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# EXPERIMENTAL STUDY AND NUMERICAL MODELING OF VIBRATIONAL OXYGEN TEMPERATURE PROFILES BEHIND A STRONG SHOCK WAVE FRONT

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The evolution of oxygen molecule vibrational temperature behind the front of a shock wave was studied at shock wave velocities 3–4.5 km/s and gas pressure ahead of the shock front 1–5 Torr. The results of vibrational temperature measurement confirmed the conception of separation of vibrational relaxation and dissociation zones behind the shock wave front at  $T \leq 6500$  K. It is observed that at  $T = 6500$ – $10\,500$  K the vibrational temperature decreased in comparison with its value characterized by the achievement of vibrational–translational equilibrium before the dissociation started. It is shown that the model should be modified to describe the evolution of the oxygen vibrational temperature under the conditions of vibrational relaxation and dissociation coupling.

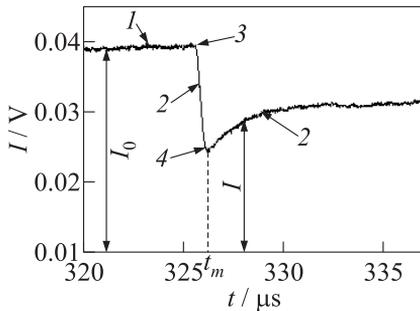
## 1 INTRODUCTION

Behind the front of a strong shock wave, the vibrational temperature depends on both the vibrational relaxation rate and the coupling of the vibrational relaxation and dissociation of molecules. Under these conditions, the processes in the gas cannot be described by a single temperature. The quantitative experimental data on the vibrational temperature of dissociating molecules are informative characteristic for the evaluation of the relationship between the rates of these processes, the determination of their rate constants, and then for the selection of suitable models of these processes at high temperatures when the possibilities of the experimental methods are exhausted. The evident lack of such data has already resulted in a catastrophic increase in the number of various dissociation models [1].

In the present work, the method of oxygen vibrational temperature determination behind the front of a shock wave is based on the comparison of oxygen molecule absorptive characteristics measured experimentally with detailed absorption spectra calculated for a number of vibrational and translational temperatures on the range 1000–11 000 K. Therefore, the requirements on the reliability of calculated absorption cross sections are very high. In this connection, the cross sections calculated for thermally equilibrium conditions in a gas using the “Spectrum” software [2] were first tested by comparing with the cross sections measured also in equilibrium conditions [3].

In the present study, the light absorption was investigated over the range of wavelengths  $\lambda = 200\text{--}260$  nm. This absorption was caused by the electronic transition of  $\text{O}_2$  molecule from the excited vibrational levels of the ground electronic state  $X^3\Sigma_g^-$  to the excited electronic state  $B^3\Sigma_u^-$  (Schumann–Runge system). For measured cross sections to have proper absorption characteristics of this electronic transition, the oxygen concentrations behind the shock front were specified to satisfy the Beer’s law:

$$A = 1 - \frac{I}{I_0} = 1 - \exp(-\sigma nl) \approx \sigma nl$$



**Figure 1** The oscillogram of light absorption for  $\lambda = 230$  nm. Initial gas conditions: 100%  $\text{O}_2$ ;  $P_1 = 1$  Torr;  $V = 4.13$  km/s; and  $T_{\text{fr}} = 9410$  K. Time  $t$  is given in the laboratory coordinate system

where  $A$  is the part of light absorbed by the gas;  $I_0$  and  $I$  are the amplitudes of the signals of the probing radiation passing through the measuring section of the shock tube before and after the passage of the shock wave, respectively (Fig. 1);  $\sigma$  is the absorption cross section,  $\text{cm}^2$ ;  $n$  is the concentration of the absorbing oxygen molecules,  $\text{cm}^{-3}$ ;  $l$  is the optical path length in the absorbing gas, i. e., the inner diameter of the shock tube, cm. In experiments [4], it was found that the proportionality of the absorption  $A$  to the concentration of the absorbing molecules holds at  $\sigma nl \leq 0.4$ .

The method of oxygen vibrational temperature determination proposed in the present study is not fundamentally novel. A similar method was used for the determination of the oxygen and nitrogen vibrational temperatures at high temperatures [5, 6]. However, for determining the vibrational temperature under thermally nonequilibrium conditions, the data on the equilibrium values of the cross sections were used, disregarding that the cross sections are the functions of both the translational and vibrational temperatures. Moreover,

in experiments [5, 6] the optical thickness of the gas layer studied was not always controlled; therefore, the correctness of the cross sections obtained is doubtful.

As compared with the method used in [5, 6], in the present method there are no such deficiencies, and detailed spectroscopic calculations make it possible to improve significantly the accuracy of the vibrational temperature measurement.

In the study, the numerical simulation of a high-temperature oxygen flow was performed under the conditions of coupling the processes of vibrational relaxation and dissociation behind the front of a shock wave. Maximally simple models are taken for the dissociation rate constants as functions of the temperatures  $T_v$  and  $T$  and for the relaxation equation that takes into account the dissociation of molecules. The preliminary results of the simulation and the comparison with the experimentally measured profiles of the vibrational temperature are discussed.

## 2 DETERMINATION OF THE VIBRATIONAL OXYGEN TEMPERATURE

The determination of the vibrational temperature  $T_v$  of the  $O_2$  molecules behind the front of a shock wave is based on the comparison of the absorption cross sections measured in the experiments and the cross-sections calculated over a wide range of translational and vibrational temperatures 1000–11 000 K.

In a shock tube, the profiles of light absorption were measured for two or three different wavelengths in experiments with the same initial gas mixture composition and gas pressure ahead of the shock front and close values of shock wave velocities  $V$ . For vibrational temperature determination, experiments for which the scatter of the velocities did not exceed 10–30 m/s (at  $V = 3$ –4.5 km/s) were chosen. The corresponding temperature scatter (for temperature  $T_{fr}$  immediately in the front of shock wave) was equal to 30–100 K.

The experimental setup and the method of oxygen absorption cross-section measurement in ultraviolet range of spectrum were described in detail in [3]. The typical oxygen absorption oscillogram is shown in Fig. 1 where the individual zones used for the determination of the vibrational temperature profile behind the shock front are marked. The radiation signals with amplitude  $I_0$  in the absence of shock wave and with amplitude  $I$ , changed by light absorption in the shock wave, are numbered by 1 and 2, respectively.

As in gas behind the shock front the molecular vibration levels corresponding to the observed optical transitions are occupied, the light absorption increases. The positions of the shock wave front and the maximum light absorption at  $t = t_m$  are numbered by 3 and 4, respectively. The gas temperature  $T_{fr}$  corresponds to the moment  $t = 0$  (position 3) when all the internal degrees of freedom of the molecules are frozen. As the vibrations are excited, the vibrational temperature  $T_v$  increases. At some moment  $t_m$ , the local vibrational–translational equilibrium is formed before the dissociation starts. In this case,  $T_v = T = T_1$ .

The similar situation takes place as the vibrational relaxation and dissociation zones are separated. For oxygen, the separation of the zones corresponds to the gas temperature not higher than 5000 K [7, 8].

When dissociation starts, the absorption decreases. During dissociation development, the gas temperature decreases, but at each moment,  $T_v = T$ . At temperatures above 5000–6000 K, the dissociation and vibrational relaxation occur simultaneously near the shock front. Though the maximum in absorption is also observed, the temperature at the moment  $t_m$  is not equal to the temperature  $T_1$ .

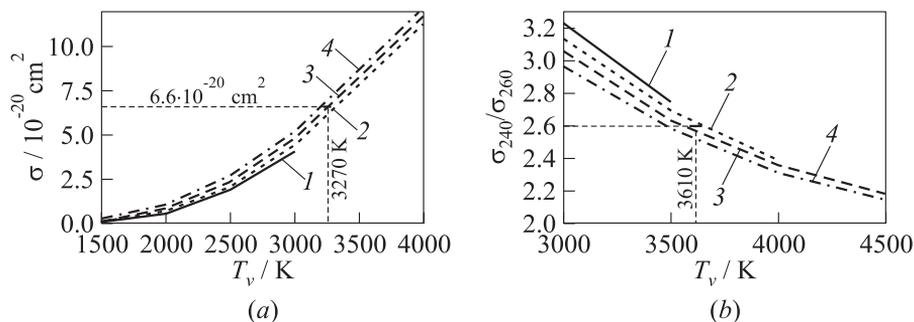
The values  $T_{fr}$ ,  $T_1$ , and the other gas flow parameters (at moments  $t = 0$  and  $t = t_m$ ) can be determined from the solution of the standard system of equations for the conservation of the mass, momentum, and energy fluxes on the shock discontinuity, together with the equation of state, for known gas parameters ahead of the shock front and the velocity of shock wave propagation over the gas [9].

At recording the oscillograms of light absorption behind the shock front, the time resolution is closely related with the accuracy of the temperature measurement. During the movement of the front past, the test section windows of the shock tube, the time for integrally averaging the radiation signal over the width of the optical slit (0.3 mm) was equal to 0.1–0.07  $\mu\text{s}$  at  $V = 3\text{--}4.5$  km/s, respectively. The indications from oscillograms were taken in each 0.1  $\mu\text{s}$ . Precisely on this time interval, the complete replacement of heated gas portions that moved past the optical slits occurred.

## 2.1 Temperature $T_{fr} \leq 6000$ K

For the determination of the  $\text{O}_2$  molecule vibrational temperature, the profiles of the quantities  $I/I_0$  were measured from the oscillograms. At temperatures not higher than 6000 K, the idea of separation of the vibrational relaxation and dissociation zones was used. In this case, the determinations of the vibrational temperature are methodically different at moments  $t \leq t_m$  and  $t > t_m$ .

**Vibrational relaxation zone.** At  $t \leq t_m$ , the concentration of the oxygen molecules  $n$  changes during vibration excitation only slightly and this variation is taken into account in processing the experimental data. The temperature  $T_v$  increases and can be determined from a single experiment by comparing the cross-section measured  $\sigma$  with the value  $\bar{\sigma} = f(T, T_v)$  calculated using the “Spectrum” software [2]. The cross-section measured can be calculated from the relation  $\sigma = -\ln(I/I_0)/(nl)$ . The cross-sections calculated  $\bar{\sigma}$  are presented for  $\lambda = 240$  nm as functions of the vibrational temperature in Fig. 2a. In the calculations, the gas temperature  $T$  (translational temperature) was the parameter. It can be seen that on the temperature range considered, the absorption cross sections weakly depend on temperature  $T$ . Figure 2a shows the determination



**Figure 2** Examples of vibrational temperature determination at  $T_{fr} \leq 6000$  K (a) before the dissociation started; absorption cross section was calculated for  $\lambda = 240$  nm; and (b) after the dissociation started; absorption cross-section ratio was calculated for  $\lambda = 240$  and 260 nm. The gas temperature  $T$  is a parameter: 1 — 3000 K; 2 — 4000; 3 — 5000; and 4 — 6000 K

of the vibrational temperature  $T_v$  by comparing the cross-sections calculated with the cross-section measured at a certain point of the oscillogram (before dissociation started):  $\sigma = 6.6 \cdot 10^{-20}$  cm<sup>2</sup>.

**Dissociation zone.** Starting with the moment  $t = t_m$ , the local vibrational-translational equilibrium is established in the high-temperature gas and the gas is described by a single temperature ( $T_v = T$ ) which decreases during dissociation at  $t > t_m$ . The concentration of absorbing molecules also decreases and it is unknown *a priori*. In this case, the profile  $T_v$  can be determined only using the relation  $\ln(I/I_0)_1 / \ln(I/I_0)_2 = \sigma_1 / \sigma_2$  from the oscillograms for two wavelengths (the subscripts 1 and 2 relate to different wavelengths) at each moment. There is no need to know the oxygen concentration at these points. As mentioned above, the oscillograms were obtained for conditions with equal or close values of the shock-wave velocities.

In the present study, paired experiments were carried out for wavelengths on the range 200–260 nm. Figure 2b shows an example of temperature determination at a certain point of the O<sub>2</sub> dissociation zone when the temperature drop from  $T_1$  to the equilibrium temperature  $T_{eq}$  was 4300–3300 K. In the graph, the vibrational temperature  $T_v = 3610 \pm 50$  K was determined at the moment on the oscillograms, which corresponded to the cross-sections ratio equal to 2.6. In the figure, the horizontal segment corresponds to the indicated range of temperatures and the error of this graphical procedure is estimated (not greater than  $\pm 50$  K). We used the fact that behind the shock front, the vibrational temperature was always less than or equal to the translational temperature at each moment.

The real uncertainty of temperature determination was found to be considerably greater and equal to 7%–10%. Its components are determined by both

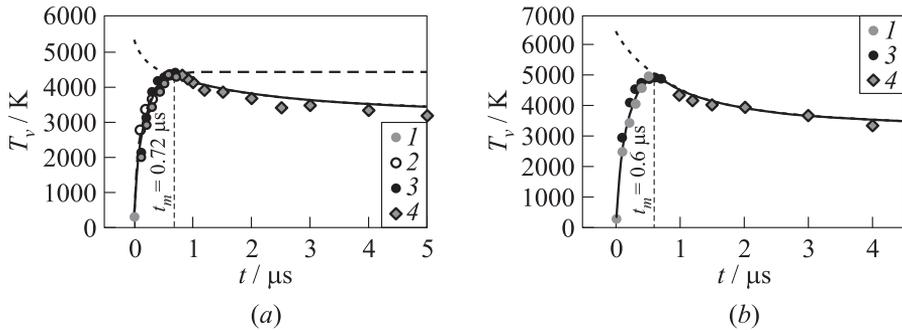
errors in shock wave velocity measurements ( $\sim 1\%$ ) and slightly different velocities of shock wave in the paired experiments. The nonsimultaneous registration of the paired oscillograms led to difficulties in determining the identity of shock front positions in them. This also increased the scatter of the measured values of  $T_v$ , especially at  $t < t_m$ , which resulted in increase in uncertainty up to 10%.

## 2.2 Temperature $T_{fr} > 6000$ K

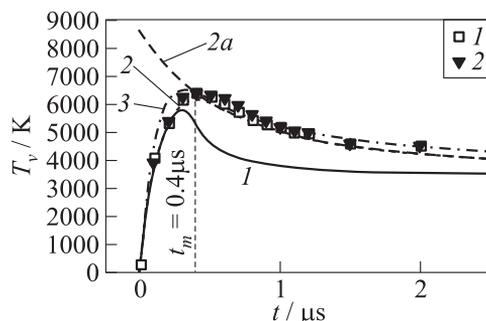
At these temperatures, it is assumed that the zones of vibrational relaxation and dissociation behind the front of the shock wave are not separated. The molecule dissociation starts close to the shock front simultaneously with vibrational relaxation. In this case, at any moment, the vibrational temperature can be determined only by comparing the calculated and measured cross-section ratios for two wavelengths.

## 3 TIME HISTORIES OF THE VIBRATIONAL TEMPERATURE

In Figs. 3 and 4, the profiles of the vibrational temperature measured behind the shock front in oxygen with different velocities of the shock wave are presented. In Fig. 3a, the temperature  $T_v$  at the initial moments ( $t \leq t_m$ ) was determined



**Figure 3** Profiles of the vibrational temperature measured behind the shock front in oxygen with  $P_1 = 2$  Torr and velocity of the shock wave  $V = 3.07$  km/s ( $T_{fr} = 5300$  K) (a) and  $P_1 = 1$  Torr and  $V = 3.4$  km/s ( $T_{fr} = 6470$  K) (b): solid curves refer to calculations using the  $O_2$  dissociation rate constant  $k_0$  from [10] and the vibrational relaxation time  $\tau_0$  from [11, 12]; dashed curve refers to calculations in the absence of  $O_2$  dissociation; dotted curves refer to the profile of the translational temperature; 1 — 240 nm; 2 — 250; 3 — 260 nm; and 4 — on ratio of  $\sigma_{240}/\sigma_{260}$



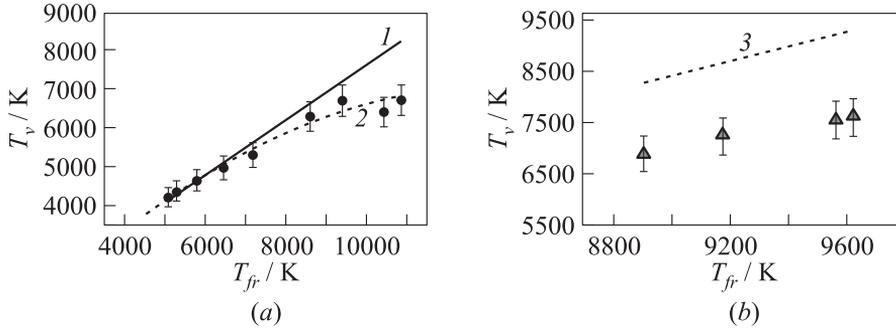
**Figure 4** Profiles of the vibrational temperature measured behind the shock front in oxygen with  $P_1 = 1$  Torr and  $V = 3.95$  km/s ( $T_{fr} = 8620$  K). The curves: 1 —  $T_v$  calculated using the  $O_2$  dissociation rate constant  $k_0$  from [10] and the vibrational relaxation time  $1.5\tau_0$ , where  $\tau_0$  was taken from [11, 12]; 2 and 2a —  $T_v$  and  $T$  calculated for  $k_0/5$  and  $1.5\tau_0$ ; 3 —  $T_v$  calculated for  $k_0/5$  and  $\tau_0$ ; squares refer to  $\sigma_{220}/\sigma_{260}$ ; and triangles refer to  $\sigma_{230}/\sigma_{260}$

separately from each oscillogram ( $\lambda = 240, 250,$  and  $260$  nm) using graphs similar to Fig. 2a. After the achievement of maximum absorption at  $t > 0.72$   $\mu$ s, the plot for the ratio of the cross sections in Fig. 2b was used for temperature determination. One notes that in Fig. 3a, the temperature calculated for conditions of local vibrational-translational equilibrium ( $T_1$ ) is equal to 4300 K. The maximum vibrational temperature  $T_v^{\max}$  measured at  $t_m = 0.72$   $\mu$ s was in good agreement with the value  $T_1$ . In Fig. 3b, the values  $T_v$  were determined similarly, the absorption oscillograms were obtained for  $\lambda = 240$  and 260 nm. The calculated temperature  $T_1 \sim 5100$  K, this value being 100 K higher than the temperature  $T_v^{\max}$  measured at  $t_m \sim 0.6$   $\mu$ s.

In Fig. 4, the profiles  $T_v$  are shown at  $T_{fr} = 8620$  K ( $T_v^{\max} = 6390$  K,  $T_1 = 6680$  K). The measured  $T_v$  values were obtained using the ratio of cross sections for two pairs of oscillograms: at  $\lambda = 220$  and 260 nm and  $\lambda = 230$  and 260 nm.

On the temperature range  $T_{fr} = 3500$ – $6500$  K, the agreement was observed between the values of temperature  $T_1$  calculated on the assumption of vibrational-translational equilibrium before the dissociation started and temperatures  $T_v^{\max}$  measured for maximum absorption. This result confirms the assumption concerning the separation of the vibrational relaxation and dissociation zones for this temperature range.

The study shows that as the shock wave velocity increases (the temperature  $T_{fr}$  increases), the maximum vibrational temperature  $T_v^{\max}$  measured in experiment lags more and more behind the temperature  $T_1$  calculated for the same experimental conditions. The vibrational temperatures measured at the



**Figure 5** Dependence of the maximum oxygen vibrational temperature behind the front of the shock wave on  $T_{fr}$ . Symbols show the maximum vibrational temperature  $T_v^{\max}$  measured at the moment  $t_m$ . Straight lines 1 and 3 represent the vibrational temperature  $T_1$  calculated for the same experimental conditions, curve 2 is an approximation of experimental points: (a) undiluted oxygen, and (b) gas mixture 20%  $O_2$  – 80% Ar

moment  $t_m$  are presented in Fig. 5 for both undiluted oxygen and gas mixture 20%  $O_2$  – 80% Ar. In undiluted oxygen, the difference of the measured temperature  $T_v^{\max}$  from the calculated one  $T_1$  (line 1) was observed already at  $T_{fr} \sim 6500$  K. Then, with increasing temperature  $T_{fr}$ , this difference increased and reached 1500 K at  $T_{fr} \sim 10500$  K. In the mixture of oxygen and argon (Fig. 5b), on the temperature interval  $T_{fr} = 8800$ – $9600$  K, the difference between the values  $T_1$  (curve 3) and  $T_v^{\max}$  was equal to 1300–1400 K. Thus, for high temperatures behind the front of the shock wave, the population of vibration levels did not reach the equilibrium values before the dissociation started and the vibrational temperatures corresponding to maximum absorption turned out to be lower than the value  $T_1$ . In undiluted oxygen, the vibrational relaxation proceeded more efficiently as compared with the gas mixture with a large content of argon due to the presence of oxygen molecules and atoms. Therefore, at the same temperatures  $T_{fr}$ , in Fig. 5a, the difference between temperatures  $T_1$  and  $T_v^{\max}$  is less than in Fig. 5b.

#### 4 PRELIMINARY RESULTS OF THE SIMULATION AND COMPARISON WITH THE EXPERIMENT

In the present study, the simulation of high-temperature gas flow behind the front of a shock wave was carried out. Together with the one-dimensional gas-dynamic equations for stationary flow [9], the system of ordinary differential equations describing the coupled oxygen dissociation and vibrational excitation in the shock

wave was solved. The Geer method was used in a standard program. The partial derivatives of right sides of the differential equations with respect to the composition parameters were calculated explicitly. Viscosity, heat conduction, and diffusion were not taken into account.

As mentioned above, at temperatures higher than 6000 K, the dissociation of molecules can occur in thermally nonequilibrium conditions when their vibration excitation (the vibrational temperature) is not in equilibrium with the translational temperature. In this case, for describing the kinetics of physicochemical processes in gas, the coupled vibration-dissociation-vibration (CVDV) model is commonly used [13]. It is assumed that the dissociation rate constant  $k_d(T, T_v)$  depends on the gas temperature  $T$  and the vibrational temperature of a dissociating molecule  $T_v$ , whereas the average vibrational energy of the molecule is determined by the change in the species concentration during the chemical reaction. Since in the present study, the processes far from the conditions of complete thermodynamic equilibrium are considered, in the relaxation equation the influence of recombination on the change in the average vibrational energy  $\varepsilon$  per  $O_2$  molecule in the dissociating gas was neglected. Then, the equation for the relaxation of the energy  $\varepsilon$  can be written in the form:

$$\frac{d\varepsilon}{dt} = \frac{\varepsilon_0 - \varepsilon}{\tau} - (E - \varepsilon) \sum_i k_{di} N_i.$$

Here,  $N_i$  is the number concentration of  $O_2$ , O, Ar per unit volume;  $\varepsilon_0$  and  $\varepsilon$  are the equilibrium and current values of the vibrational energy per molecule;  $\tau$  is the time of vibrational relaxation;  $k_{di}$  is the rate constant of dissociation  $O_2$  during the interaction with the  $i$ th particle; and  $E$  is the average vibrational energy lost in a single event of  $O_2$  dissociation.

In the literature, there is a significant number of models intended for describing the rate constants of molecule dissociation under thermal nonequilibrium conditions. These models are systematized in reviews (see, for example, [1]) and usually represent the dissociation rate constants in the form:

$$k_d(T, T_v) = k_0(T)Z(T, T_v).$$

Here,  $Z(T, T_v)$  is the nonequilibrium factor characterized by the deviation of the internal degrees of freedom from equilibrium in the course of a chemical reaction, and  $k_0(T)$  is the equilibrium value of the rate constant corresponding to the condition  $T = T_v$ , i. e., at  $Z = 1$ .

The expressions for the rate constant in different models contain their own values of the average vibrational energy  $E$  lost in a single event of  $O_2$  dissociation. This value varies from  $0.3D$  to  $D$ , where  $D$  is the energy of molecule dissociation. Kuznetsov's model [14] used in the preliminary simulation seems to be the simplest and the most comfortable:

$$k_d(T, T_v) = k_0(T) \frac{1 - \exp(-\theta/T_v)}{1 - \exp(-\theta/T)} \exp \left[ -\beta D \left( \frac{1}{T_v} - \frac{1}{T} \right) \right].$$

In [14], the parameter  $\beta \approx 0.7$  for the O<sub>2</sub> molecules.

In Figs. 3 and 4, the measured profiles of the vibrational temperature are compared with the calculated ones obtained in the simulation of the gas flow behind the front of the shock wave. In the calculations, the rate constants of oxygen dissociation were taken from [10] for all the partners O<sub>2</sub>, O, and Ar. They were presented in the form  $k_0 = AT^n \exp(-59380/T)$ , cm<sup>3</sup>/(mol·s), the  $A$  and  $n$  values being given in Table 1.

The temperature dependence of the vibrational relaxation time  $\tau_0(T)$  was taken from [11] for collisions O<sub>2</sub>–O<sub>2</sub> and from [12] for collisions O<sub>2</sub>–O. In the present study, the rate constants  $k_0$ , the vibrational relaxation time  $\tau_0$ , the coefficient  $\beta$ , and the average vibrational energy  $E$  lost in a single event of O<sub>2</sub> dissociation were varied in the simulation.

In Figs. 3 and 4, the measured and calculated profiles of the vibrational temperature behind the front of the shock wave in undiluted oxygen are shown. It can

**Table 1** The values of  $A$  and  $n$  for O<sub>2</sub>, O, and Ar [10] for temperature range 3000–18 000 K

$M$	$A$	$n$
Ar	$1.8 \cdot 10^{18}$	–1.0
O <sub>2</sub>	$9.8 \cdot 10^{24}$	–2.5
O	$3.5 \cdot 10^{25}$	–2.5

be satisfactorily described using the dissociation rate constant  $k_0$  from [10] without varying its values. All the results of the simulation shown in Figs. 3 and 4 were obtained on the assumption that the dissociation of molecules started in the shock front immediately (independently of the temperature),  $\beta = 0.7$ ,  $E = 0.2D$ .

For satisfactorily fitting the profiles at higher temperatures (see Fig. 4,  $T_{fr} = 8620$  K), the rate constants from [10] were decreased by a factor of 5 (curve 2). If the rate constants from [10] were used in simulation, the calculated profiles  $T_v$  sharply differed from the measured ones (curve 1). The similar picture was observed for other experimental conditions at  $T_{fr} = 8000$ – $10\,500$  K.

When analyzing the results of simulation, the authors observed a contradiction. In Figs. 3a and 3b, the both regimes were satisfactorily simulated when the rate constant  $k_0$  from [10] was used. This is not surprising because the recommendation for  $k_0$  was obtained using the known experimental data on O<sub>2</sub> dissociation on the temperature interval 2500–5500 K. At the same time, in Fig. 4, a part of the measured profile  $T_v$  after maximum (at  $t > t_m$ ) corresponds to almost the same temperatures and the condition  $T_v = T$  but the simulated profile does not describe the measured one with  $k_0$  from [10],  $\beta = 0.7$ , and  $E = 0.2D$ .

Successively varying the model parameters ( $\beta$ ,  $E$ , and the moment at which dissociation starts for certain values of nonequilibrium factor  $Z$ ) in various combinations (for the regime shown in Fig. 4), the authors have not managed to de-

scribe the experimental profile of vibrational temperature satisfactorily in none of the cases.

All these results indicate that the prehistory of the coupled process of vibrational relaxation and dissociation from the shock wave front to the moment  $t_m$  described by the model accepted with a set of constant parameters influences the further behavior of the calculated vibrational temperature (at  $t > t_m$ ).

## 5 CONCLUDING REMARKS

Using the developed method of determination of the oxygen molecule vibrational temperature, the profiles of the vibrational temperature are measured behind the front of a shock wave for the gas temperatures on the range 4000–10500 K. The measurements were carried out for the velocities of the shock wave on the range 3–4.5 km/s and the gas pressure ahead of the shock front on the range 1–5 Torr. The profiles of the vibrational temperature were characterized by a sharp rise near the front, presence of a maximum, and a further drop. The uncertainty of the measured temperature was below 10%.

At gas temperatures immediately on the front  $T_{\text{fr}} = 3500\text{--}6500$  K, within the limits of experimental errors, the measured maximum vibrational temperature is in good agreement with the temperature calculated on the assumption that the vibrational–translational equilibrium is reached before dissociation starts. This confirms the known assumption of the separation of the vibrational relaxation and  $\text{O}_2$  dissociation zones behind the front of a shock wave under these conditions.

As the velocity of a shock wave increases, the maximum vibrational temperature lags behind the vibrational temperature calculated on the assumption that the vibrational–translational equilibrium is reached before dissociation start. This means that at  $T_{\text{fr}} > 6500$  K, the population of vibration levels of the molecule has no time to reach the equilibrium values before dissociation starts, and at an initial stage, the dissociation occurs in the absence of vibrational equilibrium.

The comparison of the experimental data on the evolution of oxygen vibrational temperature behind the front of a shock wave with the preliminary results of simulation lead to the following conclusions.

The vibrational temperature measured during the initial stage of the relaxation process can be simulated using the known Millikan–White data for the vibrational relaxation time  $\tau_{\text{MW}}(T)$  at  $T_{\text{fr}} < 6500$  K. At  $T_{\text{fr}} > 6500$  K, in order to obtain a better agreement with the measured values  $T_v$ , it is necessary to increase the time  $\tau_{\text{MW}}(T)$  by a factor of 1.5–2. The measured profiles of the vibrational temperature can be described satisfactorily using the accepted model only at  $T_{\text{fr}} < 6500$  K. At higher temperatures, the model does not describe correctly the evolution of processes in nonequilibrium zone behind the shock front.

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