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Spectroscopic Study of CO_2 Plasma in Microwave Source Designed for Hydrogen Production via Hydrocarbons Decomposition

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In this paper, results of spectroscopic study of microwave (2.45 GHz) plasma at atmospheric pressure and high CO_2 flow rate are presented. The plasma was generated by waveguide-supplied nozzleless cylindrical type microwave plasma source. Working gas flow rate and microwave absorbed power varied from 50 up to 150 l/min and from 1 up to 5.5 kW, respectively. The emission spectra in the range of 300–600 nm were recorded. The rotational and vibrational temperatures of C_2 molecules, as well as the rotational temperature of OH radicals were determined by comparing the measured and simulated spectra. The plasma gas temperature inferred from rotational temperature of heavy species ranged from 4000 to 6000 K. It depended on location in plasma, microwave absorbed power and working gas flow rate. The presented microwave plasma source can be used in various gas processing applications.

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1. Introduction

Development of the microwave plasma sources (MPSs) based on the technique are of increasing interest from industrial point of view. Microwave sustained plasma has found practical applications in various fields. It could be used in sterilization [1] or technological processes like various materials surface treatment [2–4]. MPSs also found applications in the processing of various gases. Destruction of freon HFC-134a [5] and production of hydrogen via methane conversion [6] in microwave atmospheric pressure plasmas were reported by us elsewhere. In papers [5] and [6] a waveguide-supplied nozzleless cylindrical type MPS was used.

The gas temperature is one of the most important parameter in plasma technology and applications. Optical emission spectroscopy (OES) is a non-invasive but very useful and powerful tool in the study of plasma properties, contributing significantly to the development of microwave plasma. In the thermal equilibrium plasmas the temperature measurements using OES are usually based on the absolute or relative intensities of various atomic lines of oxygen and nitrogen.

In the case of non-equilibrium plasmas at atmospheric pressure, the techniques used for the temperature measurements in the equilibrium plasmas may not provide reliable information about the gas temperature because the population distribution of internal energy states tends to depart from the Boltzmann distribution. This concerns mainly the case of the electronic and vibrational population distributions, but the rotational populations tend to follow the Boltzmann distribution owing to fast rotational relaxation at atmospheric pressure. Thus, the gas temperature can often be inferred from the rotational temperature of the heavy species of the gas [7–10].

Various transitions of N_2, N_2^+, and NO (in dry air), OH (in humid air) and other molecules present in the plasma can be used for the temperature measurements, depending on the level of plasma excitation and interference of the other transitions.

The rotational and vibrational temperatures can be obtained from the Boltzmann plot [8] in case of resolved spectra. But, also in case of unresolved spectra some methods were developed to determine temperatures [7, 10]. Rotational and vibrational temperatures in plasmas are often determined comparing relative intensities of experimental and simulated optical spectra [9].

2. Experiments

The plasma was generated by waveguide-supplied nozzleless cylindrical type MPS based on a standard WR 430 rectangular waveguide with a section of reduced-height, preceded and followed by tapered sections. The tapered sections assured smooth transition from the standard waveguide dimensions to the waveguide of reduced height. The plasma flame was generated inside a quartz tube which penetrated MPS through circular gaps on the axis of the waveguide wide wall and protruded below bottom waveguide wall. On the outside of the waveguide the quartz tube was surrounded by a cylindrical metal shield with a slit for visualization. The MPS was described in detail in [11].

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The experimental setup (Fig. 1) consisted of a 2.45 GHz magnetron generator, microwave power supplying and measuring system, MPS, movable plunger for impedance matching, gas supplying and flow control system, spectrometer [DK-480 (CVI), 1200 and 3600 grooves/mm grating] for spectral emission measurements, equipped with a CCD camera and a PC computer. An absorbed power P_A was obtained from the $P_I - P_R$, where P_I and P_R are the incident and reflected microwave powers, respectively.

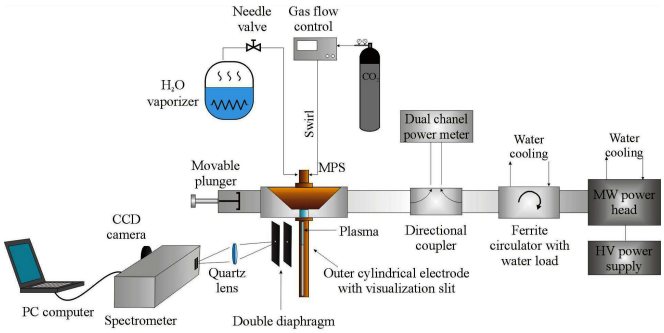

Fig. 1. Experimental setup.

Pure CO_2 was used as working gas. It was introduced to the plasma by four gas ducts which formed a swirl flow inside the quartz tube. A small amount of water vapor was added optionally to swirl gas flow in order to achieve detectable intensity of OH spectra. Working gas flow rate and microwave absorbed power varied from 50 up to 150 l/min and from 1 up to 5.5 kW, respectively.

The light emitted by the plasma was focused with a quartz lens (50 mm in diameter, focal length — 75 mm) onto the entrance slit of the spectrometer (see Fig. 1). Double diaphragm of a 1 mm diameter was placed near the plasma. We estimate that in this experiment the measured area was about 8 mm diameter. Spectra were recorded and then corrected according to the wavelength sensitivity of CCD camera. The wavelength sensitivity of CCD camera was determined using a tungsten halogen calibration lamp. Using a Hg–Ne low-pressure calibration lamp we measured that the Gaussian instrumental line profile FWHM was about 0.12 nm and 0.05 nm for 1200 and 3600 grooves/mm grating, respectively. Spectra were measured with 1200 grooves/mm grating. Only for OH (A–X) rotational band measurements the 3600 grooves/mm grating was used.

In this experiment, for the temperatures determination we used the OH (A–X, 306–310 nm band) and C_2 Swan system (A–X, 506–518 nm band). Simulation of the optical spectra were performed with Specair [12] and Lifbase [13] programs.

3. Results

Figure 2a shows spectrum emitted by the microwave CO_2 plasma. As seen, the dominant spectrum was C_2 Swan system ($A^3\Pi \rightarrow X^3\Pi$). The spectrum contained also very weak CN violet system ($C^3\Pi \rightarrow B^3\Pi$) due to probably small leaks of surrounded air into MPS. A small amount of water vapor was added to the swirl CO_2 flow. This addition of water vapor did not change the plasma significantly: the microwave incident and reflected powers, as well as the plasma length remained unchanged. The benefit of such addition was occurring of OH ($A^2\Sigma \rightarrow X^2\Pi$) rotational band. This band is widely used for gas temperature estimations, e.g. [7, 10].

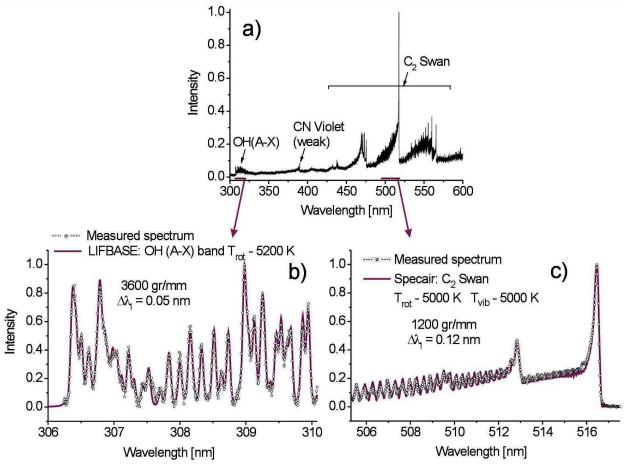

Fig. 2. Measured emission spectrum of CO_2 plasma (a) and comparison of the measured and simulated emission spectra of OH (A–X) band (b), and C_2 Swan system (c) (P_A — 3 kW, CO_2 flow rate — 50 l/min, 15 mm below waveguide).

After having the experimental spectra, a simulation of these spectra was carried out using Lifbase (for OH) and Specair (for C_2) program. The simulated spectrum was fitted to the experimental one by variation of the rotational T_{rot} in case of rotational OH (A–X) band and the rotational T_{rot} and vibrational T_{vib} temperatures in case of rotation-vibrational C_2 Swan band. The comparison of measured and simulated spectra of OH (A–X) (Fig. 2b) and C_2 second positive system (Fig. 2c) were performed and rotational T_{rot} and vibrational T_{vib} temperatures were determined.

The measured rotational temperature of OH radicals and the rotational and vibrational temperatures of C_2 molecules as a function of distance below the waveguide (distance BW) in CO_2 plasma (P_A — 3 kW, CO_2 flow rate — 50 l/min) are presented in Fig. 3. At this condition the plasma length (visible) was about 70 mm. Regardless the visible plasma length it was possible to detect OH (A–X) and determine the rotational temperature of OH also at the further area of plasma. As seen in the figure the rotational and vibrational temperature (which mean the energy) of heavier C_2 molecules decreased further from the waveguide. The rotational temperature of OH radicals increased up to 5400 K at 65 mm from the waveguide where the visible plasma was ending. Then the rotational temperature of OH radicals

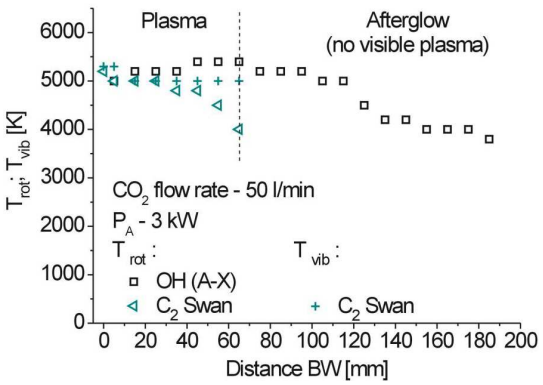

Fig. 3. Measured rotational temperature of OH radicals and rotational and vibrational temperatures of C_2 molecules as a function of distance below waveguide (distance BW) (P_A — 3 kW, CO_2 flow rate — 50 l/min).

decreased to 4000 K at the distance of 195 mm below waveguide. Further the OH (A–X) spectra was not detected. It could be assumed that the rotational temperature of OH radicals was good estimation of plasma gas temperature [7, 10].

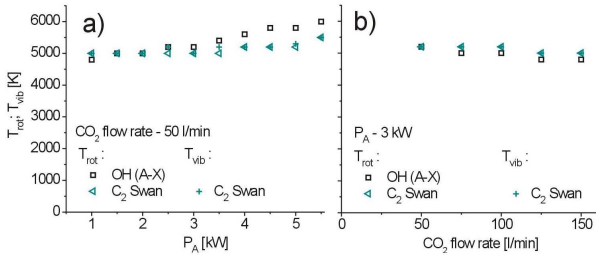

Fig. 4. Measured rotational temperature of OH radicals and rotational and vibrational temperatures C_2 molecules as a function of microwave absorbed power (a) at CO_2 flow rate — 50 l/min and as a function of CO_2 flow rate (b) at P_A — 3 kW (15 mm below waveguide).

The rotational temperature of OH radicals and the rotational and vibrational temperatures of C_2 molecules increased with microwave absorbed power (Fig. 4a) at location in the plasma placed 15 mm below the waveguide. This increase was not significant. The increase of the microwave power caused almost proportional increase of the plasma length and thus the plasma volume. It could be concluded that the microwave power influences the plasma volume and much less the plasma gas temperature. The influence of CO_2 flow rate was even less apparent. Increasing the flow caused slight decrease of temperatures (Fig. 4b). In this case the increased flow caused decrease of plasma length.

4. Conclusion

Spectroscopic study of CO_2 microwave (2.45 GHz) plasma at atmospheric pressure and high flow rates was presented in this work. The study concerns the rotational and vibrational temperatures of selected heavy species present in plasma in order to estimate gas temperature. The plasma gas temperature inferred from rotational temperature of OH radicals ranged from 4000 to 6000 K. It depended on location in plasma, microwave absorbed power and working gas flow rate.

The investigated nozzleless, waveguide-supplied, cylindrical type MPS works very stable with various working gases. The parameters of the plasma can be changed in wide range. The high gas temperature makes it attractive tool for different gas processing at high flow rates. MPS was successfully used for freon destruction [5], as well as for hydrogen production via methane conversion [6].

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