Detection of NH Molecular Spectra In Expanding Thermal Plasma Jet

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Abstract: Thermal plasma jet expanding into the low pressure chamber was studied by means of OES. Addition of small amount of nitrogen into the plasma gas allows observing spectrum of molecule NH. Rotational and vibrational temperatures from NH are compared with the temperature from OH molecule. Also map of calibrated intensity of NH from the jet is presented.

Keywords: thermal plasma jet, NH molecule, rotational temperature, vibrational temperature

1. Introduction

Operating of the plasma jets at low-pressure conditions brings advantages especially from the point of view of application in deposition of different coatings. Lower amount of oxygen is appreciated because of increased quality of the deposited layer. Our previous research was devoted to study of the argon-water thermal plasma jet by optical emission spectroscopy. We aimed our effort to investigation of atomic and ionic emission lines as well as emission bands of molecule OH along the jet [1]. However the spectrum of the jet does not contain any other molecular emissions to compare with the data from OH molecule. Even in the distance further from the nozzle exit, where mixing with ambient atmosphere has to be taken into account, there were not found any other spectra of molecules with adequate intensity. This situation is different than, for instance, in the plasma jet operated at atmospheric pressure, where entrainment of the air causes presence of lines of atomic nitrogen and molecules of NH and N_2^+ in some distance downstream from the nozzle. Therefore we decided to add small amount of nitrogen into the plasma gas, which should cause the presence of nitrogen atomic lines and molecules containing nitrogen in spectrum.

NH molecule is frequently observed in different kinds of plasmas containing nitrogen and hydrogen. However, analysis of NH spectra is rarely found in literature. One of the reasons for this fact is that molecular nitrogen usually accompanies NH radical in plasmas and spectra of N_2 and N_2^+ give more straightforward information about plasma parameters. There is also principal difference between homonuclear diatomic molecules and polar molecules such as NH or OH; for the latter ones the deexcitation process is often faster than collisional excitation and therefore the association of calculated and kinetic temperatures is questionable. Modeling of spectrum of NH $A^2\Sigma^+$ - $X^2\Pi$ electronic transition is included in program SPECAIR [2] and calculation of rotational temperature from NH spectra of DC plasma jet is part of the study of Tahara et al. [3]. Laux et al. [4] used absolute intensity of NH $A^2\Sigma^+$ - $X^2\Pi$ (0,0) band to calculate LTE temperature in nitrogen arc plasma.

2. Experimental Setup

The plasma jet is generated by the plasma torch with hybrid water-argon stabilization, where the argon is supplied along the cathode and the water vortex is created around the plasma column in the second part of the arc chamber [5]. The water-cooled anode is located outside the arc chamber, while the nozzle is not used as an electrode because of very high thermal load. Schematic view of this device is shown in Fig. 1. The plasma jet is expanding into the chamber, where the pressure can be kept

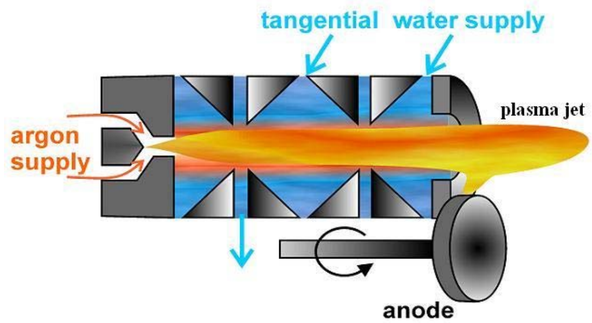

Fig. 1 Schematic view of the plasma torch with hybrid water-argon stabilization

between 1 kPa and atmospheric pressure. Commonly the plasma at the nozzle exit is composed from the atoms and ions of argon, oxygen and hydrogen and possibly some admixture of chemically active radical OH. For this experiment we added small amount of nitrogen into the plasma gas. Operating parameters were then: current 200 A, voltage 140 V, argon flow rate 10.5 slm, nitrogen flow rate 2 slm and chamber pressure 10 kPa. We decided to use this chamber pressure because of the supersonic structure of the jet, which has the best stability and visibility for these conditions. Optical emission spectroscopy diagnostics is made by means of monochromator Jobin Yvon – Spex Triax 550 equipped with gratings 300, 1200

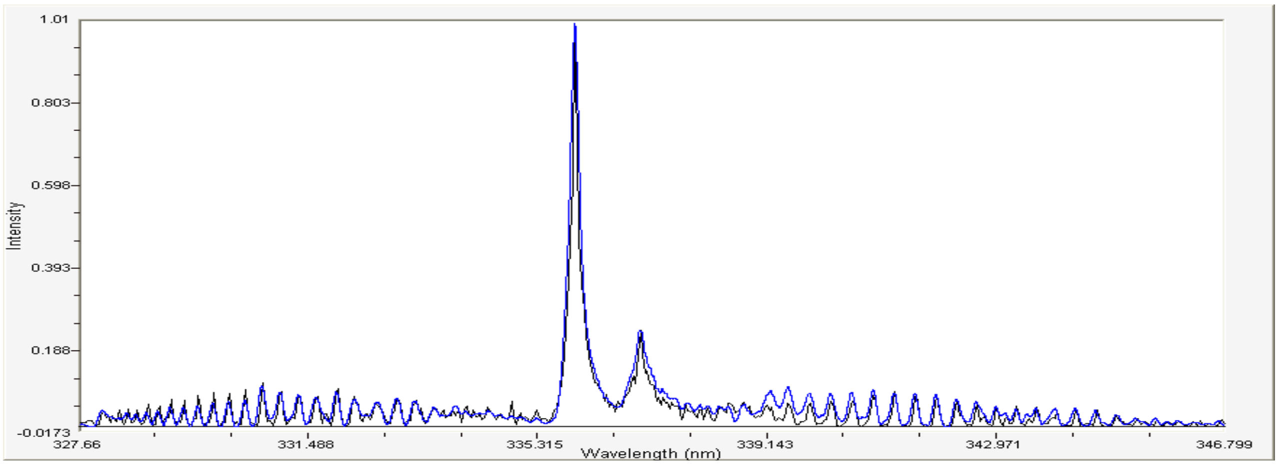

Fig. 2 Comparison of experimental (gray line) and simulated (blue line) spectra of NH in SPECAIR software

and 3600 grooves/mm. The output spectrum is detected with MTE CCD 1024x256 detector connected to the CCD 3000 controller and to the PC.

3. Results and Discussion

Admixture of nitrogen enriched the spectrum of the jet with the lines of neutral nitrogen and molecules NH and N_2^+. However, the amount of nitrogen was small and only spectrum of NH was intensive enough to be processed further. NH radical has similar characteristics as OH; both NH and OH are composed from heavy (nitrogen or oxygen) and light atom (hydrogen). They are rather different than the monoatomic molecules like N_2 for instance. NH is abundant in many types of plasma for wide range of properties and also in our plasma it was created after adding a little nitrogen.

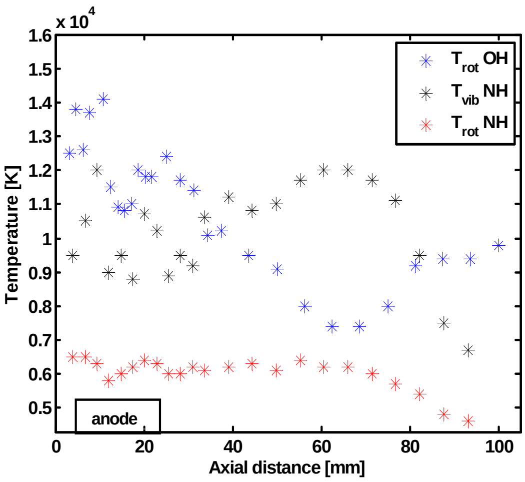

Fig. 3 Axial profile of vibrational and rotational temperatures from the spectrum of NH. Rotational temperature from OH is included for comparison

We measured radial profiles of NH spectra in different distances from the nozzle of the torch. Assuming that small amount of nitrogen do not influence the plasma properties substantially, we compared the calculated rotational temperatures with the previously studied temperatures from OH. Temperatures were calculated using the software SPECAIR [2], in which comparison of simulated and experimental spectra for various temperature distributions is possible. Fig. 2 shows an example of such comparison in graphical output. One can see well-resolved rotational lines, which allow us to determine rotational temperature with good accuracy. Spectrum is composed from several partially overlapped vibrational bands, which give possibility to evaluate also vibrational temperature.

The position of the jet axis was determined according to the position of the nozzle. However, because of asymmetrically located anode the jet is not parallel with the nozzle axis. Therefore, downstream from the nozzle the position of the jet axis was estimated from the maximum intensity of atomic and ionic lines, e.g. Balmer H_β line and several argon and oxygen lines. Fig. 3 shows values of temperatures along the jet axis. It includes vibrational and rotational temperatures from NH and rotational temperature from OH. Temperatures do not correspond to each other, which points out different way of creation of excited states of NH and of OH, and for NH it shows also difference between rotational and vibrational populations. OH radical is partly created by collisional or radiative dissociation of water and such OH can be in excited electronic state:

$$e + H_2O \rightarrow H + OH(A^2\Sigma^+) + e$$

$$H_2O + h\nu \rightarrow H + OH(A^2\Sigma^+)$$

Moreover, products of dissociation have higher rotational populations, especially for high rotational quantum num-

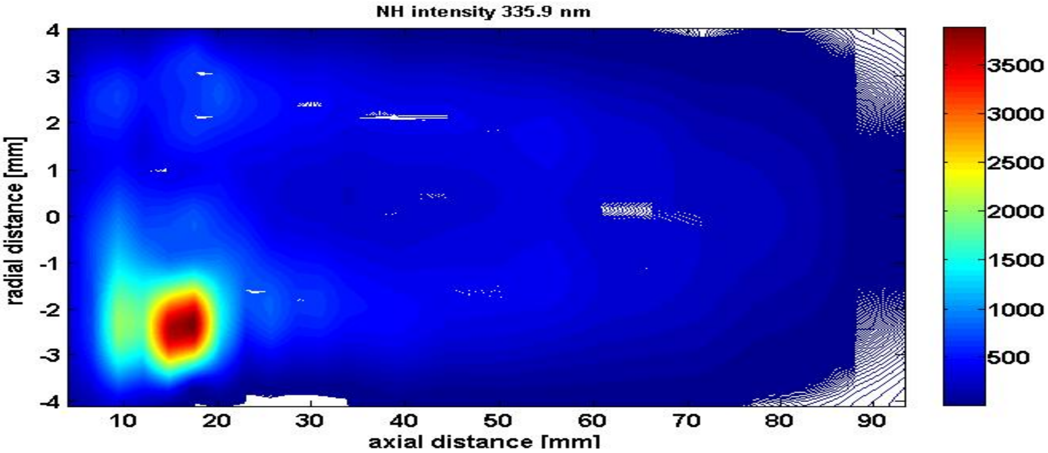

Fig. 4a Intensity of NH spectrum at 335.9 nm in the jet

bers and this effect is stronger for low vibrational quantum numbers. On the other side, nitrogen is supplied in the form of N_2 molecules and thus NH originates from the reaction of free nitrogen and hydrogen and only after it is excited by collisions. However, the time between collisions is not much shorter than the lifetime of excited state and therefore the NH rotational temperature cannot reach Boltzmann kinetic temperature. This is the reason of the difference between NH and OH rotational temperatures. It can be also seen that NH rotational temperature has almost the same value along the axis of the jet, which corresponds to the described process of NH creation, because NH rotational excitation has approximately the same efficiency for the range of conditions in the plasma jet. There are two exceptions. For the first we have the expansion region of the jet where there is lower density of the plasma and lower pressure, which corresponds to the lower efficiency of the collisional processes; consequently we can see decrease of the NH rotational temperature in the axial distance of 10 mm, where the center of the expansion region is supposed to be. Second exception occurs in the high axial distances where the plasma becomes so cold that the collisions cannot keep the temperature on the constant value. On the contrary, OH rotational temperature is more sensitive to the changes of the plasma properties, but the OH excited state is mostly the result of the dissociation of water and thus the identification with the kinetic temperature is not possible. As for vibrational excitation of NH, it is likely reached by collisional processes and thus the NH vibrational temperature might be associated with the kinetic temperature of the plasma components. We can see that in the axial positions between the nozzle and z = 30 mm the NH vibrational temperature is a little lower than OH rotational temperature. It corresponds to the supposed kinetic temperature. For further distances the non-thermal processes already play non-negligible role.

We were able to construct also the map of calibrated intensities of NH along the jet, from which it can be seen the distribution of this molecule in the jet and also the influence of the entrainment of ambient air. Resulting map is shown in Fig. 4a. Maximum intensity is concentrated in the region next to the anode. In our previous work we obtained similar result with the OH intensity, as

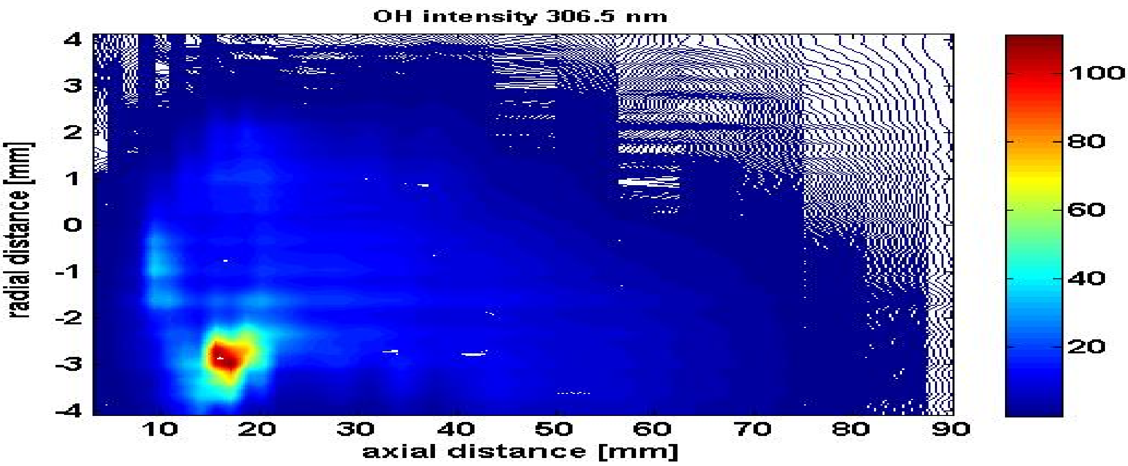

Fig. 4b Intensity of OH spectrum at 306.5 nm in the jet

it is shown in Fig. 4b. It seems that anode processes are significant for creation of these molecules. Another, but weaker, maximum is observed also in the edge of the jet opposite from the anode. In the centerline of the jet, where there is the highest temperature, the intensity of radiation from molecules is lower. For higher axial distances the intensity of NH becomes radially symmetric and centerline minimum disappears. On the other side, for OH the maximum intensity is in the jet periphery even for high axial distances. This difference can be explained by the entrainment of ambient air into the jet, which supplies more nitrogen than oxygen and this supplement is cylindrically symmetric. However, strong asymmetry of radial profiles of NH and OH intensities in the nozzle region prevents the possibility of using Abel inversion to calculate local emission coefficients of molecular spectra. Thus the temperatures are calculated from the calibrated intensities, which are composed from line of sight integrated spectra.

4. Conclusion

We made comparison of rotational and vibrational temperatures from NH and rotational temperature from OH along the jet axis. In spite OH and NH are similar molecules, their properties in our plasma are quite different, which is caused by their different origin. While OH can be created by the dissociation of water, NH has origin only in reaction of free nitrogen and hydrogen. NH would offer similar characteristics in the plasmas created by dissociation of NH_x molecules, as it is reported in [3].

Map of calibrated intensities of NH shows strong asymmetry of distribution of this molecule along the jet, especially in the nozzle region. It is in contradiction with photographs of the jet in visible light and with measurements of atomic and ionic species, which show adequate cylindrical symmetry with the maximum intensity on the jet axis.

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