VIBRATIONAL RELAXATION AND EMISSION OF H_2O DURING THE SHOCK HEATING OF A LOW-DENSITY GAS MIXTURE

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Great interest in the influence of flights of spacecraft (SC) on the state of the atmosphere has recently developed in connection with the active conquest of space [1, 2]. This is connected with the fact that during SC flights large amounts of combustion products are thrown off which can perform various physicochemical actions on the atmosphere, and this action can be quite significant, since in upper layers of the atmosphere, even when the combustion products expand to volumes with a linear size of tens of kilometers, their concentration remains comparable with the concentration of the atmospheric gas.

An SC moves with velocities on the order of several kilometers per second, so that as a result of the gasdynamic interaction of combustion products with the atmospheric gas they are heated to temperatures of several thousand degrees. It is very important to estimate the physicochemical interaction of this gasdynamic stage, since physicochemical processes are sharply activated at high temperatures. The description of the gasdynamic process of interaction of the combustion products of SC engines with the atmosphere is very complicated and, generally speaking, depends on the concrete conditions. From the point of view of relaxation processes, however, it has one common feature. Because of the low density, the combustion products are mixed rapidly with the atmospheric gas. Rapid relaxation of the combustion products with respect to translational degrees of freedom occurs during mixing, while relaxation with respect to internal degrees of freedom is retarded. Such a situation can be modeled by shock heating of a gas mixture containing a polyatomic gas which relaxes with respect to internal degrees of freedom.

In the present article we examine, within the framework of this model, one example of a physicochemical interaction – the problem of the vibrational relaxation of H_2O molecules in a mixture with N_2 behind a shock wave front. At low densities the relaxation of the internal degrees of freedom of molecular gases has a specific character. The specifics consist in the fact that in this case the relaxation times become longer than the lifetimes of the excited levels and emission strongly affects the relaxation process. It should be noted that relaxation of this character is practically unreproducible under laboratory conditions.

1. Structure of the H_2O Molecule and Properties of Vibrational Relaxation

The water molecule is nonlinear and has three fundamental frequencies, corresponding to the symmetric (ν_1), deformation (ν_2), and asymmetric (ν_3) types of vibrations (Fig. 1). Being confined to temperature on the order of 4000°K, we shall consider only the lower vibrational levels with energies $E_1 = 5265°K$, $E_2 = 2300°K$, and $E_3 = 5409°K$. A diagram of them is also presented in Fig. 1. Emission from the levels ν_1 and ν_3, which are close to each other, to the ground level takes place at the wavelength of ~ 2.7 μm, while emission from the level ν_2 takes place at the wavelength of ~ 6.3 μm. The lifetimes of the levels ν_1, ν_2, and ν_3 are $\tau_1 = 0.59$ sec, $\tau_2 = 0.12$ sec, and $\tau_3 = 0.03$ sec, respectively [3]. The levels ν_2 and $2\nu_2$ can be treated as levels of a harmonic oscillator [4], so that the lifetime of $2\nu_2$ is $(1/2)\tau_2$.

The vibrational relaxation of the H_2O molecule has not been studied sufficiently well. The most reliable seem to be the experimental data, in agreement with each other, on the rate constants of the vibrational relaxation of water obtained in [5], where the emission of H_2O vapor upon the passage of a shock wave through a gas mixture was measured, and in [6], where the relaxation of the H_2O molecule with excitation of vibrational degrees by a laser pulse was studied. The results of these reports agree with theoretical results for the vibrational relaxation of the deformation mode obtained in [7, 8]. The rate constants of vibrational relaxation for all possible transitions of vibrational energy between lower levels of the H_2O molecule are brought together in [10] on the basis of these data and the data from [9]. We note that vibrational relaxation in the collision of water

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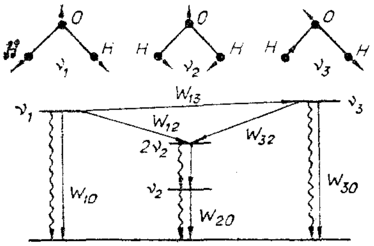

Fig. 1

molecules with each other takes place very rapidly. For example, three collisions are sufficient for excitation of the mode ν_2 from the ground to the first vibrational level. Evidently, this takes place through the active participation of rotational degrees of freedom in vibrational relaxation [5].

The possible relaxation channels are shown schematically in Fig. 1. Estimates made for a temperature of 3500°K show that energy transitions between the following levels take place most rapidly: (010) ⟷ (000), (100) ⟷ (020), and (001) ⟷ (020). The vibrational relaxation constants for these processes are $W_{20}^{H_2O} = 3.8 \cdot 10^{-10}$ cm³/sec, $W_{12}^{H_2O} = 6 \cdot 10^{-10}$ cm³/sec, and $W_{32}^{H_2O} = 3 \cdot 10^{-10}$ cm³/sec. The rate constants of the remaining transitions are considerably lower: $W_{10}^{H_2O} = 1.5 \cdot 10^{-11}$ cm³/sec, $W_{30}^{H_2O} = 1.5 \cdot 10^{-13}$ cm³/sec, and $W_{13}^{H_2O} = 1.7 \cdot 10^{-11}$ cm³/sec. Energy exchange between vibrational levels of the H_2O molecule in the case when the partners in the collision are N_2, O_2, and Ar molecules takes place about 150 times slower than the exchange of vibrational energy of water molecules with each other [5, 6].

The vibrational relaxation of water molecules in a mixture with N_2 at a total density $n_0 = 10^7$–10^{14} cm^{-3} is analyzed in the report. Estimates show that for $n_0 \lesssim 10^{10}$ cm^{-3} the relaxation times of vibrational levels considerably exceed the lifetimes of these levels (for $n_0 = 10^{10}$ cm^{-3} the shortest times of energy exchange between the (100) and (020) levels is about 50 sec). Therefore, at these densities the relaxation process takes place as follows: All vibrational modes are excited independently, there are no transitions between modes, and deactivation proceeds through spontaneous emission. For $n_0 \gtrsim 10^{12}$ cm^{-3} the times of vibrational relaxation become less than the lifetimes of the excited levels, and energy exchange between modes starts to play an important role in the process of vibrational relaxation.

2. Statement of the Problem

Let us consider the vibrational relaxation of H_2O molecules behind a shock wave passing through a mixture of gases $N_2 + H_2O$. As already mentioned, water molecules relax rapidly in collisions with each other. In order to ignore vibrational relaxation in the shock wave front, we assume that the water vapor concentration is low (~1%). At the given concentration the times of vibrational relaxation of H_2O molecules on N_2 are comparable with the times of vibrational relaxation in collisions of H_2O molecules with each other, so that we must also allow for relaxation of H_2O on N_2. The vibrational relaxation of N_2 molecules itself can be ignored, since ~10^4 collisions are needed for N_2 relaxation at $T_t \approx 3000$–4000°K, as estimates show.

The system of equations describing the behavior of the gasdynamic parameters and the populations of vibrational levels behind a shock wave front has the form

$$\left(m^{H_2O}n^{H_2O} + m^{N_2}n^{N_2}\right)u = \left(m^{H_2O}n_0^{H_2O} + m^{N_2}n_0^{N_2}\right)u_0,$$

$$\left(m^{H_2O}n^{H_2O} + m^{N_2}n^{N_2}\right)u^2 + \left(n^{H_2O} + n^{N_2}\right)kT_t = \left(m^{H_2O}n_0^{H_2O} + m^{N_2}n_0^{N_2}\right)u_0^2 + \left(n_0^{H_2O} + n_0^{N_2}\right)kT_{t0},$$

$$\left(m^{H_2O}n^{H_2O} + m^{N_2}n^{N_2}\right)u^3/2 + n^{N_2}uc_pkT_t + n^{H_2O}u\left(c_{pf}kT_t + E_v\right) =$$

$$= \left(m^{H_2O}n_0^{H_2O} + m^{N_2}n_0^{N_2}\right)u_0^3/2 + n_0^{N_2}u_0c_pkT_{t0} + n_0^{H_2O}u_0c_{pf}kT_{t0} - Q,$$

$$\frac{d\alpha_i}{dt} = n^{H_2O}\left[\sum_j W_{ji}^{H_2O}\alpha_j - \left(\sum_j W_{ij}^{H_2O}\right)\alpha_i\right] - \frac{\alpha_i}{\tau_i} + n^{N_2}\left[\sum_j W_{ji}^{N_2}\alpha_j - \left(\sum_j W_{ij}^{N_2}\right)\alpha_i\right],$$

where m^{H_2O} and m^{N_2} are the masses of the H_2O and N_2 molecules; t, u, T_t, n^{N_2}, and n^{H_2O} are the time, velocity, temperature, N_2 density, and H_2O density behind the shock wave; the corresponding parameters ahead of the wave are marked by the index 0; c_p is the heat capacity of N_2; c_{pf} is the heat capacity of water without allowance for vibrational excitation; α_i is the relative population of the i-th vibrational level of H_2O; τ_i is the lifetime of the i-th level; $W_{ij}^{H_2O}$ is the rate constant of the energy transition from the i-th to the j-th level (the partner in the collision is given at the top).

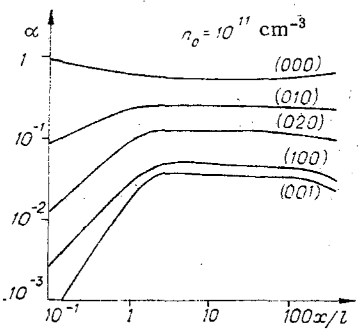

Fig. 2

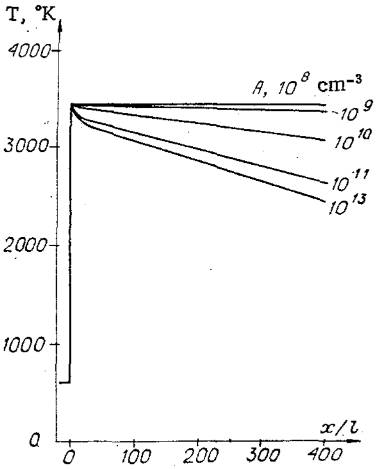

Fig. 3

At $T_t \approx 3000$°K the path length of a quantum is $l_\gamma \approx 10^{17}/n^{H_2O}$ [11], while the mean free path of molecules is $l \approx 10^{15}/n$. Estimates of the characteristic size of a cloud of combustion products give $\sim 10^2$–$10^3\, l$ [12], while the length of the zone of active relaxation is $\sim 10\, l$. Such a region can be considered as optically transparent. The quantity Q represents the energy losses due to emission, $Q = \int\limits_0^x dx \left(\sum\limits_i E_i \frac{\alpha_i}{\tau_i}\right) n^{H_2O}$, where $x = \int\limits_0^t u dt$, E_i is the energy of the i-th vibrational level, and E_V is the total vibrational energy: $E_v = \sum\limits_i E_i \alpha_i$.

The system of equations was solved numerically. The calculations were made in the range of densities $n_0 = n_0^{H_2O} + n_0^{N_2} = 10^7$–$10^{14}$ cm^{-3} for different temperatures T_{t0} and Mach numbers M_0. We considered waves of not too high intensity, such that the temperature of the mixture behind the shock wave did not exceed 3000-4000°K and the excitation predominantly of lower vibrational levels took place. Typical results of the calculations ($T_{t0} = 600$°K, $M_0 = 5$) are presented below.

3. Discussion of Results

The pattern of behavior of the populations of vibrational levels of the H_2O molecule behind a shock wave for $n_0 = 10^{11}$ cm^{-3} is presented in Fig. 2. The distance from the shock wave front, normalized to the local mean free path, is laid out along the abscissa. Immediately behind the front the populations of the excited levels grow sharply, and then at $x/l \approx 1$ a certain quasistationary distribution is established, determined by the balance of vibrational relaxation and emission. This quasistationary distribution slowly varies with time, mainly because the temperature of the mixture decreases due to the removal of radiant energy.

The temperature dependence on the distance behind the shock wave front is presented in Fig. 3. The case when emission is absent is marked by the letter A (we shall call this case adiabatic). For high densities the gas temperature behind the shock wave decreases considerably faster than for low densities. This is connected with the fact that at high densities vibrational relaxation proceeds rapidly and the energy-sink channel through the levels $2\nu_2$ and ν_3 is actively engaged. In this case, therefore, a relatively larger fraction of the energy is emitted than in a less dense gas. The gas velocity behind the shock wave front decreases in accordance with the law of reversal of action, although considerably slower than the temperature.

The maximum populations (along x) of the excited levels and the minimum population of the ground level as functions of the initial density of the mixture are shown in Fig. 4a. The effective vibrational temperature T_V as a function of the initial density n_0 of the mixture is also presented in Fig. 4b as an illustration. The effective vibrational temperature was defined as the temperature corresponding to a given relative population of the level with respect to the Boltzmann distribution. At low densities ($<10^{11}$ cm^{-3}), when the times of vibrational relaxation are longer than the lifetimes of the corresponding levels, the influence of emission on the process of vibrational relaxation is great and the levels are strongly depleted in comparison with the adiabatic case. The effective vibrational temperature naturally proves to be considerably lower than the translational temperature. From this, in particular, we get the important result that at such densities, despite the high translational temperature, dissociation of molecules behind the shock wave will be unlikely, since dissociation takes place through cascade excitation of molecules to high vibrational levels [13].

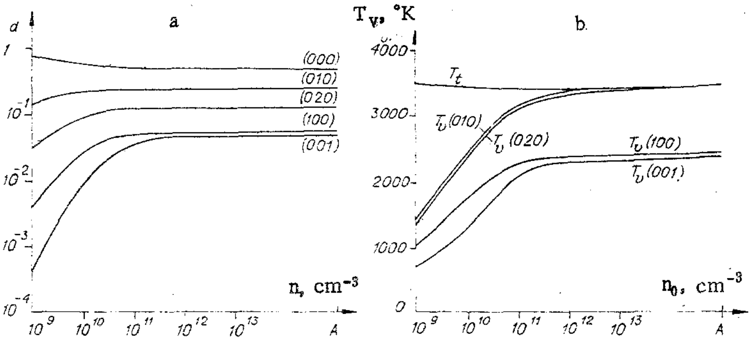

Fig. 4

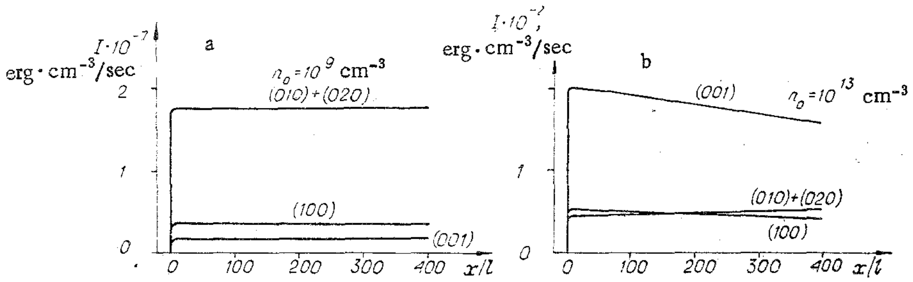

Fig. 5

For densities $n_0 = 10^{11}$ cm^{-3} and higher the populations of the vibrational levels and the vibrational temperature approach their values in the adiabatic case. This happens because the times of vibrational relaxation become small compared with the lifetimes of the corresponding levels, and the levels depleted through emission are rapidly restored through collisions of molecules.

The channels of vibrational relaxation are different in these two limiting cases of low and high densities. At low densities the times of transitions between modes in collisions of molecules are considerably longer than the lifetimes of the excited levels, so that the relaxation of each mode takes place independently. At high densities the opposite situation is observed, and in this case the following relaxation channel becomes dominant: stepwise excitation of the mode ν_2 to the level (020), then energy exchange (020) → (001), and emission (001) → (000). The variations of the emission intensities I of the different modes (Fig. 5a and b) can serve as an illustration of the different character of the relaxation in these two limiting cases. Data for a mixture density $n_0 = 10^9$ cm^{-3} are presented in Fig. 5a. The vibrational modes are excited independently of one another and the emission intensity in each mode is proportional to the population of that mode, so that emission occurs with the maximum intensity in mode ν_2, which has the highest value of α_i/τ_i. At the density $n_0 = 10^{13}$ cm^{-3} (see Fig. 5b) the character of the emission is sharply altered. The level (001), which has the shortest lifetime, mainly radiates owing to the short lifetime and the strong connection with other modes.

LITERATURE CITED

1. A. K. Rebrov, "Modern problems of rarefied gasdynamics," in: Nonequilibrium Processes in Rarefied-Gas Streams [in Russian], Izd. Inst. Teor. Fiz., Sib. Otd. Akad. Nauk SSSR, Novosibirsk (1977).
2. M. Mendillo and J. M. Forbes, "Artificially created holes in the ionosphere," J. Geophys. Res., 83, 151 (1978).
3. R. Goody, Atmospheric Radiation, Clarendon Press, Oxford (1964).
4. G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, van Nostrand, New York (1945).
5. R. T. V. Kung and R. E. Center, "High temperature vibrational relaxation of H_2O by H_2O, He, Ar and N_2," J. Chem. Phys., 62, 2187 (1975).
6. J. Finzi, F. E. Hovis, et al., "Vibrational relaxation of water vapor," J. Chem. Phys., 67, No. 9 (1977).
7. H. K. Shin, "Vibrational relaxation of water at high temperature," J. Phys. Chem., 81, No. 11 (1977).
8. H. K. Shin, "Vibrational relaxation of water molecules near room temperature," J. Chem. Phys., 69, No. 3 (1978).
9. J. A. Blauer and G. R. Nickerson, "A survey of vibrational relaxation data for processes important to $CO_2-N_2-H_2O$ infrared plume radiation," AIAA Pap. No. 74-536 (1974).

10. V. A. Levin and A. M. Starik, "Vibrational energy exchange in H_2O-H_2 mixtures in shock waves," Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 1 (1979).
11. V. B. Berestetskii, E. M. Lifshits, and L. P. Pitaevskii, Relativistic Quantum Theory [in Russian], Part 1, Nauka, Moscow (1968).
12. G. A. Simons, "Rarefaction effect in high-altitude rocket plumes," AIAA J., 10, No. 3 (1972).
13. B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Kinetic Processes in Gases and Molecular Lasers [in Russian], Nauka, Moscow (1980).

ELECTRIFICATION IN TUBE FLOW OF ORGANIC LIQUIDS WITH AN ADMIXTURE OF STRONG ELECTROLYTE

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The electrification of weakly conducting organic liquids is investigated within the framework of continuum mechanics [1]. When such liquids (e.g., hydrocarbons) flow through tubes they acquire an electric charge [2-5]. This leads to the risk of electric discharges and explosions [4]. The conductivity of the considered liquids is due to a small amount of impurity electrolyte, whose molecules dissociate into positive and negative ions. According to recent ideas [2-5], the electrification of organic liquids is due to electrochemical reactions occurring on the tube walls, as a result of which the positive or negative ions of the impurity electrolyte are converted to neutral molecules. The problem of electrification of a liquid in the case of a completely dissociated electrolyte was examined in [5], where the effect of the electric field was ignored. The electrification of a weakly conducting liquid, in the case where the impurity electrolyte dissociates slightly and the dissociation can be regarded as an equilibrium reaction, was investigated in [6].

In this paper we examine the problem of electrification of an initially unchanged weakly conducting organic liquid in laminar flow in a metal tube, where the impurity electrolyte molecules are completely dissociated, and the electric field produced has a significant effect on electrification. The diffusion coefficients and charge numbers of the positive and negative ions are assumed to be equal. In addition, for definiteness we assume that only negative ions are involved in the electrochemical reactions on the tube walls, and the neutral molecules formed are present in excess in comparison with ions. The solution obtained can easily be extended to the case of arbitrary ion charge numbers and electrochemical reactions involving ions of both kinds on the tube walls.

1. The system of differential equations and boundary conditions at the tube entrance B and on the wall S, describing the electrification of an organic liquid, has the form

$$\begin{gathered}\operatorname{div}\left(n_{\pm}\mathbf{u} \pm \frac{ezD}{kT} n_{\pm}\mathbf{E} - D\nabla n_{\pm}\right) = 0,\\ \varepsilon \operatorname{div}\mathbf{E} = 4\pi ez(n_{+} - n_{-}),\ \operatorname{rot}\mathbf{E} = 0,\ n_{\pm}|_{B} = n^{0},\\ \left(\left[\frac{ezD}{kT} n_{+}\mathbf{E} - D\nabla n_{+}\right]\cdot\mathbf{v}\right)\Big|_{S} = 0,\ \left(\left[-\frac{ezD}{kT} n_{-}\mathbf{E} - D\nabla n_{-}\right]\cdot\mathbf{v}\right)\Big|_{S} = K(n_{-} - n_{\omega})|_{S},\end{gathered} \tag{1.1}$$

where $n_{\pm}$ is the concentration of positive and negative ions; **u**, liquid velocity; e, proton charge; z, D, charge number and diffusion coefficient of the ions; k, Boltzmann constant; T, temperature of the liquid, which is assumed to be constant; **E**, electric field; ε, dielectric constant of the liquid; n^0, concentration of positive or negative ions at the tube entrance; n_{ω}, equilibrium concentration of negative ions at the tube wall, which is attained at the end of an infinitely long tube; K, constant of electrochemical neutralization of negative ions; ν, normal to the inside surface of the tube.

The last boundary condition (1.1) is fulfilled in the case where the neutral molecules formed by neutralization of negative ions on the tube walls are present in the solution in concentration n_S, which is much greater than the ion concentration. We then have the relation

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