

DESTRUCTION OF METHANE BY NANOSECOND HIGH-VOLTAGE DISCHARGE

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Abstract

Investigation of the combustible mixture ignition by nanosecond high-voltage volume discharge requires the detail knowledge of kinetic processes in the discharge itself and its afterglow. Main electrodynamic characteristics, such as velocity of discharge propagation and energy consumption were measured in methane and methane-air stoichiometric mixture in a pressure range 1-20 Torr under the action of 11 kV, 5 ns rise time and 25 ns duration high voltage pulses of negative polarity with a repetitive frequency of 40 Hz. Simultaneous control of time-resolved (both in nanosecond and tenth-second time scale) behaviour of emission of different excited components in the wavelength range of 190-800 nm gives data set for detail analysis of the chemical kinetics in discharge and its afterglow in methane-air mixtures.

1 Introduction

The problem of fast and homogeneous ignition of combustible mixture is extremely pressing [1] – [3]. The laser methods of ignition have severe disadvantages related to the impossibility to provide the high uniformity of ignition initiation in large gas volumes. The spark ignition imposes essentially restrictions on the system geometry. Ignition by arc injection make it possible to operate only in flow velocity range which is comparable or lesser than the velocity of the injected plasma jet. The homogeneous ignition method which is fast in comparison with characteristic times of combustion processes and gas dynamic times may be based on the use of the nanosecond high-voltage discharge as a source of active particles.

The pulsed electric discharge in gases at essentially high overvoltage develops in the form of so called “fast ionization wave”(FIW) which propagates with a velocity of 10^9 – 10^{10} cm/s from high-voltage electrode to the low-voltage one [4]. High electric fields in the FIW front and behind it lead to the effective gas ionization, dissociation and excitation, at the same time the gas translation temperature does not essentially change. Important advantages of FIW application in this case are the spatial uniformity and short time of active particle generation (difference between the characteristic time of particle formation in FIW and the combustion and gas dynamic processes times is about three orders of magnitude).

Our previous calculations [5] demonstrate the real possibility to diminish induction time due to the nanosecond discharge treatment of combustible mixtures. So, the first step to study experimentally ignition of combustible mixtures by FIW is an investigation of hydrogen [6] and methane destruction in stoichiometric mixtures with air at room temperature.

2 Experiment

The experimental setup is shown in Fig.1a. The discharge cell consists of quartz tube 1 of length $l = 200$ mm and diameter of 47 mm with conical high-voltage electrode 2 and ringed low-voltage electrode 3. There is an optical window 4 of CaF₂ in the low-voltage electrode. The electrode is shorted to a grounded shield of the supply cable with the help of thick brass buses. Pulses of negative polarity of $|U| \sim 11$ kV amplitude, 25 ns duration at half-height and 2 ns rise time are fed with repetition frequency of $f = 40$ Hz from pulse voltage generator 5 to the high-voltage electrode of the discharge tube. The discharge tube is evacuated through a hole in the low-voltage electrode and filled with the mixture under study at the specified pressure. Pressure change during the discharge is controlled with a special gauge. Experiments were performed in methane and methane-air stoichiometric mixture.

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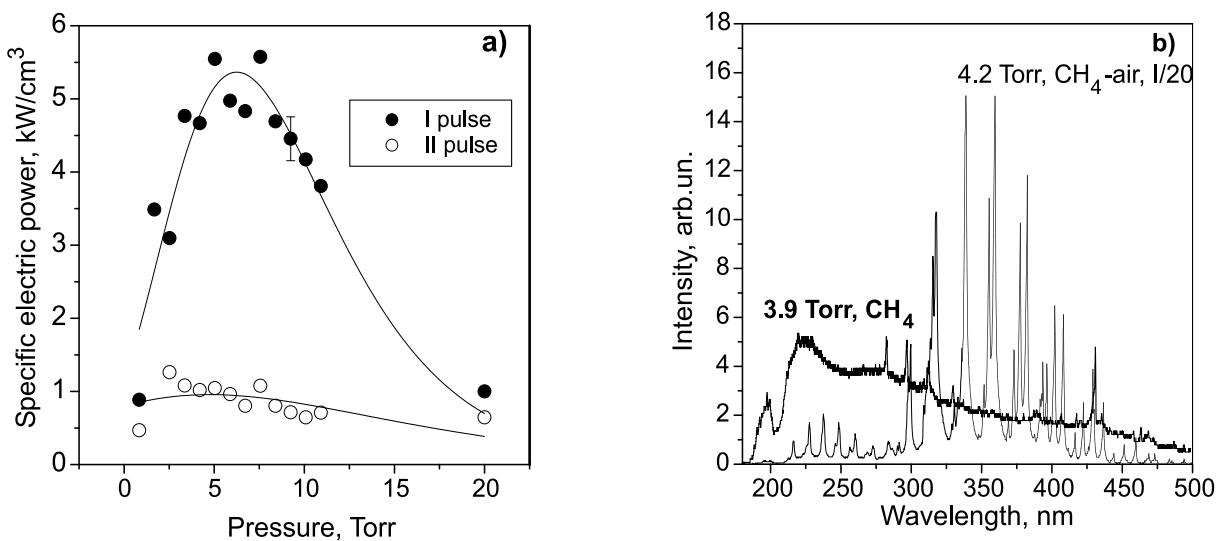
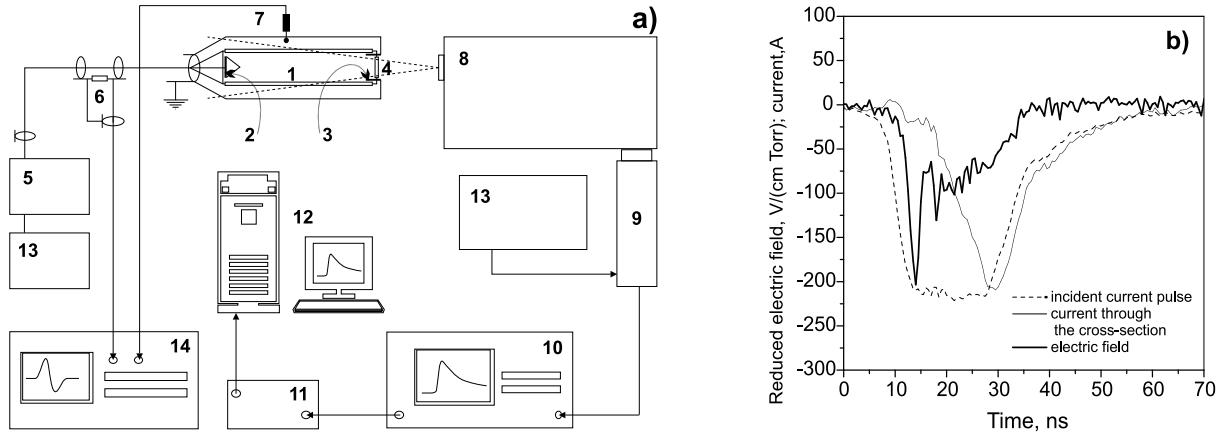


Figure 2: Maximum specific electric power vs pressure at a cross-section 9 cm separated from the high-voltage electrode. CH₄-air mixture, 7 Torr, -11 kV, 40 Hz. b) Typical emission spectrum of pulsed nanosecond breakdown in methane (-11 kV) and methane-air mixture (-11 kV).

The electric parameter recording system consists of calibrated current shunt 6 and capacitance sensor 7 which can move along the discharge tube. They allow to measure absolute values of current and voltage with temporal resolution no worse than 1ns. Electric sensors were used to measure the shape and amplitude of the high-voltage pulse, breakdown front propagation velocity, current, energy contribution into the gas. The discharge emission was observed in the mode of signal accumulation with the use of monochromator MDR-23 8 (1.2 nm/mm, 1.2 m, 1200 lines/mm, $\Delta\lambda = 2.4 \text{ \AA}$), photomultiplier FEU-100 9, RC-filter and digital oscilloscope S9-8 10, mated through interface card 11 to a computer 12. The time constant of the integrating circuit was 0.25 s and provided for operations with low noise level. To register discharge emission with nanosecond temporal resolution we used high-current photomultiplier 14ELY-F7S and oscilloscope Tektronix TDS-380 14.

3 Results

Typical shape of the electric pulse is represented in Fig.1b together with longitudinal electric field in the tube cross section at a distance of 10 cm from the electrode and a current through this cross-section. Electric field was determined as $E(x, t) \approx -\partial\varphi(x, t)/\partial x$, where potential in the cross-section $\varphi(x, t)$ was measured by a capacitance gauge with a 3.5 cm step along the discharge tube. It is seen that, in accordance with our previous investigations [7], the electric field has a sharp and narrow (a few ns) maximum. Secondary maximum, 4 ns later,

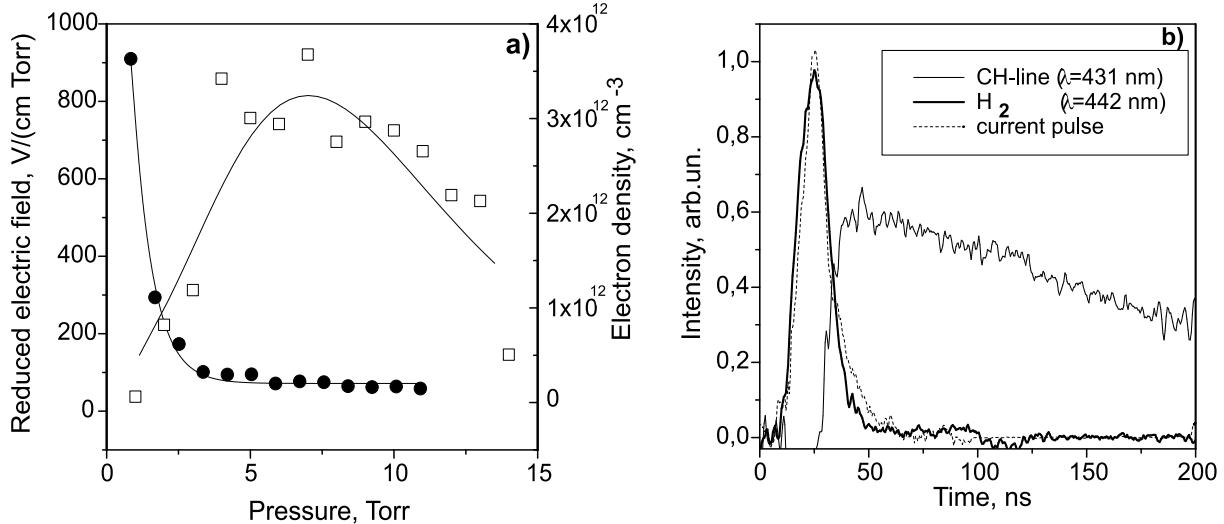


Figure 3: a) Reduced electric field E and electron density n_e at a distance of 9 cm from the high-voltage electrode. Time moment at fixed pressure corresponds to the maximum specific electric power input. CH₄:air=9.5%:90.5% mixture, -11 kV, 40 Hz; b) Typical behaviour of hydrogen and CH radical emission in nanosecond time scale. Methane, initial pressure is 4.3 Torr, -11 kV, 40 Hz.

which is clearly seen from the figure, is due to initiation of a back wave from the low-voltage electrode. Current increase up to 200 A corresponds to the overlap of the discharge gap.

In regime represented in the figure, maximum specific electric power $\omega = jE$, where $j(x, t)$ is a current density in the cross-section and $E(x, t)$ is an appropriate electric field is consumed in gas far behind the electric field front. It is so for the pressure range 5-20 Torr, while at low pressures (< 5 Torr) maximum power input corresponds to very high electric field in the front. Pressure dependence of maximum specific electric power is represented in Fig.2a for the first pulse incident on the discharge gap and for the second one, reflected from the high voltage generator. The curve has a well-defined maximum, the shape of $\omega(P)$ curve is close to the velocity dependence upon pressure, which is in good correlation with previous results. It is seen that for our conditions the specific electric power in the second pulse is 3-5 times lower practically within all the pressure range.

Discharge emission in methane is characterized by a presence of molecular hydrogen continuum ($a^3\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ transition) and CH radical line ($A^2\Delta \rightarrow X^2\Pi$). We registered also violet system of CN ($^2\Sigma \rightarrow ^2\Sigma$, $\lambda = 388.3$ nm) and 3rd positive system of CO (in the wavelength range 280 – 330 nm), which, possible, were caused by a trace amount of air in the discharge cell. Nevertheless no nitrogen systems emission was found in the spectrum. In the UV range the spectrum demonstrates two well-defined depressions. The first one, at $\lambda = 250$ nm is explained by an absorption of ozone, which creates in the air due to UV radiation from the discharge. The second one is situated at $\lambda = 205$ nm. It arises immediately after discharge is switched on and does not depend upon operation time. In methane-air mixture we observed strong emission of second positive, first positive and first negative systems of molecular nitrogen, NO lines in UV range of spectrum, CO and CH lines, H-atom lines. Fig.2b gives typical integrated in time spectrum of nanosecond pulsed discharge. It should be mentioned that in discharge in methane during quite a short time (about of an hour) brown deposit covers discharge tube and high-voltage electrode, and UV-transmission also decreases considerably. This effect is negligible in methane-air mixture.

Electron density was estimated from the current under known electric field (Fig.3a). It is clearly seen that both specific power and electron density reach maximum at the same pressure (about of 7 Torr for our case). Reduced electric field sharply decreases with pressure. There are two reasons for that. First, reduced field E/N decreases due to pressure increase, since electric field E does not change more than twice in the considering pressure range. Second, the point of maximum energy input moves from the front, in the direction in which the electric field $E(t)$ is decreasing.

It is interesting to compare time-resolved emission and electric current behaviour (Fig.3b). They practically coincide for hydrogen and differ significantly for CH-radical. Hydrogen excitation takes place at the phase of strong conductivity current, while CH radical excites only at the end of this phase. Hydrogen radiative depopulation and quenching are quite strong and, so, emission repeats the shape of the current pulse. CH radical emission decay is about of 250 ns in our conditions.

Emission on the discharge phase gives an information about population of different levels in the discharge itself, while a long-term emission represents changes in the chemical composition of mixture from pulse to pulse. Typical emission of different excited molecules in methane-air mixture is represented in Fig.4a. Here represented curves for the first negative ($B^2\Sigma, v' = 0 \rightarrow X^2\Sigma, v'' = 2, \lambda = 470.9$ nm) and second positive ($C^3\Pi, v' = 1 \rightarrow B^3\Pi, v'' = 7, \lambda = 491.7$ nm) systems of molecular nitrogen, CH-line ($A^2\Delta, v' = 0 \rightarrow X^2\Pi, v'' = 0$,

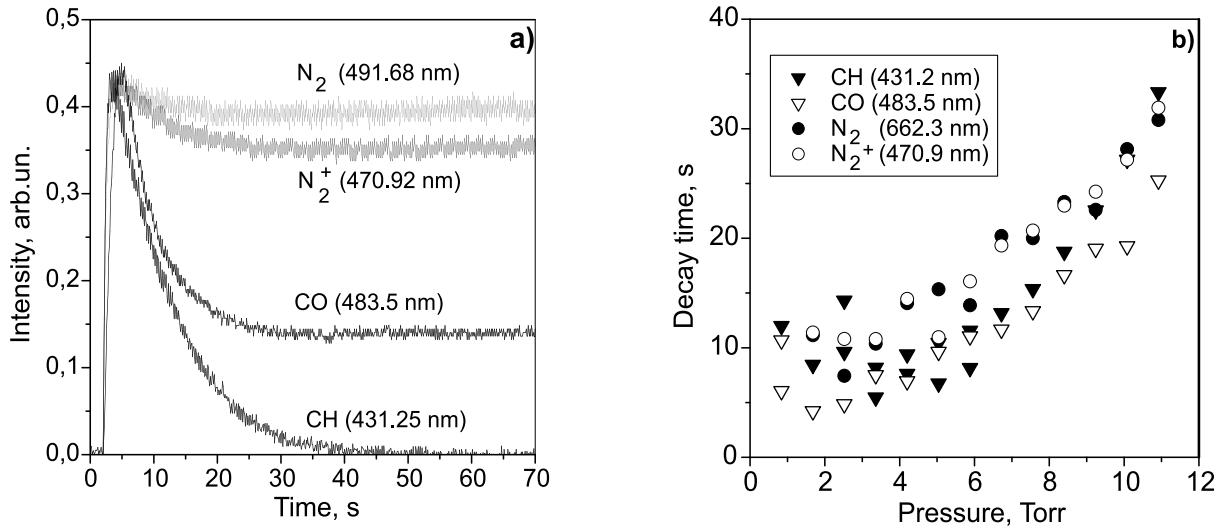


Figure 4: a)Typical behaviour of the emission in a long-time scale. CH₄-air mixture, 4.2 Torr, -11 kV, 40 Hz. b)Emission decay time for different excited states. CH₄-air mixture, -11 kV, 40 Hz.

$\lambda = 431.2$ nm) and Angstrom system of CO ($B^1\Sigma, v' = 0 \rightarrow A^1\Pi, v'' = 1, \lambda = 483.5$ nm). It is obvious that these curves are similar to each other: on discharge initiation emission begins to grow. Each subsequent nanosecond pulse leads to further growth of the emission. In the 2-3 seconds (that is after ~ 100 pulses) the value of $I(t)$ passes through a maximum, then curve slow reaches its stationary value. The time taken to reach stationary level is about of 30 s (or 1200 pulses), and it changes significantly with pressure. For example, Fig.4b demonstrates time of exponential decay of emission between maximum and stationary value for different excited levels, including first positive system of molecular nitrogen ($B^3\Pi, v' = 6 \rightarrow A^3\Sigma, v'' = 3, \lambda = 662.3$ nm).

Thus, methane decomposition in nanosecond discharge has been investigated for methane and methane-air stoichiometric mixtures in a pressure range 1-20 Torr. Obtained data are useful both for verification of numerical code developed for the modeling of ignition by nanosecond discharge and for understanding of the main perculiarities of nanosecond high-voltage breakdown in combustible mixtures.

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