance for this relaxation[8,9]. Particularly strongly dependent on n is the effective vibrational temperature Θ_n, which characterizes the relative population of the levels n and n − 1. On the upper levels, Θ_n decreases sharply with increasing n, tending to the value of the gas temperature. For levels close to the dissociation boundary, the quantity T_n^{vib}, which characterizes the absolute population of the level n, can be either larger or smaller than T_n^{vib} or the temperature of the harmonic oscillators, depending on the initial parameters. Therefore the rate of dissociation of the molecules, determined by the population of the levels close to the dissociation boundary and calculated for the model of the anharmonic oscillator under non-equilibrium conditions, may differ strongly from the corresponding value obtained, for example, for the most frequently employed model of a cut-off harmonic oscillator. Thus, the results obtained here may be of importance for the theory of non-equilibrium dissociation.

Figure 2 shows also the gain γ_n in the vibrational-rotational transition $(n, J) \rightarrow (n - 1, J + 1)$ as a function of the level number n. Since γ_n depends strongly on Θ_n, the largest value of γ_n is obtained for the pair of levels where the temperature Θ_n is maximal, and the plot of γ_n against n approximately duplicates the plot of Θ_n.

Figure 3 illustrates the dependence of the gain on the total pressure p_Σ. With increasing p_Σ, the value of γ_n first increases sharply, since the decrease of the diffusion decay causes an increase of the vibrational energies E_X^{vib} and E_Y^{vib}, and consequently also of the temperatures Θ_n and T_n^{vib}. With further increase of pressure, however, the gas temperature and the rate of collision relaxation increase, and this leads to a decrease in the gap between Θ_n and the gas temperature, and consequently to a decrease of γ_n. Attention should be called to the strong dependence of the gain on p_Σ. Similar dependences were obtained experimentally for a stationary laser based on the mixture CO-N_2-He[11].

Besides the plots shown in Fig. 3, we calculated also the influence exerted on γ_n by the partial pressures of nitrogen, helium, and by the concentration of the electrons N_e. Addition of N_2 and He increases γ_n, and there is an optimal value of N_e. For example, an increase of the He pressure decreases the probability of the diffusion decay and the gas temperature, and consequently increases γ_n. It must be noted that owing to the inaccurate determination of E^{vib} and of the parameters Θ_{1X}, X_0, Θ_{1Y}, and Y_0, and also of the vibrational temperatures Θ_{1Y}^0 and Θ_{1Y}^0 for the X_i^0 and Y_i^0 distributions, the calculated values of the coefficients γ_n turn out to be too high. In spite of this, however, we can expect large gains ($\gtrsim 10^{-3}$ cm^{-1}) and high generation power in the indicated mixtures in the case of an electric discharge. The influence of the possible dissociation of the hydrogen halides can be greatly decreased by using systems with gas flow, with separate electric excitation of the nitrogen, or by using pulsed operation.

4. AMPLIFICATION OF RADIATION OF THE VIBRATIONAL-ROTATIONAL TRANSITIONS WITH CHEMICAL PUMPING (THE REACTION $Cl_2 + H_2 \rightarrow HCl$)

Let us consider the distribution of the vibrational energy and the amplification of the radiation in anharmonic oscillators, using as an example a chemical laser based on the mixture $Cl_2 + H_2$, with photo-initiation of the chain reaction of HCl production. In this case, the nonstationary equations of type (2) for HCl must be solved simultaneously with the chemical-kinetics equations that determine the rates of creation B_n and annihilation C_n of the HCl molecules at the

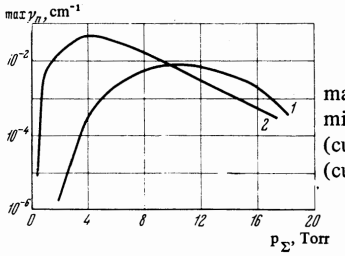

FIG. 3. Dependence of the gain max γ_n on the total pressure for the mixtures HCl:N$_2$:He = 1:10:10 (curve 1) and HI:N$_2$:He = 1:10:10 (curve 2)($N_e = 3 \times 10^9$ cm^{-3}).

different vibrational levels. The first such analysis was performed by Igoshin and Oraevskiĭ[10], who obtained interesting data on the time evolution and on the influence exerted by the photoinitiation intensity on the inverted population. In[10], however, they investigated only the initial period of the reaction, when only the vibrational-vibrational relaxation is of importance. Processes of deactivation of vibrational energy were not taken into account, and the quantum-exchange probabilities were calculated by the Herzfeld procedure, which does not take into account the contribution made to the relaxation by the rotation, a contribution of importance for hydrogen halides. In addition, in[10] they considered only the five lowest levels of HCl. When anharmonicity of the molecules is taken into account, however, it is of interest to consider also the higher levels.

The chemical reactions describing the formation of HCl in the summary reaction $Cl_2 + H_2 + h\nu \rightarrow HCl$, as well as their constants, are given in[10,15,16]. The vibrationally-excited molecules HCl are produced in the reactions

$$H + Cl_2 \rightarrow HCl^* + Cl. \qquad (11)$$

The shape of the light pulse acting on the Cl_2 was chosen to be the same as in[10]. To find the relative rates of the reaction (11), which lead to the formation of excited HCl molecules, we used the data of[17,18] and considered two models:

a) The fraction of the energy released in reaction (1) in the form of vibrational energy amounts to ~40%. In this case the relative rates α_n of the reaction (11) in the excited states n are[17] $\alpha_0 = 0$, $\alpha_1 = 0.134$, $\alpha_2 = 0.482$, $\alpha_3 = 0.362$, $\alpha_4 = 0.022$, and $\alpha_{n\geq 5} = 0$;

b) The fraction of the vibrational energy amounts to 10%[18]. Then $\alpha_0 = 0.7539$, $\alpha_1 = 3.2 \cdot 10^{-2}$, $\alpha_2 = 1.185 \cdot 10^{-1}$, $\alpha_3 = 8.9 \cdot 10^{-2}$, $\alpha_4 = 5.7 \cdot 10^{-3}$, and $\alpha_{n\geq 5} = 0$.

The chemical-kinetics differential equations were solved with a computer simultaneously with the relaxation equations (2) for nine levels of HCl and with the nonstationary heat-conduction equation that determines the gas temperature. The same heat-conduction equation was considered as in[2], and the rate W of energy release per unit volume of gas was determined from the formula

$$W = -\sum_{m=0}^{8}[E_1 - (m-1)\Delta E]\, m \left(\frac{dX_m}{dt}\right)_{\text{col}} \qquad (12)$$

$$+\left[\sum_{m=0}^{8} \alpha_m \{E_{\text{chem}} - [E_1 - (m-1)\Delta E]\}\right] k_{11} N_{\text{H}} N_{\text{Cl}_2} + [h\bar{\nu} - D_{\text{Cl}_2}] A t e^{-t/\tau} N_{\text{Cl}_2},$$

where $(dX_m/dt)_{\text{col}}$ is the rate of collisional relaxation of the level m of the HCl molecule, obtained from (2):

$$\left(\frac{dX_m}{dt}\right)_{\text{col}} = \frac{dX_m}{dt} - (A_{m+1,\,m}X_{m+1} - A_{m,\,m-1}X_m + B_m - C_m X_m);$$

E_{chem} is the total energy released in the reaction (11), $h\bar{\nu}$ is the average energy of the photon absorbed by the Cl_2($h\bar{\nu} \approx 3.8$ eV[16]), D_{Cl_2} is the dissociation energy of the Cl_2 molecules, N_H and N_{Cl_2} are the concentrations of the H and Cl_2 molecules, and k_{11} is the constant of the reaction (11).

The third term in (12) describes the formation of "hot" Cl atoms in the photodissociation of chlorine molecules. We note that the contribution of this term to the total rate is quite large. The solution was obtained for a tube of radius 1.7 cm with wall temperature 300°K.

The results of the calculations are shown in Figs. 4–10. Figure 4 shows a typical time variation of the effective vibrational temperatures Θ_n for the lower pair of HCl levels. At the initial instants of time, when there is no vibrational exchange, these temperatures characterize the relative values of the rates of population of different excited states of HCl in the reaction (11). After some time, equal to the average time of quantum exchange, a quasistationary essentially non-Boltzmann molecule-level distribution is established. The dependence of the effective operational temperatures Θ_n and T_n^{vib} on the number of the level n is shown for this case in Fig. 5.

Just as for the stationary regime with electric pumping, considered in the preceding section under certain assumptions, the exact solution is obtained from population and temperature distributions that differ from either the Boltzmann or Treanor distribution[8], and this difference is larger, naturally, for the model in which 40% of the energy released in the chemical reaction (11) goes over into the vibrational degree of freedom (Fig. 5a). Figures 5a and b indicate the temperatures for the model of a harmonic oscillator having the same reserve of vibrational energy. When account is taken of the anharmonicity, owing to the transfer of energy to the upper vibrational states, the effective temperatures will be lower at the lower levels and higher at the upper levels than in the case of a harmonic oscillator. Figures 5a and b show also the dependence of the gain on the number of levels at instants of time larger than the characteristic time of exchange of vibrations. In the case of Fig. 5b, the fraction of the energy released in the chemical reaction in the form of vibrational energy (~10%) is insufficient for obtaining the gains required for generation at these instants of time.

The time variation of the gains for different vibrational transitions is illustrated by Fig. 6. At the first

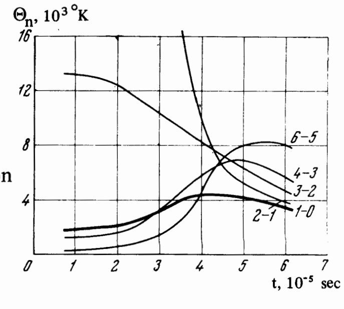

FIG. 4. Time variation of the effective vibrational temperatures for different pairs of HCl levels in the process of the chemical reaction (initial mixture: 1 Torr Cl$_2$ + 1 Torr H$_2$ + 10 Torr He, $A = 10^9$, $\tau = 10^{-4}$ sec).

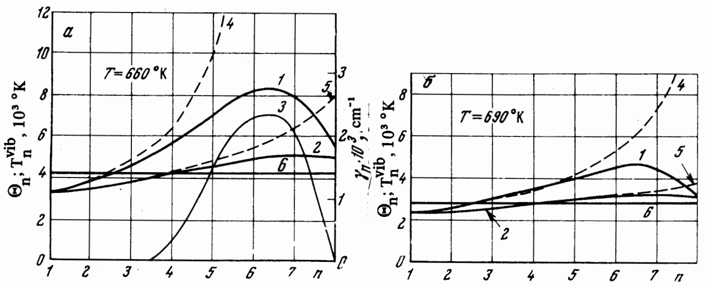

FIG. 5. Dependences of Θ_n (curve 1), T_n^{vib} (curve 2), and γ_n (curve 3) on the number of the HCl level in the chemical reaction (initial mixture 1 Torr Cl_2 + 1 Torr H_2 + 10 Torr He, A = 10^9, τ = 10^{-4} sec). Curves 6—temperature for the model of a harmonic oscillator having the same reserve of vibrational energy: a—40% of the chemical energy is converted into vibrational energy, instant of time t = 6 × 10^{-5} sec, b—10% of the chemical energy is converted into vibrational energy, instant of time t = 5.8 × 10^{-5} sec. Curves 4 and 5—temperatures Θ_n and T_n^{vib} for the Treanor distribution.

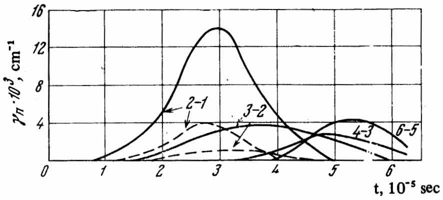

FIG. 6. Time variation of the gain γ_n for different pairs of HCl levels in the process of chemical reaction (initial mixture: 1 Torr Cl_2 + 1 Torr H_2 + 10 Torr He, A = 10^9, τ = 10^{-4} sec). The solid and dashed curves, respectively, are for the model when 40% or 10% of the chemical energy goes over into vibrational energy.

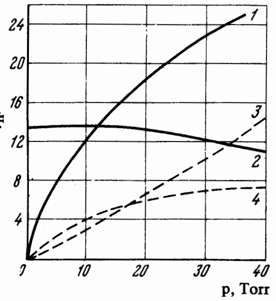

FIG. 7. Dependence of the gains max γ_2 (curves 1, 2) and max γ_6 (curves 3, 4) on the total pressure (curves 1, 3) for the mixture Cl_2 : H_2 : He = 1 : 1 : 10 and on the partial pressure of the helium (curves 2, 4) for the mixture 1 Torr Cl_2 + 1 Torr H_2 + 1 Torr He (A = 10^9, τ = 10^{-4} sec).

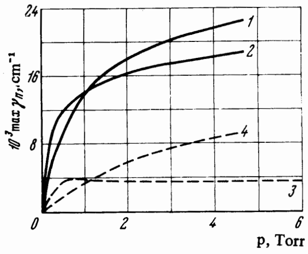

FIG. 8. Dependence of max γ_2 (curves 1, 2) and max γ_6 (curves 3, 4) on the partial pressure of Cl_2 (curves 1, 3) for the mixture 1 Torr H_2 + p Torr Cl_2 + 10 Torr He and A_2 (curves 2, 4) for the mixture 1 Torr Cl_2 + p Torr H_2 + 10 Torr He (A = 10^9, τ = 10^{-4} sec).

instant of time, when the populations of the HCl levels are proportional to the relative rates of population of the excited states in reaction (11), amplification is possible only on the transitions 2—1 (owing to the presence of absolute inverted population of the levels 2—1) and 3—2 (owing to the large effective temperature Θ_3). As the HCl molecules accumulate, the gain γ_n first increases with time, and then, owing to vibrational exchange and to a decrease of Θ_2 and Θ_3, it begins to decrease. However, for the case when 40% of the chemical energy goes over into vibrational energy, exchange of quanta leads to the occurrence of a second maximum in the gain already at the upper levels.

Figure 7 shows the dependence of the maximum gain in the pulse, max γ_n, on the partial pressure of the helium p_{He} and on the total initial pressure p_Σ for the mixture $p_{Cl_2} : p_{H_2} : p_{He} = 1 : 1 : 10$. When helium is added, owing to the decrease of the gas temperature, max γ_2 decreased somewhat and max γ_6 increases, since, according to (8), the effective temperature Θ_6 increases with decreasing temperature T. We note that an appreciable increase at the upper levels can be obtained only in the presence of a buffer gas that lowers the gas temperature. For the increasing total pressure, max γ_2 and max γ_6 increase. However, if account is taken of the broadening of the emission lines as a result of the pressure, a broadening which is appreciable at $p_\Sigma \gtrsim 10-20$ Torr, then the gain will be maximal at these pressures, after which it starts to decrease.

Figure 8 shows the dependence of max γ_n on the partial pressures of Cl_2 and H_2 for the initial mixtures 1 Torr H_2 + p Torr Cl_2 + 10 Torr He and 1 Torr Cl_2 + p Torr A_2 + 10 Torr He. We see that the gain in the transition 2—1, at the same total pressure, will always be larger if $p_{Cl_2} > p_{H_2}$. This is caused by the fact that in this case the rate of the reaction (11) is increased as a result of the increase of the concentrations of Cl and H and of the increase of the gas temperature. On the other hand, the value of max γ_6 at p_Σ = const and $p_{Cl_2} > p_{H_2}$ is always smaller than for the case $p_{Cl_2} < p_{H_2}$. The reason is that when $p_{Cl_2} > p_{H_2}$ the gas temperature T increases more rapidly because of the increase of the relative fraction of "hot" Cl atoms produced in the reaction, and because of the decrease of the thermal conductivity coefficient of the mixture.

The dependence of max γ_n on the amplitude A of the light pulse initiating the chemical reaction, with a characteristic flash time $\tau = 10^{-4}$ sec, is shown in Fig. 9. Both quantities, max γ_2 and max γ_6, depend relatively weakly on the flash amplitude, with max γ_2 increasing monotonically with increasing A, while max γ_6 has an optimum at A ~ 10^8. The presence of this optimum is connected with the fact that on the one hand, with decreasing A, the gas temperature contributing to the growth of max γ_6 decreases, and on the other hand, a smaller number of HCl molecules is produced, the process of production of HCl stretches out in time, so that the vibrational-translation relaxation, which decreases max γ_6, begins to exert a strong influence.

Finally, Fig. 10 shows plots of max γ_n against the characteristic duration of the photo-initiating pulse τ at a constant total energy and a constant maximal pulse intensity (for the considered pulse form $Ate^{-t/\tau}$, these two conditions denote constancy of the quantities $A\tau^2$ and $A\tau$, respectively). The growth of max γ_2 at

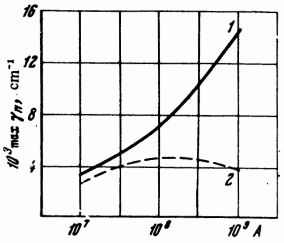

FIG. 9

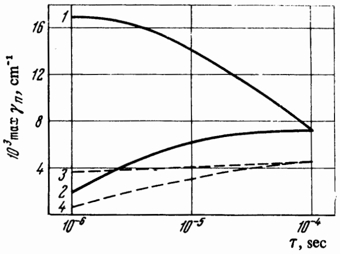

FIG. 10

FIG. 9. Dependence of max γ_2 (curve 1) and max γ_6 (curve 2) on the flash amplitude A (initial mixture 1 Torr Cl_2 + 1 Torr H_2 + 10 Torr He, $\tau = 10^{-4}$ sec).

FIG. 10. Dependence of max γ_2 (curves 1, 2) and max γ_6 (curves 3, 4) on the characteristic flash time τ at a constant total flash energy (curves 1, 3, $A\tau^2$ = const = 1 and a constant maximal flash power (curves 2, 4, $A\tau$ = const = 10^4). Initial mixture 1 Torr Cl_2 + 1 Torr H_2 + 10 Torr He.

$A\tau^2$ = const is connected with the increase of the gas temperature (since the thermal conductivity does not yet begin to play a noticeable role) and the rate of the reaction (11) at the instant of the start of the vibrational exchange.

It must be noted that at relatively low light-pulse energies, when the reaction does not run its course and a small number of HCl molecules is produced, constituting a small admixture to the gases Cl_2H_2, and He, the vibrational-translation relaxation for the probabilities in question may assume a dominating role at levels below the sixth (see Fig. 1). Then the character of the distribution over the levels will differ from that shown in Fig. 5, and the maximum values of $\odot_n$, T_n^{vib}, and γ_2 will be located at lower levels.

The data shown in Figs. 7—10 were obtained for a model in which 40% of the chemical energy in the reaction (11) goes over into vibrational energy. If this energy constitutes a smaller fraction, then the qualitative dependences for max γ_2 remain the same as before, and there may be no gain at the upper levels (for example, $\gamma_6 = 0$ for the case when p_{Cl_2} = 1 Torr, p_{H_2} = 1 Torr, p_{He} = 10 Torr, A = 10^9, and $\tau = 10^{-4}$, and only 10% of the chemical energy is transformed into vibrational energy). At the present time there are no reliable experimental data for this fraction of energy.

We have considered in this section the concrete reaction $H_2 + Cl_2 \rightarrow HCl$. However, the general relations noticed here are characteristic of a large number of chemical reactions accompanied by a release of energy into vibrational degrees of freedom.

CONCLUSION

We have obtained in this paper the real distribution of the vibrational energy of the molecules over the levels. An important role in the formation of the deviations from the Boltzmann distribution in vibrational exchange is played by anharmonicity of the molecules. The results uncover new possibilities for the organization of experiments. Thus, for example, great interest attaches, in our opinion, to the measurement of the real distributions and to a comparison of these distributions with the calculated ones.

The problems considered here are of particular significance for molecular lasers, where the generation may take place at levels other than those on which the pumping is effected. The operating mechanism of a stationary laser with electric discharge in a CO-N_2-He gas mixture[11] can be explained on the basis of the results obtained here without resorting to other hypotheses (for example, the hypothesis of selective pumping as a result of the chemical reactions). The electrically-excited hydrogen-halide lasers proposed in this paper may offer (if dissociation in the discharge is avoided) considerable advantages over a CO laser, owing to the large number of rotational quanta and the anharmonicity of the molecules.

The results obtained for a chemical laser based on the reaction $H_2 + Cl_2$ may be useful also in the analysis of other exothermal reactions, where the fraction of the chemical energy released in the form of vibrational energy is large. For example, it is of interest to investigate a chemical laser based on the reaction $CS_2 + N_2 \rightarrow CO^*$ [19]. In this laser, generation is observed on transitions from the seventh through the thirteenth levels.

Estimates show that if ~50% of the chemical energy of this reaction (~87 kcal) is released in the form of vibrational energy the distribution over the levels, which becomes established as a result of the vibrational exchange, will be strongly nonequilibrium, such that generation is possible for levels with $n \gtrsim 7$. Therefore, unlike the prevalent opinion[19], generation on the upper levels of CO, just as in the case of the stationary CO laser with electric excitation, may be connected not with the relative rates of the reaction of CO production in different excited states, but with vibrational exchange, the anharmonicity of the molecule, and the non-equilibrium value of the vibrational energy obtained in the chemical reaction.

On the whole, the approach developed in the present paper is necessary for the analysis of vibrational relaxation in molecular gases at large rates of pumping of energy into the vibrational degrees of freedom. Only when account is taken of the real distributions of the populations is it possible to perform a correct analysis of the chemical lasers and lasers with electric pumping (in the case of generation at high levels), to solve problems of vibrational relaxation (particularly, non-equilibrium dissociation), and to search for new chemical reactions for the development of molecular lasers.

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