

# CARS and Fluorescent study of ignition of H<sub>2</sub>/O<sub>2</sub> mixtures upon photodissociation of O<sub>2</sub> molecular

*Vitaly Kobtsev*<sup>1</sup>, *Sergey Kostritsa*<sup>1\*</sup>, *Dmitrii Kozlov*<sup>2</sup>, *Alexey Pelevkin*<sup>1,3</sup>, *Valery Smirnov*<sup>2</sup>, *Natalia Titova*<sup>1</sup>, *Sergey Torokhov*<sup>1</sup>, *Konstantin Vereshchagin*<sup>2</sup>, *Sergey Volkov*<sup>2</sup>

<sup>1</sup> Central Institute of Aviation Motors, Moscow, Russia

<sup>2</sup> Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia

<sup>3</sup> Moskow Institute of Physics and Technology, Dolgoprudny, Moscow region, Russia

**Abstract.** The research is devoted to gas mixtures ignition by UV laser radiation. The dissociation of O<sub>2</sub> molecules by a pulse of excimer ArF-laser radiation at 193-nm wavelength with formation of the chemically active oxygen atoms initiating chain reactions which cause ignition of H<sub>2</sub>/O<sub>2</sub> mixture was employed. The experimental test bench was created with CARS and fluorescent techniques for experimental investigation of some peculiarities of mixture ignition and combustion caused by such photo-dissociation, at conditions typical for combustion chamber. Two-dimensional numerical modeling of combustion process in model combustion chamber, based on kinetic mechanism of H<sub>2</sub> oxidation including atom O(<sup>1</sup>P) and radicals OH(A<sup>2</sup>Σ<sup>+</sup>), was performed.

## 1 Introduction

Among different methods of gas mixture ignition, the considerable attention is paid to the burning initiation by laser radiation. In the overviews [1,2], the methods of resonant and non-resonant impact on the molecules of combustible gas mixture leading to heating, optical breakdown, photo-ionization or photo-dissociation are discussed. This work is devoted to the experimental and numerical study of temporal and space behavior of such important parameters of combustion development as temperature and concentration of radicals OH at the initial stage of ignition and combustion (~5–50 μs) of H<sub>2</sub>-O<sub>2</sub> mixture upon the photo dissociation of O<sub>2</sub> molecules by the focused resonance laser radiation with a wavelength of 193 nm.

## 2 Experimental setup

For the investigation of photochemical ignition of gas mixtures at the pressure of 1–10 atm, the experimental setup was built. It consists of an excimer ArF-laser, a model combustion chamber provided with the glow plug for heating the gas mixture, and an optical diagnostic system. Fast processes in the chamber were studied using chemiluminescence emission (CLE) for detecting the electronically excited OH(A<sup>2</sup>Σ<sup>+</sup>) radicals (this species is denoted

---

\* Corresponding author: [sergey.kostritsa@gmail.com](mailto:sergey.kostritsa@gmail.com)

below as OH\*), laser-induced fluorescence (LIF) for observation of OH radicals in the ground electronic state, and coherent anti-Stokes Raman spectroscopy (CARS) for measuring the temperature. The combustion of the preheated gas mixture was initiated by the pulse of the excimer ArF-laser, which irradiates at the wavelength of  $\lambda=193$  nm. Such a radiation causes the excitation of O<sub>2</sub> molecules to the B<sup>3</sup>Σ<sub>u</sub><sup>-</sup> electronic state with the following dissociation of these molecules on two oxygen atoms. The laser pulse duration is  $\tau_p=15$  ns, the energy in the pulse varies in the range  $E_s=25-150$  mJ. Laser beam is focused by a lens with a focal length of 200 mm at the distance of 1 mm above the glow plug.

## 2.1 Temperature measurements

The gas mixture temperature was measured using both thermocouples and CARS techniques. At first, the temperature was measured by thermocouples at different pressure values in the case of absence of initiating laser radiation. For measurement of the temperature of the initial mixture and combustion products in the focus area of the excimer laser radiation both before and after the impact of excimer laser pulse, the broadband CARS spectrometer [3], which allows registering CARS spectra of a Q-branch of hydrogen molecules during one laser shot, was also used. The temperature can be determined in this way in the range of 500–3500 K with an accuracy of  $\pm 7\%$ . The spatial resolution was  $\sim 1.7 \times 0.15 \times 0.15$  mm<sup>3</sup>. For the improvement of the CARS spatial resolution in the longitudinal direction, the scheme with the crossed beams radiated by the pump laser "planar CARS" [4], which were focused by the lens with the focus length of  $f=250$  mm, was applied.

## 3 Modeling

### 3.1 O<sub>2</sub> molecule photo dissociation

For the analysis of the ignition and combustion process in the H<sub>2</sub>-O<sub>2</sub> mixture under the exposure of laser radiation with the wavelength  $\lambda=193.3$  nm, the numerical simulation was carried out. At the first stage, the absorption of laser radiation and the composition of the mixture in the irradiation region to the end of the laser pulse ( $\tau_p=15$  ns) were calculated. Computations shows that mostly oxygen atoms O(3P) form to the end of the pulse. Their mole fraction is maximal in the focal area due to the greatest values of temperature and radiation intensity in this region. According to calculations, the concentration of O atoms in the focal area can amount to 1% of total O<sub>2</sub> concentration at maximal energy  $E_s \sim 150$  mJ in the laser pulse.

### 3.2 Photochemical ignition of H<sub>2</sub>-O<sub>2</sub> mixture

At the second stage, the numerical simulation of the ignition and combustion of H<sub>2</sub>-O<sub>2</sub> mixture just after finishing the laser pulse was carried out with the usage of the program FLUENT from the ANSYS-CFD software package [5].

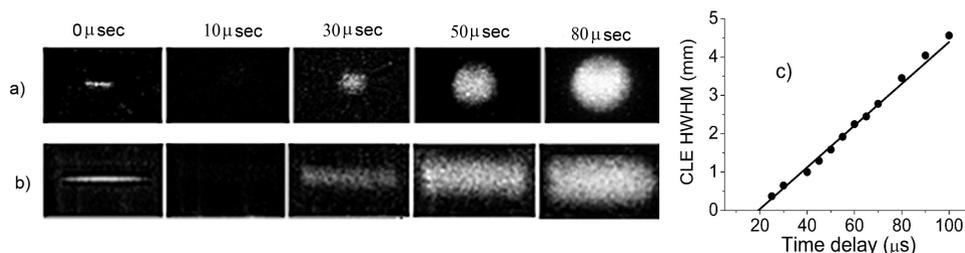
### 3.3 Kinetic mechanism

The reaction mechanism of H<sub>2</sub> oxidation [6] was used as basic one. This mechanism was supplemented by the set of reactions describing the formation of electronically excited radical OH\* [7].

## 4 Results and discussion

### 4.1 LIF and CLE

The space-time distributions of OH and OH\* radicals obtained during laser-induced ignition of the H<sub>2</sub>/O<sub>2</sub> mixture with  $\phi=1$ ,  $T_0=713$  K,  $P_0=1$  atm and  $E_s=107$  mJ have been studied. Two parameters of focusing of excimer laser radiation were used: a) in the chamber with the glow plug, the confocal parameter of focusing was equal to 8 mm, while b) in the chamber with the resistive heating, it was 24 mm. The results of experiments are compared in Fig. 1. In the first column ( $t=0$   $\mu$ s) are shown the images, which were registered at the moment of the UV laser radiation pulse and represent the luminescence of laser-excited O<sub>2</sub>(B<sup>3</sup> $\Sigma_u^-$ ) molecules within the Schumann-Runge band in the focal area. The second column ( $t=10$   $\mu$ s) represents images corresponding to the induction period when the O<sub>2</sub> luminescence already finished, but the mixture burning did not start yet. The third images ( $t=30$   $\mu$ s) display the appearance of CLE signals of OH\* radicals in the vicinity of the focal area, attesting that the ignition has occurred. Further evolution of the chemiluminescence zone is illustrated by the images with  $t=50$  and 80  $\mu$ s. It is seen that in the case b), ignition starts simultaneously with a) but in a larger area. It is evident that a total time needed for complete combustion of the mixture will be smaller in the case b) than that in the case a). It means that using the excimer laser radiation, one can ignite simultaneously a large volume of a flammable mixture.

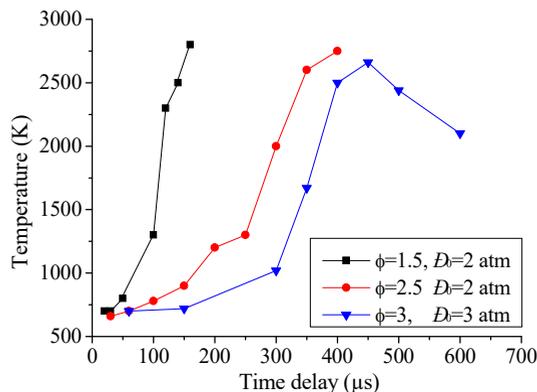


**Fig. 1.** a, b) The sequences of images of a chemiluminescence area of the OH\* radicals depending on the time delay from the excimer laser pulse in a stoichiometric H<sub>2</sub>/O<sub>2</sub> mixture with  $P_0=1$  atm and  $E_s=107$  mJ. c) Sizes of chemiluminescence area at different delay time.

The obtained images a) were processed as follows. The half-width at half-maximum ( $I_{ch})_{max}/2$  (HWHM) of the chemiluminescence intensity profile in the observed region was determined at each time delay and presented at graph (c picture). The point of intersection of the straight line  $r_{ch}(t)$  with the abscissa axis (in this point the combustion region seems to converge to zero size) can be treated as the ignition delay (induction) time  $t_{ind}$  (see Fig. 1 c).

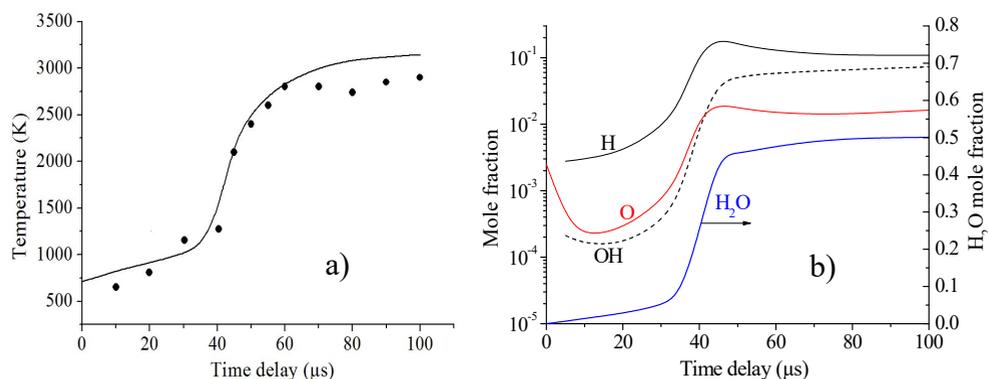
### 4.2 CARS thermometry

The evolution of temperature in the focal region was measured using coherent anti-Stokes Raman spectroscopy (CARS). The results of temperature measurements in the focal region as a function of time for different values of  $\phi$  are given in Fig. 2.



**Fig. 2.** Evolution of gas temperature in the focal zone profiles during the ignition of the H<sub>2</sub>-O<sub>2</sub> mixture with different values of  $\phi$ ,  $T_0=713$  K and  $E_s=107$  mJ.

These dependencies show that, after a certain delay (induction period), the temperature rapidly increases up to value of  $\sim 2700$  K. The decrease of the temperature at large values of  $t$  (this is shown for the case with  $\phi=3$ ) is due to the cooling of the gas due to the heat release through the chamber walls. One can also see from Fig. 2 that the induction time  $t_{ind}$  increases with increasing value of  $\phi$ . In Fig. 3a is shown the comparison of the measured and calculated values of the temperature in the focal zone during the ignition of the H<sub>2</sub>-O<sub>2</sub> mixture with  $\phi=1.3$ ,  $T_0=713$  K,  $P_0=2$  atm and  $E_s=105$  mJ. One can see that the calculation results describe the dynamics of the temperature change in this region sufficiently well. A weak linear growth in calculated temperature is observed at the initial stage ( $t \leq 35$   $\mu$ s). At this stage, O atoms, produced by laser radiation, initiate the chain reactions, which lead to a gradual increase in the concentration of O, H atoms and OH radicals and to a slow release of heat due to the H<sub>2</sub>O formation (see Fig. 3b). After the concentrations of active components reach a certain value, the mixture ignites. This is characterized by a sharp increase in the H<sub>2</sub>O concentration and temperature, which reaches the value of  $\sim 2800$  K to the time  $t=60$   $\mu$ s both in the calculation and in experiment.



**Fig. 3** Measured (points) and computed (curve) evolution of gas temperature (a) species mole fractions (b) at the focal zone during the ignition of the H<sub>2</sub>-O<sub>2</sub> mixture with  $\phi=1.3$ ,  $T_0=713$  K,  $P_0=2$  atm and  $E_s=105$  mJ.

The difference between the calculated and measured temperature at  $t \leq 35$   $\mu$ s is likely related to the above-described features of temperature measurements when the size of the high-temperature zone is less than the spatial resolution of CARS. At  $t \sim 60$   $\mu$ s, the mixture burns out in the focus area and the gas temperature changes only slightly. The calculated

temperature of the combustion products turned out to be a little higher than measured one due to the neglect of the heat losses through the chamber walls during modeling.

## Conclusions

An experimental setup was created allows to investigate the ignition process of various gaseous fuels with oxygen, the reactivity of which is instantly (within 20 nsec) activated in relation to the chain reactions by oxygen atoms obtained as a result of dissociation of O<sub>2</sub> molecules. This type of ignition does not contain impurities of the recombining plasma characteristic of spark methods of optical or electrical breakdown.

Based on the space-time distributions of OH and OH\* radicals obtained during laser-induced ignition of H<sub>2</sub>-O<sub>2</sub> mixture at the mixture temperatures below the autoignition temperature, the quantitative data of the induction time and the velocity of the flame front were obtained for various parameters of the mixture and different values of the energy in the laser pulse.

The temperature measurements by CARS-spectroscopy has allowed to getting information about the temperature evolution at the initial stage of the burning process register experimentally the presence of high temperature  $\geq 1000$  K at time delays starting from 30  $\mu$ sec and to confirm the fact of mixture ignition with transition to steady burning, obtained on the basis of observation of the emission of OH and OH\* radicals.

## References

1. P.D. Ronney, Laser versus conventional ignition of flames, *Optical Engineering* **33**(2), 510–521 (1994)
2. S.A. O'Briant, S.B. Gupta, S.S. Vasu, Review: laser ignition for aerospace propulsion, *Propulsion and Power Research* **5**(1), 1–21(2016)
3. V.V. Smirnov, S.A. Kostritsa, V.D. Kobtsev, N.S. Titova, A.M. Starik, Experimental study of combustion of composite fuel comprising *n*-decane and aluminum nanoparticles, *Combust. Flame* **162**(10) 3554–3561 (2015)
4. A.C. Eckbreth, BOXCARS: Crossed-beam phase-matched CARS generation in gases, *Appl. Phys. Letts.* **32**, 421-423 (1978)
5. ANSYS FLUENT. Version 12. ANSYS Inc.; January (2009)
6. Bezin L.V., Kopchenov V.I., Sharipov A.S., Titova N.S., Starik A.M. Evaluation of prediction ability of detailed reaction mechanisms in the combustion performance in hydrogen-air supersonic flows. *Combustion Science and Technology*, 2013, V.**185**, N.1, P. 62-94 (2013)
7. T. Kathrotia, M. Fikri, M. Bozkurt, M. Hartmann, U. Riedel, C. Schulz. Study of the H+O+M reaction forming OH\*: Kinetics of OH\* chemiluminescence in hydrogen combustion systems. *Combustion and Flame* **157** (2010) 1261–1273(2010)