

Determination of local concentration of H₂O molecules and gas temperature in the process of hydrogen–oxygen gas mixture heating by means of linear and nonlinear laser spectroscopy

D.N. Kozlov, V.D. Kobtsev, O.M. Stel'makh, V.V. Smirnov, E.V. Stepanov

Employing the methods of linear absorption spectroscopy and nonlinear four-wave mixing spectroscopy using laser-induced gratings we have simultaneously measured the local concentrations of H₂O molecules and the gas temperature in the process of the H₂–O₂ mixture heating. During the measurements of the deactivation rates of pulsed-laser excited singlet oxygen O₂ (b¹Σ_g⁺) in collisions with H₂ in the range 294–850 K, the joint use of the two methods made it possible to determine the degree of hydrogen oxidation at a given temperature. As the mixture is heated, H₂O molecules are formed by ‘dark’ reactions of H₂ with O₂ in the ground state. The experiments have shown that the measurements of tunable diode laser radiation absorption along an optical path through the inhomogeneously heated gas mixture in a cell allows high-accuracy determination of the local H₂O concentration in the O₂ laser excitation volume, if the gas temperature in this volume is known. When studying the collisional deactivation of O₂ (b¹Σ_g⁺) molecules, the necessary measurements of the local temperature can be implemented using laser-induced gratings, arising due to spatially periodic excitation of O₂ (X³Σ_g⁻) molecules to the b¹Σ_g⁺ state by radiation of the pump laser of the four-wave mixing spectrometer.

Keywords: laser absorption spectroscopy, four-wave mixing spectroscopy, laser-induced gratings, optical diagnostics of gas media, temperature, concentration, water molecule.

1. Introduction

Description and modelling of complex branching chemical processes in a gas phase, e.g., such as combustion, requires the knowledge of rates of elementary reactions between the initial components, intermediate and final products. In particular, the study of reactions with participation of O₂ molecules in singlet b¹Σ_g⁺ or a¹Δ_g excited electronic states in gas mixtures is necessary for specifying kinetic schemes, used in modelling of the combustion processes for a number of important practical applications aimed, e.g., at intensifying chain reactions, ignition and combustion [1, 2]. One of the

simplest reactions of this type is the reaction H₂ + O₂(b¹Σ_g⁺) in the hydrogen–oxygen mixture.

The measurements of physical and chemical deactivation rate constants of excited molecular components require the knowledge of composition and temperature of the reacting mixture. At relatively low temperatures the reactions are slow, and the mixture composition may *a priori* be considered constant, i.e., given by the initial conditions of the experiment. Increasing mixture temperature accelerates all chemical processes, although to a different degree. In this case, to find the rate constants one should directly determine the concentrations of the main mixture components, able to change as a result of side reactions, which should be taken into account in calculations when processing the experimental results. Thus, in our measurements of the temperature dependence of the deactivation rate constant of O₂ molecules, laser-excited to the b¹Σ_g⁺ state by H₂ molecules in the H₂–O₂ mixture, the side reaction is the ‘dark’ reaction of oxidation 2H₂ + O₂(X³Σ_g⁻) → 2H₂O that occurs in the heated gas without ignition. This reaction leads to a decrease in the H₂ concentration in the cell and to the appearance of H₂O molecules, physically deactivating the b¹Σ_g⁺ state at a rate nearly seven times greater than that provided by H₂ molecules [3]. Hence, alongside with determination of the local gas temperature in the excitation volume of O₂ molecules, it is necessary to control the H₂O molecule concentration in this volume when measuring the deactivation rate constant of the O₂(b¹Σ_g⁺) molecules.

The aim of this work was to clarify the possibility of simultaneous determination of the local concentration of H₂O molecules and the gas temperature in the process of the H₂–O₂ mixture heating in the temperature range 294–850 K using jointly the linear spectroscopy of radiation absorption from a tunable diode laser [4] and the nonlinear spectroscopy of four-wave mixing employing laser-induced gratings (see the review [5]). The tunable diode laser spectroscopy (TDLS) was used to determine from the absorption spectra the local concentration of H₂O molecules in the excitation volume at a known gas temperature in this volume. The nonlinear spectroscopy of four-wave mixing (FWM) using resonantly excited laser-induced gratings (LIGs), i.e., spatially periodic modulations of the refractive index, allowed simultaneous determination of the local values of the gas temperature and the concentration of H₂O molecules.

It is worth noting that TDLS, in which a single tunable laser is used, is a simpler method from the point of view of both the experiment and the measurement data processing. However, as well known, the recorded absorption spectra are

D.N. Kozlov, V.D. Kobtsev, O.M. Stel'makh, V.V. Smirnov, E.V. Stepanov
A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia;
e-mail: dnk@kapella.gpi.ru, kobtsev.vitaly@gmail.ru, stelmakh@kapella.gpi.ru, vvs@kapella.gpi.ru, EugeneStepanov@yandex.ru

Received 1 August 2012

Kvantovaya Elektronika 43 (1) 79–86 (2013)

Translated by V.L. Derbov

formed along the entire optical path of laser light propagation from the source to the detector and, therefore, the absorption spectrum is generally an integral rather than a local characteristic of the distributions of the absorbing molecule concentration and gas temperature, particularly, in the case of a medium, subjected to spatially inhomogeneous heating. On the contrary, the nonlinear-optical LIG-based technique, which is experimentally more complicated, because it implies precise overlapping of a pulsed pump and a cw probe laser beams and finding the spatial direction of the signal beam diffracted from the grating, provides simultaneous measurements of abovementioned parameters of the mixture directly within the probe volume. In our experiments this method is used, first of all, for measuring the temperature dependence of the collisional deactivation rate constant of the $b^1\Sigma_g^+$ state of O_2 molecules after their laser excitation in the mixture with H_2 , as well as the gas temperature. Additionally this method offers a possibility to verify the measurements of the concentration of H_2O molecules, performed using TDLS. This explains the interest in the joint application of these complementary spectroscopic techniques for determining the local characteristics of the gas mixture.

2. Experiment

The diagnostic setup comprises a diode laser spectrometer and a four-wave mixing spectrometer.

The diode laser spectrometer includes (Fig. 1) an InGaAsP-based distributed-feedback diode laser with the wavelength, tunable near $1.36 \mu\text{m}$, equipped with an analogue housing temperature stabiliser and a pump current driver, a low-noise non-cooled photodiode (InGaAs, area $1 \times 1 \text{ mm}$), a

digital programmable control and data recording unit, and a personal computer. The frequency $\nu(t)$ of the repetitively pulsed diode laser linearly changes in time with the rate $d\nu(t)/dt \approx 1000 \text{ cm}^{-1} \text{ s}^{-1}$ due to heating of the laser crystal during the pump current pulse with linearly growing amplitude. The duration of laser pulses amounts to 3.5 ms with the repetition rate 100 Hz , the mean power of radiation being as large as 0.5 mW . The time-resolved signal from the photodetector is recorded using the 16-bit sigma-delta ADC with the sampling frequency 5 MHz . The spectral resolution of the spectrometer is estimated to exceed 0.001 cm^{-1} . A more detailed description of the spectrometer design and operation of its components can be found elsewhere [4, 6]. The adjustment of the diode laser operation allows one to record the IR radiation absorption by water vapour in the range $7353\text{--}7356.5 \text{ cm}^{-1}$, which contains several important rovibrational lines of H_2O molecules belonging to the combination vibrational band $\nu_1 + \nu_3$, or (101), namely, two strong lines $|6\ 0\ 6\rangle \leftarrow |5\ 0\ 5\rangle$ ($7355.57865 \text{ cm}^{-1}$) and $|6\ 1\ 6\rangle \leftarrow |5\ 1\ 5\rangle$ ($7354.58745 \text{ cm}^{-1}$) with the intensities 10.8×10^{-21} and $3.4 \times 10^{-21} \text{ cm}^{-1} \text{ molecule}^{-1} \text{ cm}^2$ at the temperature $T = 300 \text{ K}$, as well as a few weaker lines [7]. Here and below for rotational levels of H_2O molecules we use the notation $|J\ K_a\ K_c\rangle$, generally accepted in the literature, where J , K_a , and K_c are the quantum numbers of the total angular momentum of an asymmetric top and two its projections.

The FWM spectrometer employing the laser-induced gratings (see Fig. 1) consists of a wavelength-tunable narrow-band $Ti^{3+}:\text{Al}_2\text{O}_3$ excitation laser (LT-2211A, Lotis TII), pumped by the radiation of the second harmonic of a $Nd^{3+}:\text{YAG}$ laser (LS-2137/2, Lotis TII) with pulse repetition rate 10 Hz ; a high-speed photomultiplier (XP2020, Philips); a digital oscilloscope (TDS 620B, Tektronix) with the bandwidth 500 MHz and sampling frequency up to 2 GHz , trig-

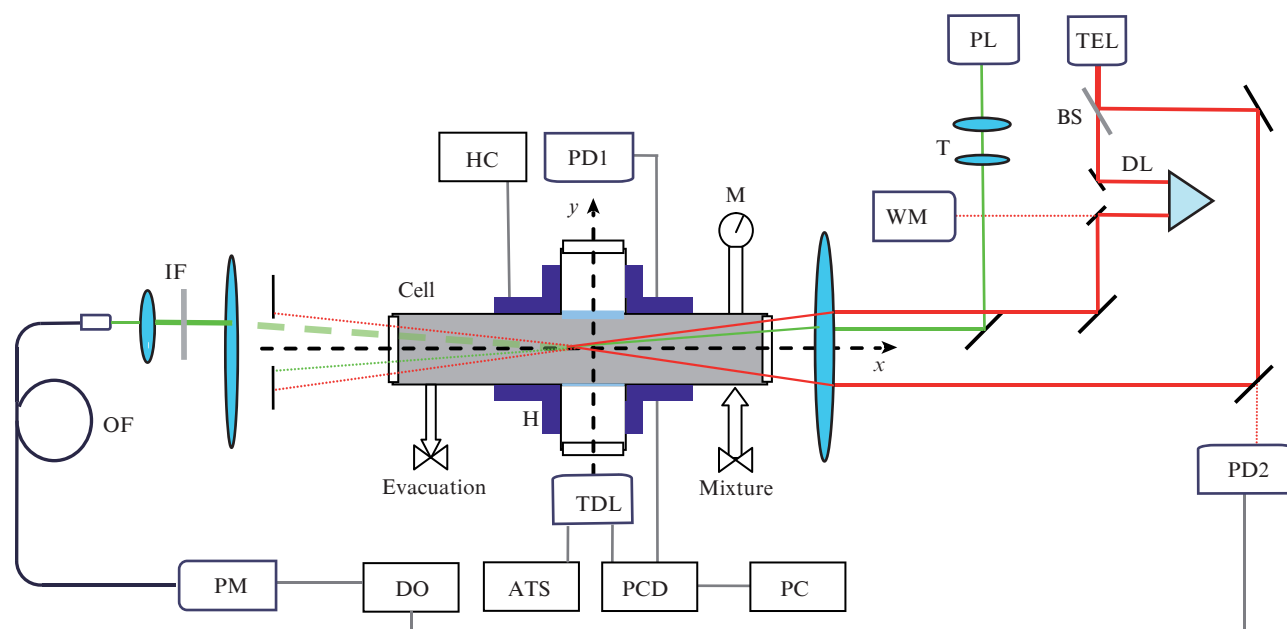


Figure 1. Schematic diagram of the experimental setup.

The diode laser absorption spectrometer: (TDL) tunable diode laser; (ATS) analogue temperature stabiliser; (PCD) pump current driver; (PD1) photodiode; (PC) personal computer. The four-wave mixing spectrometer: (TEL) tunable excitation laser ($Ti^{3+}:\text{Al}_2\text{O}_3$ laser pumped by the second harmonic of the radiation from the $Nd^{3+}:\text{YAG}$ laser); (WM) wavelength meter; (BS) beam splitter; (PL) probe Ar^+ laser; (T) telescope; (DL) delay line; (IF) interference filter; (OF) optical fibre; (PM) photomultiplier; (DO) digital oscilloscope; (PD2) trigger photodiode. The heatable cell: (H) heater; (HC) heater controller with thermocouple sensor; (M) digital manometer.

gered by the pulses of pump radiation by means of a fast photodiode; and a wavelength meter based on Fizeau interferometers (LM-007, Cluster Ltd.). The set of the optical elements includes mirrors and prisms, splitting and folding the laser beams, a telescope for matching the confocal parameters of the pump and probe beams, focusing and collimating lenses, apertures, an interference filter and a multimode optical fibre. The energy of pump pulses at the wavelength $\lambda_p \approx 785$ nm approaches 20 mJ at the duration $\tau_L \approx 10$ ns, while their spectral width equals ~ 0.04 cm⁻¹. The power of cw probe radiation ($\lambda_r = 515$ nm) amounts to 200 mW. The gratings are excited by the radiation at the frequency 12741.3955 cm⁻¹ ($\lambda_p = 784.843$ nm), coincident with the frequency of the single-photon rovibrational transition $|8\ 2\ 6\rangle \leftarrow |7\ 2\ 5\rangle$ of H₂O molecules in the combination vibrational band $\nu_2 + 3\nu_3$, or (013), with the intensity 2.7×10^{-25} cm⁻¹ molecule⁻¹ cm² at $T = 300$ K [7].

The measurements were carried out in a cross-shaped cell, made of fused silica tubes 27 mm in diameter and having 1.5-mm-thick walls. The cell had two pairs of optical windows, the axes of which were perpendicular to each other (see Fig. 1). The separations between the two pairs of the windows were 225 and 400 mm, respectively. The cell design allows registration of luminescence radiation from the O₂ (molecules) laser excitation volume, as well as probing this volume by means of laser-induced fluorescence and spontaneous Raman scattering spectroscopy. The central part of the cell is located inside the heater and can be heated up to the temperature of 900–1000 K. The outer surface of the heated walls of the central part of the cell temperature stabilisation is provided by a thermocontroller with a thermocouple sensor and a microprocessor PID regulator (TC4L, Autonics). Besides, a separate thermocouple is used to measure the temperature of the optical windows located outside the heater, which, e.g., can achieve ~ 360 K, when the central part of the cell is heated up to 850 K. The cell is equipped with a digital manometer and a system of gas mixture supply and evacuation.

In the linear absorption measurements the collimated diode laser beam 3 mm in diameter passes along the axis of the short part of the cell (in the transverse direction, the y axis) and is focused onto the detecting area of the photodiode. The recorded transmission spectrum (the temporal scan of the transmitted radiation pulse) represents the frequency dependence of the integral absorption of radiation along the entire optical path between the source and the detector.

In the FWM spectrometer the vertically polarised pulsed pump laser radiation is split into two parallel beams of nearly equal intensity, which are passed through a focusing lens ($f \approx 1100$ mm) and directed into the cell along its long axis (the longitudinal direction, x axis) to provide crossing at the angle $\theta_p \approx 0.96^\circ$ in the lens focus located in the centre of the most heated part of the cell on its axis. In this case the spatial modulation period of the pump radiation intensity (the fringe spacing) in the beam crossing region, having ~ 0.5 mm in diameter and ~ 20 mm in length is $\Lambda = \lambda_p / 2 \sin(\theta_p/2) \approx 47$ μ m. The beam of cw probe radiation is incident onto the lens parallel to the pump beams in such a way that the angle of its incidence onto the planes of the interference fringes is equal to the Bragg angle $\theta_r \approx 0.31^\circ$, determined from the relation $\sin \theta_r = \lambda_r / 2\Lambda$. A part of probe radiation, diffracted by the generated LIGs, passes along the long part of the cell, is collimated, spectrally and spatially filtered and detected by the photomultiplier. The temporal profile of the pulsed signal from the

photomultiplier (LIG signal) having the duration of a few microseconds is recorded by the digital oscilloscope. The LIG signal profile contains information about the local temperature and concentration of absorbing molecules in the region of pump beams crossing (the probe volume).

In the process of measurements the cell was filled with a hydrogen–oxygen mixture at room temperature up to the pressure, corresponding to a definite molecular number density, and then gradually heated. The measurements were performed in the temperature range 294–850 K in the H₂–O₂ mixture with the molar fraction of hydrogen $c_{\text{H}_2} = 4.3\%$ at the densities 1.5 and 2 Amagat. Since the cell is heated only in its central part, a temperature gradient and, therefore, a density gradient are produced. To keep the density in the probe volume located in the most heated zone inside the cell at a given level, the mixture pressure was increased with growing temperature by additional gas puffing. In this process the gas temperature value in the probe volume, needed for calculating the appropriate pressure, was estimated from the readings of the thermocouple sensor, which was calibrated by simultaneous measurement of the temperature in the central part of the cell using the LIG signals.

3. Physical principles and methods of measurements

At a given mixture pressure, the intensities and spectral line widths of molecular absorption of IR radiation depend on the local gas temperature T . Due to the presence of the temperature gradient along the path of the absorption measurement, the absorbance $A(\nu(t))$ is determined by both the spatial distribution of the concentration of absorbing molecules and the superposition of differently broadened spectral lines, and can be described by the integral expression

$$A(\nu(t)) \equiv -\ln[I(\nu(t))/I_0(\nu(t))] \\ = \int_0^L \sigma(\nu(t), T(y))n(T(y))dy. \quad (1)$$

Here $I(\nu(t))$ and $I_0(\nu(t))$ are the values of the diode laser radiation power, registered by the photodetector in the presence and in the absence of absorbing molecules along the optical path; $\sigma(\nu(t), T(y))$ [cm² molecule⁻¹], and $n(T(y))$ [molecule cm⁻³] are the absorption spectral cross section and the concentration of absorbing molecules at a given coordinate y along the axis of the absorption measurement; and L is the optical path length from the emitter to the detector. As an example Fig. 2 shows the time and, respectively, frequency (within the range 7353–7356.5 cm⁻¹) dependence of the photodetector signals $I_0(t)$ and $I(t)$, recorded with averaging over 10 pulses, and the calculated absorbance $A(t)$ of H₂O vapour at the mixture pressure in the cell $P = 5.65$ bar and the temperature of its walls in the most heated part 823 K, i.e., at the mixture number density of about 1.9 Amagat. Under these conditions a partial overlapping of the spectral lines occurs due to the collisional broadening.

One can assume that at a given point on the axis [i.e., at given temperature $T(y)$] within the spectral range $\nu_1(t_1) - \nu_2(t_2)$, in which the spectrum is recorded and which is sufficiently broader than the homogeneous line widths (~ 0.4 cm⁻¹ at the densities used), the area under the curve of the absorption

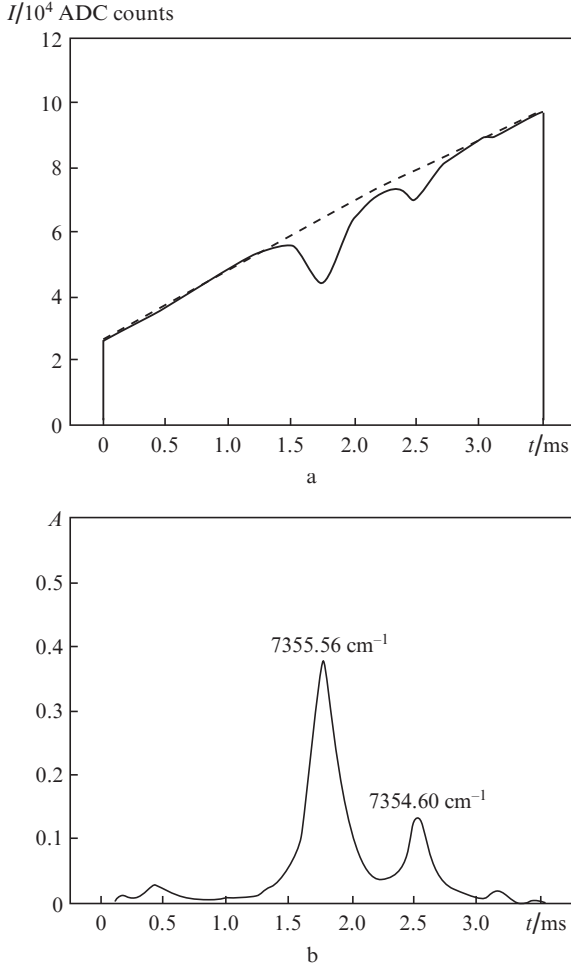


Figure 2. Recorded signals from the photodetector: the power of the diode laser radiation averaged over 10 measurements in the absence of absorption $I_0(t)$ (dashed line) and in the presence of H₂O vapour in the cell $I(t)$ (solid line) (the pressure of mixture 5.65 bar, the temperature of heated walls in the centre 823 K, the temperature of windows 352 K) (a); the calculated spectral absorbance of H₂O vapour along the optical path, $A(t)$; the frequencies are indicated for the strongest absorption lines of H₂O molecules in the selected range (b).

cross section $\sigma(\nu)$ is determined by the intensities of absorption lines that fall within this range, $S_k(T)$ [cm⁻¹ molecule⁻¹ cm²], $k = 1, 2, \dots$. The temperature dependences $S_k(T)$ for H₂O molecules are well known (see, e.g., [7]). Therefore, the calculated spectrally integrated absorbance A_i will be expressed as

$$A_i = \int_{\nu_1}^{\nu_2} A(\nu) d\nu = \int_{t_1}^{t_2} A(t) \left(\frac{d\nu}{dt} \right) dt \approx \int_0^{L_c} n(T(y)) \sum_k S_k(T(y)) dy + A_{i0}, \quad (2)$$

where L_c is the cell length; $d\nu/dt$ is the rate of frequency variation; and A_{i0} is the calibration constant, determined by the absorption of laser radiation along the short optical path in the atmosphere outside the cell, which can be assumed constant during the measurements. If the gas temperature T is uniform over the entire cell volume, then relation (2) is simplified, and the concentration of absorbing molecules in the cell can be calculated using the formula

$$n(T) = \frac{A_i - A_{i0}}{L_c \sum_k S_k(T)}. \quad (3)$$

Thus, the measurement of radiation absorption in air at temperature 296.5 K and relative humidity 54% and the calculation of concentration of H₂O molecules using Eqn (3) yields $n_{\text{H}_2\text{O}} = 3.0 \times 10^{17}$ molecule cm⁻³. Whereas the accuracy of the line intensities S_k , given in [7], amounts to $\sim 10\%$, the agreement between the obtained value and the tabulated value 3.8×10^{17} molecule cm⁻³ may be considered satisfactory.

Under the conditions of heating in the presence of the gas temperature and density gradients, Eqn (3) is not valid for estimating the concentration of H₂O molecules in the homogeneously heated hottest part of the mixture in the centre of the cell with the temperature T_{max} . However, if the relation between the temperature T_{max} and the readings of the thermocouple sensor, measuring the temperature of the heated cell walls, is established in advance and the dimensions of the homogeneously heated region are determined, then, assuming the linear mixture temperature decrease along the axis of the cell from the boundary of this region to the windows, the temperature of which is measured directly, approximating the temperature dependences $S_k(T)$ with a cubic polynomial and assuming that $n_{\text{H}_2\text{O}}(T) = n_{\text{H}_2\text{O}}(T_{\text{max}})(T_{\text{max}}/T)$, one can calculate the integral in the right-hand side of Eqn (2) and find the value $n_{\text{H}_2\text{O}}(T_{\text{max}})$ in the central part of the cell. This approach allows measurement of the temperature dependence of the concentration of H₂O molecules, produced in the course of the H₂-O₂ mixture heating.

As mentioned above, for precise gas temperature measurements in the centre of the cell the FWM spectrometer was used. The appearance of laser-induced gratings in the region of interference of the pump beams is caused by both nonresonant and resonant interactions of radiation with the medium [5]. The nonresonant contribution to the modulation of the refractive index arises due to the adiabatic compression of the gas because of electrostriction. The resonant contributions may be caused by the change in molecular polarisability at excitation, as well as by processes of heat release as a result of collisional relaxation of energy, stored in the internal molecular degrees of freedom subjected to excitation. The interference of different contributions determines the character of the temporal evolution of the grating and its diffractive efficiency (i.e., the LIG signal).

The formation of LIGs under resonant laser excitation of H₂O molecules to the rotational levels of highly excited combination-vibrational states in gas mixtures was considered in [8]. In that paper the expression for the temporal profile of the LIG signal $S(t)$ (the power of radiation, diffracted by the grating) is also presented for the conditions of weak damping of the refractive index modulation. The main parameters entering this expression are the dimensionless amplitude M_e of electrostrictive contribution; the frequency Ω_a of acoustic waves, caused by fast spatially periodic variations of the gas density due to electrostrictive and heat release; the dimensionless amplitudes M_i and M_f of the contributions, related to the 'instantaneous' and 'fast' heat release; the characteristic time τ_f of LIG evolution, caused by the 'fast' heat release and diffusion of excited molecules across the 'grooves' of the grating, the characteristic time τ_{th} of heat conduction; and a number of other parameters, characterising the velocity of acoustic waves leaving the probed volume and their damping in the gas.

An example of the LIG signal, recorded at $\lambda_p = 784.84$ nm in the central part of the cell in the mixture with the temperature $T_{\max} = 790$ K at $P = 5.65$ bar is presented in Fig. 3. The observed regular oscillation of the diffraction efficiency of the excited LIGs is associated with the acoustic standing wave arising in the probe volume. The characteristic temporal profile of the signal with alternating intensities of even and odd oscillation peaks is determined by the interference of electrostrictive and thermal contributions forming the grating. The appearance of the thermal contribution is caused by the presence of a certain amount of H₂O molecules that arose in the mixture in the process of heating. The period of oscillation T_{LIG} in the initial part of the signal ($t \leq 0.4$ μs) is determined by the adiabatic sound velocity v_s in the gas

$$T_{\text{LIG}} = \frac{2\pi}{2\Omega_a} = \frac{\Lambda}{2v_s}. \quad (4)$$

It is seen that at $t > 0.4$ μs , when after the damping of the electrostrictive contribution only the thermal one remains, the value of the period is doubled, i.e. $T_{\text{LIG}} = 2\pi/\Omega_a \equiv T_a$.

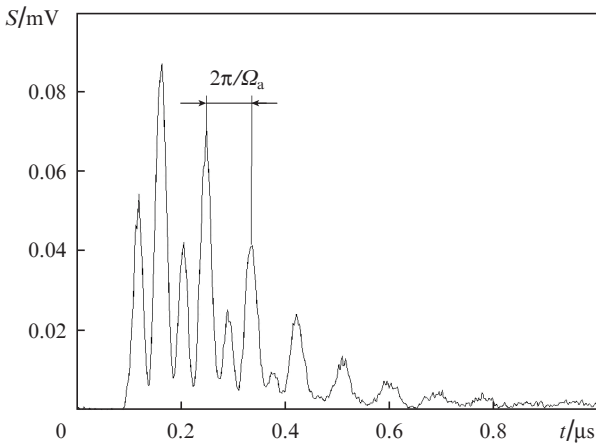


Figure 3. LIG signal at the gas temperature $T_{\max} = 790$ K and the H₂-O₂ mixture pressure of 5.65 bar. The oscillations of the signal amplitude are caused by the appearance of a standing acoustic wave due to electrostriction and heat release.

Analysing the temporal profile of the LIG signal, one can find the frequency Ω_a and, provided that the fringe spacing Λ is known and remains constant under the variations of the gas pressure and temperature, determine the sound velocity in the probe volume. In an ideal gas the adiabatic sound velocity does not depend on the pressure and is expressed by the known relation

$$v_s = \sqrt{\gamma \frac{R}{M} T}, \quad (5)$$

where $\gamma = c_p/c_V$ is the ratio of specific heat capacities (the adiabatic exponent), $R = 8.31441$ J mole⁻¹ K⁻¹ is the universal gas constant, and M is the molar mass. In gas mixtures the values of M and specific heat capacities c_p and c_V are sums of appropriate quantities for the mixture components, multiplied by their molar fractions. Obviously, in the case of a relatively small amount of admixture molecules in the buffer gas, the velocity v_s will be close to its value in the pure gas. It is

also worth noting that the dependence of γ on the temperature T is weak enough and can be, if necessary, taken into account using polynomial approximation of the tabular values [9]. Hence, having found the sound velocity from the LIG signal and assuming the mixture to be an ideal gas, one can find its local temperature from Eqn (5).

The frequency Ω_a can be rather simply determined from the Fourier spectrum $F(\Omega)$ of the signal $S(t)$, namely, $F(\Omega) = |\int S(t) \exp(-i\Omega t) dt|$. Then, with Eqns (4) and (5) taken into account, the temperature T can be calculated from the relation

$$T = T_0 \left(\frac{\Omega_a}{\Omega_{a0}} \right)^2 \left(\frac{\gamma_0}{\gamma} \right), \quad (6)$$

where Ω_{a0} and γ_0 are the values of the parameters at room temperature T_0 .

From the expressions for the amplitudes M_e and M_i of the electrostrictive and thermal contributions to the signal under the conditions of resonant excitation of laser-induced gratings given in [8], one can draw a conclusion that, if the weak temperature dependence of the specific heat capacity $c_p(T)$ of the mixture is neglected, the relation $(M_i/M_e)(P/P_0)^2(T_0/T) \times (S(T_0)/S(T)) \propto n(T)$ is valid, where P_0 is the pressure at room temperature T_0 . Thus, having fitted the temporal shape of the LIG signal to find the ratio of the parameters M_e and M_i , and using the known temperature dependence $S(T)$ [7] for the known pressure P and temperature T , one can calculate the local concentration of H₂O molecules in the most heated part of the cell, $n_{\text{H}_2\text{O}}^r(T_{\max})$ in relative units. To find this quantity in absolute units (cm⁻³) the calibration measurements in the cell, filled with the mixture with the known concentration of H₂O at known temperature, are required.

4. Results

The local measurements of the deactivation rate of O₂(b¹Σ_g⁺) by the H₂ temperature dependence in the H₂-O₂ mixture using the LIG signals at $\lambda_p = 760.565$ nm were performed at the cell axis in its most heated part. In the same part of the cell the chemical transformation of H₂ molecules into H₂O molecules, providing a larger deactivation rate of the b¹Σ_g⁺ state than that caused by H₂ is the most efficient. To choose the position of the probe volume in the heated cell, we determined the gas temperature profiles along the axes x and y and found the dimensions of the homogeneously heated regions, which are required to derive the concentration $n_{\text{H}_2\text{O}}(T_{\max})$ by means of TDLS. These measurements were also performed using LIGs, but at $\lambda_p = 784.84$ nm in the mixture at the temperature $T_{\max} \approx 625$ K and pressure $P = 4.64$ bar (the density 2.1 Amagat). To find the frequency Ω_a we applied the built-in signal fast Fourier transform function of the digital oscilloscope, averaging the signal over 200 pulses, and for calculation of the temperature we used Eqn (6). An example of the Fourier spectrum of the LIG signal, presented in Fig. 3, is shown in Fig. 4a. The spectrum corresponds to the interference of the electrostrictive contribution to the signal (producing the high-frequency peak at the frequency $2\Omega_a = 144$ μs^{-1}) and the thermal one (producing the low-frequency peak at the frequency $\Omega_a = 72$ μs^{-1}). In the spectra of signals, recorded at different temperatures, the amplitude of the low-frequency peak becomes greater with the growth of the water vapour density, as the temperature increases, so that, in principle, it is possible

to use the ratio of peak amplitudes in the Fourier spectrum of the LIG signal as a measure of concentration of H_2O molecules. It is worth noting, that this approach allows measurements in real time with the period 1–10 s (depending on the required number of averagings).

The measurements of temperature profiles along the x axis show that the centre of the most heated region with the temperature T_{max}^x is shifted by nearly 30 mm along the x axis from the cell centre ($x = y = 0$), and its length $L_h^x \approx 40$ mm noticeably exceeds the length of the probe volume (~ 20 mm). The region of homogeneous heating along the y axis is located symmetrically with respect to the origin of the coordinate frame and has the length $L_h^y \approx 16$ mm. The temperature T_{max}^y is practically the same as in the most heated region, $T_{\text{max}}^y \approx 0.96T_{\text{max}}^x$.

The correlation between the temperature T_{max}^x in the gas and the readings of the heated wall temperature sensor, shown in Fig. 4b, was established in the range $T_{\text{max}} \leq 790$ K by calibration measurements with the resonant excitation of O_2 molecules at $\lambda_p = 760.565$ nm and the mixture density 1.9 Amagat.

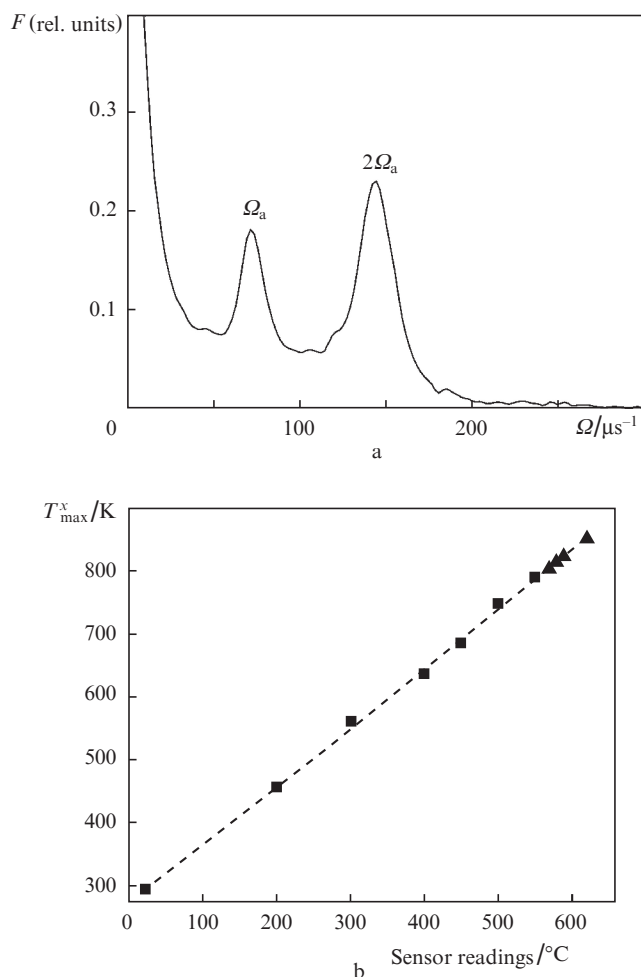


Figure 4. Local temperature measurements using LIG: Fourier spectrum of the LIG signal at the gas temperature 790 K and the pressure 5.65 bar, the frequencies of thermal (Ω_a) and electrostriction ($2\Omega_a$) peaks are shown (a) and the correlation between the temperature T_{max}^x in the gas and the heated wall temperature, measured by the sensor: ■ – experimental points, dashed line – the result of linear fitting, ▲ – the result of extrapolation of the experimental data into the region of significant concentrations of water vapours (b).

The processing of signals, averaged over 200 pulses, was carried out using the fast Fourier transform, while the temperature was calculated from Eqn (6). With very good accuracy this correlation is described by a linear dependence. Heating the mixture above 790 K was accompanied by simultaneous appearance of an appreciable ($c_{\text{H}_2\text{O}} \leq 1\%$) amount of H_2O molecules and decrease in the concentration of H_2 molecules, which leads to the change of the mixture composition and, therefore, modifies the law, describing the increase in the sound velocity with temperature. This effect is large enough to make Ω_a nearly constant within the range 790–820 K. This does not allow former accuracy of LIG temperature measurements to be achieved; therefore, at temperatures above 790 K we calculated the values of T_{max}^x using a linear extrapolation of the dependence, found at low concentrations of H_2O .

The fitting of temporal profiles of the LIG signals with determination of their characteristic parameters requires the knowledge of the grating period Λ . The period $\Lambda = 46.50 \pm 0.04 \mu\text{m}$ was determined from Eqn (4) using the value of Ω_a , found from electrostrictive LIG signals, recorded at room temperature with averaging over 100 pulses in the gas mixture with known composition. While processing the temporal profiles of the LIG signals in the heated gas this value of Λ was fixed.

The local gas temperature and the concentration of H_2O molecules in the course of the H_2 – O_2 mixture heating using LIGs were simultaneously determined in the same range of temperatures as used for studying the temperature dependence of the $\text{O}_2(\text{b}^1\Sigma_g^+)$ deactivation rate in collisions with H_2 . The analysis of temporal profiles of the recorded LIG signals allows determination of the temperature T_{max}^x from the value of Ω_a , while the defined ratio M_i/M_e , with the line intensity $S(T_{\text{max}}^x)$ taken into account, offers the possibility to find the local concentration of H_2O molecules at a given temperature in relative units, $n_{\text{H}_2\text{O}}^r(T) = (M_i/M_e)(P/P_0)^2 \times (T_0/T)(S(T_0)/S(T))$. The resulting values of $n_{\text{H}_2\text{O}}^r(T_{\text{max}}^x)$, demonstrating that the efficient conversion of H_2 molecules into H_2O molecules occurs in the narrow range of temperatures 790–820 K, are presented in Fig. 5a.

In the process of mixture heating, alongside with LIG signal registration, enabling the determination of the local gas temperature and concentration of H_2O molecules, the transmission spectrum of the gas in the cell was recorded, its processing allowing the calculation of the concentration $n_{\text{H}_2\text{O}}$ in the most heated central part of the cell. In this calculation of $n_{\text{H}_2\text{O}}$, performed with the help of Eqns (1) and (2), the function $I_0(v(t))$ is used, which is the power of the diode laser radiation, recorded in the absence of absorbing molecules along the laser beam path. One more quantity required is the calibration constant A_{i0} , determined by the atmospheric absorption of the laser radiation outside the cell. Since the diode laser radiation always passes at least a small distance through the surrounding air, containing a certain amount of water vapour, it appears impossible to register the signal $I_0(v(t))$ experimentally. Therefore, the function $I_0(v(t))$ is interpolated with a cubic polynomial using the values of the signal $I(v(t))$, obtained with the evacuated cell in the frequency range beyond the recorded absorption lines of H_2O , and then the calibration constant A_{i0} is calculated. For the absorption spectrum, recorded at the given temperature T_{max}^y in the chosen range, the spectrally integral absorbance A_i [the left-hand side of Eqn (2)] is calculated, and using the approximation of the $T(x)$ dependence, described above, the integral in the right-hand side of Eqn (2) is calculated. Finally, the value of

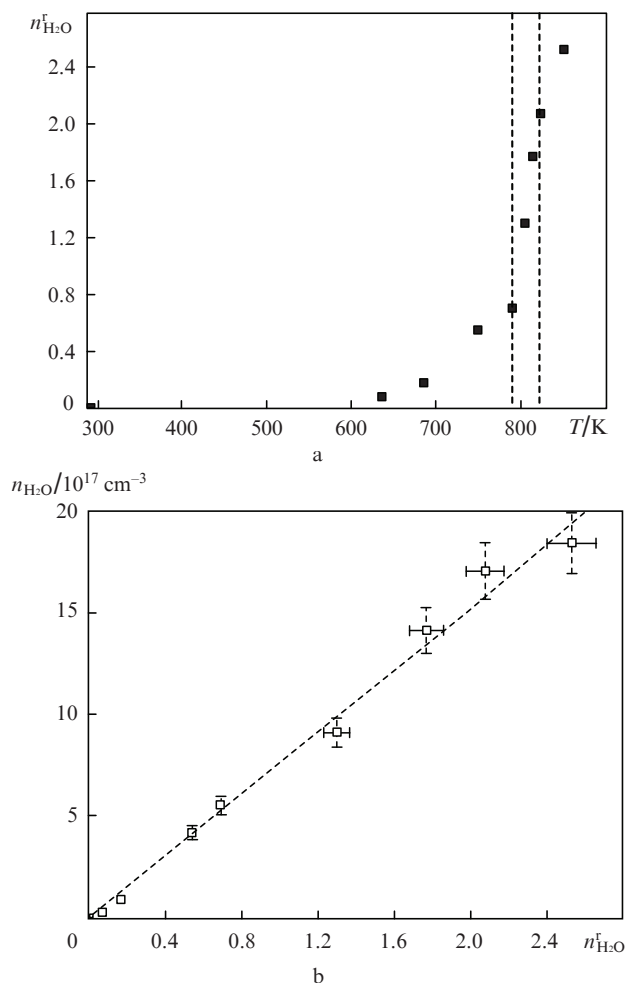


Figure 5. Concentration of H₂O molecules in the most heated region of the cell as a function of the temperature, determined using LIGs (a) and the correlation between the concentrations $n_{\text{H}_2\text{O}}(T_{\text{max}}^y)$ and $n_{\text{H}_2\text{O}}(T_{\text{max}}^x)$ (b).

$n_{\text{H}_2\text{O}}(T_{\text{max}}^y)$ is found. The correlation between the concentration $n_{\text{H}_2\text{O}}(T_{\text{max}}^x)$ in the most heated part of the cell, determined by means of TDLS, and the relative concentration $n_{\text{H}_2\text{O}}^r(T_{\text{max}}^x)$, obtained using LIGs, is illustrated in Fig. 5b. As it was expected, within the measurement errors this correlation is described by the linear dependence $n_{\text{H}_2\text{O}}(T_{\text{max}}^y) = (6.7 \pm 0.2) \times 10^{17} \text{ cm}^{-3} n_{\text{H}_2\text{O}}^r(T_{\text{max}}^x)$.

The obtained results show that, in spite of the presence of temperature gradients in the cell, the use of TDLS provides good accuracy in determining the variations of H₂O molecule concentration in the most heated part of the cell. The necessary values of the gas temperature in this region can be obtained as the LIG signal or, with less accuracy, based on the readings from the wall temperature sensor. Hence, for sufficiently accurate quantitative detection of H₂O molecules, arising in the course of heating the H₂–O₂ mixtures, when measuring the temperature dependence of the deactivation rate of O₂(b¹Σ_g⁺) molecules, excited by laser radiation in the described experimental configuration, one can confine himself to the use of the diode laser spectrometer. In this case the FWM spectrometer is used for resonance spatially periodic laser excitation of O₂ molecules and generation of LIGs that allows local measurement of the gas temperature.

5. Conclusions

In the present paper we study the capabilities of joint application of the linear absorption spectroscopy and the nonlinear spectroscopy of four-wave mixing using laser-induced gratings for diagnostics of physical and chemical processes in gas media with a spatially inhomogeneous temperature and density distributions. In the measurements of the temperature dependence of the deactivation rate of the laser-excited O₂(b¹Σ_g⁺), caused by collisions with H₂, these spectroscopic techniques were used to simultaneously determine the local concentration of H₂O molecules and the gas temperature. The measurements were carried out in a cell in the process of the H₂–O₂ mixture heating with the molar fraction of hydrogen $c_{\text{H}_2} = 4.3\%$ in the range 294–850 K without ignition. The water molecules appeared due to the dark reactions of hydrogen oxidation.

The tunable diode laser absorption spectroscopy was used to determine the local concentration of H₂O molecules in the laser excitation volume of O₂ molecules at the known gas temperature. The measurements were implemented using the absorption spectra of H₂O molecules along the optical path through the inhomogeneously heated gas mixture in the cell. The four-wave mixing spectroscopy exploiting the resonantly excited LIGs was used to derive the gas temperature within the excitation volume, as well as to independently determine the concentration of H₂O molecules.

The spectroscopic techniques employed are complementary and allow characterisation of the degree of hydrogen oxidation at a given gas temperature with high sensitivity and spatial resolution. The obtained results show that, in spite of the presence of temperature gradients, the TDLS provides good accuracy in determining the concentration of H₂O molecules in the most heated region of the cell, the gas temperature in this region being found from the temporal profile of the LIG signals.

Acknowledgements. The authors are grateful to A.N. Klimov for providing the Ar⁺ laser for carrying out the measurements and to A.V. Koval for the help in setting-up and launching the diode laser spectrometer. The work was supported by the Russian Foundation for Basic Research (Grant Nos 10-08-01315-a and 11-02-01296-a), and by the Federal Target Program ‘Scientists and Science Educators of Innovative Russia’ (State Contract No. 16.740.11.0010).

References

1. Starik A.M., Titova N.S. *Zh. Tekh. Fiz.*, **73**, 59 (2003) [*Tech. Phys.*, **48** (3), 334 (2003)].
2. Popov N.A. *Teplofiz. Vysok. Temp.*, **45** (2), 296 (2007) [*High Temp.*, **45** (2), 261 (2007)].
3. Wayne R.P., in *Singlet O₂. Vol. 1. Physical-chemical Aspects*. Ed. by Frimer A.A. (Boca Raton, FL: CRC Press Inc., 1985).
4. Stepanov E.V. *Diodnaya lazernaya spektroskopiya i analiz molekul-biomarkerov* (Diode Laser Spectroscopy and Analysis of Biomarker Molecules) (Moscow: Fizmatlit, 2009).
5. Stampanoni-Panariello A., Kozlov D.N., Radi P.P., Hemmerling B. *Appl. Phys., B*, **81**, 113 (2005).
6. Stepanov E.V., Zyrianov P.V., Milyaev V.A. *Phys. Wave Phenomena*, **18**, 33 (2010).
7. Rothman L.S., Gordon I.E., Barbe A., Benner D.C., Bernath P.F., Birk M., Boudon V., Brown L.R., Campargue A., Champion J.-P., Chance K., Coudert L.H., Dana V., Devi V.M., Fally S., Flaud J.-M., Gamache R.R., Goldman A., Jacquemart D., Kleiner I., Lacombe N., Lafferty W., Mandin J.-Y., Massie S.T.,

- Mikhailenko S.N., Miller C.E., Moazzen-Ahmadi N., Naumenko O.V., Nikitin A.V., Orphal J., Perevalov V.I., Perrin A., Predoi-Cross A., Rinsland C.P., Rotger M., Simeckova M., Smith M.A.H., Sung K., Tashkun S.A., Tennyson J., Toth R.A., Vandaele A.C., Vander Auwera J. *J. Quantum Spectrosc. Radiat. Transfer*, **110**, 533 (2009); <http://www.hitran.com>.
8. Hemmerling B., Kozlov D.N., Stel'makh O.M., Attal-Trétout B. *Chem. Phys.*, **320**, 103 (2006).
 9. <http://webbook.nist.gov/chemistry/>.