

# On the Initiation of Combustion of O<sub>2</sub>–O<sub>3</sub> Mixtures in the Course of Laser-Induced Asymmetrical Ozone Vibrations

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**Abstract**—The kinetics of ignition of O<sub>2</sub>–O<sub>3</sub> mixtures upon the excitation of O<sub>3</sub> molecules by laser radiation with a wavelength  $\lambda_l$  of 9.695  $\mu\text{m}$  is considered. The stimulation of asymmetrical vibrations of O<sub>3</sub> molecules was shown to produce more efficient dissociation of O<sub>3</sub> molecules, faster heating of the mixture, and, as a consequence, a decrease in the induction time and ignition temperature. Even when the energy of radiation applied to the gas is low ( $E_{\text{in}} \approx 0.15 \text{ J/cm}^2$ ), the ignition temperature of pure ozone can be reduced from 520 to 300 K at a pressure of  $10^3 \text{ Pa}$ .

## INTRODUCTION

The combustion of most gaseous mixtures is initiated by either chain reactions or via the mechanism of thermal explosion [1]. One of the efficient methods for controlling chain reactions in combustible mixtures is the excitation of vibrational degrees of freedom in reacting molecules. It has been shown earlier that the preliminary stimulation of vibrations of H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> molecules essentially accelerates the formation of O and H atoms and OH' radicals in an H<sub>2</sub> + O<sub>2</sub> + N<sub>2</sub> mixture, decreases the self-ignition threshold, and shortens the length of an induction period during detonation combustion in a supersonic flow [2–4]. The vibrations of dipole molecules are efficiently stimulated by IR laser radiation. The O<sub>2</sub>–O<sub>3</sub> mixture is the simplest molecular system in which laser radiation can stimulate vibrational degrees of freedom. The O<sub>3</sub> molecule possesses an intrinsic dipole moment and intensely absorbs IR radiation [5, 6]. Unlike an H<sub>2</sub>/O<sub>2</sub> mixture, the molecular O<sub>2</sub>–O<sub>3</sub> system ignites upon heating of the mixture due to the exothermic reaction (thermal explosion) [5].

Earlier, the use of laser radiation to initiate the combustion of an O<sub>2</sub>–O<sub>3</sub> mixture was considered in [7]. However, in this study, only the thermal effect of radiation was used, which led to the local heating of the medium by a laser beam. Another method of initiation with a laser beam based on photodissociation of the O<sub>2</sub> [8] and O<sub>3</sub> [9] molecules in H<sub>2</sub>–O<sub>2</sub> and H<sub>2</sub>–O<sub>2</sub>–O<sub>3</sub> mixtures was discussed. The kinetics of thermal ignition in O<sub>2</sub>–O<sub>3</sub> mixtures have been studied in detail [5, 10, 11]. This is a readily combustible mixture. The self-ignition temperature of pure ozone in a pressure range of  $P_0 = 7 \times 10^2$ – $10^4 \text{ Pa}$  varies from 673 to 423 K [5]. Ozone can also be used as an oxidizing agent for molecular hydrogen. Therefore, it was of interest to study the effect of stimulation of O<sub>3</sub> molecular vibrations by laser radiation on the ignition dynamics.

## MAIN ASSUMPTIONS AND PROBLEM STATEMENT

Let us consider a static uniform gaseous O<sub>2</sub>–O<sub>3</sub> mixture under exposure to a pulse of laser radiation with a wavelength  $\lambda_l$  of 9.69483  $\mu\text{m}$  (line P36 (00°1 → 02°0) of a CO<sub>2</sub> laser) and duration  $\tau_p$ . The frequency of this radiation is resonant to the frequency of the vibrational–rotational transition 000(12<sub>1,11</sub>) → 001(11<sub>1,10</sub>) in the O<sub>3</sub> molecules (the wavelength in the center of the spectral line  $\lambda_{\text{mm}} = 9.69486 \mu\text{m}$ ). Recall that the O<sub>3</sub> molecule has vibrations of three types: symmetrical, bending, and asymmetrical. The corresponding frequencies are  $\nu_1 = 1103.15 \text{ cm}^{-1}$ ,  $\nu_2 = 700.95 \text{ cm}^{-1}$ , and  $\nu_3 = 1042.1 \text{ cm}^{-1}$ . The O<sub>3</sub> molecule is an asymmetrical top. Its rotational levels are characterized by three quantum numbers:  $J$ ,  $K_a$ , and  $K_c$ . The first number determines the value of complete angular momentum, whereas the second and third numbers describe its projections to the axis of an elongated and flattened symmetrical top. The vibrational–rotational state of the O<sub>3</sub> molecule is determined by a set of the vibrational and rotational quantum numbers  $m \equiv V_1 V_2 V_3 (J_{K_a K_c})$ .

Let us consider the cases when  $\tau_l \gg \tau_t, \tau_r, \tau_{VV}$ , where  $\tau_l$  is the time of induced transitions,  $\tau_t$  and  $\tau_r$  are the times of translational and rotational relaxations, and  $\tau_{VV}$  is the time of the intramode vibrational–vibrational (V–V) exchange. We assume that the rotational and translational degrees of freedom of the molecules are in the thermodynamic equilibrium, and the local Boltzmann distribution with its own vibrational temperature  $T_\xi$  ( $\xi = 1, \dots, n$ , where  $n$  is the number of types of vibrations in the O<sub>2</sub> and O<sub>3</sub> molecules) exists in each mode. The modes of the O<sub>3</sub> molecule and that of the O<sub>2</sub> molecule will be labeled by numbers 1, 2, 3, and 4.

Let the gas be exposed to a pulse of laser radiation with the duration  $\tau_p$  and a Gaussian distribution of intensities

over the beam radius  $I(r, t) = I_0(t)\exp(-r^2/R_a^2)$ , where  $R_a$  is the typical beam radius, and  $I_0(t) = I_0$  at  $0 < t \leq \tau_p$  and  $I_0(t) = 0$  at  $t > \tau_p$ . We consider the cases when the value  $R_a$  is smaller than the absorption length  $L_v = k_v^{-1}$ , where  $k_v$  is the absorption coefficient at the frequency of radiation. One can neglect a change in the parameters along the longitudinal direction compared to those across the beam and consider an optically thin gas layer. In this case, a change in the hydrodynamic parameters and concentrations of the components in a section of typical size  $R_a$  is determined by a hierarchy of the characteristic times of various processes of micro- and macroscopic transfer [12, 13]. For the vibrationally nonequilibrium reacting gas, these are the time of the induced transitions,  $\tau_i$ ; the relaxation time for the energy of the vibrationally excited states,  $\tau_{VT}$ ; the duration of the affecting radiation pulse,  $\tau_p$ ; the time of the chemical reaction leading to the accumulation (decay) of a component determining the mechanism of mixture ignition,  $\tau_{iq}^{ch}$ ; the time of propagation of sonic vibrations across the beam,  $\tau_a$ ; the times of multicomponent diffusion,  $\tau_D^i$ , and thermal diffusion of the  $i$ th component,  $\tau_T^i$ ; the time of the vibrational thermal diffusion,  $\tau_{D_i}^V$ ; the time of thermal conductivity,  $\tau_\lambda$ ; the time of the vibrational thermal conductivity for the  $j$ th oscillator,  $\tau_V^j$ ; the time of convection due to viscosity,  $\tau_K$ , and the time of a change in the state of the medium due to the action of the striction force,  $\tau_F$ .

Let us estimate the characteristic times during the treatment of ozone or an  $O_2$ – $O_3$  mixture with laser radiation of the wavelength  $\lambda_l = 9.695 \mu\text{m}$  under the conditions of a numeric experiment:  $I_0 = 10$ – $100 \text{ kV/cm}^2$ ,  $R_a = 10 \text{ cm}$ ,  $P_0 = 10^3$ – $10^5 \text{ Pa}$ , and  $T_0 = 300$ – $600 \text{ K}$ . The estimates are  $\tau_l = 2 \times 10^{-3}$ – $2 \times 10^{-5} \text{ s}$ ,  $\tau_{VT} = 2 \times 10^{-3}$ – $3.4 \times 10^{-7} \text{ s}$ , and  $\tau_a = 2 \times 10^{-4} \text{ s}$  and for the lightest atoms of O determining the exothermic reactions in the  $O_2$ – $O_3$  mixtures,  $\tau_D^O \sim \tau_T^O \sim \tau_{D_{O_2}}^V \approx 0.1$ – $1 \text{ s}$ ,  $\tau_\lambda \sim \tau_V^j \approx 0.1$ – $1 \text{ s}$ ,  $\tau_K \sim \tau_F = 3$ – $10 \text{ s}$ . We will analyze the cases when  $\tau_{VT} < \tau_l \approx \tau_p < \tau_a < \tau_{ch} < \tau_D^O$ ,  $\tau_F$  (where  $\tau_{ch} = \min\{\tau_{iq}^{ch}\}$ ). The times  $\tau_{iq}^{ch}$  determine the induction period  $\tau_{in}$  (its value is at most  $3 \times 10^{-2} \text{ s}$  even in the absence of the excited  $O_3$  molecules at  $T = 600 \text{ K}$  and  $P_0 = 10^3$ – $10^5 \text{ Pa}$ ). One can neglect the mass-transfer processes in the range  $[0, \tau_{in}]$ . Since  $\tau_\lambda \gg \tau_{in}$ , the heat does not transfer from the system for considered times  $\tau \sim \tau_{in} < 0.1$ – $1 \text{ s}$ . Under these conditions,  $L_v = 18.5$ – $720 \text{ cm}$ .

We can represent the system of equations describing a change in the concentrations of the components and parameters of a medium in the central zone of the radiation action at  $r < 5 \text{ cm}$  as follows:

$$\frac{d\gamma_i}{dt} = G_i - \gamma_i \sum_{k=1}^{M_1} G_k,$$

$$\frac{d\varepsilon_\xi}{dt} = Q_{VV}^\xi + Q_{VT}^\xi + Q_{ch}^\xi + Q_I^\xi,$$

$$\frac{dH}{dt} + \sum_{i=1}^S \frac{de_v^i}{dt} = \frac{k_v I_0(t)}{\rho},$$

$$Q_{VV}^\xi = N \sum_{p=1}^{L_1} \frac{l_\xi^p L_{\xi,p}}{g_\xi^p} W_{\xi,p}^i,$$

$$Q_{VT}^\xi = N(\varepsilon_{\xi,0} - \varepsilon_\xi)(1 - y_{\xi,0}) \sum_{i=1}^{M_1} W_{\xi,0}^i \gamma_i,$$

$$Q_{ch}^\xi = \sum_{r=1}^{L_2} \frac{\alpha_{ir}^- - \alpha_{ir}^+}{N_i} [(\chi_{r\xi}^+ - \varepsilon_\xi) R_r^+ - (\chi_{r\xi}^- - \varepsilon_\xi) R_r^-],$$

$$Q_I^\xi = l_{\xi I} \frac{k_v I_0(t)}{h\nu_I N_{O_3}},$$

$$L_{\xi,p} = \varepsilon_\xi^p (g_p + \varepsilon_p)^{l_p} - \varepsilon_p^l (g_\xi + \varepsilon_\xi)^{l_\xi} \exp\left(\frac{l_\xi \theta_\xi - l_p \theta_p}{T}\right),$$

$$G_i = \sum_{q=1}^{M_2} S_{iq}, \quad S_{iq} = \frac{(\alpha_{iq}^- - \alpha_{iq}^+)}{N} (R_q^+ - R_q^-),$$

$$R_q^{+(-)} = k_{+(-)q} \prod_{j=1}^{n_q^{+(-)}} N_j^{\alpha_{jq}^{+(-)}},$$

$$k_v = \sigma_{mn} \left( \frac{g_n}{g_m} N_m - N_n \right), \quad N_m = N_{O_3} \frac{g_m}{z_m} \exp\left(-\frac{E_j}{KT}\right),$$

$$N_n = N_{O_3} \frac{g_n}{z_n} \exp\left(-\frac{E_j}{KT}\right) y_3,$$

$$z_q(q = m, n) = \frac{1}{2} \sqrt{\frac{\pi T^3}{A_v B_v C_v}} \prod_{\xi=1}^3 (1 - y_{\xi,0})^{-1},$$

$$\sigma_{mn} = \frac{\lambda_{mn}^2}{4\pi b_D} A_{mn} \sqrt{\frac{\ln 2}{\pi}} H(x, a),$$

$$H(x, a) = \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-y^2)}{a^2 + (x-y)^2} dy,$$

$$a = \frac{b_C}{b_D} \sqrt{\ln 2}, \quad x = \frac{2c \sqrt{\ln 2}}{|\lambda_l - \lambda_{mn}| b_D},$$

$$\chi_{r\xi}^{+(-)} = (E_r/K\theta_\xi)\eta_{r\xi}^{+(-)}, \quad \eta_{r\xi}^{+(-)} = \beta_{r\xi}^2 \sum_i \beta_{ri}^2,$$

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

$$H = \frac{1}{\mu} \sum_{i=1}^{M_1} h_{0i} \gamma_i + \left[ \frac{3}{2} + C_R \right] \frac{R}{\mu} T,$$

$$C_R = \sum_{i=1}^L \gamma_i + \frac{3}{2} \sum_{i=L+1}^S \gamma_i, \quad \mu = \sum_{i=1}^{M_1} \mu_i \gamma_i,$$

$$e_V^i = \gamma_i \frac{R}{\mu} \sum_{j=1}^{Z_i} \theta_{ij} \varepsilon_{ij}, \quad \varepsilon_\xi = g_\xi y_\xi / (1 - y_\xi),$$

$$\varepsilon_{\xi,0} = \varepsilon_\xi (y_\xi = y_{\xi,0}), \quad y_\xi = \exp(-\theta_\xi / T_\xi),$$

$$y_{\xi,0} = y_\xi (T_\xi = T),$$

$$P = \frac{\rho RT}{\mu}, \quad N = P/KT, \quad \gamma_i = N_i/N.$$

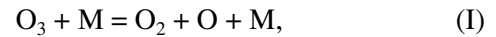
Here  $\rho$ ,  $T$ , and  $P$  are the density, temperature, and pressure of the gas;  $R$  is the universal gas constant;  $K$  is the Boltzmann constant;  $h_{0i}$  is the enthalpy of formation of the  $i$ th component of the mixture at  $T = 298$  K, and  $\mu_i$  is its molecular weight;  $S$  is the number of molecular components;  $L$  is the number of components that are linear molecules;  $\theta_\xi$  is the characteristic vibrational temperature of the  $\xi$  mode, and  $g_\xi$  is the multiplicity of its degeneration;  $Z_i$  is the number of the vibration types in the molecule of the  $i$ th type;  $W_{\xi,p}^i = \sum_{i=1}^{M_1} W_{\xi,p}^i \gamma_i$  in the case of the intramolecular V-V' exchange, and  $W_{\xi,p}^i = W_{\xi,p}^i \gamma_j$  ( $\xi \longleftrightarrow i, p \longleftrightarrow i$ ) in the case of the intermolecular V-V' exchange;  $W_{\xi,0}^i$  is the rate constant of the V-T relaxation during the collision with the  $i$ th partner;  $N_i$  is the density of the molecules of the  $i$ th type;  $M_1$  is the amount of atomic and molecular components in the mixture;  $l_\xi$  is the amount of vibrational quanta lost or acquired by the mode  $\xi$  under the V-V' exchange ( $L_1$  is the number of channels of V-V' exchange);  $\alpha_{iq}^+$  and  $\alpha_{iq}^-$  are the stoichiometric coefficients of the  $q$ th reaction leading to the formation of the  $i$ th component;  $k_{+q}$  and  $k_{-q}$  are the rate constants of the direct (+) and reverse (-)  $q$ th reactions;  $L_2$  are the number of reactions leading to the formation (or destruction) of a molecule containing mode  $\xi$ ;  $M_2$  are the number of reactions producing the  $i$ th component;  $\beta_{r\xi}$  are the coefficients of deconvolution of the reaction  $r$  over the coordinates of normal vibrations;  $E_r$  is the portion of the activation energy of the reaction  $r$  that is due to the vibrational degrees of freedom;  $l_{\xi i}$  is the number of vibrational quanta acquired (or lost) by the mode  $\xi$  under the

induced transitions;  $N_m$  and  $N_n$  are the concentrations of O<sub>3</sub> molecules in the lower and higher states of the  $m \rightarrow n$  transition, and  $g_m$  and  $g_n$  are the multiplicities of degeneration of these states;  $h$  is Plank's constant;  $\lambda_{mn}$  is the wavelength in the center of the spectral line for the absorption transition  $m \rightarrow n$ , and  $A_{mn}$  is the Einstein coefficient for this transition;  $b_D$  is the Doppler width and  $b_C$  is the collision width of the spectral line at the half-height;  $c$  is the speed of light in a vacuum;  $H(x, a)$  is the Voigt function; and  $A_V$ ,  $B_V$ , and  $C_V$  are the rotational constants of the O<sub>3</sub> molecule in the ( $V_1 V_2 V_3$ ) state, and  $E_j^m$  and  $E_j^n$  are the rotational energies of the O<sub>3</sub> molecule in the  $m$  and  $n$  states. To calculate  $H(x, a)$ , the coefficients  $b_C^M$  of the collision broadening of the spectral lines 000(12<sub>1,11</sub>)  $\rightarrow$  001(11<sub>1,10</sub>) in the O<sub>3</sub> molecule ( $M = O, O_2, O_3$ ) were estimated under assumption that the gas-kinetic and optical sections are the same. The  $\beta_{r\xi}$  values, as those in [3, 4], were taken to be equal to unity. In the framework of the mode approximation, when the translational and vibrational degrees of freedom of the molecules participating in the reaction are not equilibrated, the rate constant of the chemical reaction is a function of  $T$  and  $T_\xi$  and can be represented as

$$k_q = \varphi_q(T, T_\xi) k_q^0(T).$$

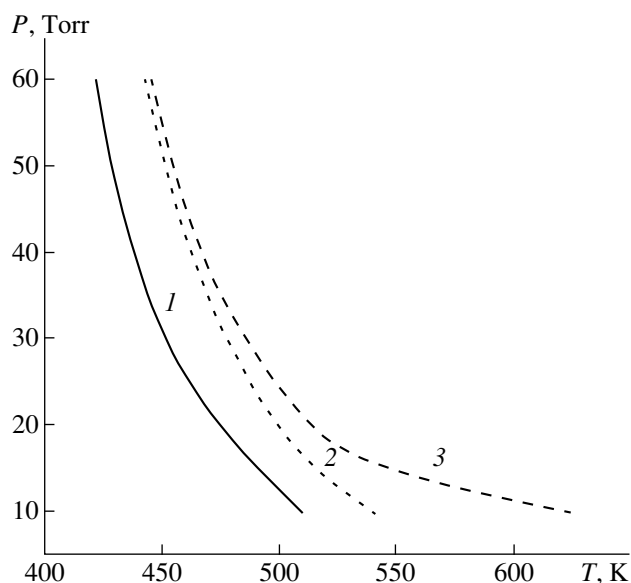
Here  $k_q^0(T)$  is the rate constant of the  $q$ th chemical reaction at  $T_\xi = T$ , and  $\varphi_q(T, T_\xi)$  is the nonequilibrium factor, which was calculated for the specified  $T$  and  $T_\xi$  as it was done in [13].

**Kinetic model.** A scheme of the chemical transformations in the O<sub>2</sub>-O<sub>3</sub> mixture without participation of electronically excited molecules involves only three reversible reactions [5]:



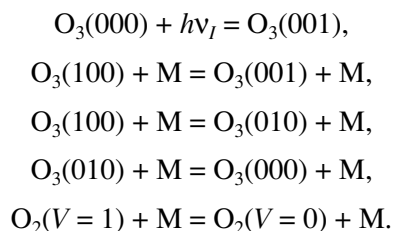
This scheme describes well experimental data on ozone self-ignition. Figure 1 compares (in the  $P$ - $T$  coordinates) the curve for ozone ignition in a closed reactor with the radius  $R_a = 3$  cm [11] and the curve calculated according to schemes (I)-(III) using the temperature dependences  $k_{+q}(T)$  and  $k_{-q}(T)$  borrowed from [13] (curve 2). Evidently, the calculated and observed data are in satisfactory agreement.

Note that the account of processes involving the electronically excited O<sub>2</sub>( $a^1\Delta_g$ ) and O<sub>2</sub>( $b^1\Sigma_g^+$ ) molecules using a model described in [14] does not noticeably alter the ignition curve for O<sub>3</sub> calculated using schemes (I)-(III). The electronically excited O<sub>2</sub> molecules are not likely to contribute to the ignition kinetics of the O<sub>2</sub>-O<sub>3</sub> mixture. In the framework of the mode model of the vibrational-energy exchange and chemical reactions (I)-(III), we analyzed the following processes

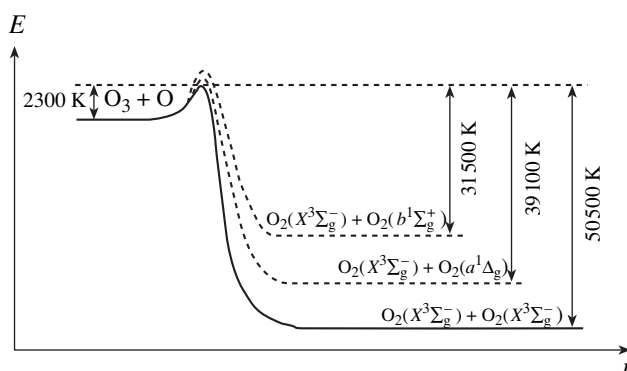


**Fig. 1.** Curves of ozone ignition in a closed reactor with the radius  $R_a = 3$  cm: (1) experimental data of [11], (2) calculation according to the thermal-nonequilibrium model of this study, (3) calculations of this study for determination of  $\alpha_r$  by formulas (1) and (2) for all electronically excited states of  $O_2$ .

of the intramode vibrational–vibrational (V–V') and vibrational–translational (V–T) exchange and the stimulation of asymmetrical vibrations of the  $O_3$  molecule with laser radiation:



The relaxation equations suggested that the exact resonance exists between the  $\nu_1$  and  $\nu_3$  modes of the  $O_3$  molecule, and we analyzed corelaxation of the  $\nu_1$  and  $\nu_3$  modes. The rate constants of (V–V') and (V–T) exchanges were taken as those in [13]. Developing a model that takes into account the mutual influence of nonequilibrium stimulation of vibrations of reacting molecules and chemical transformations involves an important problem of estimation of the vibrational energy  $E_r$  of the molecule formed in the elementary chemical reaction. In the mode model,  $E_r$  is a portion of energy released during the reaction leading to the formation of this molecule [15]:  $E_r = \alpha_r E_a$ . The value  $\alpha_r$  largely depends on vibrational levels of the reacting molecule (higher or lower) from which the reaction occurs; it belongs to the range  $0 \leq \alpha_r \leq 1$  [15]. For the calculation of  $E_r$ , it was suggested in [16] that when the chemical reaction forms a molecule, the vibrational degrees of freedom acquire the released energy, which



**Fig. 2.** Energy diagram of the  $O + O_3 = 2O_2$  reaction.

is equal to the vibrational energy of the molecule participating in overcoming the activation barrier of the chemical reaction that leads to the destruction of this molecule. Then,

$$E_r = \alpha_r E_{a_r}^+, \quad (1)$$

where  $\alpha_r$  is the coefficient of utilization of the vibrational energy, which was proposed in [17]. Its value is determined by the expression

$$\alpha_r = \frac{E_{a_r}^+}{E_{a_r}^+ + E_{a_r}^-}. \quad (2)$$

Here  $E_{a_r}^+$  is the activation energy of the  $r$ th chemical reaction occurring in the direction of destruction of the vibrationally excited molecule, and  $E_{a_r}^-$  is the activation energy of the reaction leading to its formation. The estimation of  $E_r$  using formulas (1) and (2) gives reasonable results for the recombination and exchange reactions in which the vibrationally excited molecule in the ground electron state is formed. In reactions (I)–(III), the  $O_2$  molecule can also be formed in the electronically excited states  $a^1\Delta_g$  and  $b^1\Sigma_g^+$ . This can be seen in Fig. 2, which shows the energy diagram of reaction (II). Therefore, a portion of energy released in this chemical reaction (as well as in reaction (I)) will be consumed for vibrations of the electron states  $a^1\Delta_g$  and  $b^1\Sigma_g^+$ . On the contrary, the vibrational energy of  $O_2$  molecules not only in the ground electron state but also in the  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  states will be consumed to overcome the activation barrier of the reverse reaction (II) ( $E_a = 50500$  K). To determine the  $\alpha_r$  value for reactions (I)–(III), we suggested that the  $O_2(X^3\Sigma_g^-)$  molecules are excited to the lower vibrational levels  $V = 1–5$  (the energy of the level with  $V = 5$   $E_{V=5}$  is 11300 K, and the energy of the  $O_2$  molecule in the state  $a^1\Delta_g$  with  $V = 0$  is 11391 K). In this case, the  $\alpha_r$  value for these reactions can be taken to be 0.2–0.3 [15]. Therefore, we

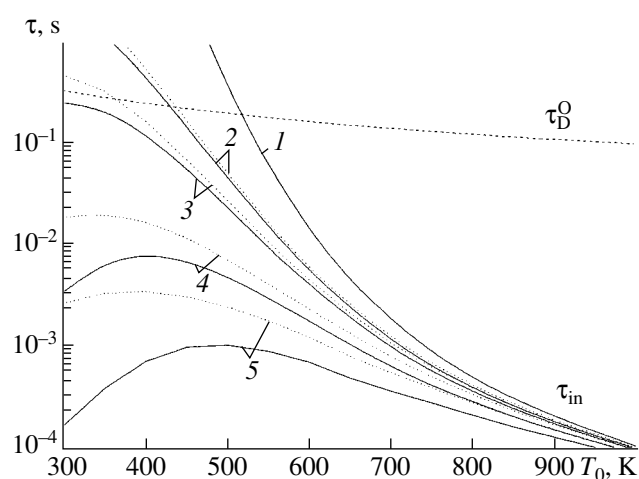
assumed  $\alpha_r = 0.7$  for the calculations of the O<sub>2</sub>( $a^1\Delta_g$ ) state and  $\alpha_r$  was calculated according to formula (1) and (2) for the O<sub>2</sub>( $b^1\Sigma_g^+$ ) state; for the O<sub>2</sub>( $X^3\Sigma_g^-$ ) state, we suggested  $\alpha_r = 0.2$ . With these  $\alpha_r$  values, the model taking into account the mutual influence of the vibrational kinetics and chemical transformations (the thermal-nonequilibrium model of chemical kinetics) results in the same curve for ozone ignition as the model of the conventional thermal equilibrium of chemical kinetics, which describes the experimental data with an error of at most 7% (curve 2 in Fig. 1). At the same time, when  $\alpha_r$  is estimated according to formulas (1) and (2) for all O<sub>2</sub> states ( $X^3\Sigma_g^-$ ,  $a^1\Delta_g$ , and  $b^1\Sigma_g^+$ ), the model significantly overestimates the ignition temperature (Fig. 1, curve 3).

### INITIATION OF COMBUSTION OF THE O<sub>2</sub>-O<sub>3</sub> MIXTURE BY RADIATION WITH $\lambda_l = 9.695 \mu\text{m}$

The mixture in an adiabatic reactor with radius  $R_a$  can self-ignite when the following condition is fulfilled:  $\tau_{iq}^{\text{ch}} \leq \tau_D^i$  [1]. In this case,  $\tau_D^i = R_a^2/D_O$ , where  $D_O$  is the diffusivity of O atoms that participate in the reaction  $O + O_3 = 2O_2$  responsible for the heating of the mixture. Therefore, in the first approximation, the ignition temperature  $T_{\text{ign}}$  can be estimated from the relation  $\tau_{\text{in}}(T_{\text{ign}}, P_0) = \tau_D^i(T_{\text{ign}}, P_0)$ . Upon exposure to laser radiation, the  $\tau_{\text{in}}$  value depends not only on the initial parameters of the mixture but also on the vibration temperature of the asymmetrical vibrations of the O<sub>3</sub> molecule. The latter is determined by the radiation intensity  $I_0$  and pulse duration  $\tau_p$ .

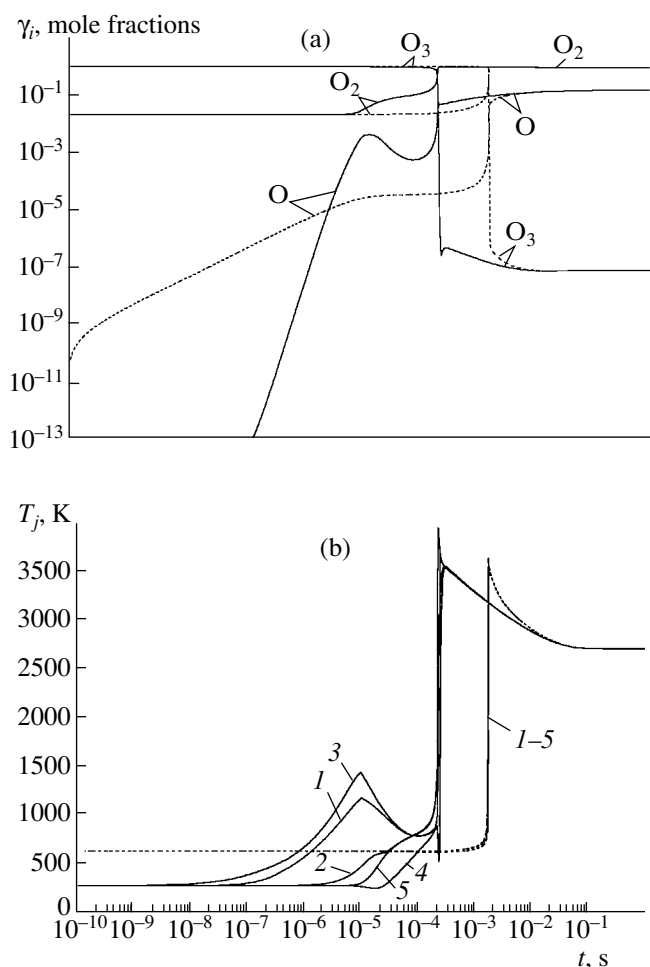
Figure 3 presents the period  $\tau_{\text{in}}$  and diffusion time  $\tau_D^i$  as the functions of ozone initial temperature  $T_0$  at  $P_0 = 10^3$  Pa for  $R_a = 10$  cm and radiation with  $\lambda_l = 9.695 \mu\text{m}$  and  $\tau_p = 10^{-5}$  s at various laser radiation fluxes applied to the gas,  $E_{\text{in}} = I_0\tau_p$ . It can be seen that the induction period and ignition temperature substantially decrease after treatment with radiation even at small  $E_{\text{in}} = 0.15 \text{ J/cm}^2$ . When the radiation is absent,  $T_{\text{ign}} = 520$  K and decreases to 300 K at  $E_{\text{in}} = 0.15 \text{ J/cm}^2$ . Note that at this  $E_{\text{in}}$ ,  $P_0 = 10^3$  Pa, and  $T_0 = 300$  K, the radiation energy consumed by one O<sub>3</sub> molecule,  $E_s$ , is  $6.79 \times 10^{-2}$  eV.

When  $E_{\text{in}}$  increases,  $\tau_{\text{in}}$  continues to decrease. This decrease is observed upon both a purely thermal effect of laser radiation and stimulation of the asymmetrical vibrations of O<sub>3</sub>. However, in the latter case, a decrease in  $\tau_{\text{in}}$  is much greater. At  $E_{\text{in}} = 0.5 \text{ J/cm}^2$  and  $T_0 = 300$  K ( $E_s = 1.46 \times 10^{-1}$  eV/molecule), the  $\tau_{\text{in}}$  values under both purely thermal initiation of the O<sub>3</sub> combustion and nonequilibrium stimulation of the vibrations of the O<sub>3</sub> molecule differ by 16 times. This can be due to the fact



**Fig. 3.** A plot of  $\tau_D^i$  (dashed line) and  $\tau_{\text{in}}$  vs. the initial temperature of O<sub>3</sub> at  $P_0 = 10^3$  Pa for various laser radiant fluxes  $E_{\text{in}}$  applied to the gas ( $\text{J/cm}^2$ ): (1) 0, (2) 0.1, (3) 0.15, (4) 0.3, (5) 0.5;  $\tau_p = 10^{-5}$  s at  $R_a = 10$  cm; the purely thermal effect is shown by a dotted line and stimulation of the asymmetrical mode of O<sub>3</sub> is shown by a solid line.

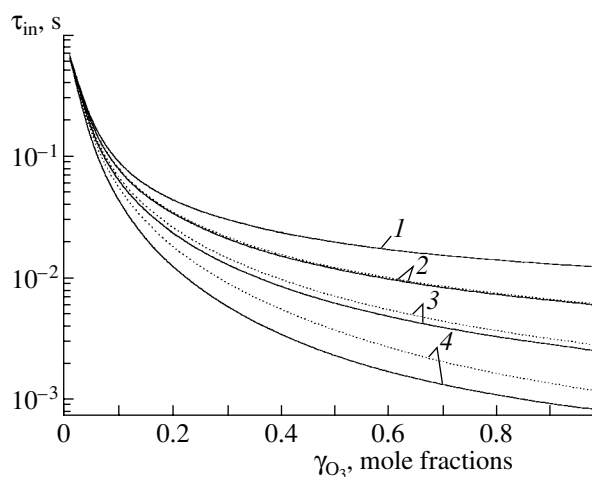
that the stimulation of asymmetrical vibrations of O<sub>3</sub> by radiation with  $\lambda_l = 9.695 \mu\text{m}$  accelerates the formation of active O atoms because of an increase in the rate of reaction (I) in the presence of excited molecules of O<sub>3</sub>(001, 100) (nonequilibrium factor  $\phi(T, T_j > 1$  at  $T_3, T_1 > T$ ). An increase in the concentration of O atoms leads to an increase in the rate of the reaction  $O + O_3 = 2O_2$  in which the energy is released. As a result, the mixture is heated more rapidly and thermal explosion is initiated. Figure 4 illustrates the dynamics of the concentrations of the mixture components as well as  $T$  and  $T_j$  ( $j = 1, 2, 3$ , and 4) for various ozone treatments by the radiation with  $\lambda_l = 9.695 \mu\text{m}$  (the purely thermal effect and excitation of the  $\nu_3$  mode of the O<sub>3</sub> molecule). As can be seen, the excitation of ozone to the 001 state with laser radiation sharply increases the concentration of O atoms at  $t = \tau_p$  and  $\tau_p = 10^{-5}$  compared to the case of instant release of the radiation energy consumed by the O<sub>3</sub> molecules at the translational degrees of freedom (in this case, the temperature increases from 300 to 654 K). When O<sub>3</sub> is excited to the 001 state,  $T$  does not exceed 330 K at the moment  $t = \tau_p$ . Despite such a substantial difference in the translational temperatures in the  $[0, \tau_p]$  range, the ignition of the mixture upon excitation of the O<sub>3</sub> molecules occurs much more rapidly because the reaction  $O + O_3 = 2O_2$ , which is largely responsible for an increase in the temperature in the induction period, is additionally accelerated due to an increase in the concentration of O atoms. Note that when the thermal nonequilibrium state ( $T_j \neq T$ ) is taken into account, the translational and vibrational temperatures at  $t < \tau_{\text{in}}$  become different. However, the final  $T$  value, as should be expected, coincides with the thermodynamic-equilibrium value



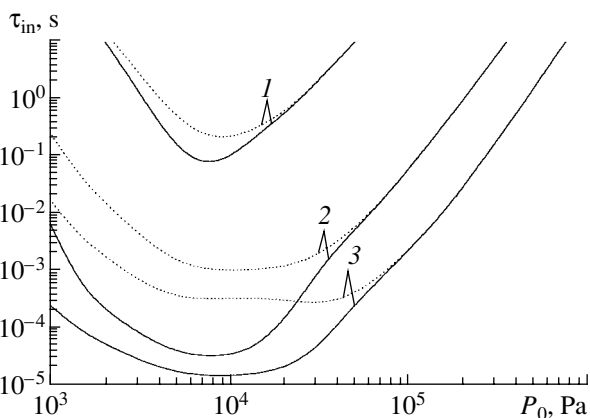
**Fig. 4.** Variation in time of (a) concentrations of the components of the mixture  $\gamma_i$ , (b) vibrational temperatures  $T_j$  ((1)  $T_1$ , (2)  $T_2$ , (3)  $T_3$ , and (4)  $T_4$ ) and (5) translational temperature  $T$  under the purely thermal action of laser radiation (dotted lines) on the 0.015 : 0.985  $O_2$ - $O_3$  mixture at  $T_0 = 300$  K and  $P_0 = 10^3$  Pa and excitation of the asymmetrical mode of  $O_3$  by radiation with  $\lambda_l = 9.695$   $\mu\text{m}$ ,  $\tau_p = 10^{-5}$  s, and  $E_{in} = 0.5$   $\text{J}/\text{cm}^2$  (solid lines).

and the  $T$  value, which is observed for the combustion products under the use of the thermally equilibrium model ( $T_j = T$ ) of chemical kinetics.

The addition of molecular oxygen to ozone enhances an ignition delay and decreases the final temperature. However, the excitation of the  $\nu_3$  mode of the  $O_3$  molecule also results in a substantial decrease in the induction period; this is more efficient than the purely thermal effect. This fact is illustrated in Fig. 5, which presents  $\tau_{in}$  as a function of the  $O_3$  molar fraction in the mixture at  $P_0 = 10^3$  Pa,  $T_0 = 600$  K, and various values of  $E_{in}$  for two cases of the irradiation effect. At  $E_{in} = 0.5$   $\text{J}/\text{cm}^2$ , the difference in the  $\tau_{in}$  values under the purely thermal effect of radiation and the excitation of 001



**Fig. 5.** A plot of the induction period ( $\tau_{in}$  vs. molar fraction of  $O_3$  in the  $O_2$ - $O_3$  mixture at  $P_0 = 10^3$  Pa,  $T_0 = 600$  K for  $E_{in}$ ,  $\text{J}/\text{cm}^2$ : (1) 0, (2) 0.1, (3) 0.25, and (4) 0.5 during the purely thermal action of the radiation (dotted lines) and excitation of the asymmetrical mode of  $O_3$  by radiation with  $\lambda_l = 9.695$   $\mu\text{m}$  (solid lines).



**Fig. 6.** A plot of the induction period ( $\tau_{in}$  vs. the initial pressure of the 3 : 2  $O_2$ - $O_3$  mixture at  $T_0 = 300$  K,  $\tau_p = 10^{-5}$  s for  $E_{in}$ ,  $\text{J}/\text{cm}^2$ : (1) 0.1, (2) 0.5, (3) 1.0 under the purely thermal action of the radiation (dotted lines) and excitation of the asymmetrical mode of  $O_3$  by radiation with  $\lambda_l = 9.695$   $\mu\text{m}$  (solid lines).

state of the  $O_3$  molecule for the mixture with  $\gamma_{O_2} = 0.5$  is 60%.

However, the numeric analysis shows that both methods of mixture ignition become equally efficient when a pressure increases. This is due to the fact that an increase in  $P_0$  results in the accelerated energy relaxation of the vibrationally excited  $O_3$  molecules; in this case, the whole effect is reduced to the thermal action of radiation. These regimes were studied in [7]. The dependence  $\tau_{in}(P_0)$  for the 3 : 2  $O_2$ - $O_3$  mixture at

$T_0 = 300$  K and various  $E_{in}$  values is shown in Fig. 6. As can be seen, the greater the radiation energy applied to the gas, the greater the boundary pressure at which the two methods become equally efficient. In the region of low pressures  $P_0$  ( $\sim 10^3$ – $10^4$  Pa), the efficiency of the method based on the nonequilibrium stimulation of the asymmetrical vibrations of the O<sub>3</sub> molecule is 10–30 times higher.

### CONCLUSION

The stimulation of asymmetrical vibrations of the O<sub>3</sub> molecule by the radiation of a CO<sub>2</sub> laser ( $\lambda_l = 9.695$   $\mu\text{m}$ ) accelerates ozone dissociation and sharply increases the concentration of O atoms to produce the enhanced heating of the O<sub>2</sub>-O<sub>3</sub> mixture and, as a consequence, a decrease in the induction period and ignition temperature. The excitation of the O<sub>3</sub> molecules to the 001 state by the resonant laser radiation is several times more efficient from the standpoint of combustion initiation than the local heating of the O<sub>2</sub>-O<sub>3</sub> mixture with the IR radiation in the region of parameters where the rate of induced transitions is much higher than the rate of the V-T relaxation. A pressure increase at the same applied radiation energy decreases the effect of the nonequilibrium vibrational excitation of the O<sub>3</sub> molecules. However, this effect remains essential up to  $P_0 = 2 \times 10^4$  Pa even at low values of  $E_{in}$  ( $\sim 0.5$  J/cm<sup>2</sup>). The results obtained show that the stimulation of molecular vibrations of the initial reactants allows one to accelerate the ignition process occurring not only through chain reactions but also through the mechanism of thermal explosion.

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