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Kirill Kozlov, Emmanuel Odic, P.A. Tatarenko, Bénédicte Dodet, G.S. Fedoseev, et al.. RADIATION KINETICS AND CHEMICAL REACTIVITY OF BARRIER DISCHARGES IN HUMID ARGON. 10th International Symp. on High Pres. Low Temp. Plasma, Sep 2006, SAGA, Japan. pp.124-127. hal-00221303

HAL Id: hal-00221303

<https://centralesupelec.hal.science/hal-00221303>

Submitted on 28 Jan 2008

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RADIATION KINETICS AND CHEMICAL REACTIVITY OF BARRIER DISCHARGES IN HUMID ARGON

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ABSTRACT. The technique of spatially resolved cross-correlation spectroscopy was used to record two-dimensional luminosity distributions for the selected spectral bands of molecular nitrogen ($\lambda=337.1$ nm), OH-radical ($\lambda=308$ nm), and two spectral lines of excited Ar ($\lambda=750.4$ nm and $\lambda=763.5$ nm) emitted by the microdischarges of the barrier discharge in flowing humid argon at atmospheric pressure. Concentrations of two stable reaction products of H₂O decomposition (H₂ and O₂) in argon plasma were determined experimentally as functions of humidity. Comparison of these results with the corresponding measurements of radiation kinetics permitted a detailed analysis of the influence of the discharge mechanism on its chemical reactivity in humid argon to be accomplished.

1. INTRODUCTION

Barrier discharges (BDs) in humid argon can be regarded not only as prospective plasma chemical reactors for H₂O₂ synthesis [1], but also as useful UV-radiation sources [2]. The objective of this research was to carry out a complete plasma diagnostics (including electrical measurements, spatially resolved kinetic spectroscopy, and chemical analysis of the stable reaction products) of the BD in humid argon, in order to improve understanding of the discharge development mechanism and to determine its influence upon the kinetics of the decomposition of H₂O molecules. The technique of cross-correlation spectroscopy (CCS) was a basic tool to investigate radiation kinetics, and the method of gas chromatography was used to determine the concentration of reaction products (H₂ and O₂) in the gas phase.

2. EXPERIMENTAL SET-UP AND PROCEDURE

The experimental set-up for spatially resolved spectroscopic measurements and the CCS-method are described in detail elsewhere [3,4]. In order to localize repetitive microdischarges (MDs) at a fixed position, a discharge cell consisting of two semi-spherical electrodes (radius of curvature $R = 7.5$ mm, see fig.1-a), both covered with glass was used. This electrode arrangement provided the possibility to observe not only the bulk volume portion of the MD, but also its surface components. The BD was operated by sinusoidal voltage at a frequency of 5 kHz. The discharge gap width (the distance between the electrode tips) was equal to 1.9 mm. The spatio-temporal distributions of radiation intensity for the selected wavelengths within the MD channels were recorded by means of the technique of CCS with spatial and temporal resolutions of 0.1 mm and 0.05 ns, respectively.

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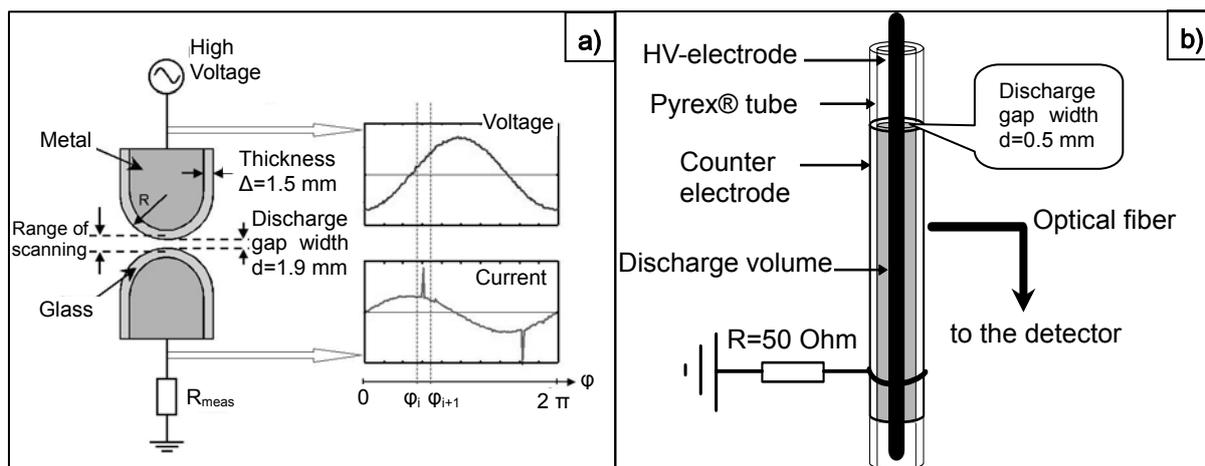


FIGURE 1. a) General scheme of the discharge cell used for spatially resolved CCS-measurements with the indicated range of optical scanning and typical examples of the oscillograms of voltage and current; b) Sketch of the discharge cell used for the investigations of chemical reactivity and for time-space integrated spectroscopic measurements. See explanations in the text.

The reactor used for the experiments on H_2O decomposition and for the time-space integrated spectroscopic measurements, was based on a coaxial electrode arrangement (see fig.1-b). The inner electrode was a stainless steel rod of 2 mm diameter, centered in a Pyrex tube (inner diameter 3 mm), wrapped with a copper foil (45 mm length). The inner electrode was energized using a 28.6 kHz high voltage power supply. The copper foil was connected to ground through a 50 Ω resistor for discharge current measurements. The reactor was fed with humid argon with variable water vapor content (1.8-23 g/m^3). The flow rate ranged from 0.2 to 2 L/min. The input power range was: 0.5-3 W.

3. RESULTS AND DISCUSSION

In the emission spectrum of the BD in flowing humid argon, the spectral bands of the second positive system of nitrogen as well as of OH-radical were observed along with the peaks of argon. The following four spectral indicators were selected to record the spatio-temporal distributions of the MD luminosity: Ar(I), $E_{exc} = 13.48$ eV, $\lambda = 750.4$ nm; Ar(I), $E_{exc} = 13.17$ eV, $\lambda = 763.5$ nm; $N_2(C^3\Pi_u)$, $E_{exc} = 11.0$ eV, $\lambda = 337$ nm; and $OH(A^2\Sigma^+)$, $E_{exc} = 9.1$ eV, $\lambda = 308$ nm. The CCS-measurements were carried out for several different levels of relative humidity in the range 3-95%. Some results of these experiments are shown in fig.2.

Generally, spatial distributions of light intensity of the radiating species being considered are determined by the corresponding distributions of electric field strength and electron density within the MD channel. However, these functional dependences are different for different spectral indicators, and the following simple rule may be used to provide a qualitative interpretation of experimental results: the greater the threshold energy E_{exc} of a spectral indicator, the stronger the dependence of its excitation rate (consequently, of its radiation intensity) upon electric field strength [3]. Using this rule to analyze the luminosity distributions shown in fig.2 and taking into account the values E_{exc} listed above, we can assume that the structure of the MD channel is similar to that one found earlier for the BD in air [3]. There are two active zones near the electrodes, and electric field is higher near the cathode, while electron density is greater near the anode.

The influence of argon humidity on the radiation kinetics within the MD channel can be considered as a superposition of the following two effects: (i) the dependence of collisional quenching rate of the radiating species upon H_2O concentration and, (ii) the influence of water vapour on electron energy distribution. Since the rate of collisional quenching of the radiating species by H_2O molecules is proportional to the humidity, an increase in water vapour content

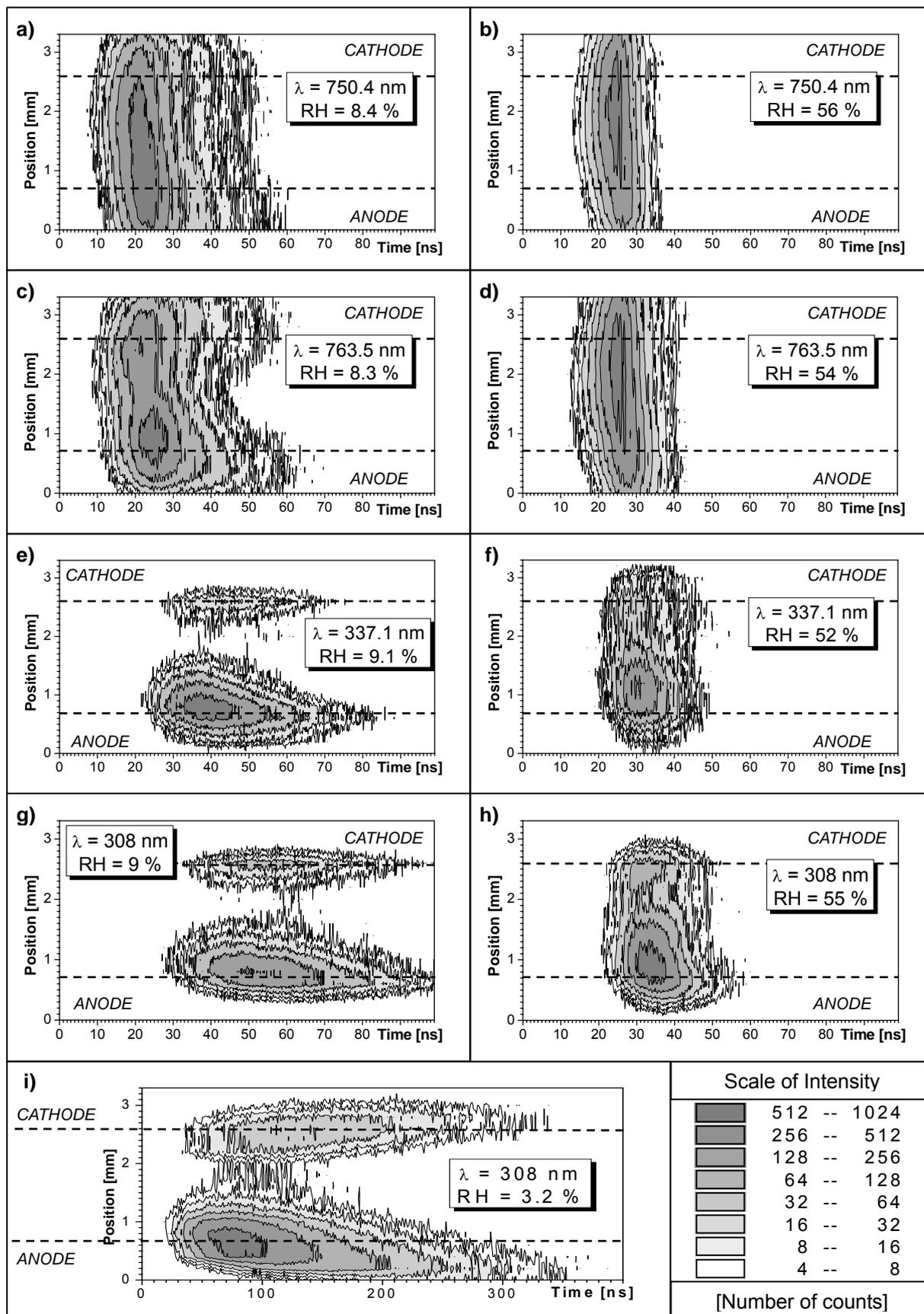


FIGURE 2. Spatio-temporal distributions of the MD luminosity for the selected wavelengths. Experimental conditions: $p=1.05$ bar; $d=1.9$ mm; gas flow rate 8 l/h; voltage frequency 5 kHz. RH denotes relative humidity.

results in a noticeable shortening of light emission duration for all spectral indicators being considered (compare the left and right columns of the plots (a-f) in fig.2, and the plots (g,h,i)).

An addition of molecular gas admixture to argon plasma results in a decrease in electron energy [4]. This effect can explain the difference between the luminosity distributions shown in fig.2-c,d. For relative humidity (RH) of 54%, the electron energy is lower than for RH=8.3% and therefore the local intensity maximum near the anode on fig.2-c is not seen in fig.2-d. This influence of humidity on electron energy is also clearly seen from the results on chemical reactivity measurements presented in fig.3.

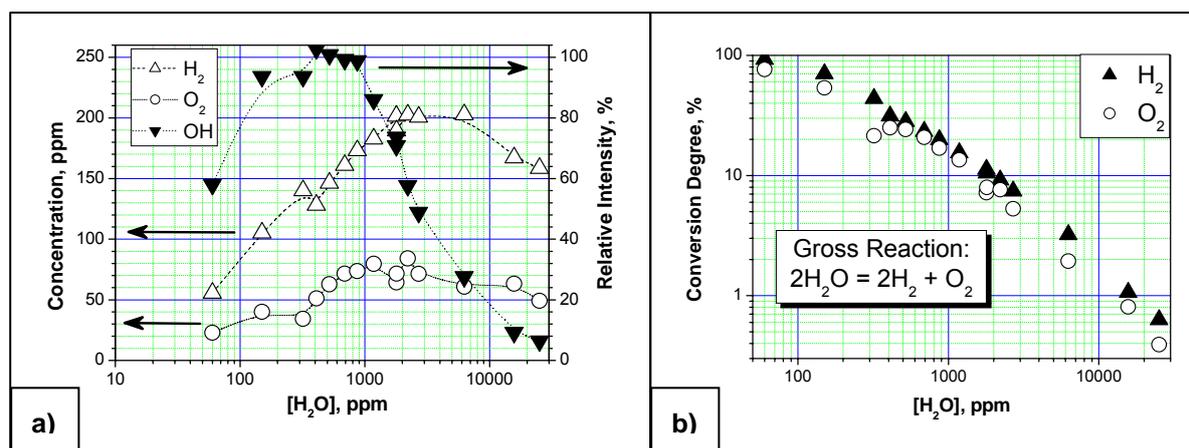


FIGURE 3. Dependences of the reaction product yields and light emission intensity for $\lambda = 308$ nm (a), and of the corresponding chemical conversion degrees (b) upon the humidity of argon.

The shapes of the curves for reaction product concentrations (fig.3-a) are determined by the following two kinetic effects of humidity acting in opposite directions. First, the dissociation rate of H₂O molecules is proportional to the concentration of water vapour. Second, the rate constant of this process decreases with the humidity due to the decrease in electron energy. For the H₂O concentrations greater than 1000 ppm, the second effect begins to dominate and the concentration curves for H₂ and O₂ fall down. The shape of the curve for integral emission intensity of the radicals OH($A^2\Sigma^+$) at $\lambda = 308$ nm (see fig.3-a) can be explained in a similar way. However in the latter case, the influence of collisional quenching of the radiating species by H₂O molecules should be taken into account. This influence results in a shift of the maximum to a lower humidity as compared to the curves for H₂ and O₂. The dependence of the conversion degrees of H₂O to H₂ and O₂ on the humidity (see fig.3-b) demonstrates that an increase in water content in argon exerts a profound negative influence on the chemical reactivity of the BD in the entire concentration range of water vapour.

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