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FORMATION OF A NONEQUILIBRIUM ENERGY DISTRIBUTION OVER VIBRATIONAL DEGREES OF FREEDOM OF THE H_2O MOLECULE AS WATER VAPOR EXPANDS IN A SUPERSONIC NOZZLE

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The study of the kinetics of inelastic collisions and the construction of models of vibrational energy transfer in mixtures containing water vapor are needed not only because of interest in the possibility of obtaining emission in the far-infrared and submillimeter ranges using a (H_2O-H_2-He) mixture as the active medium [1-7] and modeling the characteristics of such lasers, but also for the analysis of nonequilibrium processes in chemically reactive gases ($H_2 + O_2$) with excited vibrational degrees of freedom and in the passage of strong IR radiation through the atmosphere [8, 9]. Moreover, water vapor is always present in the products of combustion of hydrocarbons in air, which are used in CO_2 gas-dynamic lasers (GDLs) [10].

A small number of experimental papers have been devoted to the kinetics of vibrational energy transfer in mixtures based on water vapor. The excitation and subsequent relaxation

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of vibrational states of H_2O in an electric discharge were studied in [3, 4, 11, 12], nonequilibrium excitation behind a shock in [13], and that produced by resonance radiation was studied in [14]. On the basis of those results, a model of vibrational energy transfer in ($H_2O-H_2-O_2$) and (H_2O-H_2-He) mixtures has been suggested in [15-17]. Calculations using it have shown the possibility of producing a nonequilibrium energy distribution over vibrational degrees of freedom of the H_2O molecule and even obtaining a population inversion between levels of the asymmetric (symmetric) and deformation H_2O modes [001(100) → 020 transitions] as water vapor or a (H_2O-H_2-He) mixture expands in a supersonic nozzle. No experimental analysis of that possibility has yet been made, however.

The purpose of the present work is a comprehensive calculated-experimental study of the production of a nonequilibrium energy distribution over vibrational degrees of freedom of H_2O molecules as water vapor expands in a supersonic nozzle and improvement of the previously developed model of vibrational energy transfer.

1. Model of Vibrational Energy Transfer in Water Vapor. The earlier analysis [15-18] showed that the model of local vibrational temperatures can be used to describe vibrational energy transfer as water vapor expands in a nozzle or is heated in a shock in the absence of condensation or the formation of complex compounds and dimers, just as for other polyatomic molecules (CO_2, N_2O, CS_2, etc.). The following energy transfer channels are the most likely here:

$$1)\ H_2O(001) + M \rightleftarrows H_2O(100) + M \quad (W^M_{3,1}),$$

$$2)\ H_2O(001) + M \rightleftarrows H_2O(020) + M \quad (W^M_{3,2}),$$

$$3)\ H_2O(100) + M \rightleftarrows H_2O(020) + M \quad (W^M_{1,2}),$$

$$4)\ H_2O(010) + M \rightleftarrows H_2O(000) + M \quad (W^M_{2,0}).$$

Here $W^M_{p,k}$ are the rate constants of intramolecular energy transfer between states p and k in a collision with particles M (M = H_2O or other structureless particles such as He or Ar); p, k = 1, 2, 3 correspond to symmetric, deformation, and asymmetric types of vibrations of the H_2O molecule, and k = 0 corresponds to its unexcited state. The system of equations describing energy transfer through the identified channels under the adopted assumptions can be represented in the form

$$\frac{d\varepsilon_1}{dt} = \frac{P}{KT}[L_{3,1}W_{3,1} - L_{1,2}W_{1,2}]; \tag{1.1}$$

$$\frac{d\varepsilon_2}{dt} = \frac{P}{KT}[2L_{1,2}W_{1,2} + 2L_{3,2}W_{3,2} - L_{2,0}W_{2,0}]; \tag{1.2}$$

$$\frac{d\varepsilon_3}{dt} = \frac{P}{KT}[-L_{3,1}W_{3,1} - L_{3,2}W_{3,2}],$$

$$L_{p,k} = \frac{y_p^{r_p} - y_k^{r_k}\exp[(r_k\theta_k - r_p\theta_p)/T]}{\prod\limits_{i=p,k}(1-y_i)^{r_i}}, \tag{1.3}$$

$$y_p = \exp(-\theta_p/T_p),\ y_{p0} = \exp(-\theta_p/T),$$

$$\varepsilon_p = \frac{y_p}{1-y_p}, \quad L_{p,0} = \frac{y_p - y_{p0}}{1-y_p}, \quad W_{p,k} = \sum_i W^i_{p,k} j_i.$$

Here P and T are the gas pressure and temperature; K is Boltzmann's constant; θ_p and T_p are the characteristic and local vibrational temperatures of the p model (θ_1 = 5264 K, θ_2 = 2796.48 K, θ_3 = 5408.6 K); $r_{k(p)}$ are the numbers of vibrational quanta gained or lost by mode k(p) in VV' or VT transfer; j_i is the molar fraction of the i-th component in the mixture; i = (H_2O, He, H_2).

Let us consider in more detail the choice of the temperature dependences $W_{p,k}(T)$, since the correct determination of $W_{p,k}$ has considerable influence on the agreement of the model with reality. Both theoretical and experimental data on the kinetics of vibrational energy transfer in water vapor are inadequate. In earlier calculations of water vapor flow in [15-18], therefore, estimates were used for $W_{1,2}$ and $W_{3,1}$ Significant material has now been accumulated only on $W^{H_2O}_{2,0}$ [13, 14, 19-31]. Measurements in the range T = 255-2500 K indicate an anomalously high rate of VT relaxation in comparison with other triatomic molecules - CO_2, N_2O, and CS_2. According to [32], all experimental results can be divided into three groups. In the first, data on $W^{H_2O}_{2,0}$ were obtained at low partial water vapor pressures or in mixtures with Ar and N_2 [13, 14, 19-24], the second contains all results [25-29] for mixtures

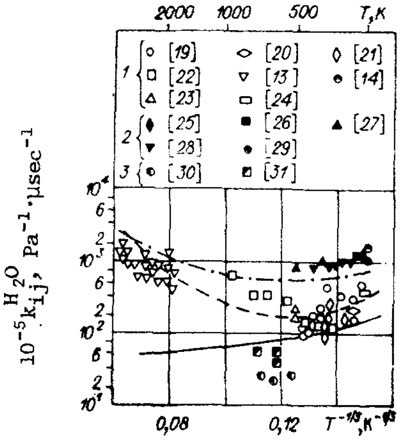

Fig. 1

containing O_2, and the third contains results [30, 31] found at high water vapor pressures, (1-2.71)·10^5 Pa (Fig. 1, points 1-3, respectively). It has been suggested [32] that the data of the first group be interpreted as intrinsic VT relaxation of the $H_2O(010)$ state. At the same time, in interpreting results in the second group one must allow for the possible production of excited $(H_2O)_2^*$ complexes, with their subsequent spontaneous decay, accelerated by VT relaxation, while for the third group one must allow for the production and decay of $(H_2O)_2$ dimers, which retard the deactivation of the $H_2O(010)$ state. Conditions under which no $(H_2O)_2^*$ or dimers are produced (pure water vapor and $P < 0.1$ MPa) are considered in the present paper. We therefore ignored data in the second and third groups in determining $W_{2,0}^{H_2O}\times(T)$. As follows from [33, 34], in molecules containing H and D atoms and having large rotational quantum numbers (H_2O, D_2O, NH_3, etc.), vibrational–rotational (VR) transfer can significantly affect VT relaxation, which leads to a significant difference of $W_{2,0}(T)$ from the Landau–Taylor relationship at low temperatures. In constructing the approximating function $W_{2,0}(T)$ from the experiments of [13, 19-24], therefore, we allowed for the fact that resonance VR transfer contributes significantly to $H_2O(010)$ deactivation at $T < T_*$ ($T_* = 513$ K for H_2O deformation vibrations, where T_* is the characteristic temperature [34]), while at $T > T_*$ the experimental data are described by the Landau–Taylor relationship. The approximating formula for $W_{2,0}^{H_2O}(T)$ can then be represented in the form

$$W^{H_2O}(T) = KT\,10^{8,273-99,1T^{-1/3}+408,127T^{-2/3}}\ \text{cm}^3/\text{sec}. \tag{1.4}$$

The approximating function $W_{2,0}^{H_2O}(T)$ used in [17] was obtained with allowance for data in the second group, and at $T \lesssim 700$ K it yields exaggerated values in comparison with (1.4) (they differ fourfold at $T = 300$ K).

There are considerably fewer published experimental data on $W_{1,2}^{H_2O}$, $W_{3,2}^{H_2O}$, and $W_{1,3}^{H_2O}$. An indirect determination of $W_{1,2}^{H_2O}$ and $W_{3,2}^{H_2O}$, based on the time variation of the gain and generation power of a pulsed, electric-discharge H_2O laser, yielded $W_{1,2}^{H_2O} = 4.53\cdot10^{-11}$ cm³/sec and $W_{3,2}^{H_2O} = 2.2\cdot10^{-11}$ cm³/sec [12]. Here it is not clear, however, to what temperature these results should be ascribed (presumably [14], $T = 600$ K in this experiment). Moreover, an analysis shows that these values of $W_{1,2}^{H_2O}$ and $W_{3,2}^{H_2O}$ might have been considerably exaggerated in analyzing the experimental results, since Sarjeant et al. [12] used a simplified two-level model. Direct measurements of $W_{1,2}^{H_2O}$ by the laser fluorescence method for the $H_2{}^{18}O$ molecule at $T = 298$ K have been carried out in [13]. In analyzing the data, it was assumed that quasi-equilibrium exists between the $H_2O(001)$ and $H_2O(100)$ states, and simultaneous energy relaxation of the ν_1 and ν_2 modes of H_2O by the channel $H_2O(001, 100) + M \rightarrow H_2O(020) + M$ was analyzed. It was found that $W_{1,2}^{H_2O}$ is smaller than $W_{2,0}^{H_2O}$, which was also determined in that paper [$W_{1,2}^{H_2O} = 2.2\cdot10^{-11}$ cm³/sec and $W_{2,0}^{H_2O} = (5.5\text{-}9.1)\cdot10^{-11}$ cm³/sec]. With allowance for the accuracy in determining $W_{2,0}^{H_2O}$, we have $W_{1,2}^{H_2O} = 0.293W_{2,0}^{H_2O}$. The value of $W_{2,0}^{H_2O}$ measured in [14] is more than four times the rate constant of VT relaxation of the $H_2O(010)$ state obtained by other authors and given by the approximating formula (1.4). In the suggested model we shall assume that at $T = 300$ K the ratio of $W_{1,2}^{H_2O}$ and $W_{2,0}^{H_2O}$ from [14] is preserved, but $W_{2,0}^{H_2O}$ is determined from (1.4) and agrees with the data of [13, 20, 24] (i.e., in our model $W_{1,2}^{H_2O}$ = $4.9 \cdot 10^{-12}$ cm³/sec at T = 300 K). The temperature dependence $W_{1,2}^{H_2O}(T)$ was calculated from the theory of [34]. Here the approximating formula for $W_{1,2}^{H_2O}(T)$ is

$$W_{1,2}^{H_2O} = 10^{-9,339-25,61T^{-1/3}+82,943T^{-2/3}}\ \mathrm{cm^3/sec}. \tag{1.5}$$

The temperature dependence $k_{1,2}^{H_2O}(T)$ corresponding to (1.5) is shown by a solid curve in Fig. 1, while $k_{2,0}^{H_2O}(T)$ corresponding to (1.4) is shown by a dashed curve ($k_{ij} = W_{ij}/kT$). In [17] it was suggested taking $W_{1,2}^{H_2O} = 0.1935W_{2,0}^{H_2O}$ in the range T = 300-2500 K. For $W_{3,2}^{H_2O}(T)$ in the entire range of T (T = 300-2500 K), as in [17], we took $W_{3,2}^{H_2O}(T) = 0.486W_{1,2}^{H_2O}(T)$. We could find no published experimental data on $W_{3,1}^{H_2O}$. In the analysis of experimental results in [14], it was assumed that VV' transfer by channel 1 occurs considerably faster than all other VV' and VT processes. In the present paper we determined $W_{3,1}^{H_2O}$ at T = 300-2500 K as follows. Calculations based on the theory of [34, 35] showed that $W_{3,1}^{H_2O} = 7.53W_{1,2}^{H_2O}$ at T = 300 K. Using the value of $W_{1,2}^{H_2O}$ (T = 300 K) found from (1.5), we obtain $W_{3,1}^{H_2O}$ (T = 300 K) = $2.18 \cdot 10^{-11}$ cm³/sec. This was taken as the reference point, and the temperature dependence was determined from the theory of [34]. The approximating formula for $W_{3,1}^{H_2O}(T)$ is then

$$W_{3,1}^{H_2O}(T) = 10^{-6,246-55,25T^{-1/3}+172,069T^{-2/3}}\ \mathrm{cm^3/sec}. \tag{1.6}$$

This function for $k_{3,1}^{H_2O}$ is shown by a dash-dot line in Fig. 1.

2. Analysis of the Results. One way to investigate a nonequilibrium energy distribution over internal degrees of freedom of molecules in gas streams and to test theoretical models is to compare the calculated absorption coefficient with experimental measurements. Here it is desirable to probe the stream with radiation at the resonance frequency of the center of the line of a vibrational-translational transition whose upper and lower states belong to modes with considerably different relaxation times. For the H_2O molecule, the $020(5_{50}) \rightarrow 001(6_{33})$ transition satisfies this condition. The absorption coefficient for the i-th line of the vibraitonal-rotational transition $m(v_1', v_2', v_3', j', k_a', k_c') \rightarrow n(v_1'', v_2'', v_3'', j'', k_a'', k_c'')$. of the H_2O molecules, where v_i (i = 1, 2, 3) are vibrational and j, k_q, and k_c are rotational quantum numbers, is determined by the following equation, assuming a local Boltzmann distribution within each mode:

$$k_\nu = \frac{\lambda_{mn}^3}{8\pi}\left(\frac{\mu_{H_2O}}{2\pi RT}\right)^{1/2} A_{mn}\left(\frac{g_n}{g_m}N_m - N_n\right)H_\Phi(\tilde{x}, a),$$

$$N_m = \frac{P}{KT}\gamma_{H_2O}\frac{g_m}{Z_v Z_r^m}\exp\left(-\frac{E_v^m}{kT_m} - \frac{E_r^m}{KT}\right),$$

$$N_n = \frac{P}{KT}\gamma_{H_2O}\frac{g_n}{Z_v Z_r^n}\exp\left(-\frac{E_v^n}{KT_n} - \frac{E_r^n}{KT}\right),$$

$$Z_r^v = 2\left(\frac{\pi T^3}{A_v B_v C_v}\right)^{1/2}, \quad Z_v = \prod_{i=1}^{3}[1 - \exp(-\theta_i/T_i)]^{-1}.$$

Here λ_{mn} is the wavelength at the line center of the absorbing transition; μ_{H_2O} is the molecular mass of water vapor; R is the universal gas constant; E_v^q and E_r^q are the vibrational and rotational energies of the molecule in the q state (q = m, n); A_v, B_v, and C_v are the rotational constants in the $v = v_1v_2v_3$ state; A_{mn} is the Einstein coefficient; $H_\Phi(\tilde{x}, a)$ ($a = \sqrt{\ln 2}bc/b_D$, $\tilde{x} = 2\Delta\nu\sqrt{\ln 2}/b_D$, and $\Delta\nu$ is the off-resonance amount) is the Voigt function; g_q is the multiplicity of degeneracy of the q state ($g_q = g_v^q g_j^q g_I^q$), where g_v^q, g_j^q, and g_I^q are the multiplicities of degeneracy with respect to vibration, rotation, and nuclear spin; for the H_2O molecule $g_v = 1$ and $g_j = 2j + 1$, while $g_I = 3$ for antisymmetric and $g_I = 1$ for symmetric levels.

In calculating the absorption coefficient at the frequency of the probe laser (ν_I = 356.15 cm⁻¹), we allowed for the possible overlap of spectral lines of purely rotational transitions in the range $\Delta\nu$ = 356.5-358.5 cm⁻¹ at adjacent frequencies toward the center of the main $020(5_{50}) \rightarrow 001(6_{33})$ transition. Here we used the model analyzed in [36]. The quantity A_{mn} and the collisional broadening coefficient for the main $020(5_{50}) \rightarrow 001(6_{33})$ transition were taken in accordance with [36]: 2 sec⁻¹ and $4.5 \cdot 10^{-6}$ cm⁻¹·Pa⁻¹. For it we have g_I = 3, $T_m = T_2$, and $T_n = T_3$, and for purely rotational transitions in the $(0v_20)$ state we have

$T_n = T_m = T_2$. The temperature dependence of the collisional broadening coefficients is $\sim T^{-0.62}$. To produce the supersonic stream in the experiments, we used a wedge-shaped nozzle with an opening angle $\alpha = 30°$ and critical cross sections of different sizes: $h_* = 2$, 1, and 0.5 mm. The pressure and temperature at the nozzle entrance were varied in the ranges $P_0 = 0.195\text{-}0.553$ MPa and $T_0 = 1760\text{-}2580$ K. The nozzle abutted the end of the shock tube, which has been described in [36]. The nozzle width was 98 mm. The absorption coefficient in the supersonic stream was measured, as in the case of measurements behind an incident shock [36], in a one-pass scheme (Fig. 2a). Thin polyethylene was used for the side windows 4 of the supersonic channel. The stream was probed with radiation from a continuous, electric-discharge H_2O laser 1 at $\lambda = 27.971$ µm, in resonance with the $020(5_{50}) \rightarrow 001(6_{33})$ transition of the H_2O molecule. A semiconductor detector of Si:B crystal, cooled with liquid helium, was used as the receiver 3. In the entrance part of the nozzle, a thin aluminum membrane 2 separated the channel of the shock tube from the evacuated damping vessel containing the nozzle. Evacuation assured fairly rapid startup of the nozzle and arrival of the outflow at a quasi-steady state in ≈20 µsec. This time was monitored from the delay in readings of the sensor 5 for the pressure P_0', mounted in the supersonic stream, relative to the time of appearance of the signal for the pressure P_0 at the end of the tube. For small h_*, the supersonic stream may separate from the nozzle walls in the presence of counterpressure in the damping vessel and at low P_0. To eliminate separation, the vessel was evacuated to a pressure not exceeding 13.3 Pa before an experiment. The nozzle then operated with underexpansion in all of the investigated regimes. The regime of quasi-steady outflow was monitored from the pressure sensor readings. The pressure P_0' beyond the detached shock has a well-known relationship [37] to the pressure P_0 at the nozzle entrance. The results of measurements of P_0/P_0' in nozzles with $h_* = 2$, 1, and 0.5 mm are given in Fig. 2b. The measurement accuracy is ≈30%. The values of P_0/P_0' agree, to within the measurement error, with the calculated function for an ideal gas with an adiabatic index $\gamma = 1.33$ (solid line in Fig. 2b). The value of P_0' serves as a reliable indicator of the process of opening of the membrane, since the time of appearance of the P_0' signal in the sensor coincides with the time of rupture of the membrane, as well as with the start of the signal of absorption of the probe radiation (the $\Delta\Phi$ signal in Fig. 2c).

A typical oscillogram of the variation of $\Delta\Phi$ and P_0' is given in Fig. 2c for measurements in a nozzle with $h_* = 2$ mm for $P_0 = 0.293$ MPa and $T_0 = 2020$ K. The pressure P_0' is determined by the degree of opening of the membrane, and when it did not open completely, the considerable decrease in P_0' led to an increase (more than double) in the ratio P_0/P_0' over the calculated value. Estimates show that flow in the nozzle is nearly one-dimensional, and we can ignore the influence of the boundary layer on the variation of the gas parameters and assume the existence of equilibrium between translational and rotational degrees of freedom. The approximation of one-dimensional steady-state flow of an inviscid, thermally nonconducting gas was therefore used to calculate the parameters in the expansion of water vapor in a wedge-shaped nozzle. The procedure for simultaneous integration of the equations of gas dynamics and vibrational kinetics is discussed in [15] and has been used in the present paper.

Our calculations in a nozzle with $h_* = 2$ mm showed that the flow is almost in equilibrium in the entire range of the parameters under consideration. The values of P and T in the measurement cross section, located 15 mm from the critical cross section, then coincide with the parameters beyond the shock for $P = 6.5\text{-}8.5$ kPa and $T = 950\text{-}1050$ K (for these P and T, the contribution of spectral lines at adjacent frequencies to the absorption at $\nu_I = 357.516$ cm^{-1} does not exceed 5%), at which k_ν was measured in [36]. Investigating the stream in a nozzle with $h_* = 2$ mm thus enables us to compare the flow characteristics obtained by two different ways: heating water vapor (behind an incident shock) and cooling it (in a nozzle). In experiments using a nozzle with $h_* = 2$ mm, the conditions under which water vapor is supersaturated arise in the measurement cross section near the nozzle walls, where the gas temperature is close to the temperature of the cold walls and the saturation vapor pressure is relatively low at that temperature. As a result, the vapor condenses on the inner surface of the supersonic part of the nozzle. A similar phenomenon has been observed experimentally behind an incident shock [38].

A typical feature of an oscillogram of absorption in the presence of condensation, both in measurements in a nozzle with $h_* = 2$ mm and behind an incident shock, is the continuous rise of the $\Delta\Phi$ signal (Fig. 2c), associated with absorption of radiation by the condensate film or with a change in the conditions in the entrance part of the nozzle. To determine the absorption coefficient of water vapor in the stream, values of the signal near the front were used in analyzing the oscillograms (minimizing the influence of this effect on the results).

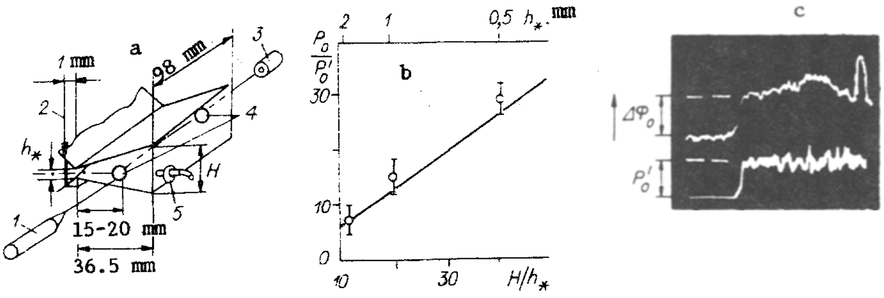

Fig. 2

In experiments using nozzles with $h_* = 1$ and 0.5 mm, water vapor in the measurement cross section was not supersaturated and the level of the absorption signal remained unchanged. The results of measuring P_0' in the stream core (Fig. 2b) agree, to within the measurement error, with the calculated function for an ideal gas with $\gamma = 1.33$. This means that under all of the analyzed conditions, attached flow of water vapor is established in the nozzles, and its condensation and other wall effects do not significantly change the outflow conditions.

In Fig. 3 we show the calculated function $k_\nu(T)$ obtained for the measurement conditions in the nozzle with $h_* = 2$ mm and behind a shock at P = 6.5-8.5 kPa, as well as experimental values of k_ν corresponding to measurements in the nozzle and behind the shock (points 1 and 2). It is seen that the model used for absorption in a water vapor stream correctly describes the experimental results in the presence of equilibrium between the transitional, rotational, and vibrational degrees of freedom of the H_2O molecule. In addition, the agreement between the experimental results obtained in a supersonic expanding stream of water vapor and behind a shock is important methodologically, since it indicates the correctness of the model concepts about the features of the formation of water vapor flow in a shock tube and a nozzle.

The calculations of water vapor flow using our model of vibrational energy transfer showed that with decreasing h_* and increasing T_0, the thermodynamic equilibrium between vibrational and translational degrees of freedom is disrupted becuase the characteristic time that the investigated gas spends in the nozzle becomes less than the greater of the times of VT and VV' transfer. Here equilibrium between deformation and asymmetric (symmetric) vibrations of H_2O molecules is primarily violated [quasi-equilibrium exists between symmetric and asymmetric H_2O vibrations for the parameters under consideration, and the VV' transfer $H_2O(100) \rightarrow H_2O(020)$ is the decisive channel of energy relaxation for these vibrations]. This is illustrated by Fig. 4a, b, in which we give distributions of vibrational temperature T_3 and of the difference $\Delta T_{32} = T_3 - T_2$ for $h_* = 1$ mm ($T_0 = 2270$ K and $P_0 = 0.287$ MPa) and $h_* = 0.5$ mm (T = 2580 K and P = 0.357 MPa), respectively (the values of P and T correspond to the experimental conditions). This is also confirmed by measurements of k_ν in nozzles with $h_* = 1$ and 0.5 mm for the indicated P and T. In Fig. 5a-c we give functions $k_\nu(x)$ corresponding to equilibrium flow (1) and calculated using our model of vibrational energy transfer (2), as well as the results of measurements in nozzles with $h_* = 2$, 1, and 0.5 mm (P = 0.202, 0.267, and 0.357 MPa and T = 2320, 2270, and 2580 K), respectively (x is distance from the critical cross section). It is seen that the theoretical values of k_ν lie somewhat above the experimental ones, but both of them differ considerably from the values of k_ν corresponding to the parameters of the equilibrium stream. These relationships are also manifested at other values of P and T. Agreement with exeriment in the entire range of variation of P, T, and h_* can be obtained by using a rate constant $W_{1,2}^{H_2O}$ for VV' transfer that is three quarters of (1.5) (curves 3 in Fig. 5; recall that it is $W_{1,2}^{H_2O}$ that determines the degree of departure of the system from equilibrium under our conditions). This is also evident from Table 1, in which we give the stagnation parameters, the coordinate $\Delta\ell$ of the measurement cross section in the nozzle, and the measured (k_ν^m) and calculated (k_ν and k_ν^e) absorption coefficients. We calculated k_ν^e under the assumption of equilibrium flow of water vapor and using our model of vibrational energy transfer with $W_{1,2}^{H_2O}$ determined from (1.5). In calculating k_ν we used a constant $W_{1,2}^{H_2O}$, three quarters of that from (1.5); the remaining constants were not changed and corresponded to the conditions of the k_ν^e calculations.

Using the system of rate constants $W_{p,k}$ from [17] leads to almost the same values of k_ν, in the investigated range of the parameters, as for the model considered here with $W_{1,2}^{H_2O}$ that is three quarters of (1.5) (the difference does not exceed 10%). In earlier calculations [17],

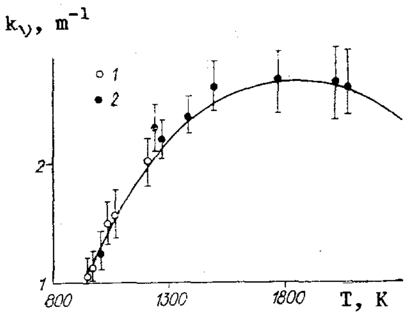

Fig. 3

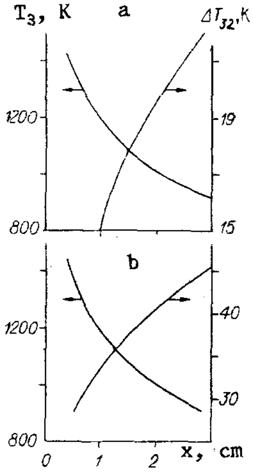

Fig. 4

TABLE 1

10 P_0, MPa	T_0, K	h_*, mm	$\Delta\ell$, mm	$k_\nu^{e\prime}$, m^{-1}	k_ν, m^{-1}	k^e_ν, m^{-1}
1,95	1760	2	15	0,86±0,18	0,89	0,89
2,18	1810	2	15	1.07±0,14	1,02	1,02
2,53	1870	2	15	1,39±0,31	1,22	1,22
2,52	1880	2	15	1,12±0,25	1,22	1,22
2,77	1960	2	15	1,22±0,2	1,41	1,41
2.93	2020	2	15	1.5±0,2	1,55	1,55
2,73	2050	1	16.8	0,61±0,15	0,66	0,82
2,86	2180	1	16.8	0,84±0,21	0,89	1,05
3.09	2200	1	16.8	0,86±0,22	0,96	1,15
4,57	2220	1	16.8	0,86±0,36	0,97	1,2
2,86	2290	1	16.8	1,0±0,17	1,03	1,4
2,18	2300	1	16,8	0,88±0,17	1,0	1,32
4,86	2340	1	16.8	1,05±0,16	1,32	1,5
5.43	2360	1	16,8	1.17±0,21	1,39	1,56
2,21	2500	1	16.8	1,25±0,11	1,27	1,68
2,67	2140	1	16,8	0,53±0,16	0,53	0,67
4,21	2170	1	16.8	0,57±0,16	0,65	0,75
4,6	2180	1	16,8	0,64±0,11	0,65	0,82
3,07	2320	1	16,8	0,69±0,12	0,82	0,975
5,53	2360	1	16.8	0,916±0,19	0,995	1,15
4,94	2360	1	16,8	0,825±0,13	0,94	1,08
3,0	1930	0,5	15	<0,2	0,15	0,28
4,23	2200	0,5	15	0,44±0,11	0,44	0,56
3,57	2580	0,5	20	0,56±0,14	0,55	0,92

the Einstein coefficient was taken, in accordance with [1], to be $A_{mn} = 6$ sec^{-1}, leading to threefold exaggeration of the calculated k_ν over the measured values. Using the results of [14] as reference points in determining $W^{H_2O}_{1,2}(T)$ and $W^{H_2O}_{1,2}(T)$ prevents one from obtaining agreement with experimental values of k_ν [a calculation using $W^{H_2O}_{1,2}(T)$ and $W^{H_2O}_{2,0}(T)$ determined in this way yields $k_\nu \simeq k^e_\nu$ in the entire range of the investigated parameters].

We can thus state that as preheated water vapor expands in a supersonic nozzle, at $\tau_R < \tau_{VV}$, (τ_R is the characteristic time the gas spends on the nozzle) there is a nonequilibrium distribution of H_2O molecules over vibrational degrees of freedom, and the proposed model of vibrational energy transfer correctly describes the experimental results on measuring the absorption coefficient for radiation with $\lambda = 27.971$ µm.

Let us use that model for a quantitative analysis of the possibility of obtaining amplification on the $001(6_{33}) \rightarrow 020(5_{50})$ transition during rapid cooling of water vapor in a supersonic nozzle. Profiled rather than wedge-shaped nozzles are usually used in gas-dynamic lasers (GDLs). This is because of the need to provide attached flow with a uniform field of the parameters at the nozzle exit and the desire to obtain the most uniform possible stream in the radiation-generation zone. We shall therefore consider flat nozzles with a profile supersonic section of minimal length, designed for attached flow with an expansion ratio $\varepsilon = 20$; its subsonic section has a wedge-shaped entrance with a 90° opening angle.

In Fig. 6 we give the distributions over the longitudinal coordinate ($\bar{x} = 2x/h_*$) of the vibrational temperatures T_i (i = 1, 2, and 3 correspond to symmetric, deformation, and asymmetric H_2O vibrations: curves 1-3) and translational temperature T (curves 4), as well as the

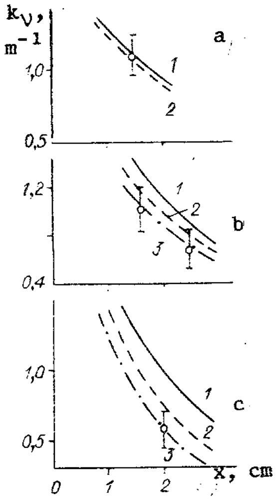

Fig. 5

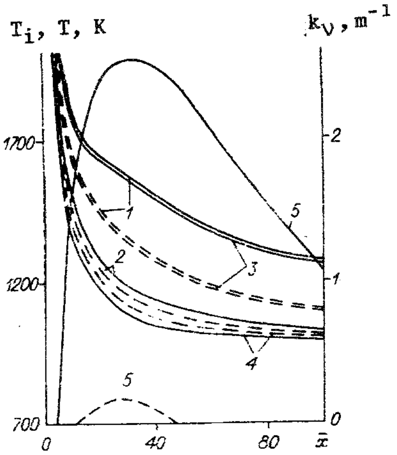

Fig. 6

gain (curves 5) for the flow of water vapor with T_0 = 2500 K and P_0 = 0.3 MPa in nozzles with h_* = 0.1 and 0.2 mm (solid and dashed curves). It is seen that in the nozzle with h_* = 0.1 mm at the given P_0 and T_0, a positive gain is reached on the $001(6_{33}) \to 020(5_{50})$ transition; the maximum in its distribution lies inside the nozzle (k_ν = 2.52 m^{-1}), and although it decreases toward the nozzle cut ($\bar{x}$ = 100), it is fairly large even there ($\approx$1 m^{-1}). For h_* = 0.2 mm, $k_\nu > 0$ occurs only inside the nozzle. The degree of nonequilibrium and the gain increase sharply with decreasing P_0. For a decrease in P_0 by one third, for example, k_ν doubles at the cut of a nozzle with h_* = 0.1 mm.

The values of k_ν obtained point to the possibility of achieving an ecologically clean water vapor GDL. A peculiarity of such a laser is the need to use nozzles with rapid expansion (axisymmetric profiled nozzles, for example) and considerably smaller values of $P_0 h_*$ (by a factor of 50-100) than in traditional CO_2 GDLs. Special experiments are needed, however, to confirm these conclusions.

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