DETERMINATION OF THE VIBRATIONAL TEMPERATURE OF MOLECULAR OXYGEN BEHIND THE SHOCK WAVE FRONT USING ABSORPTION CHARACTERISTICS IN THE SCHUMANN-RUNGE SYSTEM

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Abstract. The distributions of vibrational temperature of oxygen molecules behind the front of shock wave were obtained for temperature range 3500-6000 *K*. The method of determination of vibrational temperature is based on comparison of measured and calculated oxygen absorbing characteristics. The measurements of absorption cross-sections of O_2 in spectral region of Schumann-Runge system were carried out behind the front of shock wave using absorption technique. The calculations of absorption spectrum of O_2 molecules were made for equal and unequal vibrational and translational temperatures. The calculated absorption cross-sections were tested with the help of ones measured in shock wave for case of vibrational-translational equilibrium.

INTRODUCTION

In the present study the vibrational temperature T_v of oxygen molecules was determined behind the shock wave front under conditions of vibrational-translational non-equilibrium ($T_v \neq T$). The method is based on comparison of measured and calculated oxygen absorption characteristics.

The theoretical absorption spectrum of O_2 was calculated for the Schumann-Runge system in cases of equal and unequal vibrational and translational temperatures. Since the calculated values of absorption cross-sections were used for methodical purpose, strong demands were imposed on calculation reliability. Therefore the verification of model for O_2 absorption spectrum calculation proposed in code "Spectrum" was performed. For this purpose, the absorption cross-sections calculated in conditions of thermal equilibrium were tested with the use of cross-sections measured behind the shock front for a set of wavelengths in the ultraviolet region. The measurements of absorption cross-sections were carried out behind the front of a shock wave when the vibrational relaxation ended and the vibrational temperature became equal to the translational one ($T_v = T$).

The experiments were performed on a shock tube using absorption technique and pulse source of light with continuous spectrum in the ultraviolet range. Absorption characteristics of oxygen heated by shock wave were obtained for two (or more) wavelengths at identical conditions in gas. The gas temperature was no higher than 6000 K and therefore it is assumed that the regions of vibrational relaxation and dissociation of O_2 molecules behind the front are separated[1].

In the experiments the O_2 concentration behind the shock front satisfied the condition of small thickness of the gas optical layer. In this case the connection between light absorption, concentration of absorbing molecules and absorption coefficients follows Beer's law.

1. CALCULATION OF OXYGEN ABSORPTION SPECTRUM

In the present calculations of O_2 absorption spectra only transitions in the Schumann-Runge system were taken into account, because it is known that in the wavelength range 130-270 nm the main contribution into absorption is realized by allowed transition $X^3\Sigma_g^-$ $\rightarrow B^3\Sigma_u^-$. Transitions to other low-energy electronic levels are forbidden. Absorption caused by $X^3\Sigma_g^- \rightarrow I^3\Pi_u^-$ transition is actual for wavelengths shorter than 140 nm.

The calculations of theoretical absorption spectrum of oxygen in Schumann-Runge system were performed by help of code "Spectrum" intended for calculations of diatomic molecule spectra[2]. In calculations of absorption spectrum, the absorption coefficient for each wavelength was computed by the summation of the absorption coefficients of rotational lines over all possible rotational-vibrational transitions in the Schumann-Runge system, including transitions into the continuous energy spectrum. The rotational-vibrational interactions in the O_2 molecule were taken into account that was justified by increasing role of energy states with high values of rotation momentum at high temperatures. With this aim the effective potential included the centrifugal forces was put into Schrödinger's equation.

Necessary for calculations of absorption spectrum, the $B^3\Sigma_u^-$ energy potential function and dipole momentum of electronic transition $X^3\Sigma_g^- \rightarrow B^3\Sigma_u^-$ were taken from[3]. The energy potential function of the ground state $X^3\Sigma_g^-$ was calculated using molecular constants from databases of informational calculating complex "MSRT-RADEN"[4].

2. EXPERIMENT

2.1. Measurement of absorption cross-sections

The experiments were carried out in a shock tube with inner diameter 50 mm. The high pressure chamber was filled with hydrogen to a pressure of 10 atm, or else with a stoichiometrical mixture of hydrogen and oxygen (30%), diluted with an inert gas (70%). In the second case, the mixture was ignited by electric discharge. The gas under study was admitted to the low-pressure chamber at a pressure from 2 to 30 Torr: either undiluted oxygen, or a mixture of oxygen (10 - 50%) and argon. After rupture of the membrane separating the high-pressure and low-pressure chambers of shock tube, the shock wave propagates along the low-pressure chamber at a velocity of 1.2-3.5 km/s. The velocity of the shock wave was measured using piezoelectric transducers mounted on the walls of the shock tube. The uncertainty of the velocity measurement was no greater than 1%.

In this study the absorption technique was used. The emission of the probing pulsed source illuminated the optical windows (with slits 0.3 *mm*) of shock tube and entered the input of vacuum monochromator. The optical windows were prepared from magnesium fluoride. The spectral device isolated a narrow section of ultra-violet spectrum.

At the output of the monochromator, the radiation reached a "blind" photomultiplier with sensitivity in the region 120-300 *nm*, the electric signal from which was recorded by multichannel oscilloscopes Tektronix TDS 3012B or Ajilent Technologies HP 54624A.

In recording the radiation, the frequency characteristics of the "photomultiplier-oscilloscope" channel mainly depended on the integrating effect of the optical slits. The electrons-transit time in R6836 Hamamatsu photo-multiplier was estimated as 0.03 *μs*. A summary time resolution was $0.2 \div 0.085$ *μs* in accordance with shock wave velocities $1.5 \div 3.5$ *km/s*.

As the light source, the illumination lamp operating in pulsed mode was used. It was a quartz tube with side electrodes and a quartz end window. The lamp was filled with argon, xenon or krypton. The light from the end of the lamp entered the optical windows of the shock tube. The gas pressure in the quartz tube was 7-15 *Torr*.

Absorption signals were detected at wavelengths of 210-270 *nm* corresponding to the electronic transition $X^3\Sigma_g^- \to B^3\Sigma_u^-$. Contribution to the absorption comes from rotational-vibrational transitions falling within the spectral range 1.6 and 0.85 *nm*. A typical oscilloscope trace for absorption of light by oxygen in the shock wave is shown in Fig.1. For the selected wavelength λ, the absorption was determined from the relation:

$$A = 1 - I/I_0 \tag{1}$$

Here the values I_0 and I are the amplitudes of the signals of the probing radiation passed through the measuring section of shock tube before and after passage of the shock wave front, accordingly (Fig.1). For the optically thin layer of gas, Beer's law describes the I/I_0 ratio as:

$$I/I_0 = \exp(-\sigma n l), \tag{2}$$

where σ is the spectral absorption cross-section per molecule, cm^2; l is the optical path length in absorbing gas, i.e. the inner diameter of the shock tube, *cm*; n is the concentration of absorbing oxygen molecules, cm^{-3}. The absorption cross-section σ corresponding to the wavelength range $\lambda \pm \Delta\lambda$ was calculated by formula (2) at known concentration n and the measured values of A. For the optically thin layer of gas, the exponent in (2) $\sigma n l < 1$ and then the value A can be written as $A \approx \sigma n l$. At greater values of exponent, the influence of the optical thickness of gas layer on the σ values measured by (2) is possible[5]. In this study the experiments were carried out at $\sigma n l \le 0.3$.
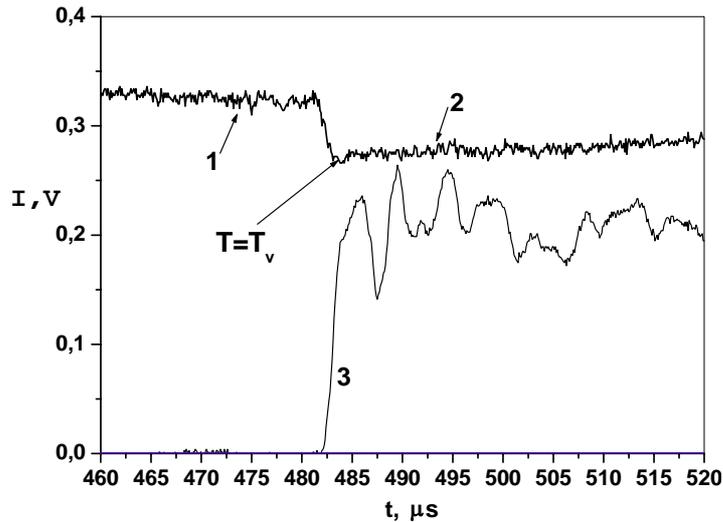
Figure 1. Oscilloscope trace for light absorption (λ=210 *nm*) behind a shock wave front. The trace 1 is a pulsed lamp emission in the absence of the shock wave. The trace 2 is a signal of pulsed lamp changed by absorption of light behind the shock wave front. The trace 3 is a signal from a piezoelectric transducer marking the arrival of the shock wave front to the optical window.

The software package "Microcal Origin" was used under oscilloscope traces handling. It enables to smooth the noisy experimental traces and to obtain averaged values of signals $\tilde{I}$ and $\tilde{I}_0$. For typical oscilloscope traces the smoothing uncertainties were 2-2.5%. Taking into account this value, the relative error of single measurement of absorption cross-section was $10\% \div 30\%$ for typical values *A*=0.15-0.25.
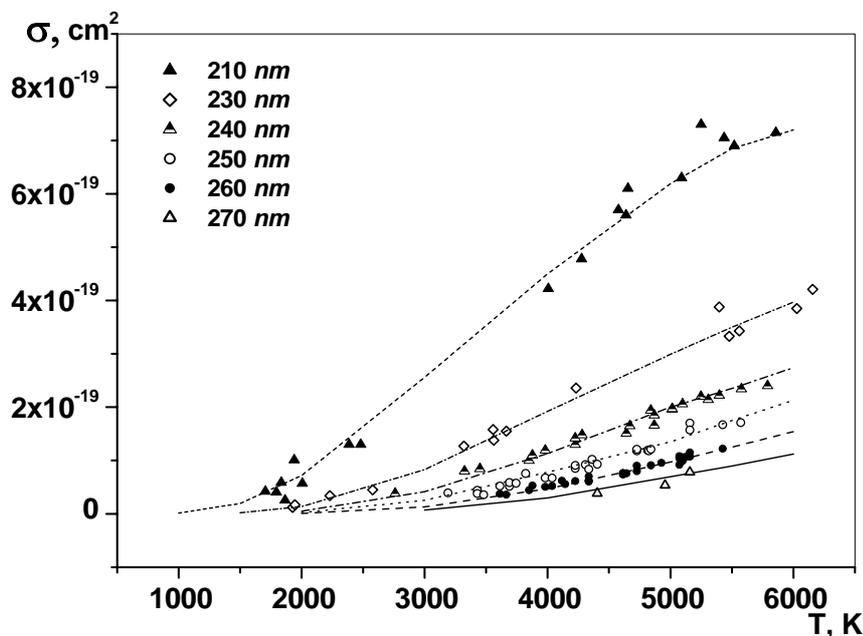

Figure 2. Absorption cross-sections of molecular oxygen in Schumann-Runge system (λ=210-270 *nm*) at high temperatures. The points represent the experiment, the curves represent calculated cross-sections.

The absorption cross-sections were determined from the oscilloscope traces at maximum absorption when vibrational relaxation of O_2 molecules has been completed, the vibrational temperature T_v became equal to translational one T (local vibrational-

translational equilibrium, $T_v = T$), but the dissociation does not start. This situation corresponds to separation of vibrational relaxation and dissociation zones at temperatures not higher than 5000-6000 K[1].

In Fig.2 the absorption cross-sections measured and calculated in conditions of vibrational-translational equilibrium are presented for wavelength interval 210-270 nm and temperature range 1500-6000 K. It is seen that the agreement of measured and calculated data is rather good. The relative root-mean-square errors due to the scatter of experimental data in reference to calculated curves are from 21% at λ=210 nm to 7-14% at λ=230-260 nm.

So, the cross-sections of molecular oxygen calculated for this spectral region are reasonably reliable that makes possible to use them as the methodic instrument for handling absorption characteristics and to obtain the kinetic coefficients described physical-chemical processes behind the shock front.

2.2.   Determination of the vibrational temperature

The light absorption at λ=210-270 nm is defined by the transitions from excited vibrational levels of ground electronic state $X^3\Sigma_g^-$ to vibrational levels of state $B^3\Sigma_u^-$. As vibrations of molecules are excited behind the front of shock wave the higher vibrational levels of state $X^3\Sigma_g^-$ are populated, and the absorption of light is observed. If the dissociation of molecules behind the front is small the absorption A increases from zero to some stationary value defined by gas parameters. With appreciable dissociation, after absorption reaches maximum value, it begins to decrease because of the O_2 concentration reduction (Fig. 1).

To determine a vibrational temperature profile of O_2 molecules behind the shock wave front, the time distributions of the I/I_0 value were measured from the oscilloscope traces for two wavelengths in experiments with close values of gas pressure and shock wave velocity. The $\ln(I/I_0)$- profiles are shown for wavelengths 240 and 260 nm in Fig.3.
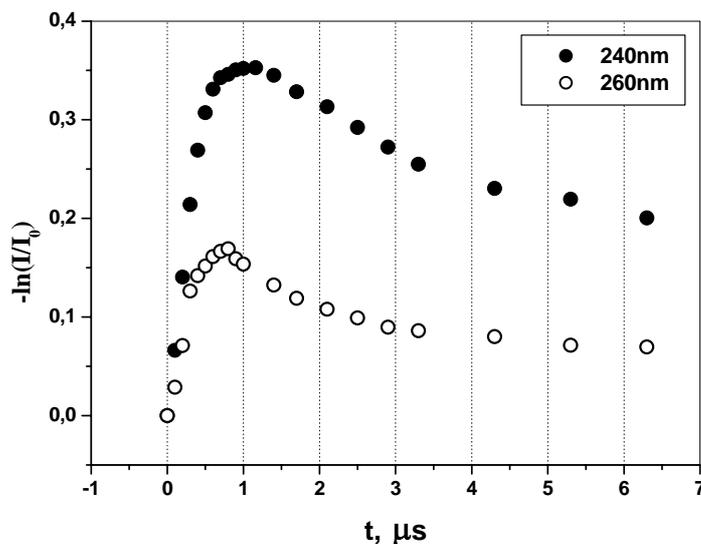

Figure 3. The profiles of the $-\ln(I/I_0)=\sigma n l$ - values behind the shock wave front measured from the absorption oscilloscope traces at wavelengths 240 (1) and 260 (2) nm. The gas ahead the shock front is 100% O_2; the initial pressure p_1 is 2 *Torr*; the velocity of shock front $V = 3.07$ *km/s* (1), 3.09 *km/s* (2).

The T_v values were determined for moments $t \le t_0$ and $t > t_0$. The moment t_0 corresponds to maximum absorption. At $t \le t_0$ the vibrational temperature increases and is not equal to the translational one ($T_v \ne T$), and the O_2 concentration changes weakly ($n \approx const$). In this case the vibrational temperature T_v may be determined from a single experiment by comparison of the measured cross-section σ with the calculated one $\overline{\sigma} = f(T, T_v)$. The cross-section σ is determined from the oscilloscope trace by formula (2). The calculated $\overline{\sigma}$-values as functions of vibrational temperature are presented in Fig.4 (a) for wavelength 240 nm with gas temperature T as a parameter. It is seen that the cross-section weakly depends on temperature T. The typical profile of T_v behind the shock wave front is presented as a function of time in Fig. 5. At $t \le t_0$ the T_v - values are obtained using oscilloscope traces for three wavelengths.
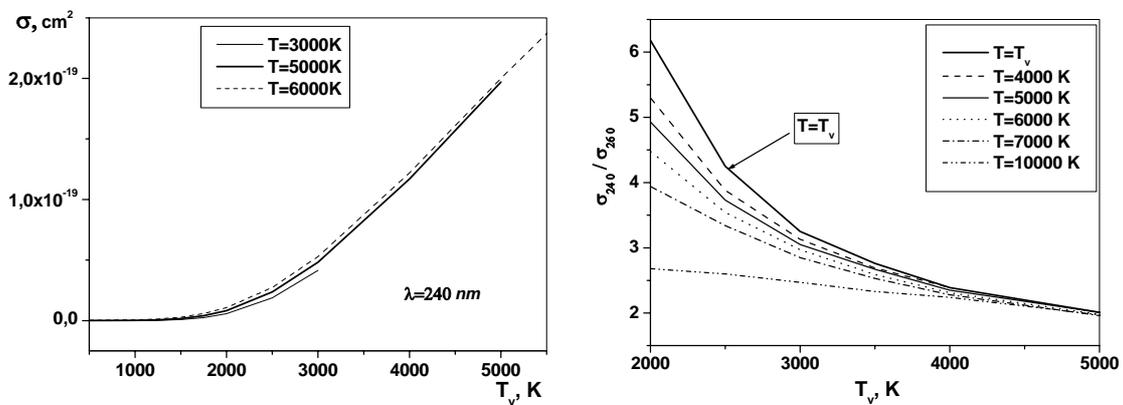

Fig. 4. Absorption cross-sections for λ=240 nm **(a)** and the ratio of absorption cross-sections for λ=240 and 260 nm **(b)** calculated as functions of vibrational temperature T_v at different gas temperature T.
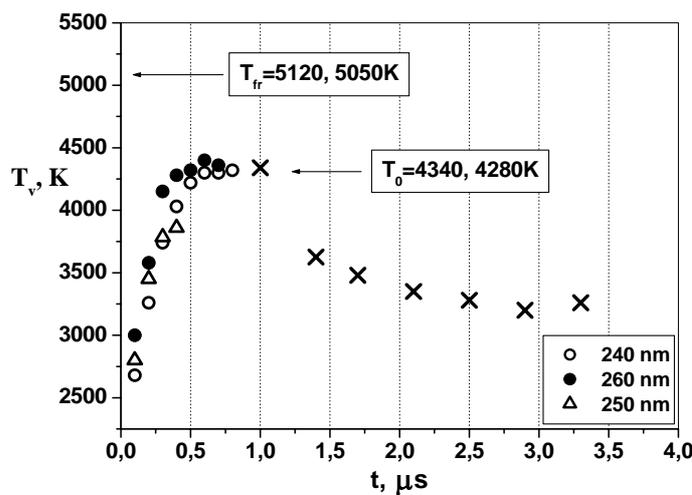

Figure 5. Distribution of the vibrational temperature T_v of the O_2 molecules behind the shock wave front. Gas parameters are the same as in Fig. 3. The values designated by crosses were obtained using ratio of absorption cross-sections for wavelengths 240 and 260 nm.

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After the onset of dissociation the O_2 concentration decreases. In this case, the ratio $\ln(I/I_0)_1/\ln(I/I_0)_2 = \sigma_1/\sigma_2$ measured from absorption oscilloscope traces for two wavelengths (Fig.3) is compared with the calculated ratio $\overline{\sigma}_1/\overline{\sigma}_2 = f(T, T_v)$ (Fig. 4b), and the value of T_v can be found.

The values of vibrational temperature obtained by means of the present method were compared with corresponding temperatures calculated for gas flow behind the front of shock wave in oxygen. For each experiment the temperature, gas pressure, and concentration of oxygen were calculated for two cases: 1) the vibrations are frozen; 2) vibrational equilibrium is established before the onset of dissociation. These parameters were determined as a solution of standard equation system for conservation of mass, momentum, and energy fluxes at the shock discontinuity, together with the equation of state:

$$\rho_1 V = \rho_2 v_2, \quad p_1 + \rho_1 V^2 = p_2 + \rho_2 v_2^2,$$
$$\sum_i \gamma_{i1} H_{i1} + V^2\!\!\Big/2 = \sum_i \gamma_{i2} H_{i2} + v_2^2, \quad p = \rho R T \sum_i \gamma_i \tag{3}$$

Here the subscripts 1 and 2 correspond to the gas parameters ahead and behind the shock wave front; p, ρ, T are the pressure, density, and gas temperature; V is the velocity of propagation of shock wave front in the gas; v_2 is the gas flow velocity behind the shock wave front (relative to the front); H_i and γ_i are the molar enthalpy and the molar-mass concentration of the i-th component of the gas mixture. In the case of completed vibrational excitation, the enthalpy of diatomic molecules is represented in the form:

$$H = \frac{7}{2}RT + \varepsilon, \quad \varepsilon = R\frac{\theta}{\exp(\theta/T_v)}$$

Here ε is the vibrational energy of the molecules calculated behind the shock wave front at $T_v = T$; ahead of the front in the unexcited gas $\varepsilon \approx 0$; θ is the characteristic vibrational temperature of O_2 equal to 2238 K.
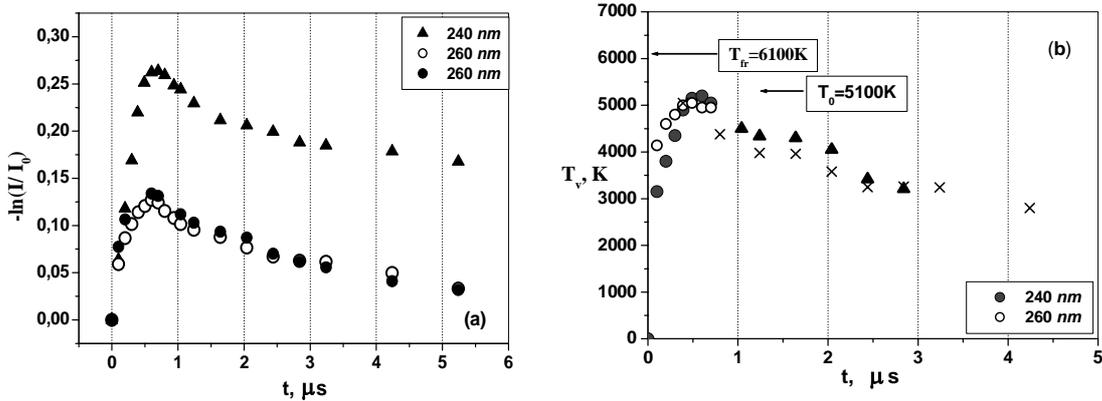

Figure 6. The profiles of $\ln(I/I_0)$ (a) and vibrational temperature T_v (b) behind the front of shock wave: the gas is 100% O_2, p_1= 1 Torr, V= 3.4 *km/s*. The oscilloscope traces were detected for wavelengths 240 and 260 *nm*. The *T*-values (crosses and black triangles) were obtained using two groups of experiments.

It is demonstrated in Fig. 5 that values T_v calculated according to the equation system (3) for vibrational-translational equilibrium (T_0=4280 and 4336 K for experiments with λ=240 и 260 nm) are in agreement with maximum temperature on the plot at $t \approx 0.8 \mu s$. This moment corresponds to maximum absorption in the absence of dissociation. The temperature T_{fr} in Fig.5 was calculated for case of unexcited vibrations immediately behind the shock front.

The comparison of the experimental ratios σ_1 / σ_2 with calculated ones shows that at $t > 1 \mu s$ (Fig. 5) the obtained T_v-values are close to gas temperature T within the limits of experimental uncertainties.

In Fig. 6 analogical profiles of $\ln(I/I_0)$ (a) and T_v (b) are presented for other conditions in heated gas with greater temperature. Calculated values of T_0 and T_{fr} are shown in boxes. At these gas conditions, the agreement between the T_0-value and temperature measured near maximum absorption is also observed.

Using the vibrational temperatures obtained here and formula (2), it is possible to determine the evolution of O_2 concentration in process of dissociation behind the shock wave front.

3. CONCLUSION

For determination of the vibrational temperature of oxygen molecules behind the shock wave front, the method based on comparison of the results of detailed calculation and measurement of oxygen absorption spectrum at high temperatures was developed.

The theoretical absorption spectrum of O_2 was calculated for the Schumann-Runge system for equal and unequal vibrational and translational temperatures. The absorption coefficients for each wavelength were computed by the summation of the absorption coefficients of rotational lines over all possible rotational-vibrational transitions in the Schumann-Runge system, including the transitions into the continuous energy spectrum. At the same time the rotational-vibrational interactions in the O_2 molecule were taken into account. The verification of the model for O_2 absorption spectrum calculation was performed using absorption cross-sections measured behind the shock front.

In experiments the distributions of light absorption in ultraviolet spectral region behind the front of shock wave were obtained. For identical conditions in heated gas, the absorption was detected for two (or more) wavelengths in the region 210-270 nm. The temperature range in experiments was 3500-6000 K. The important condition in experiments was the availability of optically thin layer of gas in question.

Earlier the analogical method was used for determination of the O_2 vibrational temperature [6], but in the work there was no constant control of the optical thickness of gas layer, and the approximate formula was used for absorption cross-section calculations.

The distributions of vibrational temperature of O_2 behind the shock wave front are obtained both in processes of vibration relaxation and dissociation. The vibrational temperature measured at maximum absorption and the temperature calculated for case of vibrational-translational equilibrium ($T_v = T$) in the absence of dissociation are

agreed within the limits of experimental errors. This confirms the validity of proposed method for determination of reliable values of molecule vibrational temperature.

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