VIBRATIONAL RELAXATION OF POLYATOMIC MOLECULES IN A FIELD OF MONOCHROMATIC RADIATION BEHIND THE LEADING EDGE OF A SHOCK WAVE

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A large number of papers have been devoted to vibrational relaxation in flows of polyatomic gases (see, for example, [1-3] and the bibliographies attached to these); processes in which the excitation and deactivation of the vibrational energy take place by way of the collision of the molecules with one another in the interior of the gas have been studied in detail. External radiation (including monochromatic) may also play a considerable part in the distribution of internal (especially vibrational) energy. Questions regarding the interaction of coherent radiation with a polyatomic gas are of interest in connection with investigations into its amplification or absorption in gasdynamic media, its action on the characteristics of gas flows around solids, the initiation of chemical reactions, and so on. We note that any theoretical analysis of this class of problems is extremely complicated and demands the use of numerical techniques. If, however, we do in fact succeed in obtaining analytical solutions, which are extremely rare in the gasdynamics of nonequilibrium flows, we should be able to make a qualitative analysis of the characteristic features of the phenomena, to separate the fundamental defining parameters, and so on. Bearing this possibility in mind, let us consider the steady-state problem of the absorption of an intense flow of monochromatic radiation behind the leading edge a shock wave. We shall solve the problem in a coordinate system linked to the leading edge of the wave ($x = 0$). Radiation may also be absorbed in front of the edge $x = \infty$, but we shall not take these processes into account. Subsequently we shall consider that the intensity of the flow of incident radiation at the leading edge of the wave $I_{x=0} = I_0$. An example having a particular relationship to the situation under consideration is that of an $SF_6 + N_2$ (air) mixture, when the Mach number in the flow $M_\infty \sim 1$ and the vibrational degrees of freedom are only excited in the SF_6 molecules behind the leading edge of the wave. It is well known that SF_6 molecules strongly absorb radiation with a wavelength of $\lambda = 10.6\ \mu$ at the resonance vibrational levels, and over a wide range of external conditions the two-temperature kinetic model of the vibrations of this molecule applies [4]. According to this model, owing to the rapid intra- and intermode quantum exchanges, all 15 vibrational degrees of freedom of the SF_6 molecules have a common vibrational temperature [5].

Taking this into account, we write the system of initial relationships in the following form:

$$\begin{gathered}\rho u = C_1;\ p + \rho u^2 = C_2;\ u^2/2 + c_pT + \beta(E_i - E_{i\infty}) - I'/\rho_0 u_0 = C_3;\\ dE_i/dx = [E_0(T) - E_i(T_i)]/u_0\tau_i + \alpha I/\rho_0 u_0 \beta;\ dI/dx = -\alpha I;\\ I' = I_0(1 - e^{-\alpha x});\ p = \rho RT,\end{gathered} \tag{1}$$

where ρ, u, p, T are the density, velocity, pressure, and temperature of the mixture; E_i is the vibrational energy; I, α are the intensity and absorption coefficient of the radiation; β is a coefficient characterizing the gravimetric or molar proportions of those components of the mixture which have their vibrational levels excited; quantities with the zero subscript correspond to the values of the gasdynamic parameters directly behind the leading edge of the wave. The structure of the leading edge at which equilibrium is established with respect to the progressive and rotational degrees of freedom is not taken into account; the edge is regarded as infinitely thin on the scale of the quantity $u_0\tau_i$ characterizing

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the extent of the zone of vibrational relaxation. It is well known that in the case of weakly relaxing gases, for which the parameter $\varepsilon = E_i/c_pT_0 \ll 1$ while $I = 0$, if τ_i = const, we may derive an analytical solution of system (1) for the structure of the zone of vibrational relaxation [6]. This solution, generalized to the case of mixtures of polyatomic gases, was used in analyzing the effects of population inversion [7]. In the case under consideration an analytical solution may be obtained subject to the conditions τ_i = const and α = const by the method of successive approximations if the quantity $\delta = |\beta(E_i - E_{i\infty}) - I'/\rho_0 u_0|/c_pT_0 \ll 1$.

In this we must distinguish two cases:

(a) $\delta \ll 1$, when $\beta(E_i - E_{i\infty})/c_pT_0 \sim \delta$, $I'/\rho_0 u_0 c_p T_0 \sim \delta$;

(b) $\delta \ll 1$ when $\beta(E_i - E_{i\infty})/c_pT_0 \sim 1$, $I'/\rho_0 u_0 c_p T_0 \sim 1$.

The quantities in the numerator of the parameter δ represent the amounts of vibrational and absorbed energy of the radiation at the point x. For $\delta \ll 1$ the perturbations of the gasdynamic quantities (primed) in the relaxation zone satisfy the conditions $p'/p_0 \ll 1$, $\rho'/\rho_0 \ll 1$, $T'/T_0 \ll 1$, etc., so that practically $\tau_i \approx$ const. As regards the assumption α = const, this is considerably less precise. Cases of practical interest are clearly those in which the intensity of the absorbed radiation is relatively high. For example, estimates show that in a mixture of 10% SF_6 + 90% N_2 for $M_\infty = 1.5$; $T_\infty = 250$°K, $p_\infty = 0.412$ atm, max $\beta\cdot(E_i - E_{i\infty})/c_pT_0 \approx 0.1$.

The corresponding value of $I_0 \sim 1$ kW/cm². Thus, as in calculations of boundary-layer absorption [8], smallness of the energy parameter $W = I/\rho_0 u_0 c_p T_0 \sim \delta \ll 1$ means that the effect of radiation in changing the parameters of the gasdynamic field is only slight. We note that, under the foregoing conditions, phenomena associated with the dependence of the coefficient α on I set in at considerably greater intensities, $I \sim 10$ kW/cm². For $\delta = 0$ the system of equations (1) separates into two independent subsystems, namely, equations representing the conservation laws for the direct jump of compaction (shock wave), and the relaxation equation, which is satisfied automatically in case (a). The solution of the equation for radiation transfer is trivial $I = I_0 e^{-\alpha x}$ and may be used in the analysis of the relaxation equation. The solution of the latter takes the form

$$E_i(x) = E_0(T) + \frac{\alpha u_0 \tau_i I_0 \left(e^{-\alpha x} - e^{-\frac{x}{u_0 \tau_i}}\right)}{\beta \rho_0 u_0 (1 - \alpha u_0 \tau_i)} - (E_0 - E_{i0})\, e^{-\frac{x}{u_0 \tau_i}}.$$

If the specific heat of the vibrational degrees of freedom c_{vi} = const, we have the following expression for the change in vibrational temperature T_i:

$$T_i(x) = T_0 + \frac{\alpha u_0 \tau_i T_R \left(e^{-\alpha x} - e^{-\frac{x}{u_0 \tau_i}}\right)}{1 - \alpha u_0 \tau_i} - (T_0 - T_{i0})\, e^{-\frac{x}{u_0 \tau_i}},$$

where the ratio $T_R = I_0/\beta c_{vi} \rho_0 u_0$ characterizes the change in T_i due to the absorption of radiation. The exact value of $T_i(x)$ may be determined from the expression for the average vibrational energy of the molecules (e.g., for the SF_6 molecules $E_i = \sum_k \frac{g_k \Theta_h R_{SF_6}}{\exp[\Theta_k/T_i(x)] - 1}$, where g_k is the degeneracy of the modes). By linearizing Eq. (1) with respect to the parameters δ we may obtain a solution in the next approximation determining the corrections p', ρ', T' to the values of p_0, ρ_0, T_0. These corrections take the form

$$T'(x) = \frac{\left(M_0^2 - \frac{1}{\gamma}\right) \gamma T_0 \delta(x)}{\left(1 - M_0^2\right)}, \quad p' = \frac{(\gamma - 1) M_0^2 \rho_0 c_p T_0 \delta(x)}{M_0^2 - 1}, \quad \rho' = \frac{p'}{u_0^2}. \tag{2}$$

If $I = 0$ and the conditions in the unperturbed flow ($x = \infty$) are equilibrium, we shall always have $T' < 0$, since the excitation of the vibrational levels of the molecules in the relaxation zone takes place by virtue of the energy of the translational and rotational degrees of freedom.

If, however, the conditions at $x = \infty$ deviate substantially from equilibrium (e.g., in the presence of population inversion in the flow), the opposite situation may arise ($T' > 0$)

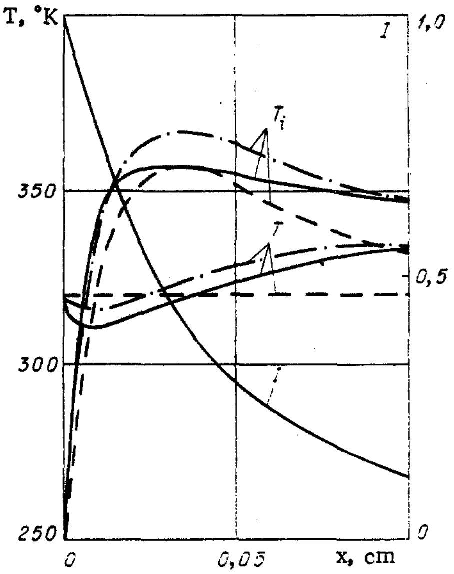

Fig. 1

[9]. For I ≠ 0 we have either heating ($T' > 0$) or cooling ($T' < 0$) of the translational–rotational degrees of freedom in the relaxation zone of the shock wave.

Let us proceed to consider some of the characteristic features of the solution of system (1). We find that for I ≠ 0 there is a maximum of T_i inside the relaxation zone at the point

$$x_{\max} = \ln \frac{\left[1 + (T_0 - T_{i0}) \dfrac{1 - \alpha u_0 \tau_i}{\alpha u_0 \tau_i T_R}\right]}{\alpha u_0 \tau_i} \Bigg/ \left[(u_0 \tau_i)^{-1} - \alpha\right],$$

exceeding the equilibrium temperature T_0. For high intensities I_0, not exceeding the saturation threshold, the relative contribution of radiation absorption and collisions to the accumulation of vibrational energy is characterized by the parameter $\alpha u_0 \tau_i$, which may assume a variety of values. Thus in an $SF_6 + N_2$ mixture for a molar composition of 1% SF_6 + 99% N_2, $\alpha u_0 \tau_i \ll 1$; for 10% SF_6 + 90% N_2, $\alpha u_0 \tau_i \sim 1$; and for 100% SF_6, $\alpha u_0 \tau_i > 1$. We note that in case (b) $\varepsilon \sim 1$ and $W \sim 1$, but the general condition of the smallness of δ which has to be satisfied at every point x within the relaxation zone imposes certain limitations on the process of vibrational relaxation involving the absorption of radiation.

The quantity δ in fact introduces an additional link between E_i and I, which should not contradict the relaxation equation. Analysis shows that case (b) applies for a value of $\alpha u_0 \tau_i \gg 1$, the order of smallness of our parameter being $\delta \sim 1/\alpha u_0 \tau_i$. Physically, this situation corresponds to infinitely rapid absorption behind the leading edge of the shock wave if $\delta = 0$ (when $E_i = E_{i0}|_{x=0}$), and to a layer of absorption which may be regarded as thin on the scale of $u_0 \tau_i$ for a small but nonzero value of δ.

Figure 1 shows the results of a calculation of the temperature T and T_i and the fall in intensity I for a mixture of 10% SF_6 + 90% N_2 subject to the following conditions in the incident flow: $M_\infty = 1.5$, $T_\infty = 250$°K, $p_\infty = 0.412$ atm, $I_\infty = I_0 = 1$ kW/cm²; in order to be specific the value of α was taken from the temperature T_0 behind the leading edge of the wave. The dashed curves correspond to the first approximation $\delta = 0$, the dashed-dot curves, to the linear approximation in δ allowing for corrections (2), and the continuous curves, to the calculations of T and T_i executed by A. Yu. Kireev in a numerical computer solution of the problem in question. For the quantities α and τ_i in the calculations we accepted the relationships presented in [4, 5, 10]. We see by comparing the results of the analytical and numerical solutions that the proposed simple model satisfactorily describes the mutual relationship between relaxation by collision and the absorption of radiation.

On the basis of the foregoing results we may note the following:

1. There are two asymptotic regions of gas flow behind the shock wave, corresponding to a layer of radiation absorption and a zone of vibrational relaxation, the relative extents of which are characterized by the parameter $\alpha u_0 \tau_i$.

2. For $M_\infty \sim 1$ and $T_\infty \sim 250-300°K$ most of the radiation manages to be absorbed in a narrow zone behind the leading edge of the wave.

3. For aerodynamic flow around complex solids interaction of the jumps in compaction with the boundary layer may change the radiation absorption characteristics by comparison with those obtained in [4, 10, 8], especially in the case of the local injection of SF_6, when the concentrations of this impurity are substantial at the outer limit of the boundary layer.

4. The effect of the heating of the internal degrees of freedom or of individual levels on account of external monochromatic radiation may be used in order to initiate chemical reactions behind the leading edge of the wave, and possibly for experimental investigations into various gasdynamic phenomena of the kind encountered in the plasma associated with laser breakdown [11]. In a polyatomic gases (mixtures incorporating SF_6 in particular) gasdynamic perturbations due to radiation absorption should be observed for relatively low intensities of the external radiation, and over volumes large compared with the ordinary laser spark.

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