CARS diagnostics of the burning of H_2–O_2 and CH_4–O_2 mixtures at high temperatures and pressures

K.A. Vereshchagin, V.V. Smirnov, O.M. Stel'makh, V.I. Fabelinsky

Abstract. **Coherent anti-Stokes Raman scattering (CARS) spectroscopy is used to determine the parameters of gaseous combustion products of hydrogen and hydrocarbon fuels with oxygen at high temperatures and pressures. The methodical aspects of CARS thermometry, which are related to the optimal choice of molecules (diagnostic references) and specific features of their spectra, dependent on temperature and pressure, are analysed. Burning is modelled under the conditions similar to those of real spacecraft propulsion systems using a specially designed laboratory combustion chamber, operating in the pulse-periodic regime at high temperatures (to 3500 K) and pressures (to 20 MPa) of combustion products.**

Keywords: *CARS thermometry, hydrocarbon burning.*

1. Introduction

Currently, burning processes and combustion chambers are often studied and optimised by laser contactless nonperturbative methods: laser-induced fluorescence (LIF) [1], laser anemometry [2], and coherent anti-Stokes Raman scattering (CARS) spectroscopy [3]. Because these methods are based on the spectra of detected molecules, atoms, and radicals, they require additional information about the spectral features that are characteristic of high temperatures and pressures. Having analysed the data obtained, one can choose the most preferred spectra for measuring the temperature and other parameters of gas media (flames). In particular, the features of the CARS spectra of hydrogen molecules at high temperatures (1000–3000 K), for example, shifts and broadening of spectral lines, are directly related to the error in determining temperature; they were investigated in [4–7].

The purpose of this study was to reveal the features of molecular CARS spectra of the combustion products of hydrocarbon fuels at high temperatures in order to establish the most informative ones for the CARS diagnostics of high-temperature reacting gas mixtures. This technique of nonperturbative diagnostics, which has a high spatial resolution, is in essence the only method that allows one to obtain information about local temperature values and flame composition in

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a pressure range of 0.1–10 MPa and a temperature range of 300–3500 K.

To test diagnostic techniques (in particular, CARS), we designed a compact combustion chamber, operating under laboratory conditions in the pulse-periodic regime. This apparatus, characterised by a small chamber volume and initial pressure of working mixture up to 2.0 MPa, provides high pressures (~20 MPa) of combustion products at temperatures up to 3000 K.

We were interested in both the results of measuring the temperature and composition of combustion products and the methodical aspects of CARS thermometry, related to the optimal choice of molecules – diagnostic references – and the specific features of their spectra, dependent on the temperature, pressure, and stoichiometry.

2. Experimental setup

2.1. System of CARS diagnostics

When choosing the CARS spectrometer scheme, we proceeded from the following considerations. The pulsed operation regime and time-dependent conditions in the combustion chamber impose the following requirements: all necessary measurements must be performed during one laser pulse with a characteristic width of ~10 ns, synchronised with the burning cycle. In addition, it is desirable to record a considerable fragment of the CARS spectrum (~300 cm^{-1}), which contains spectra of several molecules (for example, the lines of the hydrogen Q branch and the Q branch of H_2O v_1 vibration).

Hence, it is necessary to use the scheme of broadband CARS [3], where radiations of two lasers are used: pump radiation with a narrow spectrum (the second harmonic of YAG:Nd^{3+} laser), and broadband radiation of a Stokes dye laser. The difference in the radiation frequencies of these two lasers was tuned in correspondence with the Raman frequency shifts in the spectra of detected hydrogen molecules and water. The wide spectrum of the dye laser made it possible to excite and record simultaneously Q-branch transitions in these molecules during a laser pulse. Using another Stokes dye laser, pumped simultaneously with the first one and tuned, for example, to the transitions in methane molecules, one can estimate the relative concentrations of water, hydrogen, and methane molecules in the volume probed from the intensities of the transition lines observed.

Both CARS processes and Stokes lasers were pumped by the second harmonic of a single-frequency (spectral width ~100 MHz) YAG:Nd^{3+} laser (Infinity, Coherent Radiation). The typical energy of 532-nm radiation in a 3-ns pulse was

100 mJ; it was distributed as follows: 10–15 mJ for 'pumping' the CARS process and 40 mJ for pumping each Stokes laser. All Stokes lasers were designed according to the generator–amplifier scheme and based on solutions of organic dyes (Pyridine, Rhodamin) in methanol. The oscillator of the 'hydrogen-channel' Stokes laser (for measuring temperature) was a 'modeless' transversely pumped oscillator, designed according to the scheme of double-pass amplifier with one rear mirror. The radiation of the generator was amplified in a single-pass transversely pumped dye amplifier, whose output energy was ∼3 mJ at a spectral width above 500 cm^{-1}. The spatial resolution was increased using the 'planar-CARS' geometry of laser-beam interaction [3]. The pump and Stokes beams propagated in the same direction, being spaced by approximately 10 mm. They were focused by a lens (f = 300 mm) to cross in the focal region at a small angle, which made it possible to exclude generation of CARS signals from the regions beyond the zone probed. When working with two Stokes lasers, the radiation of the second dye laser propagated parallel to the first-laser radiation at a small distance from it.

The CARS spectrum was recorded by a 10-ns gated multichannel linear photodetector (Scientific Instrument), located in the focal plane of the spectrograph (Jobin Yvon, THR1000) with a focal length of 1 m.

2.2. Pulsed high-pressure combustion chamber

Various models of burners have been developed to model burning processes and verify diagnostic techniques. An example is the atmospheric-pressure McKenna burner [8], which is characterised by a high stability and reproducibility of parameters.

A specific feature of the combustion chamber proposed here is the possibility of obtaining burning products at high temperatures and pressures. The chamber geometry and sizes were chosen to provide the best efficiency and compactness for operation under laboratory conditions. Here, the CARS technique allows one to implement conditions under which the region diagnosed is much smaller than the combustion chamber volume. For a laser-beam overlap region $1 \times 0.1 \times 0.1$ mm in size, the corresponding volume of the probe region is ∼ 10^{-5} cm^3.

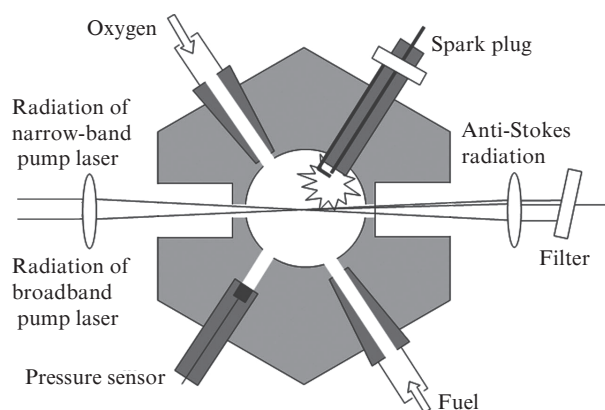Figure 1 shows schematically the design of the high-pressure pulsed combustion chamber (HPPCC). It is a cylinder

∼8 cm^3 in volume, made of heat-resistant stainless steel. There are several holes in the chamber wall for fittings of two pulsed inlet valves, a spark plug for the working mixture, and a pressure meter. The combustion products are extracted, and the chamber is cleaned before the next working cycle through two coaxial holes ∼1 mm in diameter. These holes are also used to introduce laser beams into the chamber and extract CARS radiation from it.

Controlling the delay of laser triggering pulse, one can shift the probe instant with respect to the mixture lighting pulse. As a result, CARS probing can be performed at different instants, both before and after the mixture ignition, i.e., in all stages of the HPPCC working cycle.

The pressure in the combustion chamber in the stages of mixture inlet, burning, and extraction of products in each operating cycle was measured by a Kistler 6061B piezoelectric pressure sensor, inserted in the combustion chamber wall. Figure 2 shows a typical shape of pressure pulse during methane burning and a signal from a fast photodiode, which is used to record the laser pulse, delayed with respect to the ignition instant. To obtain maximally possible pressures of combustion products, we measured the dependences of pressure on the fuel excess coefficient Φ (Fig. 3). It can be seen that, when the initial pressure of methane–oxygen mixture in the chamber is 1.5 MPa, the maximum pressure (15.8 MPa) is obtained at $\Phi = 1.5$. For comparison, Fig. 3 shows a calculated curve obtained using the GASEQ code [9] in the adiabatic-burning approximation. To estimate the HPPCC stability, we analysed pressure diagrams for a series of 50 successive cycles, implemented at specified fuel and oxidant consumptions. The pulse pressures in different cycles had a similar shape, differing only slightly in both the amplitude and peak position in time. The relative standard deviations for the peak positions and amplitudes were, respectively, ∼4% and 5%–6%.

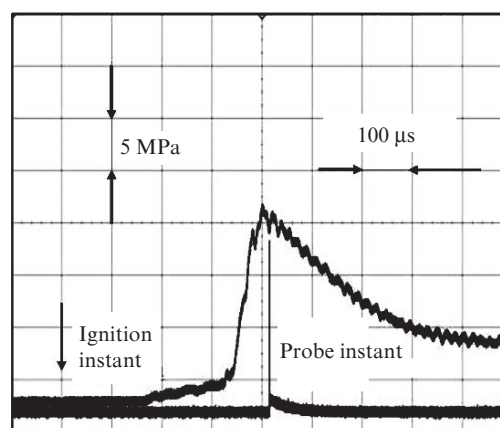**Figure 1.** Pulsed high-pressure combustion chamber.

Figure 2. Profiles of pressure pulses during methane burning (upper track) and the probe laser pulse (lower track).

Based on the studies performed, we can conclude that the HPPCC designed has reproducible and controlled parameters and is a convenient laboratory tool for optimising diagnostic techniques.

The experiment was performed as follows. The initial pressures and mass consumptions in the CH_4 and O_2 channels were specified for a burner operating at a frequency of 1 Hz.
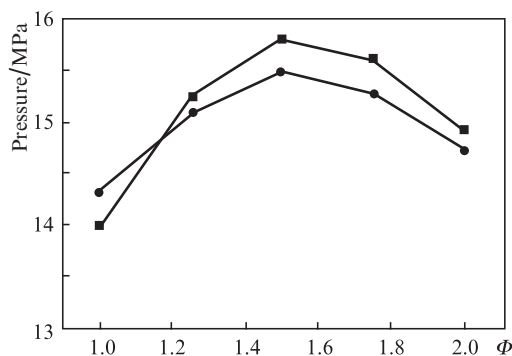
Figure 3. Dependence of the pressure pulse amplitude on the excess fuel coefficient Φ during burning of a CH_4–O_2 mixture at an initial pressure of 1.5 MPa: (■) the experimental data and (●) the result of calculation by the GASEQ program [9].
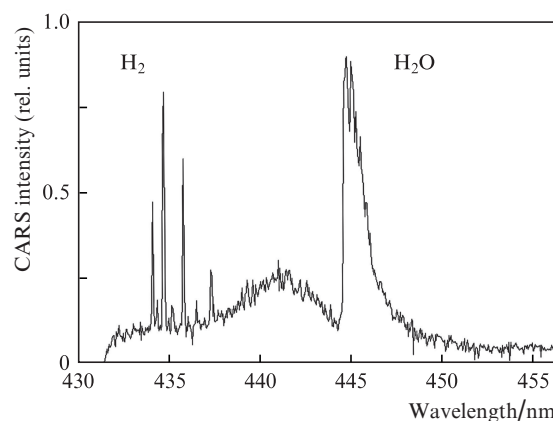

Figure 4. Fragment of a CARS spectrum with transition lines of the Q branch of hydrogen molecules and the Q branch of the v_1 vibration of water molecules.

The wavelength of the first Stokes laser was tuned to the Raman shift frequency for the lines of chosen molecules (for example, the Q-branch lines of hydrogen and water), and the wavelength of the other laser was chosen so as to overlap with the Q-branch lines of totally symmetric vibration v_1 of methane molecules. After settling the chosen delay between the ignition instants and probe laser pulses, we recorded 50 files (synchronised both with the ignition instant and with respect to each other) containing information about the CARS spectra and pressures in the combustion chamber.

3. Results

Generally, in the case of CARS diagnostics of burning, the information about the temperature and density in a medium studied is extracted from the spectra of the CARS transitions in the reference molecules in the probed volume of the combustion chamber. The temperature and density can be determined from the best coincidence between the experimental spectra and the spectra calculated with some step based on the recorded parameters. The error in their determination depends on the quality of the experimental data; the correctness of the model used to calculate the CARS spectra; and the reliability of spectroscopic information about the cross sections of the transitions in the chosen reference molecules, their frequencies, and the widths of the profiles of the spectral lines used. In particular, it is convenient to use the rotational–vibrational Q-branch spectra of hydrogen molecules, the spectroscopic constants of which are known with a high accuracy, in order to measure the temperature during burning of rich oxygen–hydrogen and hydrocarbon mixtures.

One of the purposes of our study was to reveal the potential of CARS thermometry for gas mixtures at high temperatures and pressures and lean mixtures, where other molecules (combustion products, for example, water molecules) can be used as references. Note that implementation of broadband CARS with simultaneous measurement of hydrogen and water spectra during one laser pulse increases greatly the informativeness of diagnostics, making it possible to estimate the combustion completeness and the temperature when studying time-dependent turbulent flames with a strongly varying local stoichiometry. Figure 4 shows the CARS spectra recorded during burning of H_2–O_2 mixture, which contain simultaneously recorded lines of water and hydrogen molecules.

When determining the temperature from the intensities of Q-branch lines of vibrational–rotational transitions in hydrogen, we took into account the dependence of their broadening on the rotational quantum number J; this dependence is due to the collisions with water molecules. This influence is decisive, because the water content is 40%–50% of the total mass of combustion products, and the cross section of the water-induced broadening of hydrogen lines exceeds several times the corresponding broadening cross sections for other molecules in the combustion products. The calculations were performed using the previously investigated temperature changes in this dependence in the ranges of 300–1800 K [4, 5] and 2000–3500 K [6, 7]. Figure 5 shows the result of determining the temperature based on the above-described procedure, with the best coincidence between the experimental and calculated spectra at $T = 3400$ K. The error in determining the temperature (which was measured during one laser pulse) was 4%. As was mentioned above, when diagnosing the burning of lean mixtures or local hydrogen burning out, the temperature can be determined using the lines of Q-branch transitions of the vibration v_1 in water molecules. In view of much smaller values of the rotational constant and the vibrational–rotational interaction constant of water molecules, their CARS spectrum differs from the hydrogen spectrum by a larger
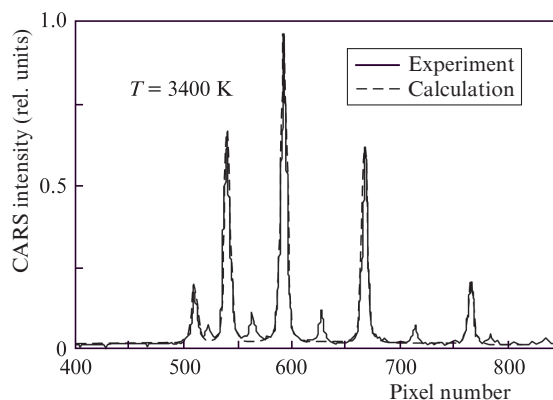

Figure 5. Procedure of fitting the experimental and calculated (only lines with odd numbers J are taken into account) Q-branch CARS spectra of hydrogen molecules.
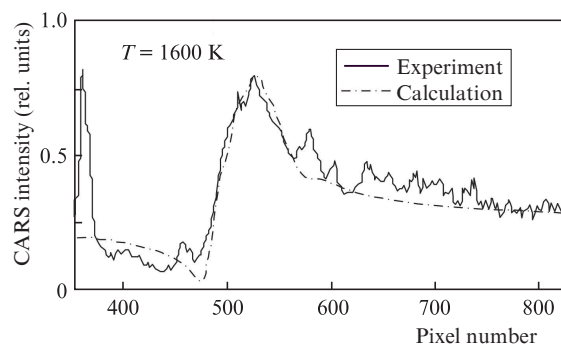
Figure 6. Procedure of fitting the experimental and calculated Q-branch CARS spectra of the ν_1 vibration of hydrogen molecules.

number of lines and their significant overlap. As a result, the spectrum of water at mixture pressures above 0.1 MPa is an unresolved profile, and the shape of its envelope, which changes with temperature and density, is used to determine the temperature (Fig. 6).

A program for calculating the spectrum of Q-branch vibration ν_1 has been developed based on the existing data on the positions of water lines and the features of their broadening [10–12]. This program was used to calculate a library of spectra. One of the spectral parameters is temperature, which is determined by fitting the calculated spectra to experimental ones according to the criterion of the best shape coincidence. Figure 6 shows the result of this procedure, which gives a temperature close to 2000 K with an error of ~6%.

When analysing the burning of CH_4–O_2 mixture, we investigated the temporal behaviour of the main gas parameters: temperature and relative concentrations of the combustion products both in the stage of burning development and the stage of their extraction from the combustion chamber. To this end, we recorded the CARS spectra in two spectral ranges, delayed in time with respect to the ignition pulse (Fig. 7). The first range (430–470 nm) contains the spectra of CH_4, H_2, and H_2O molecules, recorded simultaneously during each laser pulse. The features of the spectra obtained suggest that some of the aforementioned molecules – combustion products – can be used as references for thermometry when
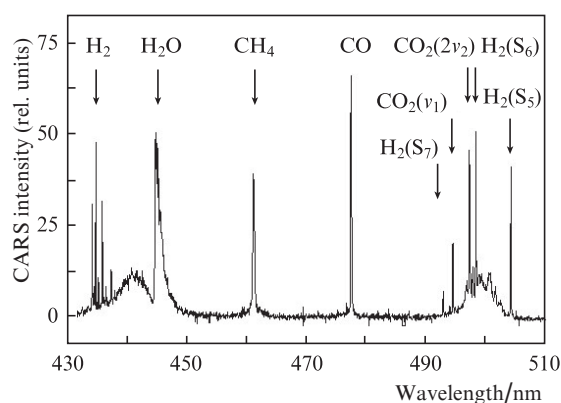
CARS spectroscopy is applied to diagnose the burning of CH_4–O_2 mixtures. Figure 8 shows a series of spectra recorded in the first range at different delays of the CARS probing instant with respect to the pressure pulse leading edge.
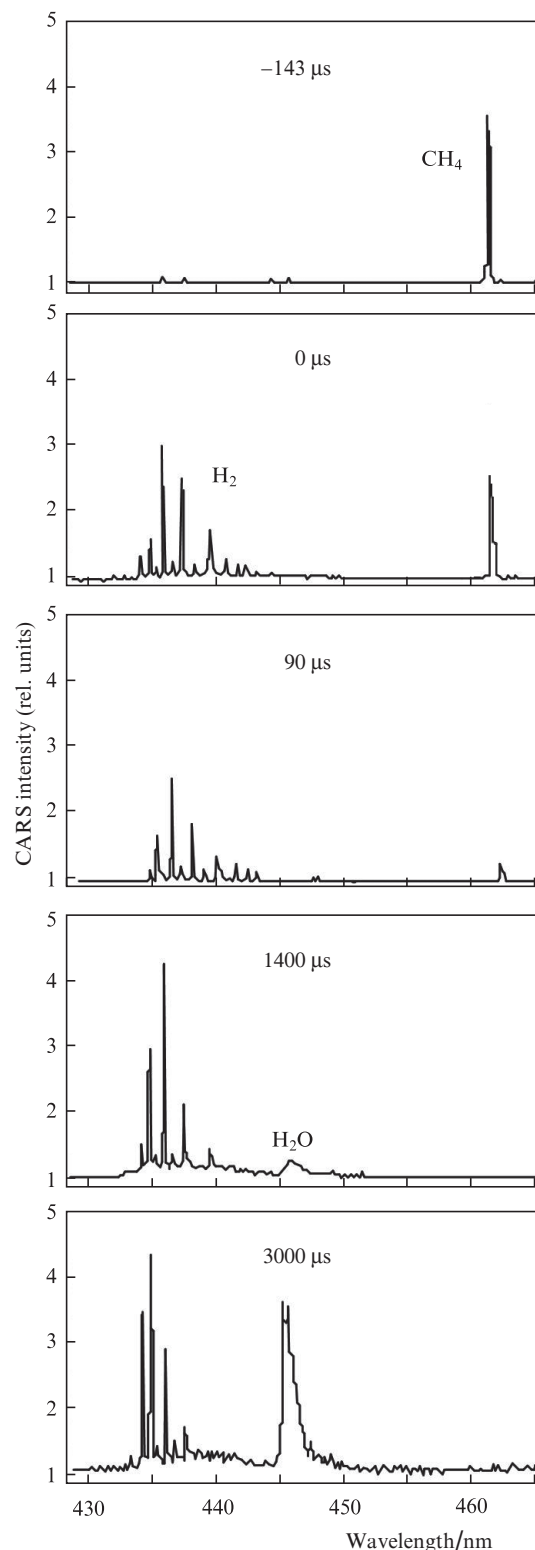

Figure 8. Series of CARS spectra of CH_4, H_2, and H_2O molecules, recorded in the range of 430–470 nm at different delay times with respect to the pressure pulse leading edge.

Figure 7. Full-range CARS spectrum of the molecules detected during burning of a CH_4–O_2 mixture in the combustion chamber.

An analysis of the spectra obtained indicates a number of features of the burning evolution. For example, one can observe intense decomposition of methane and formation of hydrogen molecules even at times covered by the pressure pulse leading edge. Since methane molecules are subjected to intense decomposition at temperatures above 1500 K, the spectra of methane molecules at high temperatures cannot be used for thermometry. The intensities of hydrogen spectral lines exceed those of water lines by an order of magnitude, because the statistical sum over rotational transitions in water molecules exceeds greatly the corresponding statistical sum for hydrogen at high temperatures (2000–3000 K). Nevertheless, the spectra of both hydrogen and water can be valid for thermometry, as well as for estimation of the qualitative characteristics of burning (mixing, combustion completeness). The CARS spectra of hydrogen recorded in this range were used to determine the dependence of the temperature in the pulsed combustion chamber on the delay of the probe instant with respect to the ignition instant. This circumstance made it possible to compare the temporal behaviour of pressure and temperature both in the burning phase and in the stage of extraction of hot combustion products (Fig. 9). It should be noted that the temperature measurement, which was implemented above for the H_2-O_2 flame and took into account the data on the temperature dependence of the broadening of different hydrogen lines by water, is not correct, because, along with water (in case of hydrogen burning), collisions with hydrogen occur with participation of other molecules (products of methane burning). Therefore, the temperature was measured using a modified CARS spectrometer scheme [13], which allows one to record simultaneously not only the intensity of hydrogen Q-branch lines but also their width.

The second spectral range (470–510 nm), which is shown in Fig.7, contains the spectra of purely rotational transitions o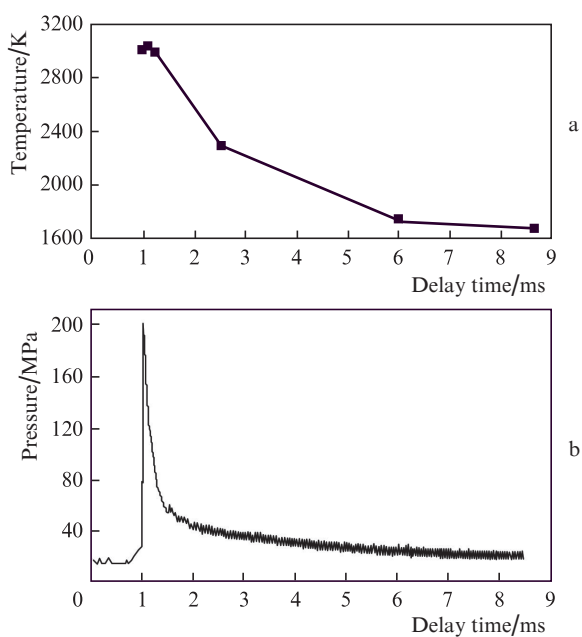f hydrogen molecules with $J = 5$, 6, and 7 (Q branch of the transition in O_2 molecules) and the vibrational–rotational bands v_1 and $2v_2$ of CO_2 molecules (as well as their 'hot' transitions). To illustrate the features of the spectra corresponding to different burning regimes, we show fragments of CARS spectra in Fig. 10; each of these fragments was recorded during one laser pulse. Fragment 1 corresponds to the inlet phase

Figure 9. Time dependences of the (a) temperature and (b) pressure, measured in the combustion chamber. The time is counted with respect to the ignition pulse.
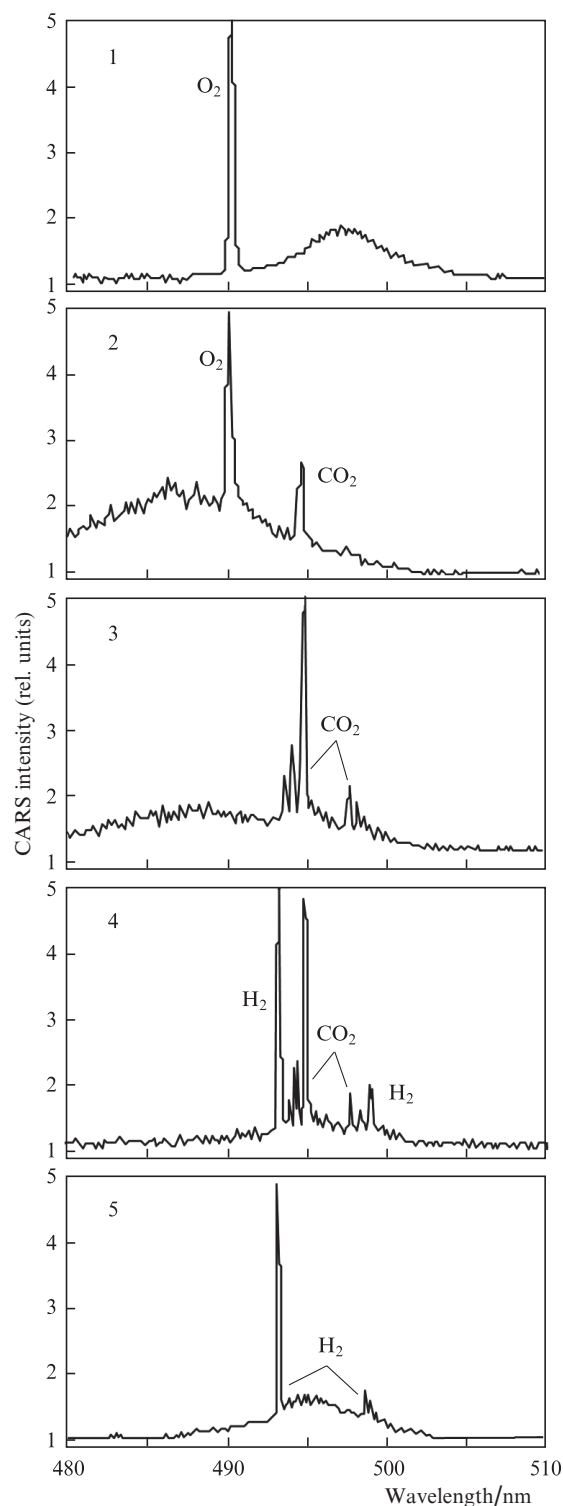

Figure 10. Fragments of CARS spectra of O_2, H_2, and CO_2 molecules, recorded at different fuel excesses and delays of the detection instant with respect to the ignition pulse.

and contains an unresolved Q-branch spectrum of oxygen molecules. Fragment 2 was recorded during lean-mixture burning, with a delay of 1000 μs with respect to the ignition; it reflects the decrease in the oxygen content and the formation of a combustion product: CO_2 molecules. Fragment 3 was also recorded for a lean mixture with a delay of 4000 μs; it indicates complete combustion of oxygen and the presence of a combustion product: CO_2. It can be seen that the spectrum contains lines of v_1 and $2v_2$ bands of CO_2 molecules and the corresponding lines of hot bands, which are characteristic of temperatures close to 1500 K. Fragment 4 was obtained for burning of a rich mixture at a delay time of 1500 μs; it contains, along with the v_1 and $2v_2$ bands of CO_2 molecules, lines of rotational transitions S_6 and S_7 of hydrogen molecules. As was noted above, hydrogen, being a product of methane decomposition, arises even in the burning phase (which corresponds to the pressure pulse leading edge) in the case of rich mixtures; this is evidenced by the spectrum recorded at a delay of 10 μs and presented by fragment 5. Based on the characterisation of the specific features of the spectra of O_2, H_2, CO, and CO_2 molecules, recorded in the second spectral range and presented in Figs 7 and 10, one can draw the following conclusions about their application in the problems of CARS thermometry of hydrocarbon–oxygen flames. First of all, we should note that the analysis performed below implies solution of the problems of express thermometry (measurements during one laser pulse) with detection of a broadband spectrum containing bands of at least two molecules, using the instruments that are most popular among experimenters: a THR-1000 spectrograph (Jobin Ivon) with a focal length of 1 m, grating 2400 lines mm^{-1}, and instrumental function ~ 0.9 cm^{-1}, in combination with a linear multichannel photodetector. The Q-branch spectra of O_2 molecules, with a characteristic spacing of 0.5 cm^{-1} between the strongest lines [14], will not be resolved even at low pressures, and the shape of the profile distorted by the instrumental function will be low-sensitive to changes in temperature. In the case of rich mixtures, along with the Q-branch lines of hydrogen, three isolated lines (S_5, S_6, and S_7), which are due to purely rotational transitions of hydrogen molecules, can also be used to determine temperatures in the range of 2000–3500 K. The procedure and error in determining the temperature from two lines of the rotational transitions in hydrogen was investigated by us in detail and reported in [15]. In the case of lean mixtures, which contain no hydrogen molecules, one can use not only water spectra but also the lines of the v_1 and $2v_2$ bands and 'hot' transitions in CO_2 molecules.

Based on the CARS spectra that are similar to those in Figs 7 and 10, with simultaneous (during one laser pulse) recording of three molecular components, we obtained qualitative information about the temporal behaviour of the relative concentrations of the initial reagents, CH_4 and O_2, and the main combustion products: H_2O, H_2 and CO_2 (Fig. 11). In the case of rich mixtures, the most characteristic processes are the fast (with delays of 0–10 μs) decomposition of methane and the formation of decomposition product: hydrogen molecules. At large (0–3000 μs) delays, the hydrogen content decreases as a result of burning, and the concentration of water molecules increases. As for burning of lean mixtures, methane decomposes as rapidly as in the previous case; however, the hydrogen concentration as a result burning is below the detection limit of the CARS method.
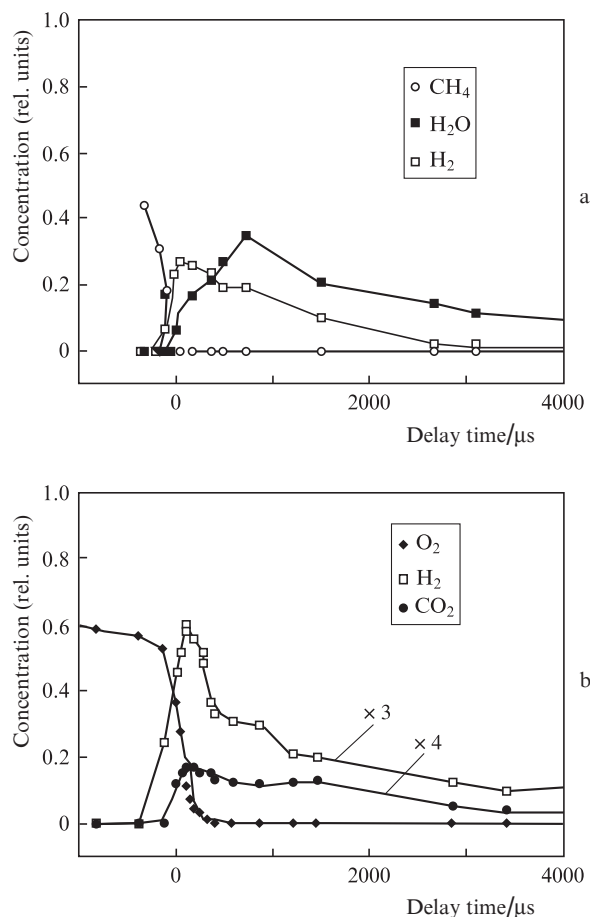

Figure 11. Time dependences of the relative concentrations of (a) CH_4, H_2O, and H_2 molecules and (b) O_2, CO_2, and H_2, measured based on CARS spectra in the ranges of 430–470 and 470–510 nm, respectively, in a pulsed high-pressure burner at mass consumptions of 1.24 g s^{-1} (O_2) and 0.52 g s^{-1} (CH_4). Time is counted with respect to the pressure-pulse leading edge.

4. Conclusions

Experiments on the diagnostics of burning of H_2-O_2 and CH_4-O_2 mixtures were performed. The CARS method with simultaneous recording spectra of several molecular components during one laser pulse (~ 10 ns) was used to measure the temperature and determine the qualitative composition of the initial materials and combustion products. The measurements were performed in a compact pulsed combustion chamber, which provides combustion products at high temperatures (to 3500 K) and pressures (to 20 MPa), which are characteristic of real combustion chambers of spacecraft propulsion systems. The specific features of the spectra of the molecules present in the chamber in different combustion modes, obtained under these conditions, allow one to choose the most preferred components to measure the temperature and mixture composition. Simultaneous recording of CARS spectra of several components (CH_4, H_2, H_2O or O_2, H_2, CO_2) during one laser pulse, synchronised with the ignition pulse, made it possible to observe the temporal evolution of the mixture temperature and composition in the combustion chamber.

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