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FULL PAPER

Optical emission spectra of microwave discharge in different liquid hydrocarbons

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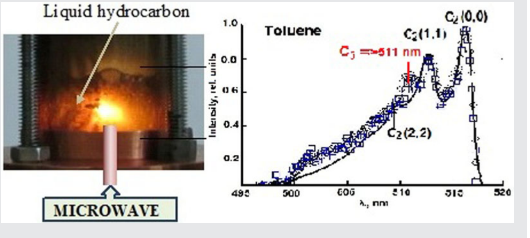
Abstract

Emission spectra of microwave discharge in liquid hydrocarbons (hexane (C_6H_{14}), *n*-heptane (C_7H_{16}), decane ($C_{10}H_{22}$), pentadecane ($C_{15}H_{32}$), cyclohexane (C_6H_{12}), toluene (C_6H_5–CH_3), *ortho*-xylene (C_6H_5–$(CH_3)_2$), and petroleum solvent nefras S2 80/120 [mixture of light hydrocarbons with boiling temperature ranging between 33°C and 205°C]) were studied in the range of wavelength 200–700 nm. The pressure above the surface of the liquid was equal to the atmospheric pressure. It was shown that in the spectra measured in aromatic hydrocarbons (toluene and *ortho*-xylene) the sequence of the Swan band with $\Delta \upsilon = 0$ was overlapped with the molecular emission band with a maximum at 511 nm never observed before. Analysis of known data allowed us to hypothesize that this emission can be attributed to the emission of linear carbon cluster C_5 (transition $C_5(^1\Pi_u \rightarrow X^1\Sigma_u^+)$). This cluster was previously observed only in absorption. Rotational temperatures determined by modeling of the sequence $\Delta \upsilon = -1$ of the Swan band were equal to $2{,}000 \pm 300$ K for all studied hydrocarbons.



KEYWORDS
discharges in liquid hydrocarbons, microwave discharge, optical emission spectroscopy

1 | INTRODUCTION

Spectroscopy of carbon-containing molecules occupies a leading place in research in various fields. First of all, interest is generated by the prevalence of such compounds in outer space and they largely determine the processes of cosmochemistry.[1,2] Hydrocarbon spectroscopy is important in the study of flames,[3] as well as in various plasma-chemical systems.[4–6] The Swan band emission ($C_2(d^3\Pi_g - a^3\Pi_u)$) is most often used to diagnose various carbon-containing systems in various conditions.

It is known that these bands, discovered in the middle of the 19th century, appear in any carbon-containing system: in flames, gas-discharge plasma, during laser ablation of a carbon target, in an interstellar medium, and so forth.[7–12] To date, the mechanism of emission excitation is not fully understood, but nevertheless, the radiation of these bands is widely used to determine the characteristics of the medium and, in particular, the rotational/translational and vibrational temperatures.[6,7,13–17]

The objective of this article is to study the optical emission of a microwave discharge in different liquid hydrocarbons, including the Swan bands. The possibilities of using these bands to determine the gas temperature in microwave discharge in liquid *n*-heptane were shown in Reference [8]. The conditions of experiments in Reference [8] were the same as in the present paper.

Discharges in liquids and in contact with it attract the attention of researchers with new phenomena occurring in such systems, and with many possibilities of their applications. They are used for the synthesis of diamonds and nanomaterials, surface modification, decomposition of toxic materials, water purification, and so forth.[9–12,18,19] All known types of electrical discharges are used for the generation of plasma in liquids but microwave discharges are less studied. Brief reviews on this topic are presented in References [20–22].

2 | EXPERIMENTAL SETUP

The experimental setup used for generation of microwave discharge in liquid hydrocarbons is described in detail in Reference [23]. It includes a microwave (2.45 GHz) magnetron generator, circulator, water attenuator, directional coupler, spectrum analyzer, and an oscilloscope. The attenuator allows a smoothly varying incident power in the range from 100 W to 2.5 kW. The discharge section is a waveguide-to-coaxial junction, the center conductor of which serves as an antenna for introducing microwave energy into the reactor. The discharge was created in liquids near the end of the antenna in a quartz reactor (diameter 55 mm) placed in a protective metal screen. The antenna part coming out to the cell is made of a copper tube with an outer diameter of 1.5 mm.

Schematically, the discharge chamber and the measurement circuit are shown in Figure 1. The volume of liquid hydrocarbon in the reactor is about 40 ml, which ensures that the end of the internal electrode of the coaxial line is located below the surface of the liquid. The experiments were carried out with an incident microwave power of about 100–150 W. The pressure above the surface of the liquid was equal to atmospheric pressure. Figure 1 includes a schematic of the discharge.

The discharge through optics was focused on the input aperture of the optical fiber, which directs radiation to the entrance slit of the AvaSpec-2048 spectrograph. The discharge averaged over time and space emission spectra in the wavelength range of 200–700 nm with a resolution of 1 nm was recorded. The relative calibration of the spectrograph was carried out using a band tungsten lamp SI-8-200. A detailed description of optical emission spectroscopy measurements is given in Reference [8]. The discharge was visualized by a digital camera with a frame rate of up to 240 frames per second.

The objective of this paper was to study the possible effect of the type of hydrocarbon on the gas temperature in the plasma. We used hydrocarbons that differ in structure, C/H ratio, and boiling points: *n*-heptane (C_7H_{16}, $T_{boil} = 98.42°C$), decane ($C_{10}H_{22}$, $T_{boil} = 174.1°C$), pentadecane ($C_{15}H_{32}$, $T_{boil} = 270.6°C$), cyclohexane (C_6H_{12}, $T_{boil} = 80.74°C$), toluene ($C_6H_5–CH_3$, $T_{boil} = 110.6°C$), *ortho*-xylene ($C_6H_5–(CH_3)_2$, $T_{boil} = 144°C$), and petroleum solvent nefras S2 80/120 (mixture of light hydrocarbons with boiling temperature ranged between 33°C and 205°C). The gas temperature was determined by modeling the Swan bands detected in the discharge radiation.[24] It was found that the sequence of the Swan band with $\Delta\upsilon = 0$ in the discharge radiation in liquid aromatic compounds is overlapped with an unknown emission band. Possible sources of the appearance of this radiation are discussed.

3 | RESULTS AND DISCUSSIONS

The spectra of the microwave discharge in all studied liquid hydrocarbons with the exception of aromatic

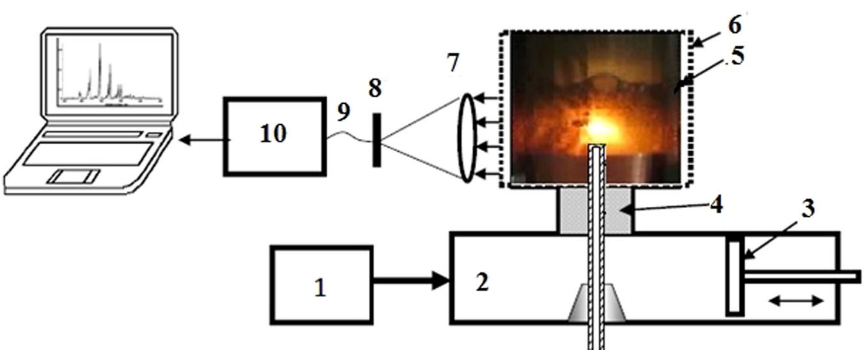


FIGURE 1 Schematic of experimental setup and optical measurements. (1) Microwave generator with circulator and water attenuator, (2) waveguide-to-coaxial junction, (3) shorting plunger, (4) dielectric, (5) quartz reactor, (6) metal mesh screen, (7) lens, (8) screen, (9) optical fiber, (10) spectrograph AvaSpec-2048

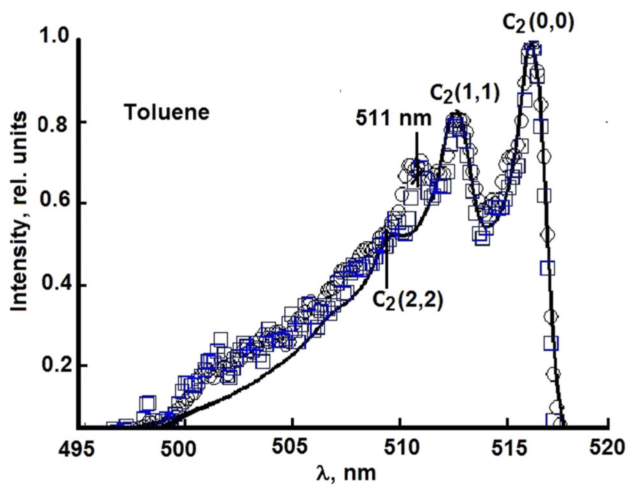


FIGURE 2 Emission of microwave discharge in liquid toluene in the range of wavelength 495–520 nm (points corresponds to the experimental data, solid line is the result of modeling of Swan band with $\Delta \upsilon = 0$). Wavelengths of the band maximum of $C_2(0,0)$, $C_2(1,1)$ and $C_2(2,2)$ transitions correspond to 516.52, 512.93, and 509.77 nm, respectively

hydrocarbons are represented by Swan bands (transition $C_2(d^3\Pi_g - a^3\Pi_u)$) sequences $\Delta \upsilon = 0$ (maximum at 516.5 nm), $\Delta \upsilon = 1$ (maximum at 563.5 nm), $\Delta \upsilon = -1$ (maximum at 473.75 nm), $\Delta \upsilon = -2$, and the band at 436.5 nm ($\Delta \upsilon = -2$) overlapped with the 0–0 emission band of CH at 431.2 nm (CH transition $CH(A^2\Delta - X^2\Pi)$). In addition, a broadband emission spectrum of solid carbon-containing particles is observed.

The sequence of the Swan band with $\Delta \upsilon = 0$ in spectra measured in aromatic hydrocarbons (toluene and *ortho*-xylene) was overlapped with the molecular emission band with a maximum at 511 nm. The most pronounced additional band was observed in experiments with toluene (Figure 2). With an increase in the number of CH_3 groups in a molecule (one group is in toluene and two groups are in *ortho*-xylene), the intensity of the additional band decreases (Figure 3) and it almost disappeared in other hydrocarbons. It seems that a trace of this band is present in the spectra of plasma in other liquid hydrocarbons (Figure 4). Attempts to measure the spectra of discharge in benzene were unsuccessful as spectra were presented by continuum emission of solid particles.

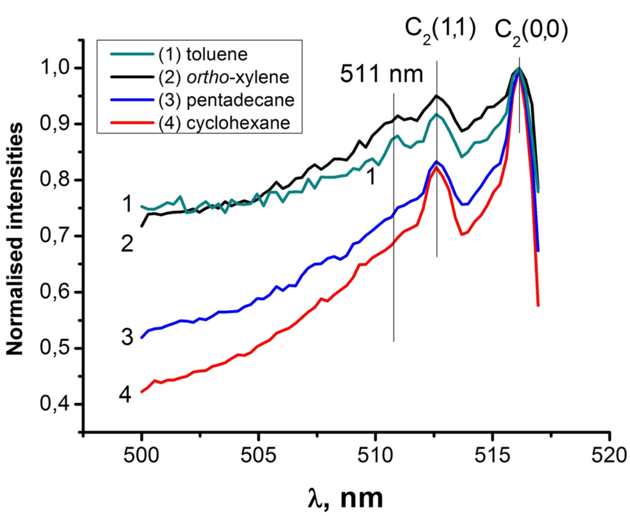


FIGURE 3 Emission spectra of toluene (1), *ortho*-xylene (2), pentadecane (3), and cyclohexane (4) in the wavelength region of emission sequence C_2 Swan band with $\Delta \upsilon = 0$

Let us consider the possible sources of the detected additional emission band. Note that the composition of the main gas-phase products in aromatic hydrocarbons differs from the composition of products in other hydrocarbons and the difference decreases with an increase in the number of CH_3 groups[25] (products of discharge in benzene and toluene did not contain C_2H_4, which is found in the products of all other hydrocarbons and also appears in *ortho*-xylene).

The radiation of a microwave discharge recorded by a spectrograph in liquid hydrocarbons consists of two parts. The first is due to plasma radiation passing through the layer of a liquid hydrocarbon. In the visible part of the spectrum, pure hydrocarbons do not absorb radiation. During experiments, solid particles are present in the liquid, which are formed in the discharge and then transferred to the liquid.[23,26] A fluid with particles is an attenuator for light emission, which leads to nonstationary detection of discharge radiation.

The second part of the detected radiation could be associated with possible luminescence of solid particles in a liquid under the influence of plasma radiation.

Let us analyze both possibilities and sources with which the observed emission of the band at about 511 nm can be associated. We repeat once more that in our experiments this radiation is observed only in a microwave discharge in liquid aromatic hydrocarbons.

In the published articles, much attention is paid to studying the emission of linear carbon clusters.[4] This interest is, in part, motivated by their relevance to astrophysics, especially to understanding the absorption features observed through diffuse interstellar clouds. Carbon chains are among the appealing candidates for the carriers of such bands. The radiation of C_2 sequences (Swan bands) is well known and used. Radiation of the C_3 cluster at 405 nm is also known.[3,27,28] The absence of the registered emission spectra of clusters of a higher order is explained by their high coagulation rate with the formation of soot.

A large amount of information about such clusters was obtained in laboratory conditions by matrix isolation and absorption of radiation. In particular, the radiation absorption of C_5 cluster at a wavelength of 511 nm was

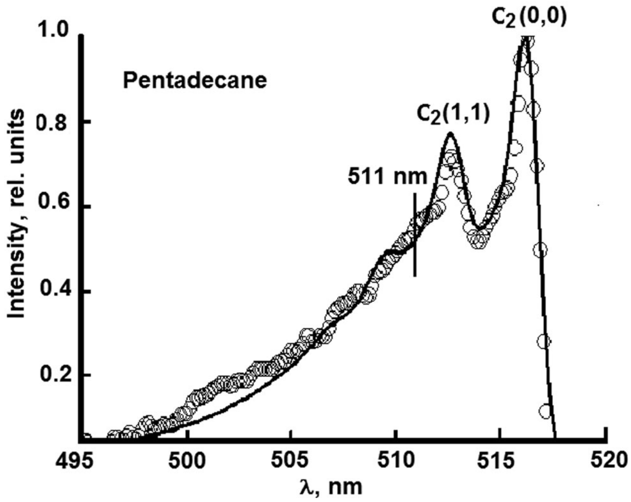


FIGURE 4 Emission of microwave discharge in liquid pentadecane in the range of wavelength 495–520 nm (points corresponds to the experimental data, solid line is the result of modeling of Swan band with $\Delta\upsilon = 0$)

recorded (transition $C_5(^1\Pi_u \leftarrow X^1\Sigma_u^+)$).[29] It can be assumed that in a microwave discharge in liquid aromatic hydrocarbons, the conditions for observing this transition in radiation are provided.

Another reason for the appearance of radiation in the spectral region of interest may be the fluorescence of solid particles in a liquid hydrocarbon—radiation of carbon dots.[30,31] Particles can be formed in plasma and then can be transferred to a liquid. It can also be formed in liquid hydrocarbon under the influence of microwave radiation. The spectral range of fluorescence depends on the method of producing particles. Fluorescence can be caused by plasma radiation.

Changes occurring in a number of liquid hydrocarbons after creating an atmospheric-pressure microwave discharge in their bulk have been studied in Reference [32]. It has been shown that all liquid hydrocarbons, which are initially colorless, acquire a yellow-brown color under room light irradiation after the plasma treatment. This color can be attributed to the presence of nanoparticles.

The photoluminescence mechanism of carbon dots is still open for discussions and its general laws are not clear. An article[31] described the possibility of obtaining radiation of carbon dots at a wavelength of 511 nm by irradiating a sample at a wavelength of 350 nm. The probability of such a coincidence of conditions in the experiments of these authors and ours seems to be small.

Therefore, the authors of this article are inclined to conclude that the observed band with a wavelength of 511 nm can be associated with radiation from an excited C_5 cluster.

What is the peculiarity of the conditions that are realized in the microwave discharge and allow observing the radiation of the C_5 linear cluster? Several reasons can lead to a high concentration of C_5 emitting states in a microwave discharge in liquid aromatic hydrocarbons. First of all, and this was noted in many studies on microwave discharges in liquids (see review[20]), the rates of product formation in microwave discharges are higher, in comparison with other discharges. This is caused by high rates of formation of active particles. Another reason for high concentration of the emitting state of the C_5 linear cluster can be effective quenching of hydrocarbon decomposition products, which is caused by a large temperature gradient: at the center, the temperature is 2,000 K, and at the boundary (bubble size is of several millimeters), this is the boiling point of the hydrocarbon. The observation of a new emission band only in aromatic hydrocarbons may be due to the fact that the rate of formation of the solid phase in them is much higher than in other hydrocarbons. This was shown by our experiments. Therefore, we can expect that the rate of formation of active particles is also high.

It is clear that additional extended studies are needed to answer all the questions that arise with the observed radiation.

From the discussion above, one more conclusion follows: Due to overlapping of the sequence $\Delta\upsilon = 0$ of the Swan band with an additional radiation band, this sequence should be used for plasma diagnostics with caution, at least in the case of discharges in liquid hydrocarbons.

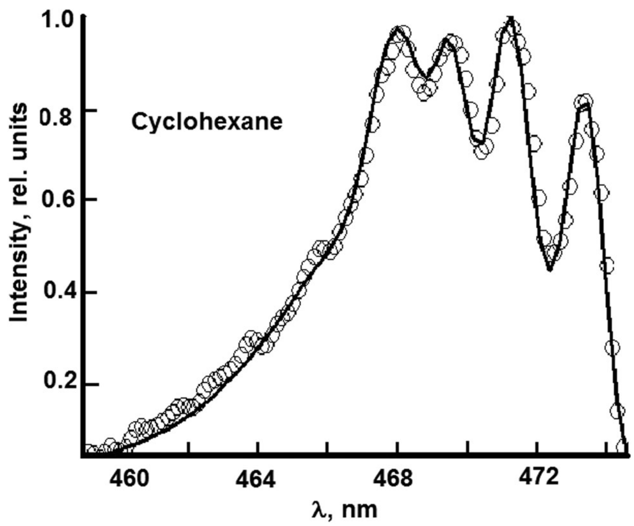


FIGURE 5 Emission of microwave discharge in liquid cyclohexane in the range of wavelength 460–476 nm (points corresponds to the experimental data, solid line is the result of modeling of Swan band with $\Delta\upsilon = -1$)

An analysis of the obtained spectra showed that the sequence $\Delta\upsilon = -1$ is the least noisy. An example of the spectrum is shown in Figure 5. This sequence was processed using the technique described in Reference [24] (the spectrum was simulated with adjustable parameters of rotational and vibrational temperatures until it coincided with the measured spectrum). In the discharge in all studied hydrocarbons, the rotational temperature T_r turned out to be the same and equal to 2,000 ± 300 K. In our experimental conditions, T_r is equal to the gas temperature T_g. The problem of equality of rotational and gas temperatures for our conditions was analyzed in detail in Reference [8]. To satisfy the equality $T_r = T_g$ it is necessary to fulfill several conditions[33]: (a) the characteristic time of energy exchange between translational and rotational degrees of freedom (τ_{exch}) is much less than the time of their radiative decay (τ_{rad}) and the processes leading to a change in the population of radiating levels of molecules; (b) τ_{exch} is much less than the residence time of molecules in the discharge zone; (c) there is no radiation distortion due to reabsorption, refraction, reflections from elements of the optical system, and so forth. Results of Reference [8] showed that in our case these requirements are satisfied.

4 | CONCLUSIONS

The radiation of microwave discharge generated within liquid hydrocarbons of various classes (alkanes, cyclic, and aromatic hydrocarbons) was studied in the wavelength range 200–700 nm at atmospheric pressure above the surface of liquids. The spectra of the microwave discharge in all studied hydrocarbons with the exception of aromatic hydrocarbons are represented by the Swan bands (transition $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$) sequences $\Delta\upsilon = 0$, 1, −1 and the band at 436.5 nm ($\Delta\upsilon = -2$) which is overlapped with the 0–0 emission band of CH at 431.2 nm. In addition, a broadband emission spectrum of solid carbon-containing particles is observed.

In the spectra measured in an aromatic hydrocarbon (toluene, *ortho*-xylene), the sequence of the Swan band with $\Delta\upsilon = 0$ was overlapped with the unknown molecular band emission with maximum at 511 nm. Analysis of literature data brings us to the conclusion that this emission can be caused by emission of linear carbon cluster C_5 (transition $C_5(^1\Pi_u \rightarrow X^1\Sigma_u^+)$). This cluster was previously observed only in absorption. This means that microwave discharge in liquid aromatic hydrocarbons produced specific conditions for C_5 generation and its emission.

Rotational temperatures determined by modeling of sequence $\Delta\upsilon = -1$ of the Swan band were the same for all studied hydrocarbons and equal to 2,000 ± 300 K. This value can be considered as the gas temperature. Therefore, the structure, C/H ratio, and boiling points of hydrocarbons do not affect the gas temperature.

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