AFTERGLOW IN PURE NITROGEN CONTAINING CHLORO- AND FLUORO-CARBON TRACES

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Abstract

The influence of small chloro- and fluoro- carbon impurities on the pure nitrogen afterglow was studied in a DC flowing plasma reactor in comparison with formerly studied methane influence [1]. The study has been done at two different wall temperatures of the observation part of the reactor (77 – 300 K). The band head intensities of the identified spectral bands have been measured by emission spectroscopy. At low wall temperatures, the high sensitivity of pure nitrogen to presence of the carbon containing additives in the discharge has been observed. These observations extend our results recently obtained for methane admixture to some other carbon containing molecules and thus they can clearly demonstrate the validity of our proposed method for the destruction of polymeric materials detected by the nitrogen afterglow that has been recently proposed [2, 3] and developed [4].

1. Introduction

The flowing nitrogen post-discharge has appeared during the last years in the new field of extremely sensitive methods and techniques using the spectral emission, designed specially for the detection of impurities containing carbon and oxygen. Emission of the CN violet and red spectral systems has been widely observed in the reaction of active nitrogen with hydrocarbons and with partially or fully halogenated hydrocarbons [5, 6]. In these studies, the halogenated hydrocarbon concentrations were in the order of a few percent and the effects have not been studied in complexity. The upper electronic states of these two spectral systems are formed mostly in selected vibrational states. There are also many state specific reactions with a vibrationally excited nitrogen ground state [4, 7]. The effects connected with these kinetic reactions have been discussed in many works [8] but only as a "parasitic effect". Therefore we started to study these interesting effects initially in nitrogen-methane mixtures and now we extended these studies by the nitrogen halogenated hydrocarbon mixtures.

The extensive research may lead to many applications in the field of environmental analysis (e.g. monitoring of hydrocarbon traces during plasma chemical nitridation processes, analyzing the qualities of air, water and food etc.) as well as in the field of basic research. The presented results considerably extend the features and fields of application concerning our recently described method concerning the estimation of polymeric materials destruction [4].

2105
2. Experimental setup

The scheme of the experimental device is presented in Fig. 1. The device is based on a long experience with the flowing post discharges; a more detailed description of this device can be found in [3]. The $N_2 + \varepsilon M$ gas mixtures (M means the halogenated hydrocarbon) have been prepared in our laboratory by random mixing. Due to this fact, the final admixture (which is the gas mixture) had to be calibrated by the ICP spectroscopy using the nitrogen + 1% of methane calibration mixture. We used the Freons R12 (CHF$_2$Cl), R22 (CF$_2$Cl$_2$) and R134a (CF$_3$-CH$_2$F) as the halogenated hydrocarbons in our study.

![Diagram of the experimental device using the flowing DC afterglow.](image)

**Figure 1:** Scheme of the experimental device using the flowing DC afterglow.

M - the halogenated hydrocarbon admixture; 1 - a copper based catalyst; 2 - rotameters; 3 - a quartz discharge tube (i. d. 14 mm, total length of 130 cm, the length of the afterglow part 90 cm); 4 - molybdenum anode; 5 - molybdenum cathode (14 cm from anode); 6 - a observation cell (may be cooled to 77 K); 7 - an optical fibre; 8 - a monochromator (Jobin Yvon HR 640); 9 - CCD; 10 - PC; 11 - a Pirani gauge; 12 - a rotary oil pump.

In our experiment, we measured optical emission spectra of the CN (violet and red systems) and nitrogen $1^\text{st}$ and $2^\text{nd}$ positive and $1^\text{st}$ negative systems during the DC flowing post-discharge. The plasma was created in the pure nitrogen containing the traces of light chloro- and fluoro-carbons. The experimental conditions were the total gas pressure of 2000 Pa and the discharge current of 125 mA at the total gas flow of 690 Sccm. We varied the impurity concentration in an active discharge in the range from 1 to 100 ppm. The optical spectra emitted during the afterglow have been recorded at the decay times of about 29, 54 and 86 ms. The temperatures of the reactor wall were 77 K and 300 K at the measured decay time ± 10 ms.

3. Experimental results

The experimental results obtained using halogenated hydrocarbons can be compared with the results obtained in the nitrogen - methane gas mixture presented in Fig. 2 [1, 4]. These figures demonstrate the significant increase (more than 3 orders) in the intensities of CN bands with the increase of methane concentration in the discharge. The small decrease in these intensities at the lower temperature and simultaneously at the highest observed
concentrations results from the kinetic processes during the afterglow (see section 5 in [4]). The changes of the intensity of both nitrogen positive systems are not so significant (less than 1 order), meanwhile the presence of methane changes in approximately 4 orders. The changes of the intensity of nitrogen 1st negative system result from the kinetic processes during the afterglow; the strong enhancement of the intensity at lower temperature at the concentration of about 10 ppm results from the CN violet 10-10 band overlapping the 1st neg. 0-0 band. Although the former experiments have been carried out in a much wider range of carbon concentration than the present measurements. The results given below can be compared with them in a wide range of concentrations and the present observations are not limited by the narrow concentration interval (the gas mixtures were prepared in our laboratory).

![Graphs of band intensities as a function of methane concentration](image)

**Figure 2:** Band head intensities of the observed spectral systems as a function of the methane concentration at the afterglow temperatures of 400 K (left) and 100 K (right) at the decay time of 25 ms. Legend: a - nitrogen 1st pos. 2 - 0 band; b - nitrogen 1st neg. 2 - 0 band; c - CN violet 0 - 0 band; d - nitrogen 2nd pos. 1 - 3 band; e - CN red 7 - 1 band.

The main results of the experimental observations are given in figures 3 - 5 with the band head intensities of some CN bands as functions of the carbon atom concentration. This parameter has been calculated from the halogenated hydrocarbon concentration estimated by ICP and from the ratio of nitrogen and admixture flows. The dependencies are presented at three different decay times and at two different wall temperatures, in accordance with the former experiments. The observations excellently correspond with each other (the experimental error of about 20% is not included in the graphs). They also correlate with the former experimental data of these systems given in Fig. 2. The other spectral bands observed (i.e. nitrogen 1st and 2nd positive and 1st negative bands) present more or less the same dependencies as in nitrogen - methane mixture and they are not presented here. These experimental results show that the kinetic processes in the nitrogen - halogenated hydrocarbons mixture are more or less the same as in the nitrogen - methane mixture that have been described recently [4].

The interesting point in these experimental observations is that at the high halogenated hydrocarbon concentration (of order of 0.1 %) the atomic spectra of a sputtered molybdenum cathode can be observed in the afterglow at the decay times higher than 100 ms. The kinetic explanation of this unexpected phenomenon will be studied in the future.

4. Conclusion

The nitrogen - halogenated hydrocarbons DC afterglow was a subject of this study in comparison with the former studies of the methane influence. The experiments have been carried out at two different wall temperatures of the reactor observation part (77 – 300 K). The band head intensities of the identified spectral bands have measured by the emission

2107
spectroscopy and some dependencies of the CN bands have been presented. The observed phenomena are in good accordance with the former results obtained for methane admixture and thus the validity of our recently proposed method for polymeric material destruction detected using nitrogen afterglow can be clearly demonstrated. From the kinetic point of view the same processes as the in nitrogen – methane mixtures play the dominant role in the afterglow kinetics. The unexpected molybdenum spectra in the afterglow will be studied in the future from the kinetic point of view.

**Figure 3:** The CN violet 1 – 1 band head intensity as a function of the carbon atom concentration in pure nitrogen at different decay times and at wall temperature. Three different Freons R12 (CHF₂Cl), R22 (CF₂Cl₂) and R134a (CF₃-CH₂F) have been used.
Figure 4: The CN violet $7-7$ band head intensity as a function of the carbon atoms concentration in pure nitrogen at different decay times and at wall temperature. Three different Freons R12 (CHF$_2$Cl), R22 (CF$_2$Cl$_2$) and R134a (CF$_3$CHF) have been used.

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References
Figure 5: The CN red $6 - 3$ band head intensity as a function of the carbon atoms concentration in pure nitrogen at different decay times and at wall temperature. Three different Freons R12 (CHF$_2$Cl), R22 (CF$_2$Cl$_2$) and R134a (CF$_3$-CH$_2$F) have been used.