33. SPECTROSCOPIC MEASUREMENT OF GAS PARAMETERS UNDER CONDITIONS OF HYDROCARBON-FUELED COMBUSTION WITH ELECTRIC-DISCHARGE ASSISTANCE

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Abstract. The development of the diagnostic methods of the gas-plasma flows at presence of electric discharge and exothermal chemical reactions is presented in this paper. Sets of radicals, used for spectroscopic analysis of gas-mixture’s parameters at hydrocarbon-fueled combustion, are well known and include the following: OH, CN, C2, CH and others [1-5]. However, it is necessary to take into account, that other molecules excited by electrons can appear in the gas when combustion is assisted by the electric discharge. Another mechanism of the excitation allows using extra methods for determination of gas parameters. Electron density, for example, can be determined by analyses of relative vibrational level populations of N2 (C3Π → B1Π; 337,1nm) and N2+ (B2Σ+ → X1Σ+; 391,4nm). Excitation of the vibrational levels of these molecules is specific for electric discharge conditions. A measurement of the gas temperature by spectrum of the CN (B2Σ+ → X2Σ+; 388,5nm) and N2 in carbon-fueled combustion at high-speed airflow is discussed in this paper. Mechanism of the rotational energy relaxation has been investigated for these molecules and correspondence between rotational and translational temperatures has been found.

Introduction

The following parameters of the gas mixture are important to know under the hydrocarbon-fueled combustion at the electric discharge assistance: gas temperature – Tg; electron temperature – Te; concentration of the electrons – ne; vibrational temperature – Tv; concentration of the radicals – Nr. There are numbers of papers devoted to the measurement of gas mixture parameters under the combustion without discharge. Papers [6-8] can be named among of them. A lot of investigations were carried out for plasma diagnostic of different types of electrical discharges [9-11]. The extra problem in diagnostic of plasma assisted flames is that chemical kinetic of the combustion is disturbed by the presence of the molecules, which were exited by the electron impact. Besides it, the parameters of gas mixture are strongly spatially nonhomogeneous as a result of the flow conditions. The search in the available literature brings us the understanding that such a problem has to be investigated in more detail. As a first step we have concentrated our efforts on finding the translational gas temperature and vibrational temperature of the CN molecules.

Methods

This paper relates to the spectroscopic methods of the vibrational and translational gas temperature measurements. The spectroscopic methods can be divided on laser methods and passive one, build upon registration plasma self emission. Among the laser methods the Raleigh and Raman Stokes and anti-Stokes scattering can be pointed. It is possible to determine vibrational and rotational distribution of molecules using Raman Stokes and anti-Stokes scattering [12,13]. Laser methods are widely used because of their advantages in high temporal and space resolution. The method of the passive spectroscopy of unresolved spectrums of diatomic molecules has been used in this investigation. The calculated spectrum was adjusted to the measured one by variation of vibrational and rotational temperature at the known apparatus function of spectrometer. The part of the spectrum (vibrational transition 0-0 of the band B2Σ+→X2Σ+) shown in Fig.5 illustrates the method of adjustment the measured spectrum and calculated one, Fig.6.

The CN molecules have been chosen to measure vibrational and rotational temperature. Such a choice is resulting from high emission intensity of vibrational-rotational bands of B2Σ+→X2Σ+ transition of this molecule. The form of CN spectrum strongly depends on vibrational and rotational temperature in this area as was shown in [14]. Therefore, the temperatures can be obtained, which are close enough to real one. Besides it, this molecule is generated and emit both under combustion of hydrocarbon fuel and under electric discharge in the air with addition of carbonic species. This fact allows us to carry out comparative analysis of these two cases.

It is necessary to compare lifetime of the level B2Σ+, τr and time of the rotational relaxation, τrot when analyzing rotational distribution of electronically exited molecules. If τrot > τr, then rotational distribution of the exited CN molecules might be nonequilibrium and rotational temperature measured by analyzing B2Σ+→X2Σ+ band could be different from translational temperature of the gas.

Lifetime of the state B2Σ+ of the CN molecule is about: τr=5·10^-8sec.

The time of the rotational relaxation can be estimated as 1/N, where N – number of the impacts causing to the rotational excitation, which
one molecule experienced during the one second on average. \( N = \sigma_{rot} \cdot n \), \( \sigma_{rot} \approx 10^{-15} \text{sm}^2 \) – cross section of the rotational excitation; \( n(p=300\text{Torr})=10^{17} \text{sm}^{-3} \) – concentration of the molecules; \( v(T=3000\text{K}) \approx 2 \times 10^5 \text{sm/sec} \).

So, \( \tau_{rot} \approx 10^{-8} \text{sec} \), and we can say that \( CN \) molecules have equilibrium distribution on rotational degrees of freedom in exited state \( B^3 \Sigma^+ \). Therefore, rotational temperature, which is measured by analyzing spectrum of \( CN \), is equal to the translational temperature of the gas. We may expect that time of V-T relaxation will be not less then \( 10^{-6} \text{sec} \) for our conditions: \( p=0.1-1\text{atm}; T_e=500-5000\text{K}; E_e=0.5\text{eV} \). [15,16]. So, if we supposed that \( CN \) have Boltzmann distribution on the vibrational degrees with temperature \( T_{vib} \), this temperature would be essentially higher then rotational one. Distribution function on vibrational states of exited state of the \( CN \) is determined by the influence of the electron impact for the first side and by \( CN \) generation in chemical reactions for another side. With high probability this function will be Boltzmann for exited state of \( CN \). Simple kinetic scheme of the hydrocarbon fuel combustion processes as applied to generation of nitrogen-containing species is in Fig.1. This scheme illustrates so-called “fuel-nitrogen” mechanism. Reactions with hydrocarbons are not included in this scheme. There are two sequences of chemical reactions are presented in the Table 1 as an example of \( CN \) generation from the hydrocarbons.

### Table 1. \( CN \) generation schemes.

<table>
<thead>
<tr>
<th>Through the HCN.</th>
<th>Through the C2O.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4H6=C2H3+C2H3;</td>
<td>C2H2+M=C2H2+H+M;</td>
</tr>
<tr>
<td>C2H3+O2=CH2O+CHO;</td>
<td>C2H2+O=CHCO+H;</td>
</tr>
<tr>
<td>CHO+N=HCN+O;</td>
<td>CHCO+H=C2O+H2;</td>
</tr>
<tr>
<td>HCN+O=CN+OH.</td>
<td>C2O+N=CN+CO.</td>
</tr>
</tbody>
</table>

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Kinetics of the combustion is complex but it is more complex with discharge assistance due to the dissociation and excitation of molecules by electron impact causes to the dramatic change of the velocities of reactions.

### Scheme of the measurement

Spectrograph with the dispersion of 13A/mm was used for spectrum registration. Radiation was exposed by CCD matrix with a resolution of about 130pixel/mm, so the spectrum was measured with resolution about 10 pixel/A. Plasma radiation was collected by the quartz lens (Fig.2) and went to the input slit of the spectrograph by the optic fiber. Spectrograph was removed from the wind channel to reduce electromagnetic noise. The width of the slit was adjusted depending on the system resolution. It was in order of 0.2mm as a rule. So, apparatus function was approximately 0.2-13-2.6A. The high-speed CCD camera Pulnix6710 was used which have rate 240 frames per second at resolution 640 on 200. We could see the ignition occurrence and what flame structure was in the region radiation was collected from.

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![Fig.2](image-url)

### Results of the experiment

Measurements of the rotational and vibrational temperature were carried out for aerodynamic duct with separation zone (Fig.2) by analyzing the spectrum of second positive system of \( N_2 \) [17] in case of electric discharge without combustion. Rotational temperature was \( 1600\pm200\text{K} \), vibrational was \( 6000\pm1000\text{K} \). We can see that this temperature less then one measured in case of discharge assistance combust ion Fig.4, 5 - \( T_{rot}=2500-3000\text{K} \), \( T_{vib}=8000\pm500\text{K} \). Dispersion of the measured temperatures can be explained by strong space nonhomogeneous, Fig.3.
Fig. 3.

W=1.2 kW/electrode; p=90 Torr;
Combustion of the hydrocarbon fuel in the channel with separation zone.
T vib=8000K; T rot=2500K.

Fig. 4.

W=1.2 kW/electrode; p=90 Torr;
Combustion of the hydrocarbon fuel in the channel with separation zone.
T vib=8000K; T rot=2500K.

Fig. 5.

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Conclusions

The strong difference between vibrational and rotational temperatures of CN molecules was found under hydrocarbon fuel combustion with electric discharge assistance. The rotational temperature of CN molecules was found to be higher than rotational temperature of N2 molecules on more than 1000K under electrical discharge in the same aerodynamic duct and under the same conditions. Electronically and vibrationally exited states of molecules must be included into the chemical kinetic scheme of combustion process due to their high temperatures.

References