

Laser induced breakdown spectroscopy for local equivalence ratio measurement of kerosene/air mixture at elevated pressure

Shaohua Zhang^a, Xilong Yu^{a,*}, Fei Li^a, Guojian Kang^b, Lihong Chen^a, Xinyu Zhang^a

^a State Key Laboratory of High Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China

^b Chinese Academy of Aerospace Aerodynamics, Beijing 100074, China

ARTICLE INFO

Article history:

Received 15 September 2011

Received in revised form

16 November 2011

Accepted 4 January 2012

Available online 31 January 2012

Keywords:

Laser induced breakdown spectroscopy

(LIBS)

Equivalence ratio

Kerosene/air mixture

Elevated pressure

ABSTRACT

The quantitative local equivalence ratio measurements of premixed kerosene/air gas at elevated pressure by the laser induced breakdown spectroscopy (LIBS) technique were performed in a high temperature test cell, which was designed and manufactured for simulated supersonic combustion state. According to in-situ experimental conditions in supersonic combustion, the correlations between the values of emission intensity ratio of H/O, H/N and the equivalence ratio of premixed kerosene/air mixture in different gas pressures was established. The dependence of the FWHM of H_α on pressure of the mixture was also measured. Therefore, the laser diagnostic method for quantitative local equivalence ratio measurements of kerosene/air mixture by the LIBS technique in supersonic combustion was developed in laboratory. The fundamental data was prepared for on-line quantitative local equivalence ratio measurements of kerosene/air mixture in supersonic combustion experiments.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

In combustion, fuels must be mixed into air in an appropriate ratio to release more energy. The mixed ratio of fuel and air (the equivalence ratio, Φ) determines the efficiency of combustion and the generation of pollutants when it affects the ignition, transitions and stability of combustion. Therefore, measurement of the local equivalence ratio is essential in maintaining the stability of the combustion process, as well as in minimizing soot emissions. It is also a key factor to keep appropriate equivalence ratio in combustion chamber for supersonic air-breathing engines, in which chemical reactions takes place in the supersonic gas flow. Hitherto, the accurate measurement for the distribution of hydrocarbon fuels is still one of the most critical keynotes in SCRAMjet that is the soul of supersonic vehicle. Therefore, the development of optical diagnostic techniques, which could measure fuel–air ratio accurately owns a great significance for the studying of high efficiency engine system and SCRAMjet.

Laser induced breakdown spectroscopy (LIBS) is a powerful diagnostic method that can be applied to combustion systems for measurements of fuel–air ratio, fuel composition and temperature. In this technique, a sufficiently high energy laser pulse is employed to create local plasma by focusing into a small volume.

The high peak power laser pulse breaks chemical bonds and initializes the fragmentation of molecules into elemental components in the focus. Then, high temperature plasma is produced while the atoms dissociated from target molecules are excited. The emission of these excited atoms in their relaxation process can be recorded and analyzed to determine the elemental compositions of sample qualitatively and quantitatively. In LIBS, if the plasma is optically thin and in local thermodynamic equilibrium (LTE), the intensity of spectral emission line has a linear correlation with the population of the atomic excited state, as the following formula:

$$I = CNh\nu \exp\left[-\frac{E}{kT}\right] \quad (1)$$

where I is the intensity of the spectral emission line, N is the population of the excited state of atomic species, $h\nu$ is the energy of single photon of excited laser, E is the excitation energy of the atomic species, k is the Boltzmann constant, T is the absolute temperature and C is the constant which relates to instrument parameters, element property and other factors. In Eq. (1), C , $h\nu$, E , k and T are all constants for the specific spectral emission lines and other given experimental conditions. That is to say, the intensity of the spectral emission line varies directly with the population of the atomic excited state in certain conditions. In LIBS experiment, the relative intensities of atomic spectral lines are often employed to get the qualitative information of the atomic species with keeping from effects of instrument parameters and the jitter of laser energy. For instance, the ratio

* Corresponding author.

E-mail address: xlyu@imech.ac.cn (X. Yu).

between emission intensity of hydrogen and oxygen (H/O) or C/N in LIBS is usually used to get the equivalence ratio of hydrocarbon fuels within the probe volume.

The LIBS technique is one of the best tools for the fuel–air ratio (the equivalence ratio) measurements in combustion. It possesses many advantages, e.g. high temporal and spatial resolution, low requirements for environment, fast response time, non-intrusiveness and so on. It collects the emission of excited atoms, which is unaffected by the molecular state (e.g. burned or unburned gas), differing from other optical diagnostic techniques, which record the emission of excited molecules. Therefore, it can be applied to analysis of any matter regardless of its physical state, providing the possibility for real time multi-element analysis. Furthermore, the LIBS technique is particularly effective in harsh, hostile, toxic or dangerous environments and it has been employed in the planetary environment exploration [1–3]. For example, the LIBS technique was utilized to analyze the components of Mars soil by NASA in MSL project in 2009 [4]. Moreover, there are many studies that have been successfully performed for local equivalence ratio measurements of lower carbon number hydrocarbon fuels (e.g. CH₄ and C₃H₈) and air flames on low pressure premixed chamber by LIBS [5–10]. Experiments in which the laser induced plasma ignition and equivalence ratio measurements by LIBS were achieved simultaneously have also been carried out [11–13]. Additionally, some LIBS on-line investigations were accomplished. e.g. Rai et al. [14] have been applied LIBS technique to in-situ component analyze in combustion and in plume of a simulated CH₄/air rocket. The quantitative local equivalence ratio measurements of methane/air in a standard motor by LIBS under laboratory conditions were also executed by Ferioli et al. [15].

However, most of the previous LIBS investigations in combustion for quantitative equivalence ratio measurements are limited in low pressure premixed combustion or in lower carbon number hydrocarbon fuels. The experimental data obtained from these investigations does not suit to kerosene, a perspective jet fuel in supersonic combustion. Since kerosene is a kind of mixed complex composed of many kinds of higher carbon number hydrocarbon fuels. Its breakdown threshold and spectra are greatly different from that of the lower carbon number hydrocarbon fuels like methane. Furthermore, it is well known that at elevated pressure, the spectral line profile, the emission efficiency and the lifetime of spectral line are all changed remarkably because of the intensified collision. The relative intensities of different spectral lines as well as the results of quantitative equivalence ratio measurements are also greatly affected. For these reasons, the LIBS experiments of kerosene in elevated pressure should be performed in detail before executing LIBS diagnostic for the supersonic combustion of kerosene. In addition, it is significant that kerosene is a complex hydrocarbon fuel mixture which owns strong regionalism. Taking jet fuel for instance, it contains hundreds of components like alkane, alkene, cyclohydrocarbon, aromatics and so on. Its exact components are usually varies with habitats, producers and vintages. Therefore, the LIBS investigation for the specific kerosene (e.g. the RP-3 model) is very necessary.

In this paper, the LIBS investigation of RP-3 kerosene was carried out in a high temperature elevated pressure test cell, which was designed and manufactured for simulated supersonic combustion state. The quantitative local equivalence ratio measurements of premixed kerosene/air gas by the LIBS technique were preformed. The correlations of values of emission intensity ratio (H/O and H/N) in LIBS with the equivalence ratio of kerosene/air mixture in different gas pressures were established. The calibration experiments of quantitative local equivalence ratio measurements of kerosene/air mixture in different gas pressures were also accomplished considering the pressure effect on the FWHM of H_α.

2. Experimental apparatus

The used kerosene in present experiment is RP-3 kerosene. It is conventional national aviation kerosene, which is composed of many kinds of alkane, alkene, cyclohydrocarbon, aromatics, etc. In this kerosene, volume percentages of saturation hydrocarbons, aromatics and unsaturated hydrocarbons are 92.5, 7 and 0.5, respectively. The molecular formula of RP-3 kerosene closes to C₁₁H₂₂. The characteristic data of the specific kerosene was summarized in Table 1.

The experimental setup of quantitative local equivalence ratio measurements for kerosene/air mixture at elevated pressure by LIBS was illustrated in Fig. 1. As shown in Fig. 1, the LIBS measurements were performed in a stainless steel flow cell designed and machined by ourselves. The cell is a high temperature elevated pressure test cell equipped with optical accessible quartz windows whose transmission region is in the range of 200–3000 nm. The temperature of the cell could be varied from room temperature to 350 °C by hiring a temperature controller while the pressure could be adjusted in 1–4 atm region with a pressure sensor. A premixed gas sample containing a suitable ratio of vaporized kerosene and air supplied from the liquid vaporizer (Model: DLILS Turbo Vaporizer, BROOKS Instrument) through stainless steel pipes and controlled by individually calibrated mass flow controller (Model: Coriolis Mass Flow meter and SLA5851S Thermal Mass Flow meter, BROOKS Instrument) was slowly passed through the cell. The LIBS signals of premixed kerosene/air gas were generated from the excited atoms in the microplasma, which was created by focusing the second harmonic output of a Nd:YAG laser (Model: Quanta-Ray190, Spectra-Physics) at 532 nm. The plasma emission was collected by a lens system, passed through a fiber and then, focused into an echelle spectrometer (Model: Mechelle5000, Spectral range: 200–850 nm, Spectral resolution: 0.125 nm at 500 nm, Andor Technology) equipped with an ICCD camera (Model: iStar DH734, minimum optical gate width < 5 ns, Andor Technology). The output of the ICCD was inputted into a digital board and then analyzed with a computer data acquisition system. Experimental synchronization is controlled through a multi-channel digital delay pulse generator (Model: DG535, Stanford Research System). The grating efficiency of the echelle spectrometer was calibrated by a NIST standard traceable tungsten halogen lamp (Model: 63976, Oriel Instruments) and wavelength calibration of the system was proceeded with a standard Hg–Ar lamp.

In experiment, the temperature of liquid vaporizer was kept at 180 °C (± 1 °C) while that of the cell was set at 200 °C (± 8 °C), in order to vaporize liquid kerosene thoroughly and avoid the condensation in the test region. The flow rate of air was set at 3 L/min while that of kerosene varied in the range of 7.5–28.5 g/h, which was corresponding to the equivalence ratio in the 0.47–1.8 region. The second harmonic output of a Nd:YAG laser was focused via a quartz lens with a focal of 150 mm to form a local plasma. The single pulse energy of excited laser was set as 120 mJ (± 5 mJ) unless otherwise specified. The emission of LIBS was collected by a 250 mm focal length quartz lens at the

Table 1
Physicochemical properties of RP-3 kerosene.

Density (g/cm ³) at 20 °C	0.8079
Flash point (°C)	50
Viscosity (mm ² /g) at 20 °C	1.67
Distillation (°C) at 10%	179
Mass ratio of C/H	6.04
Aromatics content (%) in mass	15.0
Crystallization point (°C)	–59

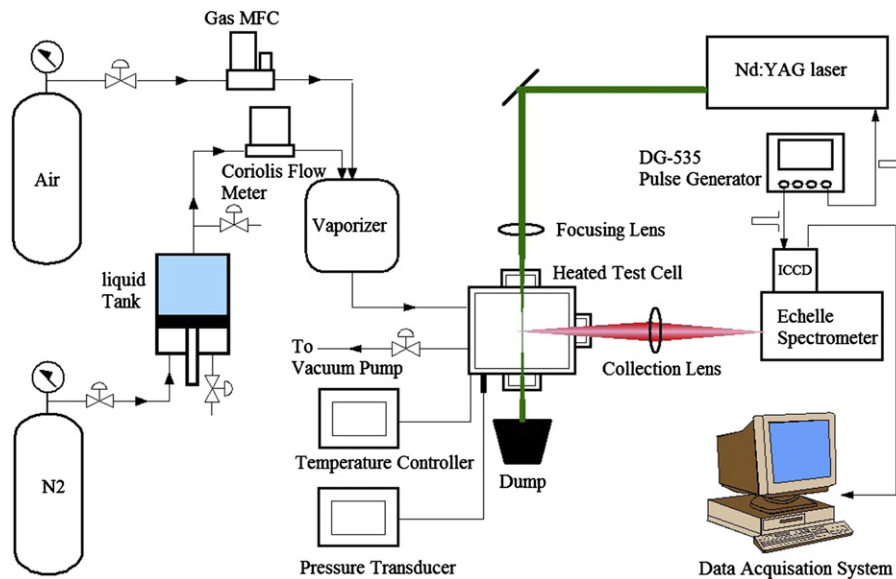


Fig. 1. A schematic diagram of LIBS setup.

perpendicular direction of the laser. Then, the LIBS signals of atoms (H, O, N, etc.) were focused into the fiber whose diameter is 1 mm and transmitted into the echelle spectrometer with a 50 μm input slit. The acquisition of data generally starts at 800 ns after the impacting of laser pulse with a 3 μs gate time to increase the intensity of LIBS signals and decrease the continuum emission from the high temperature plasma. The LIBS signals were averaged over 10 laser single shots and repeated three times for good signal noise ratio(S/N) by avoiding the influence from laser induced ignition.

3. Results and discussion

In the high temperature elevated pressure test cell that was described in Section 2, the LIBS experiments for premixed kerosene/air gas at elevated pressure were performed and the emission of spectral lines of atoms ($\text{H}\alpha \sim 656.3 \text{ nm}$, $\text{NI} \sim 742.3 \text{ nm}$, $\text{NI} \sim 744.2 \text{ nm}$, $\text{NI} \sim 746.8 \text{ nm}$ and O I triplet near 777 nm) was collected by a broadband echelle spectrometer. A typical laser induced breakdown spectrum of premixed kerosene/air gas was recorded and shown in Fig. 2 without any modification. In this typical spectrum, the delay was fixed at 800 ns with a 3 μs exposed gate of ICCD, differing from some reference in which the delay was set at 1 μs to reduce the influence of the broad background continuum from the luminous plasma induced by laser. The equivalence ratio of premixed kerosene/air gas was 0.47 and pressure was set at 1 atm. As shown in Fig. 2, the influence of the plasma broad background continuum on LIBS spectra could be neglected in the present parameter setting. Additionally, it is noted that in our laser induced breakdown spectroscopy, no spectral lines of C atom were observed, but the radiation of radical CN had been recorded.

3.1. Effective lifetimes of atomic spectral lines

The effective lifetimes of the emission lines of H, N and O atoms were investigated by the time-resolved LIBS technique to determine the suitable experimental parameters. The equivalence ratio of premixed kerosene/air gas was set at 0.47. Total pressure of gases was 1 atm, while the gate width of ICCD was programmed as 200 ns. With recording the time-resolved LIBS spectra, the spectral

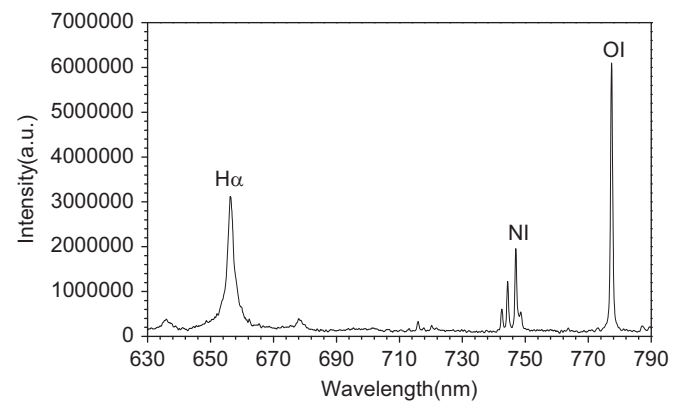


Fig. 2. A typical spectra of premixed kerosene/air gas in the LIBS experiment.

lines of H, N and O atoms ($\text{H}\alpha$, 656.3 nm, NI, $\sim 742.3 \text{ nm}$, $\sim 744.2 \text{ nm}$, $\sim 746.8 \text{ nm}$ and O I triplet near 777 nm) were measured and analyzed. The relaxation processes of these spectral lines emission were obtained and demonstrated in Fig. 3(a). In this graph, the black dots are the integrated radiation intensity of the $\text{H}\alpha$ line ($\sim 656.3 \text{ nm}$) at different delays when the triangle ones are that of O I triplet near 777 nm. The circle data points are the sum of integrated intensities of three N I lines at $\sim 742.3 \text{ nm}$, $\sim 744.2 \text{ nm}$, $\sim 746.8 \text{ nm}$ while the colored solid curves are mono-exponential fits of these data points. The lifetimes of the spectral lines emission can be derived directly from the colored solid curves. As shown in Fig. 3(a), the fitted lifetime values are $\sim 355 \text{ ns}$, $\sim 328 \text{ ns}$ and $\sim 305 \text{ ns}$ for H, N and O excited atoms, respectively, in the present LIBS experiment. It is obviously that the lifetimes of excited atoms are quite short. Intensities of the spectral lines are too weak to be detected when the data acquisition start at 1 μs after the impacting of laser pulse as described in some references. It means that, in the present LIBS experiment, the delay of data acquisition should be shorter than 1 μs for strong intensities of the emission atomic lines. At the same time, the impact from the delay shortening on the relative intensities of the atomic spectral lines should be considered carefully. Therefore, the decay processes of relative intensities of the spectral lines were also analyzed and presented in Fig. 3(b).

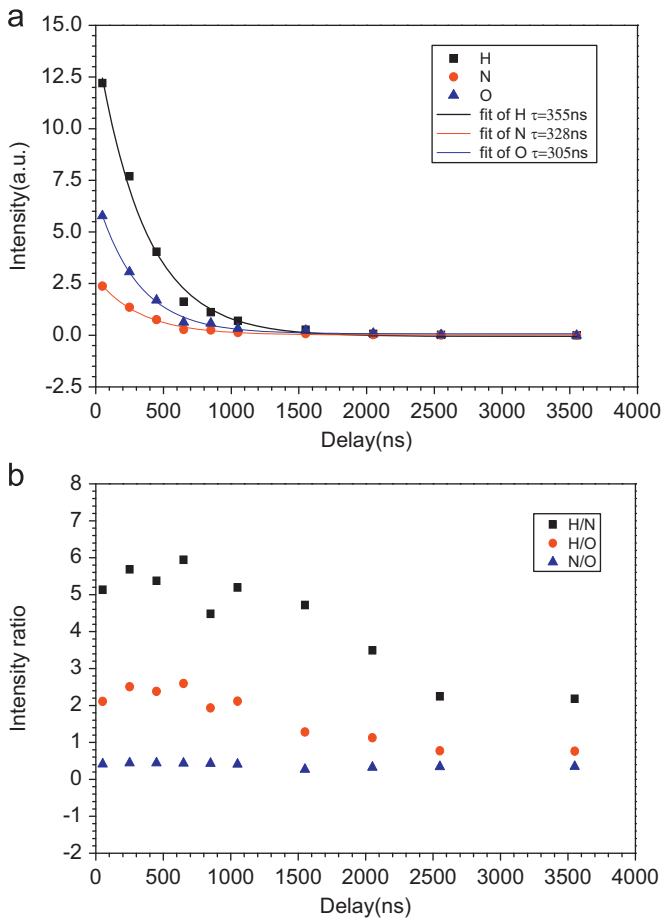


Fig. 3. Relaxation processes of the spectral lines of H, N and O atoms in absolute (a) and relative (b) intensity.

In Fig. 3(b), the different type dots relate to the different relative intensities of atomic spectral lines (square \sim H/N, circle \sim H/O and triangle \sim N/O). In the figure, it was clearly shown that the relative intensities of different atomic spectral lines are almost constants in $1 \mu\text{s}$ from the excitation of laser individually. That is to say that in this time region, the acquisition of experimental data can start at any moment, as the results of quantitative local equivalence ratio measurements would not be affected greatly. Considering the impact of the plasma broad background continuum, in the present experiment, the time of data acquisition was set at 800 ns after the coming of laser pulse to keep enough intensity of signal while preventing the broad background continuum from the luminous plasma in the LIBS of kerosene/air mixture without affecting the accurateness of quantitative measurements.

3.2. Effect of laser pulse energy on emission intensity ratio

In LIBS technique, the temperature of the laser induced local plasma must be hot enough to dissociate the target molecules into their constituent atoms. The right value of excited energy for a specific molecule should be higher than its dissociation threshold, which is different from each other for different molecules. In addition, the power density of the excited laser pulse has a considerable influence on intensities of the spectral lines. Consequently, the impact of the pulse energy on the relative intensities of spectral lines becomes very necessary to be investigated by the LIBS technique. In the present experiment, the variations between energy of excited laser in the range of 50–200 mJ and the relative

intensities of H/O and H/N of three different premixed kerosene/air gases whose equivalence ratio are 0.57, 1.23, 1.8 were investigated and shown in Fig. 4. The total pressure of gases in the experiment was set at 1 atm.

As illustrated in Fig. 4(a), when the pulse energy is lower than 90 mJ, values of H/O and H/N vary greatly with the pulse energy. The variation is greater when the equivalence ratio of premixed gas is larger. It is implied that the dissociation for the larger equivalence ratio premixed kerosene/air gas is more difficulty. When the laser pulse energy is higher than 90 mJ, ratios of the H to the O or N lines of three different equivalence ratios premixed kerosene/air gases become constants whose values increase with equivalence ratio. It is suggested that the kerosene/air mixture in the probe volume were atomized thoroughly when the pulse energy over 90 mJ. It means that the pulse energy should not be lower than 90 mJ in our LIBS experiments. Therefore, in present work, the excited laser whose single pulse energy is 120 mJ was employed to create the local plasma, with the delay and gate of 800 ns and 3 μs , respectively. The arrangement makes the LIBS signal strong enough as well as keeps from the continuum emission of luminous plasma. Furthermore, the molecules in the plasma also could be dissociated to its component atoms completely even the fluctuation of the pulse energy goes up to $\pm 10\%$.

From Fig. 4, the sequence of dissociation rate of different molecular could be inferred. In Fig. 4(a), the ratio of H/O growing with the excited energy represents that the increase of O atomic

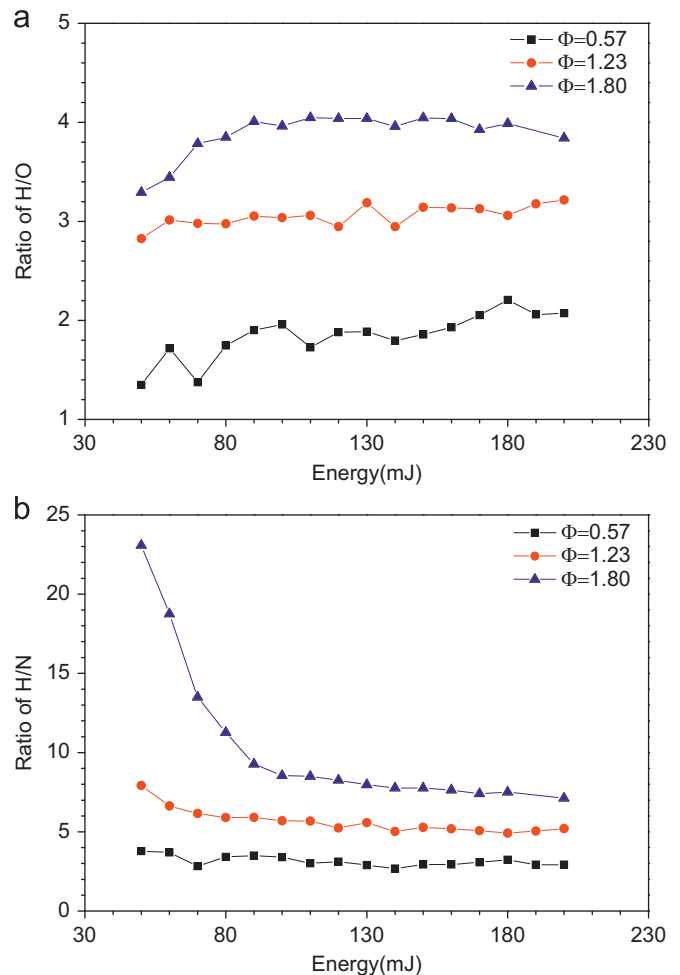


Fig. 4. Relative intensities of atomic emission lines H/O (a) and H/N (b) as a function of laser pulse energy for premixed kerosene/air gases.

emission intensity gradually lags behind the growth of H atomic emission intensity with increasing of the introduced laser energy. At the same time, the great decrease of H/N ratio with the laser energy in the *fig. 4b* indicates that the increase rate of N atomic emission intensity is greater than that of H atomic emission intensity when the energy below 100mJ. As a result, the ratio value of H/N varies greatly with the energy but the ratio of H/O is inversely proportional with the energy of laser impact in *Fig. 4*.

3.3. Correlation of equivalence ratio with relative intensity in different pressures

In LIBS experiments of premixed kerosene/air gas, the value of the H/O or H/N varies directly with the relative concentration of the atomic species. It means that the value of the H/O or H/N corresponds linearly to the equivalence ratio of the premixed kerosene/air gas in the test cell. The linear correlation called the calibration line is the fundamental data for the quantitative local equivalence ratio measurements by the LIBS technique. Therefore, the relationship between the value of relative intensity and the equivalence ratio of premixed gas must be measured in the high temperature high pressure test cell at different pressures for the simulated supersonic combustion state.

The calibration lines in different pressures obtained in LIBS experiments were obtained and presented in *Fig. 5*. Here, the experimental conditions, which had been determined in the preceding context, were hired. The temperature of liquid

vaporizer was kept at 180 °C (± 1 °C) while that of chamber was set at 200 °C (± 8 °C). The single pulse energy of excited laser was fixed at 120 mJ. The LIBS emission of atoms were focused into the fiber and then, transmitted into the echelle spectrometer with the delay and gate of 800 ns and 3 μ s, respectively. The LIBS signals were averaged over 10 laser single shots and repeated three times for high S/N with avoiding the impact from laser induced ignition. The flow rate of air was set at 3 L/min while that of kerosene varied in the range of 7.5–28.5 g/h with the pressure of cell is 1, 1.5, 2, 2.5 and 3 atm.

In *Fig. 5*, the solid lines (the calibration lines) are corresponding to the linear fits of the data, which denote H/O or H/N ratios correlated with the equivalence ratio at different pressures ($P=1, 1.5, 2, 2.5$ and 3 atm) with different types and symbols. It is clearly shown that the calibration lines between the ratios of H/O and H/N with the equivalence ratios are different in different pressures. From *Fig. 5*, slopes of the linear correlations of the equivalence ratio with the value of H/O or H/N were deduced and related with the pressure of cell, as shown in *Fig. 6*.

Fig. 6 shows that the correlation of slopes of calibration lines with the pressure in chamber. The solid lines are the mono-exponential fits of slopes of the calibration lines in different pressure, which were denoted by data dots. In *Fig. 6*, it is obvious that slopes of the calibration lines decrease exponentially with the pressure in present LIBS experiments. It is very reasonable, because the particle densities as well as the interactions are all increased with the pressure. The quenching of excited atoms was also intensified greatly by the increase of pressure while the intensities of spectral lines were weakened. Therefore, it is believed that the mono-exponential variation of slopes of calibration lines is originated from the increase of pressure.

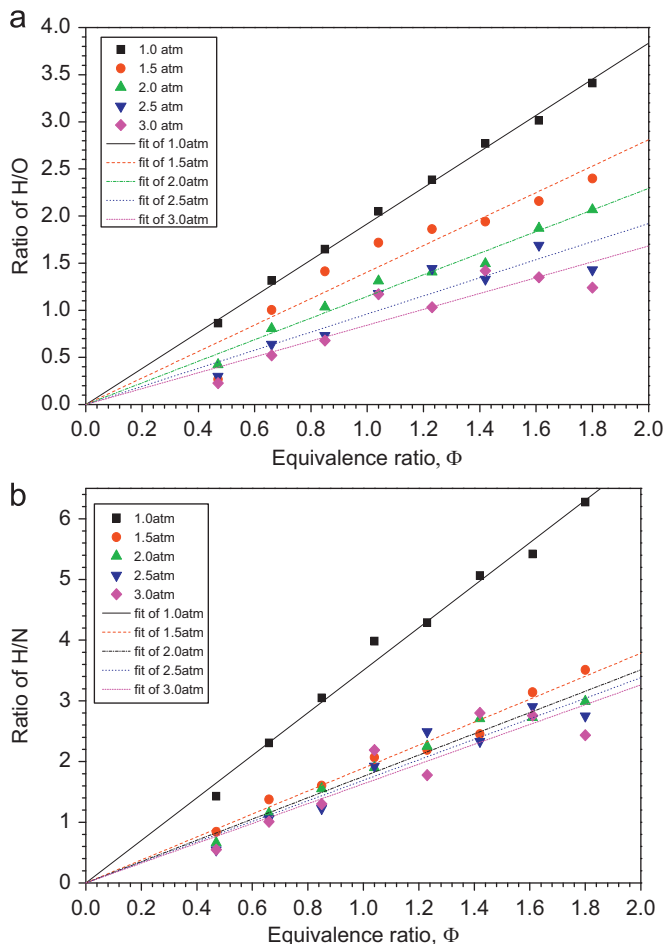


Fig. 5. Correlation of the equivalence ratio with the relative intensity of the H and O atoms (a) and that of the H and N atoms (b) at different pressures.

3.4. Effect of the gas pressure on the FWHM of H_{α}

Due to the variation of slopes of calibration lines with the pressure, the local equivalence ratio of premixed kerosene/air gas cannot be easily measured according to the calibration lines in *Fig. 5* unless the value of pressure is determined. With increasing of pressure, densities of particles are multiplied in the cell while the collision probability is improved greatly. Therefore, the interactions of different particles are enhanced. The processes of decay and collisions are accelerated. As a result, the emission width of spectral lines is broadened significantly while the line intensity is reduced greatly. It is well known that the observed line width of spectral lines is the results of the convolution of instrumental

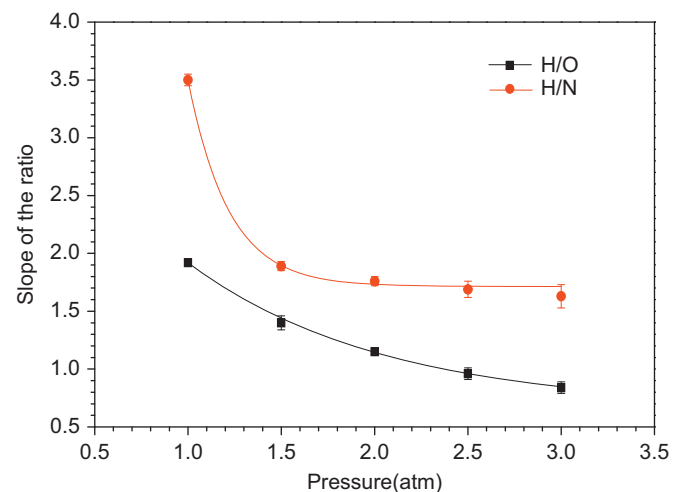


Fig. 6. Variation of slopes of calibration lines with the cell pressure.

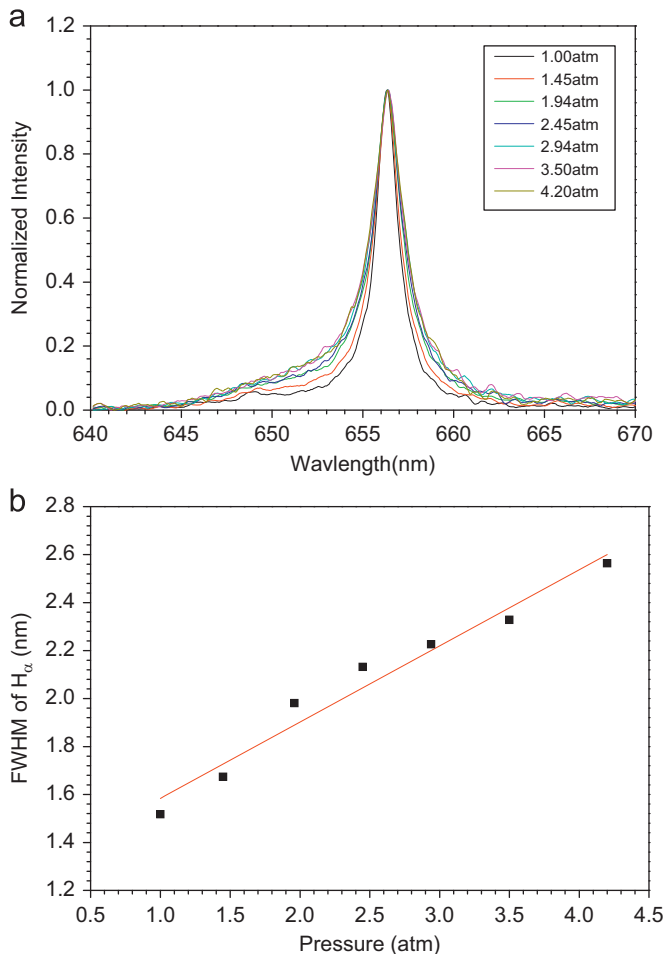


Fig. 7. Effect of the gas pressure on the full width at half maximum (FWHM) of H_{α} line (a); the linear correlation described by the Stern–Vollmer equation of FWHM of H_{α} line with the gas pressure (b) (equivalence ratio $\phi=0.47$). (For the interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

broadening, natural broadening, Doppler broadening and pressure broadening with the “true” line width. The natural broadening and the instrumental broadening are constants for the certain apparatus. The Doppler broadening only relates with the absolute temperature for the specific particle. So, in present experiment, the Doppler broadening of the atomic spectral lines also keeps constant because of the fixed cell temperature and excited energy. Therefore, the variation of observed line width of spectral lines is mainly determined by the pressure broadening in present LIBS experiment. This pressure broadening of spectral line also calls the collisional broadening. The collisional radiation spectrum has a Lorentzian line profile that is symmetrical with respect to the center wavelength. According to the Stern–Vollmer equation, the width of spectral line should increase linearly with the gas pressure as the formula $w_{FWHM}=aP+b$. It means that the values of gas pressure can be deduced from the measured width of atomic spectral line in LIBS experiments.

Based on the knowledge of spectroscopy, the pressure dependence of the FWHM of H_{α} , which is a single strong atomic spectral line was investigated and presented in Fig. 7. Here, the equivalence ratio of premixed gas is 0.47 when pulse energy was set at 120 mJ. The colorful curves in Fig. 7(a) are the normalized H_{α} spectral lines of LIBS for premixed kerosene/air gas in different pressures. The FWHM of the normalized H_{α} spectral lines was

determined by fitting with Lorentzian line profile and related with gas pressure as shown in Fig. 7(b). It is clear that the FWHM of H_{α} spectral line increase linearly with the cell pressure as described by the Stern–Vollmer equation as $H_{FWHM}=0.32P+1.27$.

4. Conclusions

In the present work, the quantitative local equivalence ratio measurements of kerosene/air mixture at elevated pressure by the LIBS technique were performed. According to on-line experimental conditions for a supersonic combustion, the calibration experiments of quantitative local equivalence ratio measurements of kerosene/air mixture in different gas pressure were accomplished with considering the pressure dependence of the FWHM of H_{α} spectral line. Therefore, the laser diagnostic method for quantitative local equivalence ratio measurements of kerosene/air at elevated pressure by LIBS is developed. The experimental experiences and data have been prepared for on-line quantitative local equivalence ratio measurements of kerosene/air mixture in supersonic combustion test.

Acknowledgments

The work is partially supported by the National Science Foundation of China (Grant no. 90816015). The authors acknowledge the technical assistance provided by D.H. Guo, D.H. Song and Z.M. Luo at the Institute of Mechanics, Chinese Academy of Sciences.

References

- [1] Awadshesh KR, Zhang HS, Yueh FY, Jagdish PS, Weisburg A. Parametric study of a fiber-optic laser-induced breakdown spectroscopy probe for analysis of aluminum alloys. *Spectrochim Acta B* 2001;56:2371–83.
- [2] Carranza JE, Hahn DW. Plasma volume considerations for analysis of gaseous and aerosol samples using laser-induced breakdown spectroscopy. *J Anal At Spectrom* 2002;17:1534–9.
- [3] Li J, Lin CH, Li SL. Determination of calcium concentration in water solution by laser-induced plasma spectroscopy. *Spectrosc Spectral Anal* 2006;26:944–6.
- [4] Fantoni R, Caneve L, Colao F. Laser induced breakdown spectroscopy (LIBS)—the process. Applications to artwork and environment. *NATO Sci Ser II: Math Phys Chem* 2006;231:229–54.
- [5] Mansour MS, Imam H, Elsayed KA, Abbass W. Local equivalence ratio measurements in turbulent partially premixed flames using laser-induced breakdown spectroscopy. *Spectrochim Acta B* 2009;64:1079–84.
- [6] Stavropoulou P, Michalakou BA, Skevis G, Uris S. Laser-induced breakdown spectroscopy as an analytical tool for equivalence ratio measurement in methane–air premixed flames. *Spectrochim Acta Part B* 2005;60:1092–7.
- [7] Michalakou A, Stavropoulos P, Couris S. Laser-induced breakdown spectroscopy in reactive flows of hydrocarbon–air mixtures. *Appl Phys Lett* 2008;92:081501.
- [8] Phuoc TX, White FP. Laser-induced spark for measurements of the fuel-to-air ratio of a combustible mixture. *Fuel* 2002;81:1761–5.
- [9] Ferioli F, Buckley SG. Measurements of hydrocarbons using laser-induced breakdown spectroscopy. *Combust Flame* 2006;144:435–47.
- [10] Sturm V, Noll R. Laser-induced breakdown spectroscopy of gas mixtures of air, CO_2 , N_2 , and C_3H_8 for simultaneous C, H, O, and N measurement. *Appl Opt* 2003;42:6221–5.
- [11] Zimmer L, Okai K, Kurosawa Y. Combined laser induced ignition and plasma spectroscopy: fundamentals and application to a hydrogen–air combustor. *Spectrochim Acta B* 2007;62:1484–95.
- [12] Phuoc TX. Laser-induced spark ignition fundamental and applications. *Opt Lasers Eng* 2006;44:351–97.
- [13] Kiefer J, Tröger JW, Li ZS, Aldén M. Laser-induced plasma in methane and dimethyl ether for flame ignition and combustion diagnostics. *Appl Phys B: Lasers Opt* 2010;103:229–36.
- [14] Rai VN, Singh PJ, Winstead C, Yueh FY, Cook RL. Laser-induced breakdown spectroscopy of hydrocarbon flame and rocket engine simulator plume. *AIAA J* 2003;41:2192–9.
- [15] Ferioli F, Puzinauskas PV, Buckley SG. Laser-induced breakdown spectroscopy for on-line engine equivalence ratio measurements. *Appl Spectrosc* 2003;57:1183–9.