In stronger shock waves, the effect can lead, in particular, to the existence of a zone with a high degree of dissociation of molecules, while the latter attains an equilibrium value behind the region in which the heavy molecules are stopped, if there are no admixtures that actively couple the reaction products.

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PROBLEM OF OBTAINING A POPULATION INVERSION IN VIBRATIONAL LEVELS OF POLYATOMIC DIPOLE MOLECULES BEHIND A SHOCK-WAVE FRONT

V. A. Levin and A. M. Starik

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The possibility for an inversion to arise with the breakdown of thermodynamic equilibrium as a result of a sharp increase in the temperature of a mixture of polyatomic molecules, having different relaxation times for free vibrations, was first examined in [1]. However, in spite of the fact that in [2] lasing was detected behind the front of an overdriven detonation wave in a F_2O-H_2-Ar mixture, in practice this method has not been widely used. This is related, apparently, to the fact that the calculations of the flow of CO_2-N_2-He (H_2O) mixtures behind the front of a strong shock wave carried out in [3, 4] indicated a very small size for the region in which the inversion exists of about 0.2 cm [4]. And, although the value of the inverted population density for the transitions $04^00 \rightarrow 00^01$ and $20^00 \rightarrow 00^01$ in the CO_2 molecule was comparable to the inverted population density of molecules with expansion in supersonic nozzles $\sim 10^{14}$-10^{15} cm^{-3}, it is very difficult to observe it and to generate laser radiation with very small gains (~ 0.005 m^{-1}) in such thin layers.

The difficulties of choosing an active medium for a laser, using the method of fast heating for disrupting thermodynamic equilibrium, are related to the necessity of providing for high pumping rates to the upper laser level. Since initially the translational temperature behind the front of a shock wave is high, while the population density of vibrational levels corresponds to the equilibrium temperature in front of the shock wave front [5], the rate of excitation of molecules in this case is determined by the rate of the V–T process for modes having the shortest relaxation time. For this reason, one of the requirements for molecules in the active medium in obtaining an inversion by the rapid heating of the mixture is a high rate for V–T processes. This is also indicated by the results of [6], wherein the possibility of the formation of an inversion behind a shock wave front as the wave passes through a mixture containing (CO_2, N_2O) molecules with different V–T relaxation times, τ_j, was analyzed.

The smallest values of τ_j, with other conditions being equal, are characteristic for unsymmetrical dipole molecules. For example, the rate of excitation of the deformation vibrations in the V–T process for H_2O molecules is 50 times greater than the corresponding value for CO_2 even in a mixture with He. The use of such molecules will also provide acceptable gains (due to the high Einstein coefficients) even with low inverted population densities of the particles. The possibility of obtaining an inverted population with rapid heating of a gas consisting of dipole molecules in shock waves was first examined in [7] for H_2O molecules.

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The purpose of this paper is to analyze further the possibility of realizing a water vapor laser by rapid heating of a molecular system and to clarify the possible magnitudes of the index of refraction, the spectral composition of the radiation, and the values of the energy stored per unit mass of gas in inverted transitions.

We examined the propagation of normal shock waves through a medium containing H_2O, H_2, and O_2 molecules. In so doing, the most probable channels for relaxation of vibrational energy were assumed to be as follows [8]:

$$
\begin{array}{ll}
H_2O\,(000) + M \rightleftarrows H_2O\,(010) + M & W_{20}^{M}, \\
H_2O\,(020) + M \rightleftarrows H_2O\,(100) + M & W_{12}^{M}, \\
H_2O\,(020) + M \rightleftarrows H_2O\,(001) + M & W_{32}^{M}, \\
H_2O\,(100) + M \rightleftarrows H_2O\,(001) + M & W_{13}^{M}, \\
H_2O\,(000) + M \rightleftarrows H_2O\,(100) + M & W_{10}^{M}, \\
H_2O\,(001) + H_2\,(V = 0) \rightleftarrows H_2O\,(000) + H_2\,(V = 1) & W_{35}, \\
H_2O\,(100) + H_2\,(V = 0) \rightleftarrows H_2O\,(000) + H_2\,(V = 1) & W_{15}, \\
H_2O\,(010) + O_2\,(V = 0) \rightleftarrows H_2O\,(000) + O_2\,(V = 1) & W_{24}, \\
H_2\,(V = 1) + M \rightleftarrows H_2\,(V = 0) + M & W_{50}^{M}, \\
O_2\,(V = 1) + M \rightleftarrows O_2\,(V = 0) + M & W_{40}^{M},
\end{array}
$$

where W_{pk} are the rate constants of elementary processes ($p = k = 1, 2, 3$ corresponds to the symmetrical, deformation, and asymmetrical type vibrations of the H_2O molecule; $p = k = 4, 5$ corresponds to the excited state of O_2 and H_2 molecules, while $k = 0$ corresponds to the unexcited state of any molecule); M is any molecule in the mixture.

The analysis carried out in [7-10] showed that in order to describe vibrational energy exchange processes in such mixtures the rotational and vibrational kinetics can be viewed separately and it is possible to use a model of local temperatures, characterizing a quasistationary distribution in each type of vibration. In what follows, the indices $j = 1, 2, 3, 4, 5$ will denote the symmetrical, deformation, and antisymmetrical vibrations of the H_2O molecule and vibrations of O_2 and H_2 molecules.

It should be noted that when water vapor condenses, the assumptions indicated are not valid. In this case, it is necessary to take into account the possibility of exciting intermolecular types of vibrations, formed with condensation of complexes, as well as the fact that for a certain ratio of the heating time of the condensate particles behind the shock wave front and the vibrational relaxation time for molecules in the gas phase, on absorption, the lower vibrational levels can be excited more rapidly than the upper levels. The kinetics of vibrational energy exchange in such media is much more complicated than in single-phase flows. In this paper, we examine a range of pressures and temperatures of the unperturbed flow in which condensed particles do not form. In order to determine the values of the probabilities of elementary processes W_{pk} for temperatures $T > 1000°K$ behind the front of shock waves, we used experimental and theoretical results [11-21]. In this case, as an analysis of data on the probability of the V–T relaxation process for the 010 state of the H_2O molecule (the measurements were carried out over a wide temperature range $T = 300$-$2600°K$ [12-16]) showed, the nature of the function $W_{20}^{M}(T)$ for low ($T < 700°K$) and high ($T \geq 700°K$) temperatures is different (for $T < 700°K$, the quantity W_{20}^{M} decreases with increasing T, while for $T \geq 700°K$ it increases). This kind of behavior for the function $W_{20}^{M}(T)$ can be explained by assuming that long-range attractive forces dominate at low temperatures and that the role of short-range repulsive forces increases with increasing T. This assumption, together with the hypothesis of a step-like V–R–T transfer of energy during collisions between molecules having high rotational quanta (H_2O, H_2), leads to good agreement between theory and experiment [20, 21].

A similar change in the nature of the interaction with increasing T was also observed for the V–V' vibrational relaxation process from the 00^01 level in the CO_2 molecule in collisions with H_2O molecules [22]. For this reason, for the probabilities of the V–V' processes $\nu_3 \rightarrow 2\nu_2 (W_{32}^{M})$ and $\nu_1 \rightarrow 2\nu_2 (W_{12}^{M})$ in the H_2O molecule, whose values were measured for $T = 600°K$ [11], the temperature dependences for $T \geq 700°K$ were chosen, in contrast to [7], to be the same as for $W_{20}^{M}(T)$, i.e., assuming that repulsive forces act at high T. The remaining probabilities, for which there are no measurements at high temperatures, were calculated in the same way as in [8].

The nonequilibrium parameters of the medium in the relaxation zone of a shock wave, as also in [6, 7], were determined from a numerical solution of the complete system of equations of gas dynamics and vibrational kinetics for a model of a nonthermally conducting ideal gas. The boundary conditions were parameters behind the shock wave front, calculated assuming that the chemical composition of the mixture and the population densities of the vibrational levels of molecules with a transition through the viscous shock remained unchanged. The gain of the medium and the energy stored per unit mass of gas in the inversion transition were calculated from the known values of the relative populations, temperature, and density in the relaxation zone at each step in the integration. At the same time, it was assumed that the rotational degrees of freedom of the H_2O molecule are in equilibrium with the translational degrees of freedom, while the distribution of rotational energy over the quantum levels can be approximated by the equation for an elongated slightly asymmetric top:

$$F(j,\tau)\approx F(j,K_a)=\frac{1}{2}(B+C)j(j+1)+\left[A-\frac{1}{2}(B+C)\right]K_a^2, \tag{1}$$

where $\tau = K_a - K_c$; j, K_a, and K_c are quantum numbers that determine the total angular momentum and its projection on the axis of the elongated and oblate symmetric top, respectively; A, B, and C are rotational constants (for the H_2O molecule:

$$A=5{,}54\cdot10^{-15}\ \text{erg},\ B=2{,}89\cdot10^{-15}\ \text{erg},\ C=1{,}85\cdot10^{-15}\ \text{erg [23]}).$$

For definiteness, we will examine transitions in the R branch. In this case, the expression for the gain for a vibrational–rotational transition $m(V_1'', V_2'', V_3'', j'', K_a'') \rightarrow n(V_1', V_2', V_3', j', K_a')$ can be represented in the form

$$\alpha_n^m=\gamma_1\frac{\lambda_0^3\rho}{8\pi\mu}N_A\sqrt{\frac{\mu_1}{2\pi RT}}\frac{2j''-1}{Z_VZ_r}H(a,y)A_n^m\delta_n^m,$$

$$\delta_n^m=Y_{[V'']}\exp\left[-\frac{F(j'',K_a'')}{kT}\right]-Y_{[V']}\exp\left[-\frac{F(j',K_a')}{kT}\right],$$

$$Z_V=\prod_{j=1}^{3}(1-Y_j)^{-1},\quad Z_r=2\sqrt{\frac{\pi}{ABC}(kT)^3},$$

where N_A is Avogadro's number; R is the universal gas constant; k is Boltzmann's constant; $\mu=\sum_{i=1}^{M}\mu_i\gamma_i$ (μ_i is the molecular weight of the i-th component, while γ_i is its mole fraction in the mixture, i = 1, 2, and 3; 1 denotes H_2O, 2 denotes O_2, and 3 denotes H_2); $Y_{[V]}=\prod_{j=1}^{3}\exp\left(-V_j\frac{\Theta_j}{T_j}\right)$ (j = 1, 2, 3); Θ_j and T_j are the characteristic and local vibrational temperatures; ρ is the density; T is the transitional temperature of the gas; $H(a, y)$ is the Voigt function, whose value was calculated for the line center (y = 0) according to the equations in [22]. The parameter a, characterizing the ratio of the Lorentz and Doppler spectral line widths, was calculated from the relation

$$a=\frac{\rho N_A}{\mu}\frac{\lambda_0}{\pi}\sqrt{\frac{4}{\pi}}\sum_{i=1}^{M}\sigma_i\gamma_i\sqrt{\frac{\mu_i+\mu_1}{\mu_i}}.$$

The values of the cross sections for impact acceleration were taken to be the same for all partners: $\sigma_1 = \sigma_2 = \sigma_3 = 2.36\cdot10^{-15}\ \text{cm}^2$ [20].

The wavelength of the radiation at line center of the given vibrational–rotational transition λ_0, in view of the absence of spectroscopic data, was determined theoretically using Eq. (1):

$$\lambda_0=\left\{\frac{K}{hc}\left[\Theta_{[V'']}-\Theta_{[V']}+\frac{F(j'',K_a'')-F(j',K_a')}{K}\right]\right\}^{-1},$$

where h is Planck's constant, c is the velocity of light in the vacuum. Einstein's coefficients A_n^m for the transitions studied in this work were calculated assuming that the square of the moduli of the matrix elements of these transitions and the transition $001(6_{33}) \rightarrow 020(5_{50})$, emitting in the far infrared region of the spectrum ($\lambda_0 = 28\ \mu\text{m}$), for which the Einstein's coefficient is known (6 sec^{-1}), are equal [24]. The energy stored per unit mass of gas in the inversion transition was calculated from the relation

$$E_n^m=\frac{R}{\mu}\Theta_{mn}\gamma_1\left[\varepsilon-\varepsilon(\alpha_n^m=0)\right],$$

where Θ_{mn} is the frequency of the transition at the line center, expressed in Kelvins; ε and $\varepsilon(\alpha_n^m = 0)$ are defined by the equations

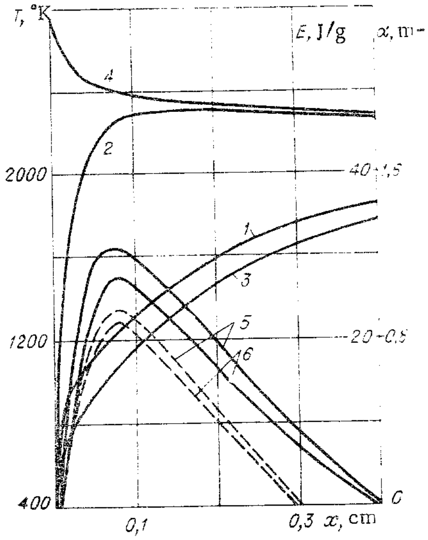

Fig. 1

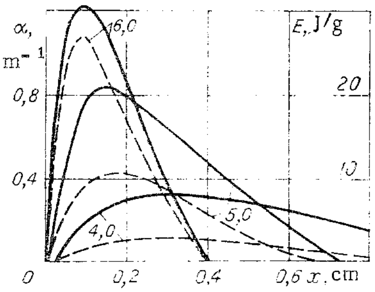

Fig. 2

$$\varepsilon = \frac{d_j Y_j}{1 - Y_j} \quad (j = 1, 3),$$

$$\varepsilon\left(\alpha_n^m = 0\right) = \frac{d_j}{(Y_2)^{-2} \exp\left[\dfrac{F(j', K_a') - F(j'', K_a'')}{kT}\right] - 1},$$

where d_j is the multiplicity of the modes to which the upper laser level belongs (for H_2O, $d_j = 1$). The calculations were carried out for Mach's numbers in front of the shock wave equal to $M_0 = 4.0$–6.0 with gas temperature $T_0 = 400$°K and static pressure $p_0 = 10$ Pa for H_2O-H_2 ($\gamma_3 = 0$–0.05) and H_2O-O_2 ($\gamma_2 = 0$–0.1) mixtures.

Figure 1 shows, for pure water vapor with $M_0 = 6.1$, a typical distribution of vibrational T_i (curve 1 is for T_1, 2 is for T_2, and 3 for T_3) and translational T (curve 4) temperatures, as well as the gains α_n^m (curve 5) and specific energy E_n^m (curve 6) for the most strongly emitting transitions in the R branch $030(5_{32}) \rightarrow 001(4_{43})$ (continuous curves) and $030(5_{32}) \rightarrow 100(4_{43})$ (dashed curves). The wavelengths of the radiation from these transitions are ~10.6 and ~9.6 μm, respectively. It is evident that positive values are already obtained for the gain at the beginning of the relaxation zone as a result of the considerably different rates at which the levels $0V_20$ and $V_100(00V_3)$ are populated with the vibration–rotational transitions indicated. The maximum values of α_n^m, as well as E_n^m, are realized at a distance of x = 0.1 cm from the shock wave front, when the temperature T_2 is nearly equal to the translational temperature ($T_2 \approx 2250$°K, while $T \approx 2400$°K), and constitute 1.25 m^{-1}, 27 J/g for the transition $030(5_{32}) \rightarrow 001(4_{43})$ and 0.9 m^{-1}, 22.5 J/g for the transition $030(5_{32}) \rightarrow 100(4_{43})$. The lower values of E_{100}^{030} compared to E_{001}^{030}, in spite of the large magnitude of the emitted quanta for the transition $030(5_{32}) \rightarrow 100(4_{43})$, are explained by the fact that the rate at which the state 100 is populated is always greater than the rate at which the state 001 is populated [7]. For this reason, in what follows, we will be interested in the value of α_n^m and E_n^m only for the transition $030(5_{32}) \rightarrow 001(4_{43})$. The positive values of α_n^m for this transition remain up to x = 0.4 cm.

We note that since the wavelength of the radiation of the transition examined is $\lambda_0 \approx 10.6$ μm, i.e., it corresponds to the wavelength of the usual CO_2 laser, for expected values of the gain ~1 m^{-1}, it is possible to check experimentally the existence of inversion of the transition 030 → 001 in the H_2O molecule behind the shock front of a normal shock wave using the usual measurement of the intensity of the weak emitted signal. The size of the zone with positive gain can be increased, as calculations have shown, by decreasing the velocity of the shock wave. This is illustrated in Fig. 2, which presents the distributions of α_n^m (continuous curves) and E_n^m (dashed curves) along the relaxation zone for different values of $M_0 = 4.0$–6.0. Although as Mach's number decreases and, therefore, the values of the translational temperature to which T_2 approaches as well, the magnitude of the gain also decreases, but even for $M_0 = 4.0$ its value is ~0.3 m^{-1} and with an inversion zone having a length of ~1.1 cm can be detected in the experiment. The difference between the dependence of the length of the inversion region on Mach's number for the short wave obtained and the dependence examined previously in [7] is explained by the difference in the temperature dependence of the rate constants for the intramolecular V–V' process $W_{12}^{H_2O}$ (and $W_{32}^{H_2O}$) in the present work and in [7]. Let us examine the effect of the presence of H_2 and O_2 molecules in water vapor on the inversion characteristics of the medium.

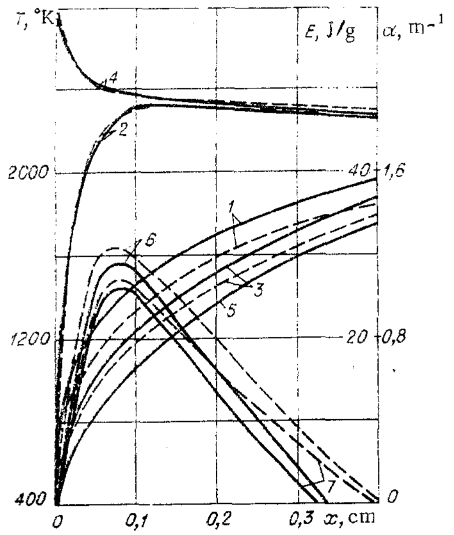

Fig. 3

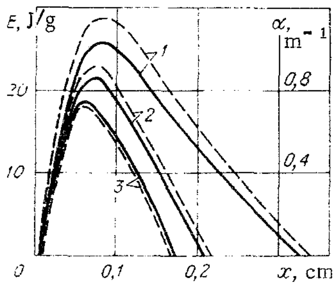

Fig. 4

Figure 3 shows the distributions of the vibrational T_i (T_1 is given by curve 1, T_2 by curve 2, T_3 by curve 3, and T_4 by curve 5) and translational T (curve 4) temperatures in the relaxation zone of the shock wave with $M_0 = 6.0$ for the mixture H_2O-H_2 ($\gamma_1 = 0.99$, $\gamma_3 = 0.01$) with $T_0 = 400°K$, $p_0 = 10$ Pa. Here, for comparison, the corresponding quantities for pure water vapor are also shown (dashed curves). It is evident that even a small amount of H_2 molecules ($\gamma_3 = 0.01$) in the mixture leads to a sharp acceleration of the relaxation of symmetrical vibrations of the H_2O molecule (temperatures T_1 and T_3 increase more rapidly than in pure H_2O). This is explained by the fact that when molecular hydrogen is added to water vapor, the rate of V−V' exchange between the deformation and symmetrical modes of the H_2O molecule increases [11] and the rate of V−T relaxation of the 100 state also increases [19]. In this case, although the molecular hydrogen is a possible "sink" of vibrational energy from the asymmetric mode along the channel $H_2(V = 0) + H_2O(001) \rightarrow H_2(V = 1) + H_2O(000)$, due to the very rapid nonresonent V−V' exchange $\nu_1 \rightleftharpoons \nu_3$, the process accelerating the relaxation of asymmetric vibrations dominates. The characteristics of vibrational energy exchange in H_2O-H_2 mixtures examined above lead to a decrease in the magnitude of the gain α_n^m and specific radiation energy E_n^m compared to the corresponding values for pure water vapor. Figure 3 shows their distributions along the length of the relaxation zone for the transitions studied − $030(5_{32}) \rightarrow 001(4_{43})$ (curves 6 and 7, respectively). Further increase in the H_2 content in the mixture leads to an even greater degradation of the inversion characteristics of the medium and shortens the amplification zone. This is illustrated in Fig. 4 where the distributions $\alpha_n^m(x)$ (dashed lines) and $E_n^m(x)$ (continuous lines) behind the shock wave front ($M_0 = 6.0$) are shown for H_2O-H_2 mixtures with different content of molecular hydrogen: $\gamma_3 = 0.01$ for curve 1, $\gamma_3 = 0.05$ for curve 2, and $\gamma_3 = 0.1$ for curve 3 with the initial parameters as before. Thus, if for $\gamma_3 = 0.01$, the length of the amplification zone is ~0.32 cm, then for $\gamma_3 = 0.1$, its magnitude decreases to ~0.17 cm, while the maximum gain in this case decreases by a factor of 1.5.

The addition of molecular oxygen to water vapor does not lead to such an appreciable, as in the case of H_2, change in the relaxation rate of the system and shortening of the amplification zone. The decrease in the values of the gain and specific radiation energy is explained in this case by the decrease in the number of inverted particles per unit volume (γ_1 decreases).

Thus, the numerical study carried out has shown that the gas dynamic water vapor laser, using the rapid increase of the translational temperature in shock waves, can serve as a powerful source of coherent radiation in the near infrared region of the spectrum. At the same time, the magnitude of the gain and the magnitude of the specific radiation energy can attain, respectively, 1.5 m^{-1} and 30 J/g.

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