

# UV Vibrational Raman Spectroscopy Flame Diagnostics System

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## ABSTRACT

A novel ultraviolet Raman spectroscopic system based on vibrational Raman scattering effect is presented. Coupling of a time-resolved diagnostic and slow spectrometer scan is used for measurements of Raman scattering intensities of combustion species to derive relative concentration and temperature of the flame.

Due to photon counting system high efficiency, relative lower energy of the incident light pulses, about 25 mJ, is required for the Raman scattering excitation. Low pulse energy application minimizes laser induced soot incandescence and vaporizations, which causing serious sample perturbations. Coupling of a time-resolved diagnostic and slow spectrometer scan allows decreasing width of the monochromator slit, which in turn increases the resolution of the system and minimizes of background radiation noise. The time resolved technique usage allows to minimize the noises in the detection system as well as the background radiation noise. The use of relative amplitude measurements technique minimizes the sensitivity of the system to fluctuations of the laser pulse energy.

Temperature measurements are derived from the Raman Stokes/anti-Stokes intensities ratio. Relative concentrations of O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, water vapor and unburned fuel are obtained from the ratio of the relevant species spectral lines strength to the nitrogen lines strength.

Fig. I represents a schematic overview of the optical configuration and the electronic data processing, used in the experiment. Fig. II shows radial temperature of the Bunsen burner flame, measured by the system. Top of Fig. II represents Stokes Raman intensity distribution, which can be used for the crude valuation of the flame temperature and shows position of the reaction zone of the flame. The system has a simple configuration and can be easily applied for combustion chamber flame diagnostics.

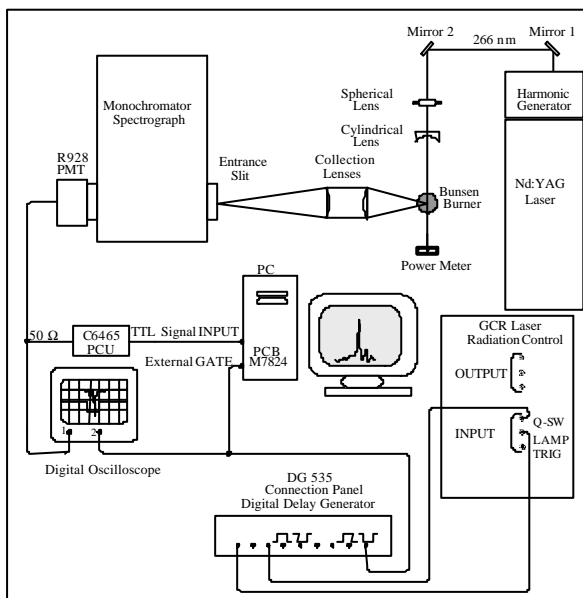


Fig. I Schematic Overview of the Optical Configuration and the Electronic Data Processing

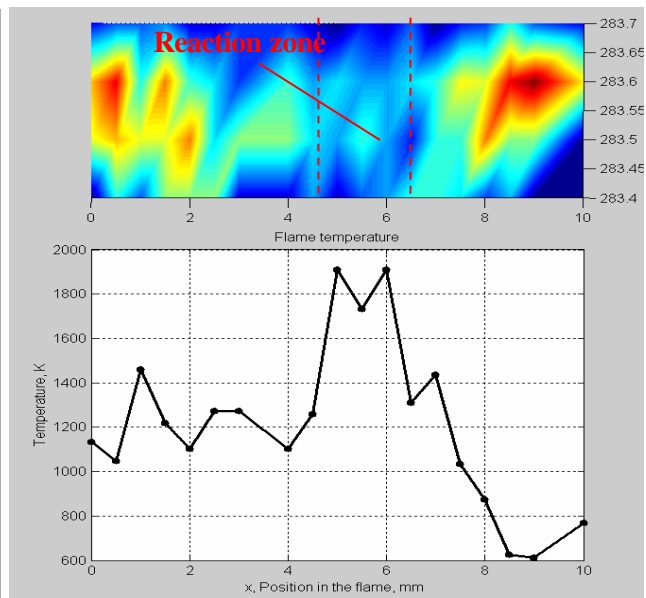


Fig. II Radial Bunsen Burner Flame Temperature and Reaction Zone Position, Determined from Nitrogen Stokes Raman Spectrum

## 1. Introduction

Of the laser spectroscopic techniques applied to combustion processes, Laser Induced Fluorescence (LIF) and Coherent Anti-Stokes Raman Scattering are among the most often used. The LIF technique allows for simple imaging of the radical species, pool OH, CH, NH, CN, C<sub>2</sub>, and pollutants, NO, CO, which often resides in concentrations below 0.01% (100 ppm) (Thomsen Douglas D. and Laurendeau Norman M., 2001; Jeffers J. B. and Grosley D.R., 1986; Grosley D.R. and Smith G.P., 1983). CARS spectra for species at high concentration can be also used in combustion diagnostics (S.A.J. Druet and J.P.E. Taran, 1981). However CARS spectroscopic modeling is considerably more complicated than spontaneous Raman scattering and determination of the temperature from Raman spectra is not simple. Majority species O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, which are not easily, or not at all, accessible to LIF, are observable by spontaneous Raman scattering (Alan C. Eckbreth, 1988). A single laser can be used for Raman excitation of the different species. Therefore, simultaneous multi-species detection is inherent in Raman spectroscopy. Raman scattering provides two independent data sources for temperature: the spectrum and the intensity. The signal obtained by spontaneous Raman scattering, is a spectrum whose intensity is linearly related to the number density of the molecular species. The Stokes anti-Stokes peaks intensity ratio for species, whose molecular concentration remains relatively constant for any given test conditions, is directly related to the temperature via Maxwell-Boltzmann statistics. Using a UV laser of 266 nm wavelength for Raman scattering excitation instead of a visible laser of 532 nm wavelength will increase the Raman signal by a factor greater than sixteen and minimize the influence of the background radiation.

The first laser excited Raman spectrum of molecular species in the environment, was demonstrated by Leonard et al. in 1967. Lapp et al. in 1971 first investigated the spontaneous Raman spectroscopy technique for combustion diagnostics. The ability to use spontaneous Raman technique for combustion diagnostics stimulated further developments of this technique (Lapp et. al, 1972). New time-resolved optical techniques (Drake M. C., et. al., 1980; Drake M. C., et. al., 1982) have been applied for measurement of probability density functions of temperature and major species densities in turbulent diffusion flame produced in a well - controlled co-flowing fan-induced combustion tunnel. In 1971 Widhopf and Lederman developed a new, method for gas diagnostics, based upon vibration Stokes/anti-Stokes ratio measurement.

In 1974 the Stokes/anti-Stokes method was first used for flame temperature measurement (S. Lederman and Glaser J. W., 1983). The work (Drake M. C., et. al., 1982) describes the gas temperature and species concentrations measurements method, using Stokes/anti-Stokes Raman scattering data.

In the work of Pitz et al. (1990), the authors used a UV excimer laser for Raman diagnostics of a hydrogen-air flame. Flame temperature is determined by vibration Raman scattering spectra of nitrogen, by the Stokes/anti-Stokes method. The broadband KrF excimer laser at 248nm excites Raman scattering and induces fluorescence of the OH radicals. Laser induced fluorescence of OH processes interferes with vibrational Raman Stokes lines of H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. In further research (T. M. Brown, et. al., 1996), the group developed a UV Raman scattering technique for diagnostics of laminar diffusion flame structure

The development of a tunable UV Raman technique and its application in harsh conditions that include strong flame luminosity and very high pressure is described in the NASA Glen Research Center work (Gu.E., et. al., 2000). NASA Glen Research Center tested low emission combustors for advanced gas turbine aircraft power plants. The spontaneous Raman technique was applied for diagnostic of the high-pressure advanced injector, burning commercial jet fuel. The results show, that UV Raman diagnostics can be used in high pressure and temperature conditions.

## 2. Background

The presented system was designed to obtain a qualitative and quantitative data on temperature and concentrations of major flame species. For this purpose a spectroscopic system, was created based upon UV vibrational Raman scattering technique. The system sensitivity allows measuring Raman scattering signals, induced by sufficiently small laser energy (about 20-25 mJ per pulse) in flames at atmospheric pressure.

The quantum theory of Raman scattering has been reported (R. H. Pantell and H. E. Puthoff, 1969; A. Weber, 1979; A., Yariv, 1980). The theory of molecular spectra of diatomic and polyatomic molecules has been reported in great detail (G. Herzberg, 1989; G. Herzberg, 1991). An equation for Raman scattering intensity, expressed in number of Raman photons, measured by the system has been obtained (Alan C. Eckbreth, 1988). Stokes intensity of gases decreases with temperature rise. Anti-Stokes intensity increases with temperature though decreasing in concentration. According analytical calculations, maximum N<sub>2</sub> anti-Stokes Raman intensity occurs at air temperature of about 2400<sup>0</sup> K. Maximum O<sub>2</sub> anti-Stokes Raman intensity occurs at the temperature of about 1500<sup>0</sup> K. Measuring flame temperature by means of Stokes/anti-Stokes technique of O<sub>2</sub> or CO<sub>2</sub> gases is not possible, because of low concentrations of these gases in the flame zone, and as a result, anti-Stokes signal cannot be measured. Calculations are carried out for the 25 mJ laser pulse energy. The system components efficiency is dependent on the measured wavelength. Relative concentrations for any specie *i* to nitrogen,  $x_i$  can be calculated as follows:

$$x_i = \frac{I}{A(T)} \cdot \frac{N_{S\_i}}{N_{S\_N_2}}, \quad (1)$$

where  $N_{S\_N_2}$  and  $N_{S\_i}$  are number of measured Stokes Raman photons of the nitrogen and specie, respectively. Coefficient *A*, correction factor, is calculated from relation of specie to nitrogen parameters, for known temperature:

$$A(T) = \frac{\left[ \frac{dS}{dW} [1 - \exp(-w_e hc/kT)] h e \right]_i}{\left[ \frac{dS}{dW} [1 - \exp(-w_e hc/kT)] h e \right]_{N_2}} \quad (5)$$

A temperature diagnostics technique, based upon the Stokes/anti-Stokes ratio, was first applied by Widhopf and Lederman and, later, by other researchers (Drake M. C., et. al., 1982; Pitz et. al., 1990). The ratio for the Stokes and anti-Stokes Raman intensities per number of photons, was obtained:

$$\frac{N_S}{N_{AS}} = \left( \frac{n_S}{n_{AS}} \right)^3 \frac{h_S e_S}{h_{AS} e_{AS}} e^{-G_0(1)hc/kT} \quad (3)$$

Thus, for the gas temperature the following correlation was achieved,

$$T = \frac{hcG_0(1)}{k} \left/ \left[ \ln \left( \frac{N_S}{N_{AS}} \right) + 3 \ln \left( \frac{n_{AS}}{n_S} \right) + \ln \left( \frac{h_{AS}}{h_S} \right) + \ln \left( \frac{e_{AS}}{e_S} \right) \right] \right. \quad (4)$$

where  $w_e$  is the vibrational frequency of the species (Herzberg, 1989);  $h$  is detection efficiency,  $e$  is collection lenses and monochromator efficiency, depended on Raman wavelength;  $n_S$  and  $n_{AS}$  is the Stokes and anti-Stokes frequency respectively;  $c$  is light velocity;  $k$  is the Boltzmann's constant and  $G_0(1)$  is the energy difference between the ground and the first excited vibrational levels of the diatomic molecule (Drake., et al., 1982; Herzberg, 1989).

Fig. 4 shows the temperature as a function of the Stokes/anti-Stokes ratio, calculated by Eq. (4) for N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> (transition Raman line 1388.1 cm<sup>-1</sup>).

The system can be used for measurement of major species concentrations. Concentrations of O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, water vapor and unburned fuel can be measured by Raman scattering technique, from ratio of the species signal intensity to intensity of nitrogen signal. Relative concentrations of relevant species can be calculated according to Eqs. (1). Measurements are possible in the reaction zone, and

regions, where flame temperature is sufficiently high, so that certain radicals are already burned and spectral lines do not overlap spectra of the measured species.

Consider a multicomponent mixture of gases in flame, composed of  $N_1$  moles of species 1,  $N_2$  moles of species 2, etc. The mole fraction of species  $i$ ,  $?_i$ , is defined as the fraction of the total number of moles in the system that are species  $i$ ; i.e. (Stephen R. Turns,1993),

$$C_i \equiv \frac{N_i}{N_1 + N_2 + \dots + N_i + \dots} = \frac{N_i}{N_{tot}} \quad (5)$$

Ratio of molar concentrations of species to nitrogen can be obtained by Raman scattering measurement. According to Eqs. (1) and (5), mole fraction of a relevant species can be calculated as following:

$$C_i \equiv \frac{x_i}{1 + x_1 + x_2 + \dots + x_i + \dots}, \quad (6)$$

where  $?_1, \dots ?_i$  are ratios of concentrations (Eq. 1) of a species to nitrogen and “1” defines nitrogen to nitrogen ratio.

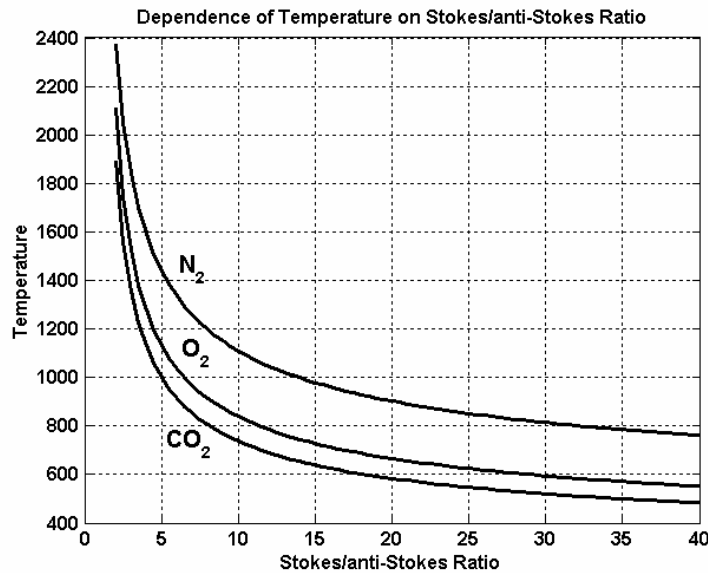


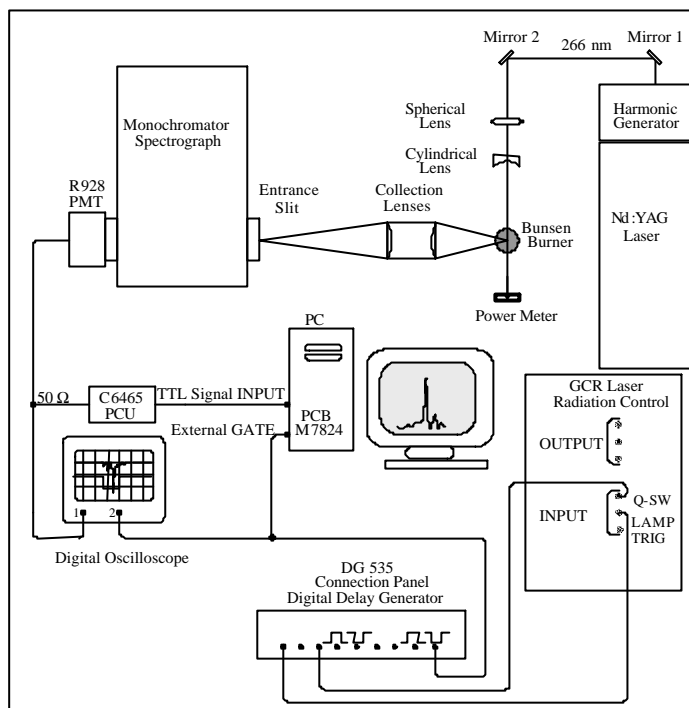
Fig. 1 Temperature (in Kelvin) Stokes/anti-Stokes Ratio Dependence, Calculated for  $N_2$ ,  $O_2$ , and  $CO_2$ .

### 3. Experimental Setup

Fig. 2 represents a schematic overview of the optical configuration and the electronic data processing, used in the experiment.

The pulsed Nd:YAG laser with 10 Hz frequency, produces a 1064 nm wavelength beam. Ultraviolet (UV) light of 266 nm wavelength, is generated by the fourth harmonic generator. The laser beam with diameter 10 mm, is focused by the spherical and cylindrical fused silica lenses, with antireflection coating, to a vertical light strip, 4mm high. The spherical plano-convex lens is 50.8 mm diameter and 308 mm focal length. The cylindrical plano-convex lens is square with 30.0 mm length and 304 mm focal length. The power meter measures the laser beam pulse energy. The laser light is focused into the flame zone of a laminar partially premixed butane/air Bunsen burner flame with 0.2 mm nozzle diameter. The burner is mounted on a horizontal and vertical driven translators, allowing

scanning of the flame along the horizontal and vertical axes. Raman signals emanating from the sample volume are collected by a 100 mm diameter, 250 mm focal length quartz lens. Another quartz lens with the same diameter and 500 mm focal length, focuses the scattered light into the entrance slit of the monochromator for dispersion and separation of the spectra of a relevant species.



*Fig. 2 Schematic Overview of the Optical Configuration and the Electronic Data processing.*

The slit width can be varied in accordance with experimental conditions, and the height of the slit is 4mm. The focal length of the monochromator is 500 mm and aperture ratio is  $f/6.5$ . The rotating diffraction grating of the monochromator (ARC SpectraPro Monochromator and Spectrograph) scans the collected light along spectra with the chosen scanning velocity (2-6 nm/min). Dispersed spectrum is re-imaged at the exit slit by the focusing mirror. Exit slit width must be equal to the width of the entrance slit. Holographic grating with groove density 2400 g/mm is used for the experiment. Nominal band pass or spectral resolution (the wavelength interval, passed through the exit slit) for 100  $\mu\text{m}$  slit width is 0.06 nm. The operation function of the monochromator slit was measured for Raman spectral lines of nitrogen in air at ambient temperature and pressure. The (HAMAMATSU R928) photomultiplier tube (PMT) is connected to the exit slit of the monochromator. It detects light exiting from the slit. The PMT output signal amplitude is directly proportional to the intensity of light, entering the photocathode, and the PMT current amplification.

The analogue signal from the PMT output is directed to the (HAMAMATSU C6465) photon-counting unit (PCU) with input impedance 500. The signal is amplified by the pulse amplifier and divided into binary signals by the discriminator. The number of pulses higher than the chosen threshold level is converted into TTL signals. The TTL signals with a high signal to noise ratio, are counted by the (HAMAMATSU M7824) photon counting board (PCB). Connecting the PCB to the personal computer allows it to function as a photon counting system. The M7824 does not contain a memory, so counted data must be transferred to the computer memory immediately. The Raman scattering event is a result of excitation of molecules of matter, occurring simultaneously with the incident laser pulse, at a frequency of 10 Hz.

The external gate mode of the photon counting system allows selective counting of pulses only during the time when Raman scattering occurs. The DG 535 digital delay generator is used to synchronize operation of the laser trigger with the external gate mode operation. The digital delay

generator generates the inverse rectangle electrical drive pulse 100ns gate, which operates in counting mode, and synchronizes the laser flash lamp trigger and Q-switch laser trigger.

The counted data is transferred to the computer memory by software. The measuring time depends on the selected spectral range. The output PMT signal can be directed to the analogue input of the 300MHz frequency digital oscilloscope LeCroy 9450A. In the present scheme, the first channel of the oscilloscope is connected to the PMT output and the second channel triggered by gate pulses of the delay generator. The PMT output impulses from Raman scattering optical signal are displayed, and signal amplitude can be measured. This option allows observation of the Raman scattering event in real time. The Raman data file stored in the computer memory from the photon counting system is a vector of zeros and ones, where ones correspond to pulses of the signal, and the vector length is the number of the measure points, which depend on measured spectral range. The pulses density is proportional to the optical signal intensity and depends on scan velocity, slit width and operation function of the monochromator. Theoretically, according to the laser operating rate of 10 Hz per second, 10 pulses of the Raman scattering can be obtained. Scanning velocity is selected according to slit width, used in the individual measurement setup, and bandpass of the monochromator. Observed spectral range determines the number of measured points and the measurement time.

For example, if a 200  $\mu\text{m}$  slit is used, the linear dispersion for a 2400 g/mm grating, according to the operation function of the monochromator, is 0.1 nm, and 6 nm/min scanning velocity is preferred. Scanning spectral range with 6 nm long, requires 60 seconds, which corresponds to 600 laser shots or 600 measured points. The measurement step is 0.01 nm (drive step size of the grating is 0.0025 nm). Each 10 points determine the spectral line bandpass according to the wavelength position, expressed in nm. If scanning velocity is decrease, the spectra resolution will be worse and intensity will decrease. The optimal scanning velocity for measurement purposes can be chosen experimentally.

Fig. 3 shows  $\text{N}_2$  vibrational Stokes Raman scattering spectra. The measurement spectral range is 282 nm – 285 nm.

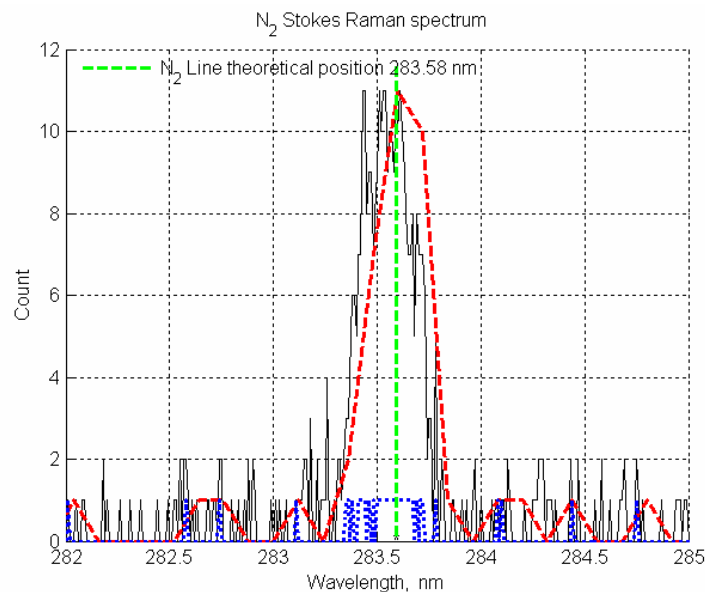


Fig. 3 Stokes Raman Scattering of Nitrogen on Flame Surface.

The solid line represents result of the sum of eleven independent measurements. A sample of these 11 measurements is plotted in a blue dotted line. The curve, plotted red dashed line is the same single measurement, but processed in the MATLAB program. This program is developed to recover from a number of counters (pulses) to the spectral lines, which contain information about amplitude.

The amplitude of the Raman spectra, shown in Fig. 3, is a relative value.

The signals from the individual specie are corrected for the measured spectral response of the monochromator – photon-counting system. We select the gain of the PMT, the PCU threshold level, the relative Raman cross-section and the temperature dependent function of each species, scan velocity and experimentally determined operation function of the monochromator.

The spectra of N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, butane and water vapor, were obtained for calibration of these spectral line positions. Experimental and theoretical data have been in good agreement.

Theoretical position of the maximum of the N<sub>2</sub> anti-Stokes Raman spectra, calculated for 266 nm of the induced wavelength, is 250.45 nm. According to experimental data, position of the maximum of the nitrogen anti-Stokes spectra was found at 250.75 nm.

The described Raman detection system must be calibrated in order to provide accurate measurements of the temperature and molecular density. Raman photon scattering of nitrogen and oxygen in air in ambient conditions (room temperature T= 300<sup>0</sup> K and atmospheric pressure P<sub>0</sub>=741 mm Hg) was measured for this purpose. Measurements were obtained by time-resolved technique with the following system parameters:

Grating 2400 g/mm;  
 Slit width  $\ell = 200 \mu\text{m}$ ;  
 Detection solid angle  $O = 0.2 \text{ sr}$ ;  
 Laser pulse energy  $I_t = 4 \text{ mJ}$ ;  
 Input PMT voltage 3 V, which corresponds to PMT gain  $1.63 \cdot 10^6$ ;  
 The anode output pulse width  $13 \pm 1 \text{ ns}$ ;  
 Detection efficiency for nitrogen 19.3 %;  
 Detection efficiency for oxygen 19.7 %;  
 Optical components efficiency for nitrogen 9.1 %;  
 Optical components efficiency for oxygen 10.2 %;  
 Grating scanning velocity 6 nm/min

The photomultiplier amplification and photon counting discrimination level depend on the optical Raman signal intensity and are selected during the experiment. For the Stokes and the anti-Stokes measurements these parameters are chosen individually. For accurate measurements, discrimination level was selected relative to the maximal signal intensity of the measured species, and this relation must be conserved during the experiment for all measurements of all species.

The Raman scattering was excited by the Nd:YAG laser with 266 nm wavelength in ambient air. The diffraction grating of the monochromator scanned an optical range with the defined velocity. The PMT output signal was discriminated by PCU discrimination level PCB, operated in external gate mode, counted the signal pulses. The optical scan range for nitrogen was from 283.4 nm to 284 nm, and for oxygen  $277.3 \pm 277.9 \text{ nm}$ . The scan time was 6 sec. By changing the discrimination level of the PCB, the nitrogen Raman scattering signal was found for levels below or equal to the value 1.4 V, which corresponds to  $N = 23 \pm 1$  photons, registered by the system.

Total number of photons, induced by one laser pulse Raman photons, viewed through the solid angle can be calculated as follows:

$$\text{Number of photons} = N / (\text{Detection efficiency} \cdot \text{Optical efficiency})$$

$$\text{Number of photons (N}_2) = 23 / (0.193 \cdot 0.091) = 1309 \text{ photons}$$

Theoretical value, calculated, according to Eq. 1, for the same conditions of measurements is 1879 scattered photons through the solid angle of the collecting lens or 33 photons, registered by the system, for a value of the Raman cross-section  $7.62 \text{ cm}^2/\text{sr}$ .

The analogically found discrimination value for oxygen was 0.87 V, which corresponds to  $12 \pm 1$  counts per one laser pulse.

The number of oxygen Raman photons was

$$\text{Number of photons (O}_2) = 12 / (0.197 \cdot 0.102) = 597 \text{ photons}$$

Theoretical value, calculated for the Raman scattering of the oxygen, for value of the Raman cross-section  $12.28 \text{ cm}^2/\text{sr}$ , is 746 scattered photons or 15 photons, registered by the system.

Nitrogen to oxygen concentrations ratio (standard air, 15 Degrees C is 78.085% / 20.947%) equals 3.728. Concentrations ratio, calculated according to Eqs.4 for nitrogen and oxygen intensities, measured by the present system, equals 3.791. The difference between theoretical results and experimentally measured results can be explained by difference in atmosphere moisture conditions and the measurement errors of the optical efficiency of the monochromator. The real optical efficiency of the monochromator was difficult to determine for light in the UV range. According to theoretical and experimental results, correction value, calculated for efficiency of the optical components for Raman scattering of nitrogen is 6.74 % and 7.9 % for oxygen. Optical components efficiency, for 250 nm (anti-Stokes) wavelength is 8.3 %.

## 4. Results and Discussion

Coupling of a time-resolved diagnostic and slow spectrometer scan is used for measurements of Raman scattering intensities of combustion species to derive the relative concentration and temperature of the flame. The developed system has been tested on a laminar partially premixed butane-air flame, produced by a Bunsen burner, with a 5 mm inlet tube diameter at atmospheric conditions. Fig. 4 shows Raman spectrum of the flame, measured at a height of 1 cm from the center of the tube.

Each species spectral line position can be determined according to known transition frequency of the specie. Spectral lines of the transient formations of the unburned radicals, presented in the rich fuel flame zone, occupy the entire spectral range. These lines can be difficult to resolve and, in some cases overlap with spectral lines of the major species. This problem can be partially solved by using a small slit width.

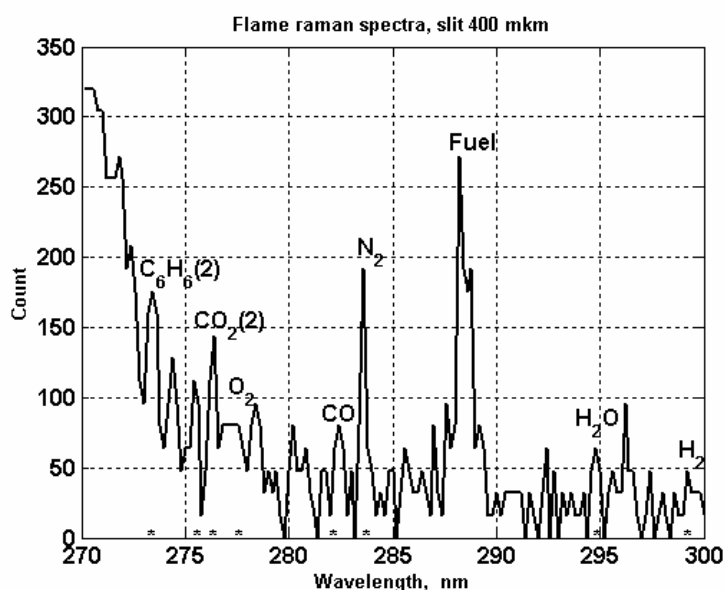
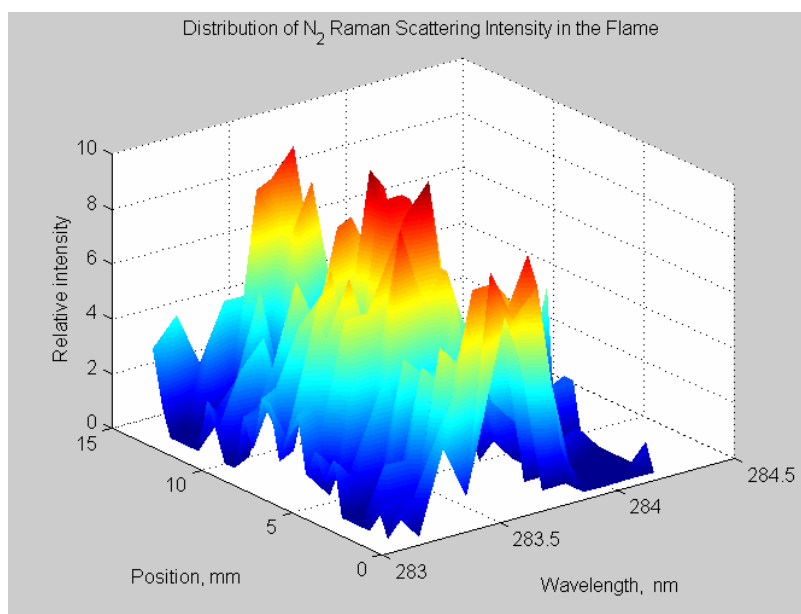


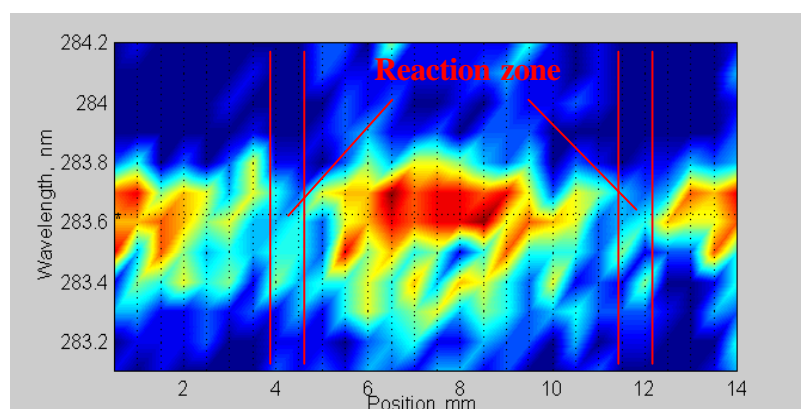
Fig. 4 Raman Spectrum of Flame.

Determining the position of the reaction zone of the Bunsen burner flame is carried out by scanning across the diameter of the flame. Fig. 5 represents nitrogen Stokes Raman scattering intensity distribution across the flame diameter.

Temperature distribution in flame can be described by Raman scattering Stokes intensity distribution. Raman scattering intensity of nitrogen was measured across the flame diameter with the step 0.5 mm, from zero point chosen on the flame surface. The visual diameter of the analyzed flame, was about 15-20 mm. The symmetrical image, demonstrated in Fig. 5, is the result of 28 measurements of the Stokes line intensity of the Raman scattering of nitrogen in the flame. Minimal scattering intensity approximately determines the position of the reaction zone of the flame, where the temperature is maximal. Rapid fall of the intensity of the Stokes scattering is explained by rapid rise of the flame temperature (rapid drop in molecular density) in the reaction zone. We can see from Fig. 6 that thickness of the reaction zone is about 1-2 mm. The internal diameter of the reaction zone is about 6-7 mm and the external is about 10 mm. Flame temperature distribution was measured in the Bunsen flame with maximal opened air vents. Zero point was aligned with the flame center. Measurements were obtained at a height of 45 mm from the top of the tube. The curve in Fig. 6 shows point measurement of radial temperature distribution inside the flame.



*Fig. 5 Nitrogen Raman Intensity Distribution Across Flame Diameter.*



*Fig. 6 Position of Reaction Zone in Flame*

Flame temperature distribution was measured in the Bunsen flame with maximal opened air vents. The focus of the collecting lens was aligned to flame center. Measurements were obtained at a height of 45 mm from top of the tube. Temperature  $1910^0$  K was recorded in the points located on distance 5mm and 6mm from the flame center, Fig. 7. Top of Fig.7 represents Stokes Raman intensity distribution, which can be used for the crude valuation of the flame temperature and shows position of the reaction zone of the flame. Temperature of the flame at the each point was calculated according Stokes/anti-Stokes ratio of the scattering intensity of nitrogen. We can see that the thickness of the zone with maximal temperature is approximately 1.5-2 mm. Temperature of  $1910^0$  K was recorded at points located 5 mm and 6 mm radially from the flame center.

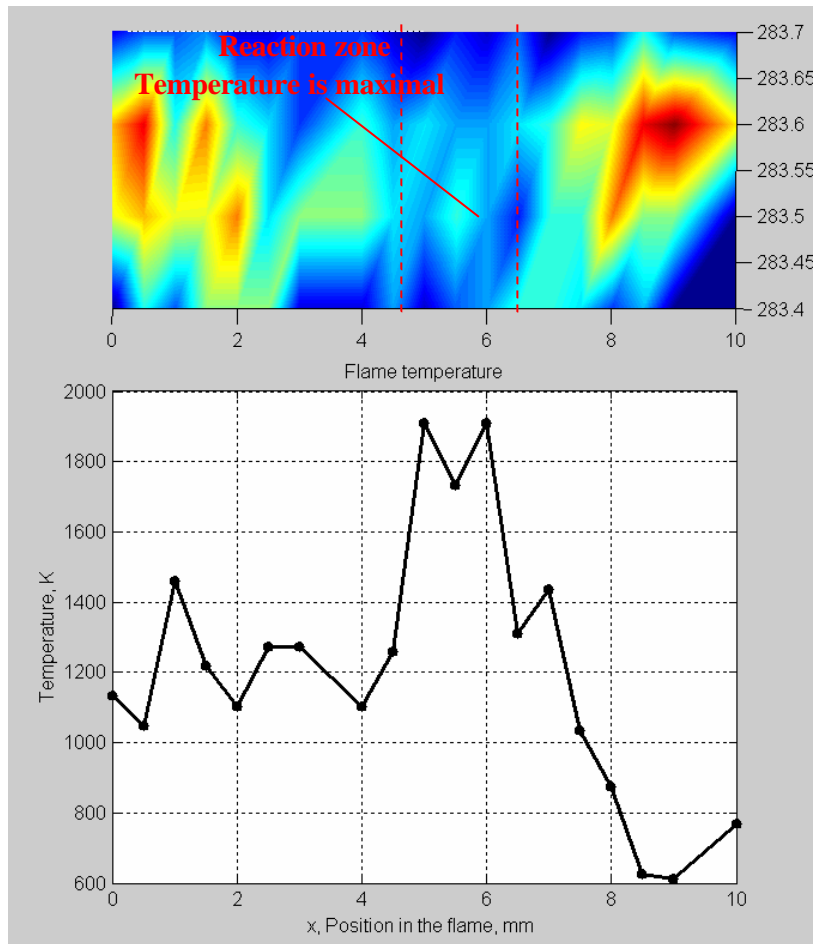


Fig. 7 Radial Flame Temperature

Temperature at the flame center, measured by Raman technique, equals  $1134^0$  K, which corresponds very accurately with thermocouple measurements  $1108-1131^0$  K. Temperature below  $800^0$  K cannot be measured correctly by means of the Raman scattering technique, because the anti-Stokes signal is not registered.

The standard deviation of the temperature of flames with local mean temperature of about  $1090^0$  K, was also measured for thermocouple and for the Raman scattering measurements. Mean temperature values were approximately equal for thermocouple and Raman measurements. The values  $1084.6^0$  K and  $1091.4^0$  K were obtained for the Raman and for the thermocouple measurements, respectively. Thermocouple measurements deviation was  $\pm 15^0$  K, which corresponds to 1.4 % error. Raman scattering measurements standard deviation of temperature was  $\pm 74.5^0$  K, or 7 % error.

The system can be used for measurement of major species concentrations. Concentrations of  $O_2$ ,  $N_2$ , CO,  $CO_2$ ,  $H_2$ , water vapor and unburned fuel can be measured by means of Raman scattering technique from ratio between species signal intensity and intensity of nitrogen signal. Relative concentrations of relevant species can be calculated according to Eqs. (4,5). Measurements are possible in the reaction zone, and regions where flame temperature is sufficiently high, so that certain radicals are already burned and spectral lines do not overlap the spectra of the measured species.

Measurements were obtained across the flame diameter in the reaction zone at a height of 45 mm from the tip of the tube, where the flame is fuel lean. Intensities of the burning species have been measured at 11 points with steps of 0.5 mm.

Mole fraction of the major species as  $O_2$ ,  $N_2$ , CO,  $CO_2$ ,  $H_2$ , water vapor and unburned fuel were calculated from species to nitrogen intensities ratios.

Figs. 8 (a) and (b) show concentrations distribution of the major species and nitrogen across flame radius respectively.

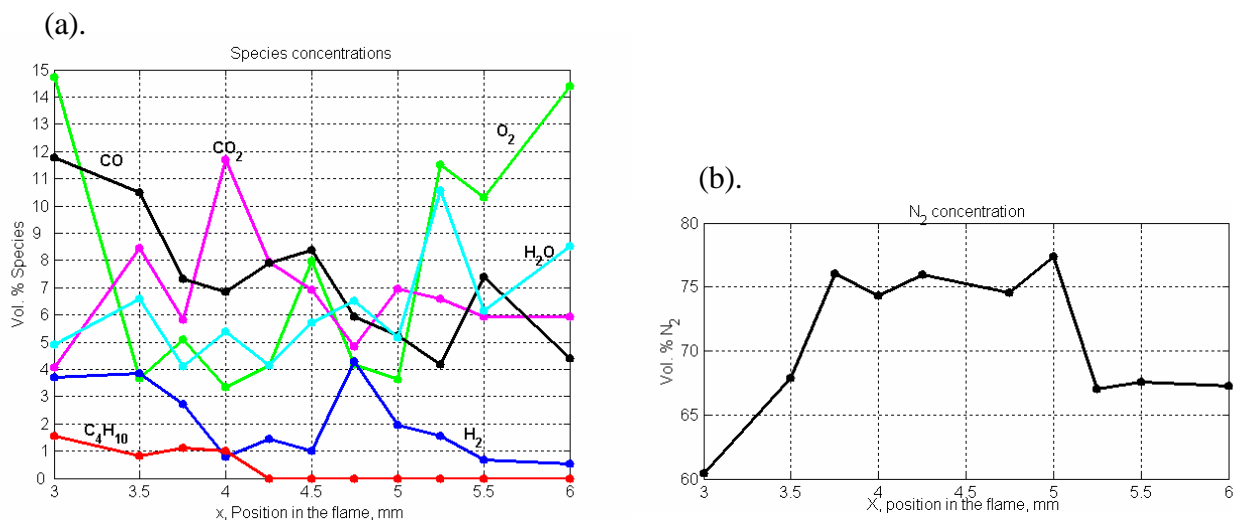


Fig. 8 Species (a) and Nitrogen (b) Concentration Distribution in the Reaction Zone,  $y = 45$  mm.

Concentration distribution in Fig. 8 shows consumption of the fuel that is followed by appearance of the intermediate species CO and the burn up of the CO to form  $CO_2$ . The  $CO_2$  has peak value at approximately the same locations where the fuel concentration reaches zero,  $CO_2$  concentration rises through oxidizing of CO and obtains a value of about 12% of the molar volume. Peak value of  $CO_2$  accords with maximal obtained temperature and minimal oxygen concentration, 3.5 % of the molar volume.  $H_2$  specie concentration rises to 4%, thereafter hydrogen is burned with formation of water. Concentration of water, obtained in the experiment is lower than the analytical value. Maximal mole fraction of nitrogen 77.3 % volume was measured in the reaction zone, where concentration of oxygen was minimal. The bulk of chemical activity is contained in the interval at about 1.5 mm. The value of a stoichiometric ratio at the point "4 mm" is about 0.8.

Fluctuation of the temperature and concentrations are explained by unstable flame structure of the Bunsen burner. Measuring results were not obtained simultaneously.

Intensities of the nitrogen and oxygen in ambient air were measured for different values of discrimination level of the photon counting system. Oxygen volume concentration was calculated on the base of Raman spectra. Calculation of oxygen concentration shows, that  $\pm 10\%$  deviation in the relative discrimination levels ratio from value 1 gives about 1% deviation from the typical 20.9 % value of oxygen concentration in ambient conditions, which corresponds to 5 - 7 % of absolute measurements error.

The error is decreased, when concentrations of the measured species are small relative to nitrogen concentration. This condition is fulfilled in the flame reaction zone.

## 5. Conclusions

The paper describes the development of a diagnostic system for combustion processes. An experimental Raman spectroscopy system was created, tested and calibrated under laboratory conditions. A Bunsen burner was used for testing the system. The objective of the measurements was to calibrate the new diagnostics system and determination of its features. The temperature and mole fractions data, obtained by the system show, that the system could be used for practical flame diagnostics. The advantage of the system is its simple configuration and usage. Due to the relative high efficiency of the photon counting system, low energy of the incident light pulses, about 25 mJ, is required for the Raman scattering excitation. Low pulse energy usage minimizes laser sample perturbations of the sample volume. Coupling of a time-resolved diagnostic and slow spectrometer scan allow for decrease of the width of the monochromator slit, which in turn increases the resolution of the

system and minimizes background radiation noise. The time-resolved technique used, eliminates noises in the detection system such as the background radiation noise. For temperature and species mole fraction calculations, measurements of the relative amplitude values are required. Relative amplitude measurements makes the system insensitive to fluctuations of the laser pulse intensity. For experimental purposes, 10 Hz frequency Nd:YAG laser was used. The measuring time and the system efficiency can be decreased, if a high frequency laser is used for Raman scattering excitation. Measurements error of the presented system is 5-7% for species mole fractions measurements and 7-9% for temperature measurements, in temperatures ranging from 800<sup>0</sup> K to 2500<sup>0</sup> K.

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