

EFFECT OF EXCITATION OF MOLECULAR VIBRATIONS ON THE DYNAMICS OF COMBUSTION OF AN $H_2 + O_2$ MIXTURE BEHIND A DETONATION SHOCKWAVE*

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A significant number of papers [1-4] have been devoted to the investigation of the detonation of an $H_2 + O_2$ (air) mixture behind shockwaves. Interest in this problem is due not only to the possibility of detailed study of the kinetics of processes under conditions which are rather "pure" from the gasdynamic standpoint, but also the potential design of hypersonic ramjet engines with the detonation scheme for combustion in a supersonic flow in [5,6]. In all these papers, it is assumed that the rate of excitation of the vibrational degrees of freedom behind the shockwave front is considerably faster than the rate of the chemical reactions, and therefore all the chemical transformations occur with an equilibrium distribution of the molecules over the vibrational levels.

At the same time, back in [7] it was shown that even in water vapor, the molecules of which have anomalously high vibrational relaxation rates, behind a shockwave a rather extended zone may exist with a nonequilibrium distribution of energy over the vibrational degrees of freedom. Another important factor indicating we need to take into account the simultaneous occurrence of chemical reactions and vibrational relaxation in theoretical modeling of detonation is the possibility of formation of reaction products in vibrationally excited states [8]. This may substantially affect the change in the dynamics of the entire process, since rate constants of chemical reactions depend on the degree of vibrational excitation of the reacting molecules [9].

The goal of this work was to investigate the effect of nonequilibrium excitation of molecular vibrations on the dynamics and the basic characteristics of detonation behind shockwaves.

In the general case, for detonation behind shockwaves, we need to carry out the analysis based on the Boltzmann equation, taking into account all the inelastic processes. However, such detail does not allow us to obtain concrete solutions for real systems, and in principle is not necessary. Presently the hydrodynamic approximation is widely used for description of relaxation processes in shockwaves. This is based on the fact that establishment of equilibrium with respect to translational and rotational degrees of freedom occurs substantially faster (hundreds or thousands of times faster) than with respect to vibrational degrees of freedom or establishment of chemical equilibrium. This allows us to consider the shockwave front as an infinitesimally narrow zone in which the temperature T , the pressure P , and the density ρ increase in a jumpwise fashion. Behind the front, there exists an extended relaxation zone in which T , P , and ρ vary rather slowly [10].

When vibrational relaxation and chemical reactions occur simultaneously behind the shockwave front, at present it is difficult to rigorously account for all the processes even for simple multicomponent systems. This is connected with the fact that according to contemporary ideas [10, 11], a molecule found in any vibrational state has nonzero probability of overcoming the activation barrier. Therefore under nonequilibrium conditions, we need to have information about the distribution functions for all the component molecules with respect to vibrational levels. At the same time, many of the probabilities for vibrational-translational VT - and vibrational-vibrational VV exchange processes needed for calculation of the distribution function are unknown. Data are also lacking on the rate constants of chemical reactions with participation of molecules excited to a specific vibrational state. All this makes it necessary to introduce certain simplifications.

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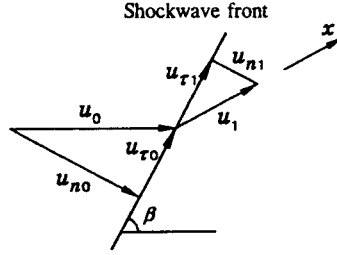


Fig. 1

Let us use the local vibrational temperature model for description of vibrational relaxation processes [11]. In this case, we match each type of vibration of the molecule with its own harmonic oscillator. Since the rate of intramode VV -exchange is considerably faster than the rates of intermode VV' -exchange and VT -relaxation, a quasiequilibrium Boltzmann distribution is very rapidly established in the mode, with its own temperature (different from T). For description of the relaxation processes, in this case we do not require detailed information on the probabilities of all the inelastic processes, as in the level representation.

Let us carry out a concrete analysis for the flow diagram shown in Fig. 1. We note that this diagram is rather often used in theoretical analysis of kinetic processes in detonation waves [2, 4]. Upon passage through the shockwave front, only the normal component of the velocity u_n changes, while the tangential component u_t remains unchanged. We will consider the change in the parameters in the reacting mixture of gases along the jet stream, the direction of which coincides with the Ox axis. In the coordinate system connected with the shockwave front, the equations describing such flow can be represented in the form

$$\begin{aligned}
 \frac{d(\rho u)}{dx} &= 0, \quad u \frac{du}{dx} + \frac{1}{\rho} \frac{dP}{dx} = 0, \quad \frac{dH}{dx} + \sum_{i=1}^S \frac{de_V^i}{dx} + u \frac{du}{dx} = 0, \\
 P &= \frac{\rho RT}{\mu}, \quad u \frac{d\gamma_i}{dx} = G_i - \gamma_i \sum_{j=1}^{M_1} G_j, \quad u \frac{d\varepsilon_\xi}{dx} = Q_V^\xi + Q_{ch}^\xi, \quad G_i = \sum_{q=1}^{M_2} S_{iq} \\
 S_{iq} &= \frac{(\alpha_{iq}^- - \alpha_{iq}^+)}{N} [R_q^+ - R_q^-], \quad R_q^{+(-)} = k_{+q(-)} \prod_{j=1}^{n_q} N_j^{\alpha_j^{+(-)}}, \quad \varepsilon_\xi = \frac{g_\xi y_\xi}{1 - y_\xi}, \\
 Q_V^\xi &= N \left[\sum_{p=1}^{L_1} \frac{l_\xi}{g_\xi g_p} L_{\xi,p} W_{\xi,p} - (\varepsilon_\xi - \varepsilon_{\xi 0})(1 - y_{\xi 0}) \sum_{i=1}^{M_1} W_{\xi,0}^i \gamma_i \right], \\
 Q_{ch}^\xi &= \sum_{r=1}^{L_2} \frac{(\alpha_{ir}^- - \alpha_{ir}^+)}{N_i} \left[(\chi_{r\xi}^+ - \varepsilon_\xi) R_r^+ - (\chi_{r\xi}^- - \varepsilon_\xi) R_r^- \right], \\
 L_{\xi,p} &= \varepsilon_\xi^{l_\xi} (\varepsilon_p + g_p)^{l_p} - \varepsilon_p^{l_p} (\varepsilon_\xi + g_\xi)^{l_\xi} \exp[(l_\xi \theta_\xi - l_p \theta_p)/T], \\
 y_\xi &= \exp(-\theta_\xi/T_\xi), \quad \varepsilon_{\xi 0} = \varepsilon_\xi (y_\xi = y_{\xi 0}), \quad y_{\xi 0} = y_\xi (T_\xi = T_{\xi 0}), \\
 H &= \sum_{i=1}^{M_1} h_{0i} \gamma_i + C_{RT} T, \quad C_{RT} = \left(\frac{5}{2} + \sum_{i=1}^L \gamma_i + \frac{3}{2} \sum_{i=1+L}^S \gamma_i \right) \frac{R}{\mu}, \\
 e_V^i &= \frac{R}{\mu} \gamma_i \sum_{j=1}^Z \theta_{ij} \varepsilon_{ij}, \quad \gamma = \frac{N_i}{N}, \quad N = \sum_{i=1}^{M_1} N_i, \quad \mu = \sum_{i=1}^{M_1} \mu_i \gamma_i.
 \end{aligned} \tag{1}$$

Here R is the universal gas constant; h_i^0 is the enthalpy of formation of the i -th component at $T = 298$ K; N_i , μ_i are the density of molecules of the i -th type and their molecular mass; M_1 is the number of atomic and molecular components in the mixture; L_2 is the number of reactions leading to formation (disappearance) of the molecule containing the mode ξ ; M_2 is the number of reactions leading to formation (disappearance) of the i -th component; θ_ξ and T_ξ are the characteristic and local temperature of the ξ -th mode; g_ξ is the degree of its degeneracy; l_ξ is the number of vibrational quanta lost or acquired by the mode x in

VV' exchange (all together there are L_1 of them); $W_{\xi,p} = \sum_{i=1}^{M_1} W_{\xi,p}^i \gamma_i$ for intramolecular VV' exchange; $W_{\xi,p} = W_{\xi,p} \gamma_i$ ($\xi \leftrightarrow i, p \leftrightarrow j$) for intermolecular VV' exchange; $W_{\xi,p}^i$ and $W_{\xi,p}$ are the rate constants for intramolecular and intermolecular VV' exchange; $W_{\xi,p}^i$ is the rate constant for VT relaxation upon collision with the i -th partner; α_{iq}^+ and α_{iq}^- are the stoichiometric coefficients of the q -th reaction; k_{+q} and k_{-q} are the rate constants of the q -th chemical reaction in the forward and backward directions; $\chi_{r\xi}^{+(-)}$ is the average number of vibrational quanta acquired (lost) by the mode x in a single event of formation (disappearance) of the molecule containing the mode ξ ($i \leftrightarrow \xi$) in the r -th reaction.

Let us dwell in more detail on determination of $k_{+(-)q}$ and $\chi_{r\xi}^{+(-)}$ in the case of a nonequilibrium distribution of molecules with respect to vibrational degrees of freedom. Within the mode approximation, the rate constant of the chemical reaction is a function of the vibrational T_j and translational T temperatures [12]. Thus for dissociation reactions

$$k_r = \varphi_r(T, T_j) k_r^0(T); \quad (2)$$

$$\varphi_r(T, T_j) = \frac{\prod_{j=1}^{n_r} (1 - y_{j0})^{-g_j}}{\prod_{j=1}^{n_r} (1 - y_j)^{-g_j}} \exp \left[\frac{E_r^*}{K} \left(\frac{1}{T} - \frac{\sum_{j=1}^{n_r} \beta_{rj}^2}{\sum_{j=1}^{n_r} \beta_{rj}^2 T_j} \right) \right], \quad (3)$$

where $k_r^0(T)$ is the equilibrium rate constant for the chemical reaction for $T_j = T$; the β_{rj} are the expansion coefficients for the coordinate of the r -th reaction with respect to the coordinates of the normal modes of vibrations; n_r is the number of modes participating in the r -th reaction; K is the Boltzmann constant; E_r^* is the energy corresponding to the vibrational level, so to speak the "bottleneck" in the transition of vibrationally excited molecules to the quasicontinuous energy continuum. Within the framework of the truncated harmonic oscillator model (this approximation is also used in this work), E_r^* corresponds to the energy of the last discrete level from which dissociation occurs. We could not find a sufficiently rigorous definition of $\varphi_r(T, T_j)$ in the literature for bimolecular exchange reactions. Often for these reactions formula (3) is used [13]. In this case, E_r^* is assumed to be equal to the activation energy of the chemical reaction occurring in the direction of disappearance of the molecule with mode j .

The quantity $\chi_{r\xi}^{+(-)}$, according to [12, 13], is defined by the formulas

$$\chi_{r\xi}^{+(-)} = (E_r / K \theta_\xi) \eta_{r\xi}^{+(-)},$$

$$\eta_{r\xi}^+ = \beta_{r\xi}^2 / \sum_j \beta_{rj}^2, \quad \eta_{r\xi}^- = \beta_{r\xi}^2 T_\xi^2 \sum_j \beta_{rj}^2 / \left(\sum_j \beta_{rj}^2 T_j \right)^2,$$

where E_r is the part of the activation energy of the r -th reaction corresponding to the vibrational degrees of freedom. For bimolecular exchange and dissociation reactions, to a first approximation we have $\eta_{r1} = \eta_{r2} = \dots = 1/n_r$. Furthermore, due to lack of information, usually the β_{rj} are assumed to be equal to each other [12, 13].

Presently the calculation of the value of E_r is the most complicated. Essentially this is the energy which is stored in the vibrational degrees of freedom of the i -th component upon its formation in the r -th chemical reactions. In nonequilibrium laser-assisted chemical reactions (for example, $F + H_2 \rightarrow HF + H$), when we need to have information about the distribution function of the molecules with respect to vibrational levels, for determination of E_r we use either the classical calculation of three-dimensional trajectories using the semiempirical potential energy surface in description of the force interaction of colliding partners, or the information theory approach in [14]. In the case under consideration (the mode model), such detailed information is not required. We will assume that upon formation of the molecule, energy equal to the vibrational energy going toward overcoming the activation barrier of the reaction occurring in the direction of disappearance of the molecule is released into the vibrational degrees of freedom. In this case, in order to calculate E_r we can introduce the vibrational energy utilization coefficient α_r , which shows what fraction of the vibrational energy of the molecule goes toward overcoming the activation barrier of the chemical reaction [15]:

$$E_r = \alpha_r E_{ar}^+, \quad \alpha_r = E_{ar}^+ / (E_{ar}^+ + E_{ar}^-).$$

Here $E_{ar}^{+(-)}$ is the activation energy of the r -th chemical reaction in the direction of disappearance (appearance) of the vibrationally excited molecule.

For solution of system (1), we need to specify the boundary conditions for $x = 0$ ($x = 0$ corresponds to the shock front). Let us use the conservation laws for this. Taking into account the fact that the gas ahead of and behind the shockwave front can be chemically and vibrationally nonequilibrium, these laws can be presented in the form

$$\rho_0 u_{n0} = \rho_1 u_{n1}; \quad (4)$$

$$P_0 + \rho_0 u_{n0}^2 = P_1 + \rho_1 u_{n1}^2; \quad (5)$$

$$H_0 + \sum_{i=1}^S e_{i0}^V + \frac{u_{n0}^2}{2} = H_1 + \sum_{i=1}^S e_{i1}^V + \frac{u_{n1}^2}{2}; \quad (6)$$

$$e_{i0}^V = e_{i1}^V; \quad (7)$$

$$\gamma_{i0} = \gamma_{i1}. \quad (8)$$

From (4)-(8) follow the relations connecting the parameters before (subscript 0) and after (subscript 1) the shockwave front

$$\begin{aligned} \frac{P_1}{P_0} &= \frac{2\alpha}{\alpha+1} M_{0n}^2 - \frac{\alpha-1}{\alpha+1}, & \frac{\rho_1}{\rho_0} &= \frac{(\alpha+1)M_{0n}^2}{(\alpha-1)M_{0n}^2 + 2}, \\ \frac{T_1}{T_0} &= \frac{P_1 \rho_0}{P_0 \rho_1}, & u_{1n} &= \sqrt{\frac{P_1 - P_0}{\rho_1 - \rho_0} \frac{\rho_0}{\rho_1}}, & u_1 &= (u_{1n}^2 + u_{1\tau}^2)^{1/2}, \\ \alpha &= 1 + \left(\frac{3}{2} + \sum_{i=1}^L \gamma_{i0} + \frac{3}{2} \sum_{i=1+L}^S \gamma_{i0} \right)^{-1}, & M_{0n} &= u_{0n} / \sqrt{\alpha \frac{R}{\mu} T_0}. \end{aligned}$$

In calculations of detonation behind shockwaves, rather often (see, for example, [1-3]) it is assumed that the rates of the VV and VT processes are considerably faster than the rates of the chemical reactions; and behind the shock front, thermodynamic equilibrium is very rapidly established between the translational, rotational, and vibrational degrees of freedom of the molecules, and the chemical reactions occur already on the background of this steady-state equilibrium (for comparison, this approximation is also used in this work). In this case, system (4)-(8) is reduced to three algebraic equations of the following form:

$$\begin{aligned} M_{n1} &= M_{n0}^{-1}, \\ h_1 - h_0 &= \frac{1}{2} \frac{P_0}{\rho_0} \left(\frac{P_1}{P_0} - 1 \right) \left(\frac{\rho_0}{\rho_1} + 1 \right), \\ -\alpha_{0e} M_{n0}^2 &= \left(\frac{P_1}{P_0} - 1 \right) / \left(\frac{\rho_0}{\rho_1} - 1 \right). \end{aligned}$$

Here

$$\begin{aligned} h &= C_{RT}^0 T + \frac{R}{\mu_0} \sum_{i=1}^S \gamma_i \sum_{j=1}^Z g_{ij} \theta_{ij} \left[\exp \left(\frac{\theta_{ij}}{T} \right) - 1 \right]^{-1}; & M_n &= u_n / \sqrt{\alpha_e \frac{R}{\mu} T}; \\ \alpha_e &= 1 + \left\{ \frac{\mu}{R} C_{RT} - 1 + \sum_{i=1}^S \gamma_i \sum_{j=1}^Z \left(\frac{\theta_{ij}}{T} \right)^2 g_{ij} \exp \left(\frac{\theta_{ij}}{T} \right) \left[\exp \left(\frac{\theta_{ij}}{T} \right) - 1 \right]^{-2} \right\}^{-1}. \end{aligned}$$

For determination of the change in the gasdynamic parameters and the concentrations of the components along the Ox axis, we use system (1) except for the last equation for ε_x , since for any x we have $T_x = T$.

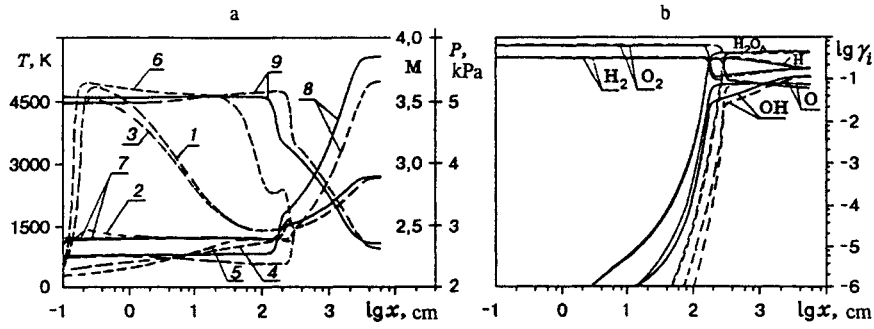


Fig. 2

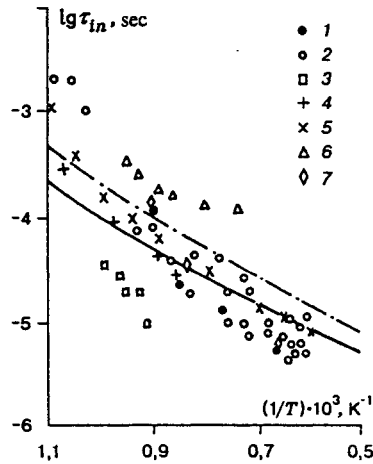


Fig. 3

As was shown in [4], a sufficiently exact description of the change in the gasdynamic parameters and also the values of the induction length L_{in} and the length of the combustion zone L_c upon detonation behind a shockwave in an $H_2 + O_2$ (air) mixture can be achieved by taking into account all nine chemical reactions with participation of H_2 , O_2 , OH , O , H in the kinetic model. The vibrational energy exchange scheme in this case contains the VV' exchange processes between symmetric, bending, and asymmetric (ν_1, ν_2, ν_3) modes of the H_2O molecule, the modes of the $H_2(\nu_4)$, $O_2(\nu_5)$, $OH(\nu_6)$ molecules, and also the VT relaxation processes of the modes $\nu_2, \nu_4, \nu_5, \nu_6$ [16]. In the case of an $H_2 + air$ mixture, we assume that N_2 does not participate in any chemical reactions, and we consider only the process of VT exchange for the mode $N_2(\nu_7)$. The expressions for $k_r^0(T)$ were taken from [2], and the expressions for $W_{\xi,0}^i(T)$ and $W_{\xi,0}^j(T)$ were taken from [16, 17]. Analysis was done on the basis of numerical integration of system (1) using an implicit second-order difference scheme.

Let us first consider how taking into account excitation of vibrations behind the shockwave affects the nature of the occurrence of chemical reactions and the change in the gasdynamic parameters. In Fig. 2a we show the distribution of vibrational temperatures ($T_i, i = \overline{1-6}$ — the lines 1-6) and also the translational temperature, pressure, and the Mach number (lines 7-9 respectively), and in Fig. 2b we show the change in the concentrations of the components along the Ox axis, obtained in calculation of the detonation of a $2H_2 + O_2$ mixtures for $T_0 = 300$ K, $P_0 = 133$ Pa, $M_0 = 8$ behind an oblique shockwave with $\beta = 30^\circ$. Here the solid lines correspond to the calculation done assuming instantaneous establishment of the equilibrium between the vibrational and translational degrees of freedom, and the dashed lines correspond to the calculation when we took into account delayed excitation of vibrations behind the shockwave and the effect of the vibrational kinetics and the chemical transformations on each other.

From comparison of the presented dependences, we see that taking into account delayed excitation of the vibrational degrees of freedom of the molecules leads to lengthening of the induction and combustion zones, and also to a change in the equilibrium values of P and M . This is because the flow in the induction zone (a consequence of the fact that $T_4, T_5 < T$) occurs with heat withdrawal from the translational degrees of freedom. Since behind the shockwave front $M_1 > 1$, in this case the temperature and pressure decrease and the velocity of the gas increases [18]. Reduction of the pressure, in turn, decreases the number of collisions and consequently the rate of all the chemical reactions. The difference of T_4 and T_5 from T leads also

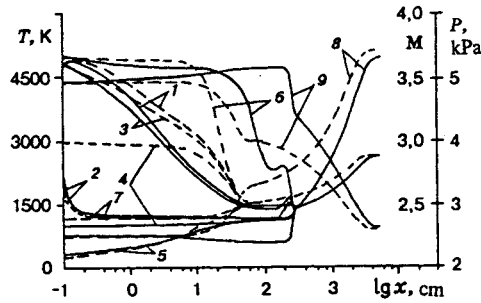


Fig. 4

to a direct decrease in the rate constants of the reactions $\text{H}_2 + \text{O}_2 \rightarrow 2\text{OH}$, $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$, $\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$, and $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$, which are the sources of reactive O and H atoms and OH radicals, the rate of formation of which is precisely what determines the burning velocity. Heat liberation as a result of the occurrence of chemical reactions (mainly recombination reactions are responsible for this) increases the temperature and pressure and decreases the velocity of the gas (for $M > 1$, the flux is slowed down). Consequently, P at the end of the induction zone when taking into account delayed excitation of vibrations is less than for their instantaneous excitation; the final value of the pressure P_e at the end of the combustion zone for an identical amount of liberated energy should also be less.

We should note that in taking into account the effect on each other of the chemical transformations and processes of vibrational energy exchange in the induction zone, we observe a significant difference in vibrational temperatures of the OH (T_6) and the symmetric and asymmetric modes of H_2O (T_1, T_3). This is due to the fact that in the reaction $\text{H}_2 + \text{O}_2 \rightarrow \text{OH} + \text{OH}$, vibrationally excited OH molecules are formed ($E_r^* = 5624$ K), while in the reaction $\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}$, vibrationally excited H_2O molecules are formed ($E_r = 8053$ K). Therefore at the beginning of the induction zone, we also observe an abrupt increase in T_1, T_2, T_3, T_6 . Due to the fast rate of VT relaxation, T_2 very rapidly decreases. At the same time, since the modes ν_1 and ν_3 are connected by rapid VV' exchange with OH ($\text{H}_2\text{O}(\nu_1, \nu_3) + \text{OH}(V=0) \rightarrow \text{H}_2\text{O}(000) + \text{OH}(V=1)$), T_1 and T_3 decrease significantly more slowly than T_2 . Since T_6 reaches 4500 K and is maintained to a length of ≈ 1 m, in principle it is not difficult to experimentally test the effect of nonequilibrium excitation by measuring the intensity of spontaneous radiation of OH at the wavelength $\lambda = 2.7$ mm.

Of course, experiment is the test for the validity of any theoretical model and the reliability of the results obtained using the model. In Fig. 3, we present the results of comparison of the measured values of the induction time τ_{in} in combustion of the mixture $\text{H}_2 + \text{air}$ ($2\text{H}_2 + \text{O}_2 + 3.76\text{N}_2$) for different values of T_0 with the dependences $\tau_{in}(T)$, first obtained theoretically in calculation of detonation behind a oblique shockwave taking into account delayed excitation of vibrations and the effect of chemical transformations and vibrational relaxation on each other, and then obtained taking into account only chemical transformations and assuming the existence of thermodynamic equilibrium between the vibrational and translational degrees of freedom (the broken line and the solid line, respectively). In Fig. 3, points 1-7 correspond to data from [1, 19-24]. In the

calculations, the value of τ_{in} was determined, as in [4], from the formula $\tau_{in} = \int_0^{L_{in}} u^{-1} dx$, where L_{in} corresponds to the cross section in which the maximum concentration of H atoms is achieved. We see that the calculated curve corresponding to the full model (taking into account delayed excitation of vibrations behind the shockwave) corresponds rather well to the experimental data, especially in the low-temperature region ($T \leq 1400$ K).

Let us now consider how preliminary excitation of vibrations of H_2 or O_2 ahead of the shockwave affects the combustion dynamics. Obviously, a substantial effect may be expected only in the case when T_{40} or T_{50} is higher than the translational temperature behind the shockwave T_1 . This also was supported by the numerical calculations performed.

In Fig. 4, we show the change in the vibrational temperatures T_i ($i = \overline{1-6}$ - lines 1-6), and also the translational temperature T , the pressure, and the Mach number (lines 7-9) along the Ox axis upon detonation of the mixture $2\text{H}_2 + \text{O}_2$ with $T_0 = 300$ K, $P_0 = 133$ Pa, $M_0 = 8$, $\beta = 30^\circ$ and T_{30} ($i \neq 4$) = T_0 in the case $T_{40} = 1000$ and 3000 K (the solid and dashed lines respectively). We see that an increase in T_{40} up to 3000 K ($T_{40} > T_1$) leads to significant shortening of the induction and combustion lengths (the combustion length is determined by the coordinate $x = L_c$, where $T = 0.95T_e$, and T_e is the equilibrium value of the temperature in the already reacted mixture of gases). At the same time, for $T_{40} = 1000$ K ($T_{40} < T_1$), there is no acceleration of combustion compared with the case $T_{40} = T_{30} = T_0$. Shortening of the length of the induction and combustion

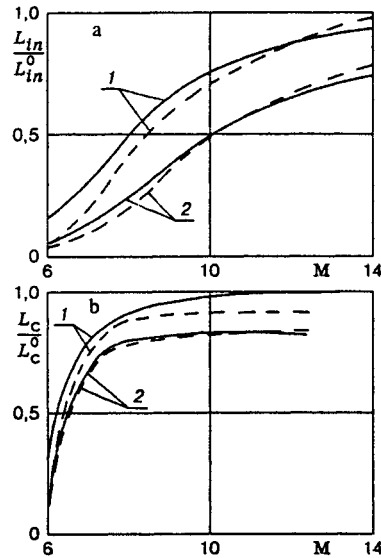


Fig. 5

zones for $T_{40} > T_1$ is due mainly to acceleration of the chain mechanism for combustion of the $H_2 + O_2$ mixture. The sequence of processes leading to this acceleration can be represented as follows.

Excitation of vibrations of H_2 up to $T_{40} > T_1$ in the initial stage leads first of all to acceleration of formation of OH radicals in the reaction $H_2 + O_2 \rightarrow OH + OH$ and H atoms upon dissociation of H_2 (it is due to the increase in the rate constants of these reactions compared with the case $T_{40} > T_1$). The appearance of OH and H initiates the reactions $OH + H_2 \rightarrow H_2O + H$ and $O_2 + H \rightarrow OH + O$, in which in addition H and O atoms are formed. Acceleration of the reaction of dissociation of OH also leads to more rapid formation of atomic hydrogen and oxygen; this acceleration is due to the more rapid production of vibrationally excited OH molecules compared with the case $T_{40} \leq T_1$. An increase in the O concentration in this case accelerates the reaction $H_2 + O \rightarrow H + OH$, which is one of the major branching chain reactions.

Excitation of vibrations of O_2 molecules also leads to acceleration of the combustion process ($T_{50} > T_1$). Also in this case, acceleration is due to more rapid production of O and H atoms and OH radicals. In contrast to the preceding case, production of atomic oxygen in the initial step occurs also upon dissociation of O_2 (the rate constant of this process increases). In this case, a considerably larger role is played in formation of OH radicals by the reaction $H_2O + O \rightarrow OH + OH$.

As shown by the calculations, the change in L_m and L_c upon excitation of vibrations of H_2 or O_2 depends considerably on the Mach number for the undisturbed flow. This dependence is determined first of all by the fact that the translational temperature of the gas behind the shockwave front changes as M_0 changes (for unchanged T_0 and β). And the change in T leads to a change in the role of vibrational excitation of molecules in overcoming the barriers of the endoergic reactions (with a decrease in temperature, this role increase). In Fig. 5a,b we show the dependences $L_m/L_m^0 = f(M_0)$ and $L_c/L_c^0 = j(M_0)$, obtained in calculation of the detonation in the mixture $2H_2 + O_2$ behind the shockwave with $b = 30^\circ$ at $T_0 = 300$ K and $P_0 = 133$ Pa in the case of excitation of molecular vibrations of H_2 and O_2 (solid and dashed lines); lines 1, 2 correspond to T_{40} (T_{50}) = 2000 and 3000 K. We see that a substantial decrease in L_c occurs for $M_0 < 8$, when T_{40} (T_{50}) $\gg T_0$. At the same time, the length of the induction zone decreases more monotonically with a decrease in M_0 . The shortening of L_m and L_c for the range of parameters considered in this work may reach 10.

Thus our calculations showed that excitation of molecular vibrations of the components participating in the reaction ahead of a shockwave front may lead to substantial acceleration of detonation and shortening of the supersonic combustion zone.

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