

Study of the dc and 100 kHz glow discharges in acetylene-nitrogen mixture by means of optical emission spectroscopy

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Abstract. The dc and 100 kHz low pressure discharges in acetylene-nitrogen mixture have been studied here. Optical emission spectroscopy was used for identification of active plasma components and to determine plasma temperature. Relative concentrations of H, CH and CN were investigated *versus* experimental conditions by optical actinometry techniques. Emission intensities of N₂ and N₂⁺ normalized to intensity of argon line were also monitored as a function of experimental parameters. The rotational temperatures from the N₂⁺ B²Σ_u⁺-X²Σ_g⁺ (0-0) and CN B²Σ⁺-X²Σ⁺ (0-0) bands and vibrational temperatures from the CN (B²Σ⁺-X²Σ⁺) and N₂ (C³Π_u-B³Π_g) spectra were determined. Plasma processes and plasma equilibrium state were discussed.

PACS. 52.70.-m Plasma diagnostic techniques and instrumentation – 52.80.-s Electric discharges – 52.20.-j Elementary processes in plasmas

1 Introduction

Since 1989 when Liu and Cohen [1] predicted theoretically very good mechanical properties of carbon nitride, process of deposition of this material was often investigated. As a result, a variety of techniques such as plasma enhanced chemical vapor deposition (PECVD) [2,3], reactive magnetron sputtering [4], laser ablation [5], dc sputtering [6] and ion beam deposition [7] have been used for deposition of carbon nitride thin films. The carbon nitride films were mostly generated by PECVD, as this technique appeared to be very promising for obtaining crystalline carbon nitride (β-C₃N₄) [3], which could be used as a superhard coating.

In order to understand mechanism leading to the formation of carbon nitride films and to control deposition processes it is necessary to investigate the phenomena, which occur in plasma phase. The nature of the film deposited by the PECVD method strongly depends on the deposition parameters. A very important parameter is temperature. Temperature influences on physical and chemical processes. Low-pressure plasma is not in thermodynamic equilibrium state. Hence it may be defined several plasma temperatures (vibrational, rotational, kinetic, etc.). Determination of these temperatures enables investigation of energy distribution in plasma [8] and equilibrium phenomena. Consequently, determination of temperatures is important to the understanding and description of various PECVD processes. The method, which

enables study of chemical and physical processes in plasma and determination of optical temperatures is optical emission spectroscopy (OES). OES, noninvasive, simple and in situ technique, was in advance used for investigation of carbon nitride deposition processes [2,9,10]. OES has been also used for determination of rotational temperature (from spectra of CN [5,6,8,11–13], H₂ [11,15], CH [14], C₂ [5,8,12], N₂ [15], N₂⁺ [16]) and vibrational temperature (from CN [5,6,12], C₂ [12], N₂ [12,17]) in low-pressure plasmas. When the rotational distribution is equilibrated, then the rotational temperature is considered to be in a good agreement with the plasma gas (kinetic) temperature. However the information obtained by OES is not complete, because it concerns only species in excited states. Optical actinometry, proposed by Coburn and Chen [18], provides a measurement of relative concentrations of species in ground state. This technique was frequently used to study various diamond and carbon nitride deposition processes [3,9].

The acetylene-nitrogen mixture without [19] or with addition of noble gases (Ar [20], He [10]) is widely employed for production of amorphous carbon nitride layers by PECVD. However only a few papers reported study of such systems by means of OES and optical actinometry. Sung *et al.* [20] studied acetylene-nitrogen-argon microwave discharge (2.45 GHz) by means of OES and investigated changes in emission intensities of N₂, CN, CH as a function of plasma gas composition and discharge power. Durrant and co-workers investigated rf discharges in acetylene-nitrogen mixture contains helium [10,21] and oxygen with argon [3] by means of optical

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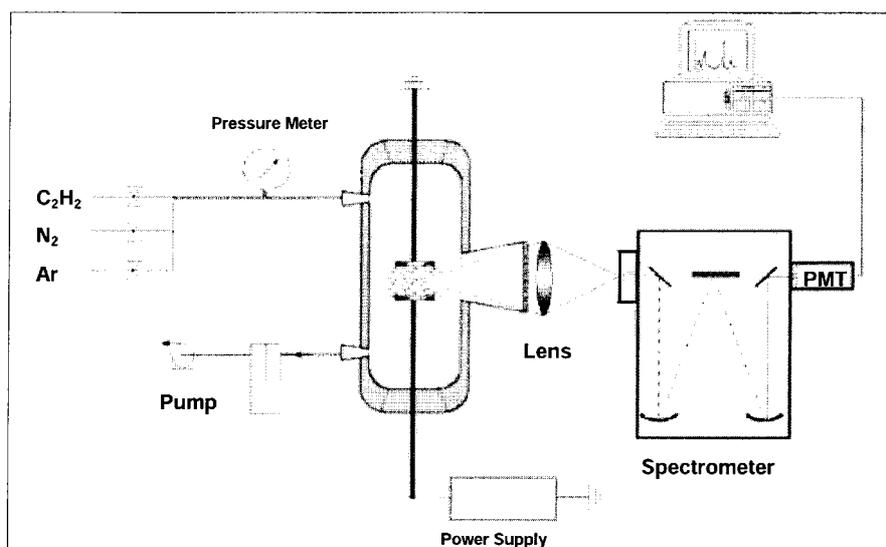


Fig. 1. The experimental set-up.

actinometry. They studied relative concentrations of CN and CH radicals as a function of gas feed composition [3, 10] and time-changes in concentrations of these species after cutoff flow of acetylene or nitrogen [21].

In the present study, optical emission spectroscopy was used for investigation of dc and 100 kHz discharges in nitrogen-acetylene mixture. Concentrations of species such as CH, H, CN in various experimental conditions were investigated by optical actinometry technique. The emission intensities of N_2 and N_2^+ normalized to intensity of argon line were also examined. The acetylene-nitrogen discharge are characterized by vibrational and rotational temperatures.

2 The experimental set-up

The experimental set-up is schematically shown in Figure 1. The plasma was generated between two circular plane steel electrodes (diameter 22 mm, thickness 2 mm, space between the electrodes 16 mm) in a circular Pyrex glass chamber. Electrodes were connected to an alternating (100 kHz) or direct current power supply. A Czerny-Tuner monochromator (Bentham M-300HR, holographic grating $1800 \text{ grooves mm}^{-1}$) with Hamamatsu DH-3 photomultiplier was used for measurements of emission intensities. The high-resolution emission spectra were measured by modified Carl Zeiss Jena PGS-2 spectrograph with electronic detection system (Hamamatsu R-928 photomultiplier) in the third and fifth orders. The UV achromatic lens ($f = 80$) was used for focusing of discharge light onto the entrance slit of the spectrometer. Variation of sensitivity of photomultiplier *versus* wavelength was taken into account and the optical system was calibrated using standard halogen lamp (Bentham). The spectra were recorded near cathode in the negative glow region (2 mm above the cathode surface). The nitrogen-acetylene mixture (3/1, 1/1 and 1/3) and pure nitrogen were employed

Table 1. Experimental conditions.

type of discharge	dc	100 kHz
max. power	160 W	200 W
voltage	500–1300 V	
range of current	60–120 mA	
range of pressure	2–4 torr (266–532 Pa)	

here. For the optical actinometry measurement a small quantity of argon ($\sim 4\%$) was added to the reactive mixture. Other experimental details are given in Table 1.

3 Results and discussion

3.1 Emission spectra of the 100 kHz and dc acetylene-nitrogen discharges

Both in dc and 100 kHz in acetylene-nitrogen plasmas many bands of N_2 (the $C^3\Pi_u-B^3\Pi_g$ system), N_2^+ (the $B^2\Sigma_u^+-X^2\Sigma_g^+$ system) and (at 742.3 and 744.1 nm) and N II (at 567.9, 500.1 and 500.5 nm) were observed. N I and N II lines in violet region were not observed. The same bands and weak lines of nitrogen were observed in pure nitrogen discharge (Fig. 2). Intensities of the N_2 bands were clearly higher in the 100 kHz discharge, than those observed in dc (Fig. 3). Additionally, in the both discharges the NH $A^3\Pi-X^3\Sigma^-$ band at 336.0 nm, partially overlapped by very intense band of N_2 (with head at 337.1 nm) and were observed. The introduction of acetylene to dc and 100 kHz nitrogen plasma caused an appearance of the most intense violet system ($B^2\Sigma^+-X^2\Sigma^+$) of cyanide radical (Figs. 2, 3) and weak bands of the red system ($A^2\Pi-X^2\Sigma$) of CN. In dc and 100 kHz acetylene-nitrogen plasma several products of acetylene dissociation: CH (the 431.4 nm band, $A^2\Delta-X^2\Pi$ system), hydrogen (the H_α at

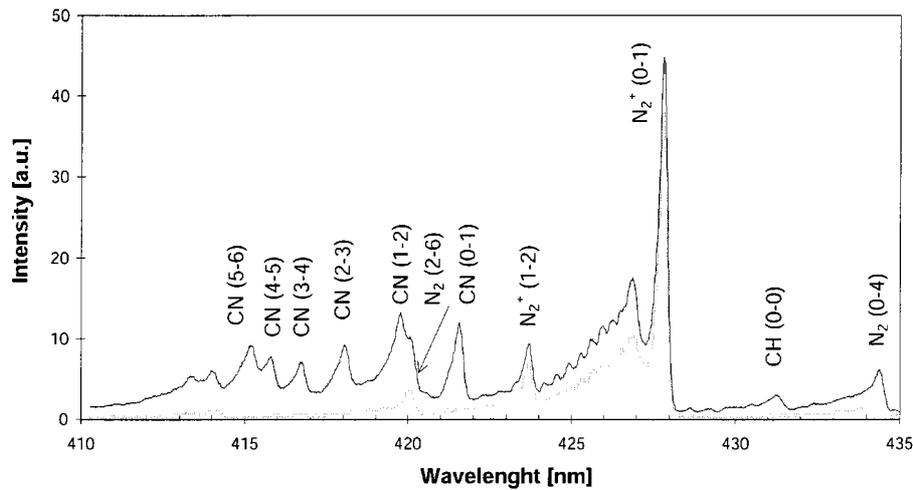


Fig. 2. Comparison of the emission spectra for acetylene-nitrogen (solid line) and nitrogen (dotted line) in 100 kHz discharges.

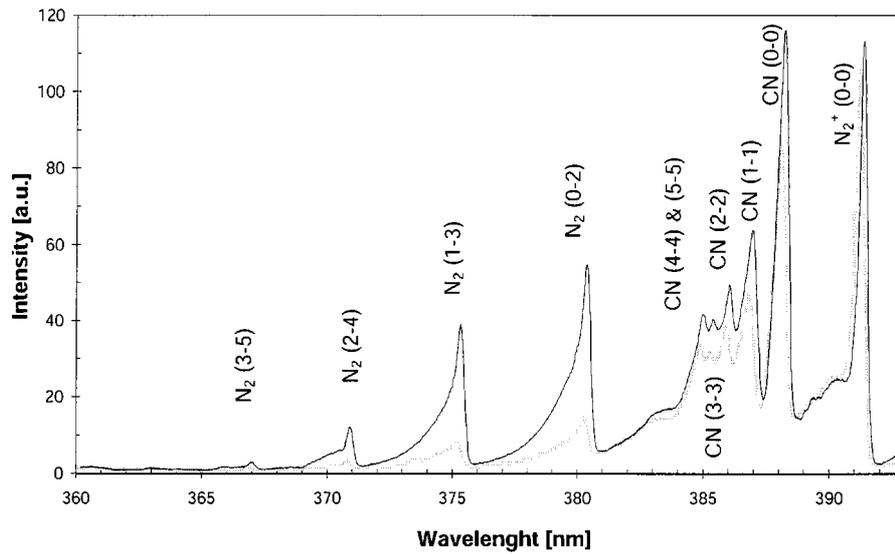


Fig. 3. Emission spectra of the dc (dotted line) and 100 kHz (solid line) discharges ($N_2/C_2H_2 = 3/1$, 100 mA, 4 torr).

656.28 nm and H_β at 486.13 nm lines) and carbon (C I at 247.86 nm) were also identified. These lines and bands were of low intensity, however a rise of their intensities with increase of acetylene in the mixture was observed. Only in the 100 kHz discharge in the mixture containing 75% acetylene ($N_2/C_2H_2 = 1/3$), a very weak spectrum of C_2 , *i.e.* the (0-0) band at 516.52 nm belonging to the $A^3\Pi_g-X'^3\Pi_g$ system was observed here. Strong spectrum of C_2 was identified by Zhou *et al.* [22] in study of methane-nitrogen microwave plasma.

3.2 Optical actinometry

Optical actinometry is based on introduction of inert tracer gas so-called-actinometer to discharge zone and investigation of emission intensity which comes from the

actinometer and unknown species. Actinometry assumes that the excited state of species is attained by electron impact. When threshold energy and electron impact cross-section of actinometer (Act) are similar to those of the unknown species (X), then the relative concentration of species in the ground state (n_x) is proportional to the ratio of the emission intensity of the species (I_x) to the emission intensity of actinometer (I_{Act}), providing, that concentration of the actinometer is constant or well known [3, 18]:

$$n_x \propto \frac{I_x}{I_{Act}}. \quad (1)$$

Noble gases are usually used as actinometer (*e.g.* Ar, He), because they are chemically neutral. Among

Table 2. Spectroscopic data of species.

Species	Wavelength [nm]	Transition	Threshold energy [eV]
H α	656.3	$3d^2D_{3/2}-2p^2P_{3/2}^0$	12.1
CH	431.4	$A^2\Delta-X^2\Pi$ (0-0)	$2.9^1; \approx 11^2$
CN	388.43	$B^2\Sigma-X^2\Sigma$ (0-0)	3.2^1
N ₂	380.49	$C^3\Pi_u-B^3\Pi_g$ (0-2)	11.2^1
N ₂ ⁺	391.44	$B^2\Sigma_u^+-X^2\Sigma_g^+$ (0-0)	18.7^1
Ar	750.3	$2p_1 - 1s_2^3$,	13.5

¹ Energy of the upper electronic state.

² Value reported in [3,10].

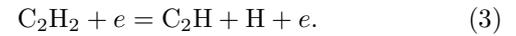
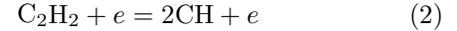
³ Paschen notation.

different gases available for optical actinometry, argon is the most popular. The threshold energy of argon $E_{th} \sim 13$ eV is quite close to the energy of the several species in their upper states *e.g.* H 12 eV, N₂ 12 eV [3].

For investigation of phenomena, which occur in plasma phase relative concentrations of CN, CH and H were determined. These species may play important role in processes of the formation and deposition of carbon nitride layer. For measurements of changes in the CN, CH and H relative concentrations equation (1) was used. Additionally, emission intensities of the N₂ and N₂⁺ headbands, normalized to the emission intensity of argon line, were also investigated as function of discharge parameters. As actinometer the Ar I 750.3 nm line was chosen. Table 2 lists main spectroscopic constants of examined species, such as wavelengths of lines and bands measured transitions and respective threshold energies. The threshold energy of CH is equal to 2.9 eV, but considering some mechanisms of formation of the CH species the value of ≈ 11 eV for CH has been reported in [3,10]. As can be seen in Table 2 the threshold energy of argon is close to the threshold energies of H and N₂ and it differs from the excitation energy of CN and CH. However, for the CH and CN species their ratio intensities to the intensity of argon has been considered as a good representation of the evolution of their relative concentration [3,9]. Therefore as it was performed by Durrant *et al.* [3,10,21] and Chanti *et al.* [9] we also used optical actinometry technique for investigation of the CN and CH relative concentration.

Changes in relative concentrations of the CH and H species as a function of discharge current at 2 and 4 torr are presented in Figure 4. At pressure of 4 torr the growth of current caused increase in concentration of H, CH both in the 100 kHz and dc discharges. For 100 kHz changes in concentration of H were more significant than those observed for CH. This effect was not noticed for the dc discharge, where the CH and H concentrations changed similarly with current. At pressure of 2 torr changes in the concentrations of H and CH with current are insignificant. Among different reactions leading to production of the CH and H species in plasma, dissociation of acetylene by

electron impact seems to be the most important:



The CH radical may also come from dissociation acetylene by high-excited states of nitrogen [10].

Both in the dc and 100 kHz discharges the concentration of CH radicals increased with pressure. This same effect was observed for H atoms, but only in the 100 kHz discharge. Relations between the CN concentration and current are presented in Figure 5. At pressure of 4 torr the increase of current caused a rise of the CN concentration both in the 100 kHz and dc discharges. A similar result was obtained at 2 torr in 100 kHz plasma. For the dc discharge at 2 torr a maximum in concentration of CN for current of 80 mA was observed. Emission intensities of N₂ and N₂⁺ (normalized to argon line) *versus* current for 2 and 4 torr were presented in Figure 5. Only the ratio of $I(N_2^+)/I(Ar)$ increased with discharge current both in dc and 100 kHz discharges. For the 100 kHz discharge the change of pressure from 2 to 4 torr led to the growth of the $I(N_2)/I(Ar)$ and $I(N_2^+)/I(Ar)$ ratios, while for the dc discharge the $I(N_2^+)/I(Ar)$ ratio decreased with pressure.

Concentrations of CN, H, N₂ and CH species *versus* gas composition are shown in Figure 6. In 100 kHz, the concentration of the CN molecule increased with content of nitrogen in mixture. In the case of the dc discharge the generation of CN is predominated for the N₂/C₂H₂ = 1/1 mixture. Both in the dc and 100 kHz discharges the CH and H concentrations depended on the gas mixture composition and decreased with nitrogen concentration. However, for the dc discharge, changes in concentration of H and CH were not meaningful. The ratio of $I(N_2)/I(Ar)$ and $I(N_2^+)/I(Ar)$ increased with nitrogen concentration in the mixture for 100 kHz discharge (Fig. 6). In the dc discharge such an effect was noticed only for the $I(N_2^+)/I(Ar)$ ratio. Analysis of the $I(N_2^+)/[I(N_2^+) + I(N_2)]$ ratio for dc and 100 kHz discharges suggests the ionization degree of molecular nitrogen increases *versus* percentage of nitrogen in dc and decreased in 100 kHz. Therefore the ratio of the $I(N_2)/I(Ar)$ with nitrogen concentration is different for dc and 100 kHz as is shown in Figure 6. The same behavior of CN and N₂ (Fig. 6) indicated that the nitrogen molecules play an essential role in the formation mechanism of CN.

The lower concentrations of CH and H species in the 100 kHz plasma than in the dc plasma may indicate that in the first case the dissociation degree of acetylene is lower and/or products of fragmentation or polymerization acetylene more efficiently react with nitrogen. Consequently, there may be formed various polyatomic organic species. Fuji [23] reported that in acetylene-nitrogen plasma: nitriles (R-CN), amines (R-NH₂) and hydrazines (R-N=NH) were produced. These species were impossible to identify by the OES method. Both in dc and 100 kHz, brown solids were observed here on cold walls of the glass chamber. Acetylene (or other hydrocarbons) could react easily and quickly with active nitrogen. As a result of that

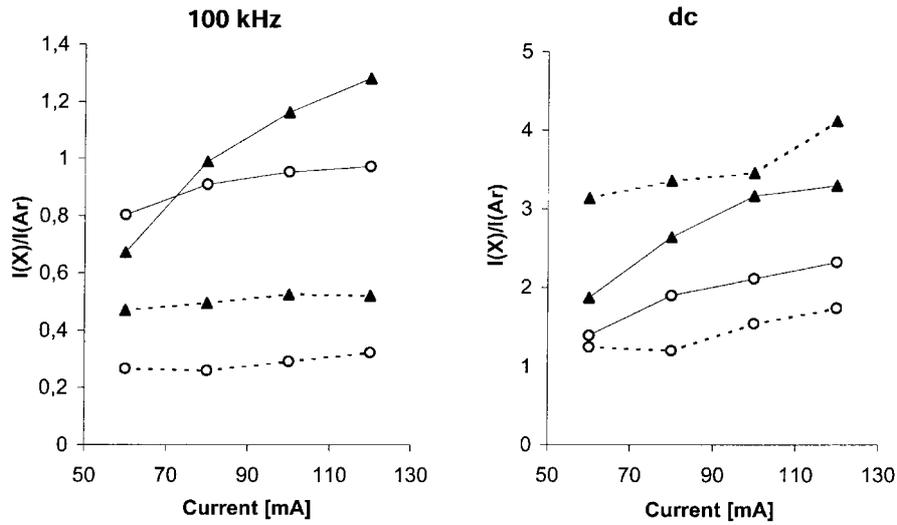


Fig. 4. Relative concentration of species *versus* current ($X = \text{CH}$ ○, H ▲) for pressures 2 torr (dashed line) and 4 torr (solid line) in the $\text{N}_2/\text{C}_2\text{H}_2 = 1/1$ mixture.

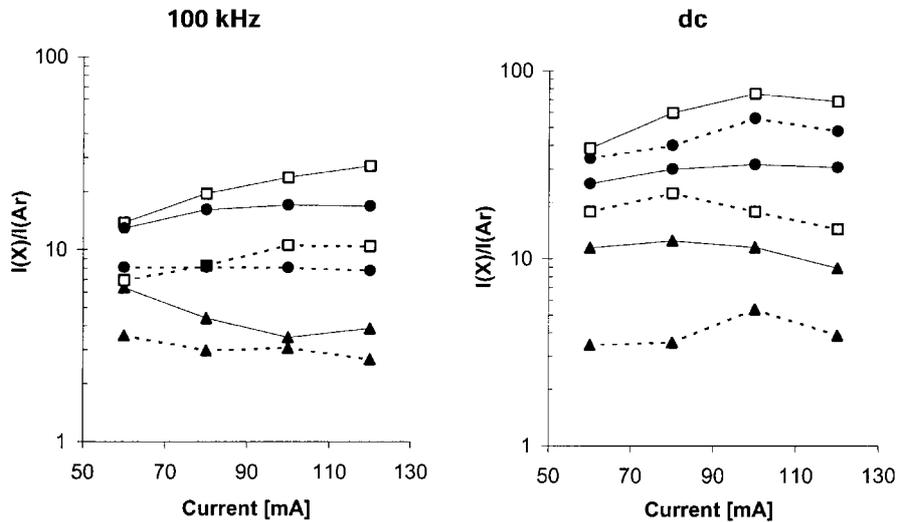
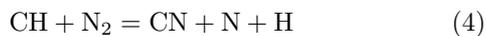


Fig. 5. The changes of $I(\text{N}_2)/I(\text{Ar})$ ▲, $I(\text{CN})/I(\text{Ar})$ □ and $I(\text{N}_2^+)/I(\text{Ar})$ ● as a function of current at 2 torr (dashed line) and 4 torr (solid line) for $\text{N}_2/\text{C}_2\text{H}_2 = 1/1$.

cyanide radical (CN) was produced. The CN molecules may originate from the reactions [2, 21]:



Some authors [13, 24] have stated that the mechanisms leading to the formation of CN in acetylene-nitrogen mixtures are extremely complex.

3.3 Measurements of the vibrational and rotational temperatures

In order to characterize the acetylene-nitrogen plasma the rotational and vibrational temperatures have been determined here. The N_2^+ $\text{B}^2\Sigma_u^+ - \text{X}^2\Sigma_g^+$ (0-0) and CN $\text{B}^2\Sigma^+$ -

$\text{X}^2\Sigma^+$ (0-0) bands were used for measurements of the rotational temperature. These molecular bands were well developed and the most intensive. For the $^2\Sigma - ^2\Sigma$ transition ($\Lambda = 0$) the emission intensity of rotational line may be written in the form [25]:

$$I_{K'K''} \propto C\nu^4(K' + K'' + 1) \exp\left(\frac{-F'(K')}{kT_{\text{rot}}}\right) \quad (6)$$

where: $I_{K'K''}$, the line intensity; K' and K'' , quantum rotational numbers; ν , transition frequency; $F'(K')$, rotational energy of the upper state; T_{rot} , rotational temperature; C , constant.

A plot of $\ln(I/(K' + K'' + 1))$ as a function of $F'(K')$ yields a straight line with a slope equal to $-1/kT_{\text{rot}}$ [25]. Rotational temperature of N_2^+ was determined using lines of the R-branch. Rotational lines of the P-branch were employed for measurements of the CN temperature. Partial

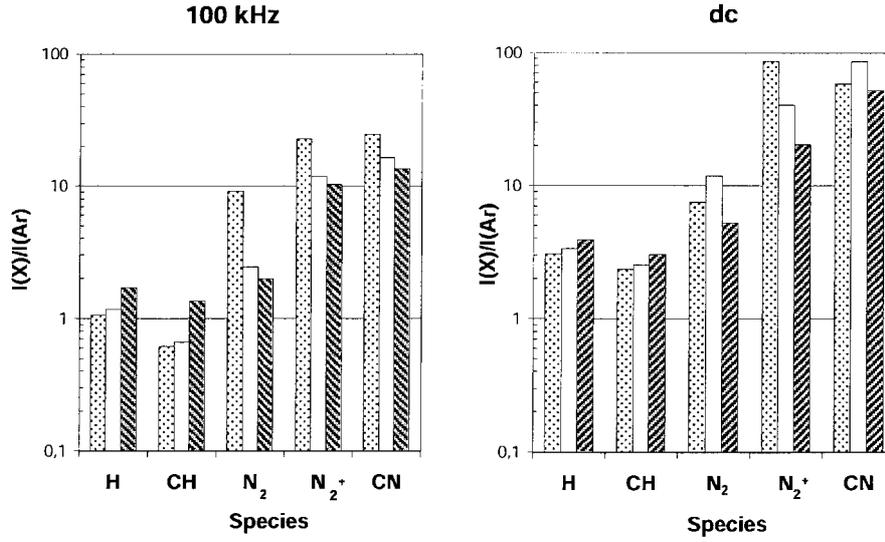


Fig. 6. Intensity ratio for different species at various concentration of nitrogen (\square 75%, \square 50%, \square 25%).

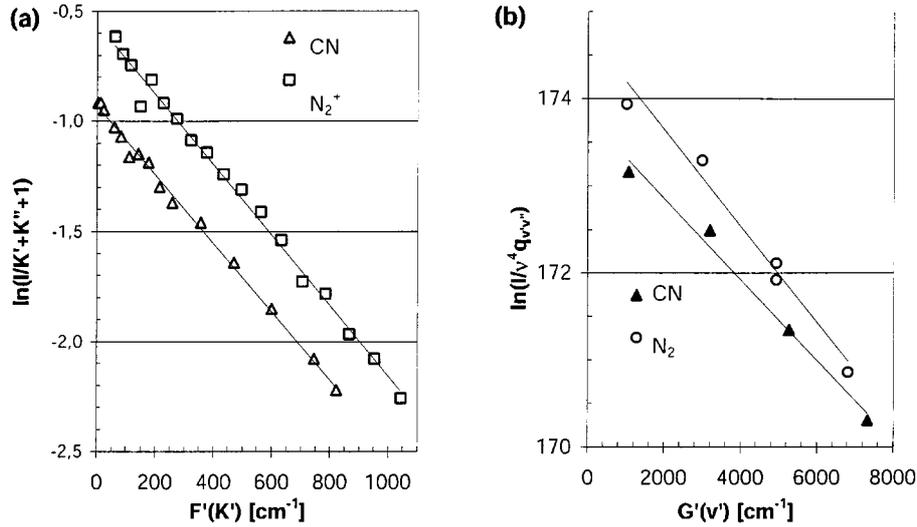


Fig. 7. (a) Vibrational and (b) rotational Boltzmann plots.

overlapping of rotational P-lines of CN were been taken into account.

The molecular constants of the N_2^+ and CN molecules were taken from Huber and Herzberg [26]. The Boltzmann plots for the N_2^+ and CN rotational lines are presented in Figure 7a. The rotational distributions are well described by the Boltzmann law.

The vibrational temperatures (T_{vib}) were calculated using the CN $B^2\Sigma^+-X^2\Sigma^+$ ($\Delta v = 0$) and N_2 $C^3\Pi_u-B^3\Pi_g$ ($\Delta v = -2, +1$) bands with the aid of equation [25]:

$$\ln\left(\frac{I_{v'v''}}{q_{v'v''}\nu_{v'v''}^A}\right) = C_1 - \frac{G'(v')}{kT_{\text{vib}}} \quad (7)$$

where: $I_{v'v''}$, emission intensity of vibrational band (measured here as the bandhead intensity); v' and v'' , vibrational quantum numbers; $G(v')$, energy of the upper

vibrational level; $q_{v'v''}$, Franck-Condon factor; $\nu_{v'v''}$, transition frequency; k , Boltzmann constant; C_1 , constant.

The N_2 and CN bands and their spectroscopic constants used for calculation of the vibrational temperatures are given in Table 3. The background corrections for CN bands partially overlapped were carried out. The Boltzmann plots for the CN and N_2 vibrational levels are shown in Figure 7b. The standard deviation uncertainties for the rotational and vibrational temperatures were 2–7% and 10–15% respectively.

Changes of the rotational and vibrational temperatures *versus* current, plasma gas composition and pressure were investigated. For $N_2/C_2H_2 = 3/1$ the relations between the temperature and current are shown in Figure 8. In the 100 kHz discharge increase of current caused rise of the rotational temperature of N_2^+ and CN from 750 to 900 K and not significant changes in vibrational temperatures of N_2 and CN. In

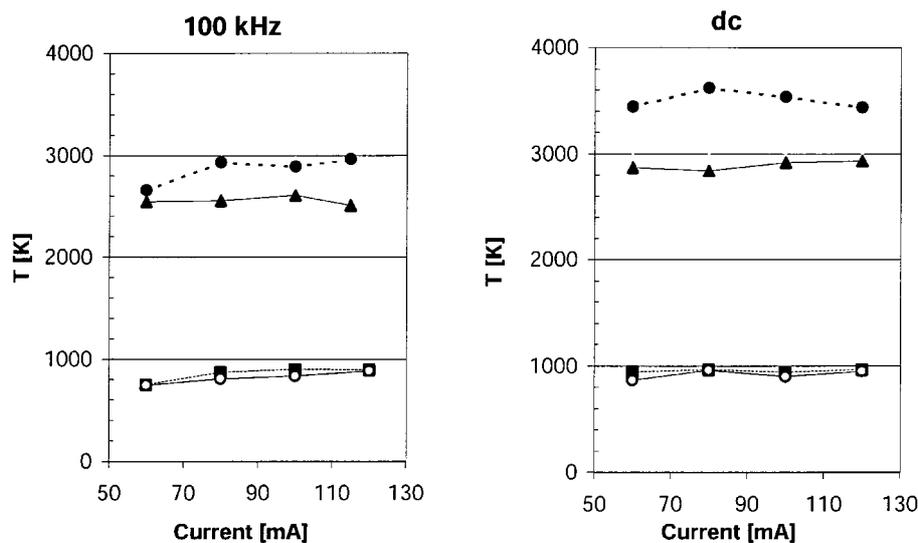


Fig. 8. The vibrational temperatures (CN ●, N₂ ▲) and the rotational temperatures (N₂⁺ ■, CN ○) versus current for N₂/C₂H₂ = 3/1 mixture.

Table 3. Molecular constants of N₂ [26,27] and CN [26,28] used for determination of the vibrational temperatures.

Species	Band	$q_{v'v''}$	$G'(v')$ [cm ⁻¹]	$\nu_{v'v''}$ [cm ⁻¹]
N ₂ (C ³ Π _u -B ³ Π _g)	0-2	0.169	1016.5	26943
	1-3	0.202	3006.7	26630
	2-4	0.145	4940.1	26289
	1-0	0.388	3006.7	31661
	2-1	0.335	4940.1	31889
	3-2	0.204	6816.6	32089
CN (B ² Σ ⁺ -X ² Σ ⁺)	0-0	0.9193	1077.0	25798
	1-1	0.7776	3200.6	25879
	2-2	0.6656	5283.8	25946
	3-3	0.5803	7326.4	25999

case of the dc discharge, there were not observed relations between the rotational and vibrational temperatures and current. The N₂⁺, CN rotational temperatures and the N₂, CN vibrational temperatures versus nitrogen percentage in the working gas are presented in Figure 9. The rotational temperatures of N₂⁺ and CN were not very sensitive for changes of the plasma gas composition. The highest rotational temperature of N₂⁺ was in pure nitrogen in dc while in 100 kHz the temperature was the lowest. Decrease of the nitrogen contribution in the gas mixture led to growth of the CN rotational temperature in 100 kHz and dc from 900 K to 1050 K and from 900 K to 940 K respectively. The vibrational temperature of CN strongly depended on the content of acetylene in the both discharges as can be seen from Figure 9, while in practice the vibrational temperature of N₂ was slightly related to plasma gas composition. Differences between the CN and N₂ vibrational temperatures were clearly observed. The

differences depended on plasma gas composition and were the greatest for the N₂/C₂H₂ = 1/3 mixture. The rotational temperatures determined from the CN (0-0) and N₂⁺ (0-0) bands were consistent for the N₂/C₂H₂ = 3/1 and 1/1 mixtures. The significant difference between the CN and N₂⁺ rotational temperatures were observed only for N₂/C₂H₂ = 1/3.

In the 100 kHz discharge the vibrational temperatures of CN and N₂ at pressure of 2 torr and 4 torr were similar as can be seen in Figure 10. The rotational temperatures of CN and N₂⁺ were sensitive on pressure changes as it was shown in Figure 10. Similar relations between the vibration and rotational temperatures and pressure were found in the dc plasma.

The vibrational temperatures of CN and N₂ in the dc and 100 kHz discharges measured here were in the range 2900–4300 K and 2500–2900 K, respectively. The rotational temperatures varied from 600–1050 K. The great differences between the rotational and vibrational temperatures indicate that the dc and 100 kHz plasma were not in equilibrium state. The largest “degree of non-equilibrium” was noticed for N₂/C₂H₂ = 1/3 mixture both in dc and 100 kHz. The differences between vibrational temperatures and as well as between rotational temperatures of CN and N₂⁺ were the largest in this mixture.

4 Conclusions

The dc and 100 kHz discharges in the acetylene-nitrogen mixture have been investigated here by optical emission spectroscopy and compared. The same active species were identified in the both discharges and the most intensive spectra were emitted by the N₂, N₂⁺ and CN molecules. However, the intensities of the N₂ and CN spectra of the 100 kHz plasma were considerably higher than those excited in the dc plasma. It was observed that fragmentation

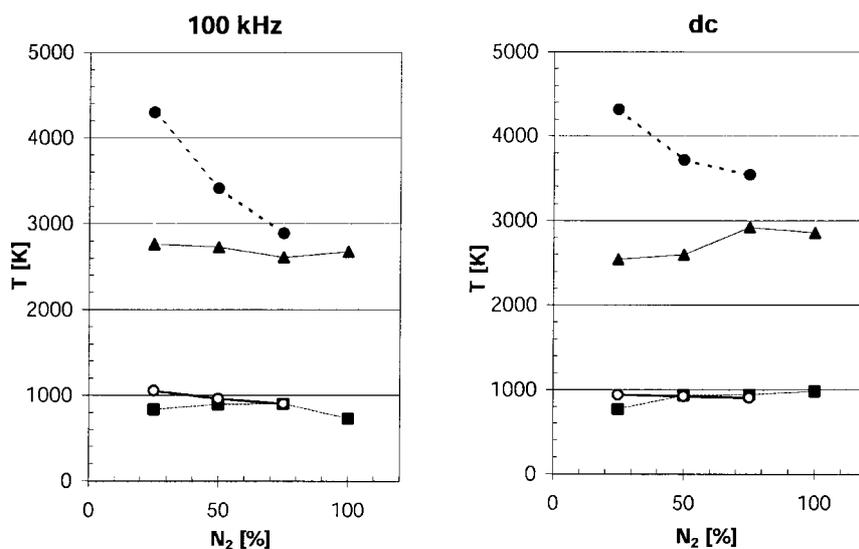


Fig. 9. Variations of the vibrational temperatures (\bullet CN, \blacktriangle N_2) and rotational temperatures (\blacksquare N_2^+ , \circ CN) versus gas composition (100 mA, $p = 4$ torr).

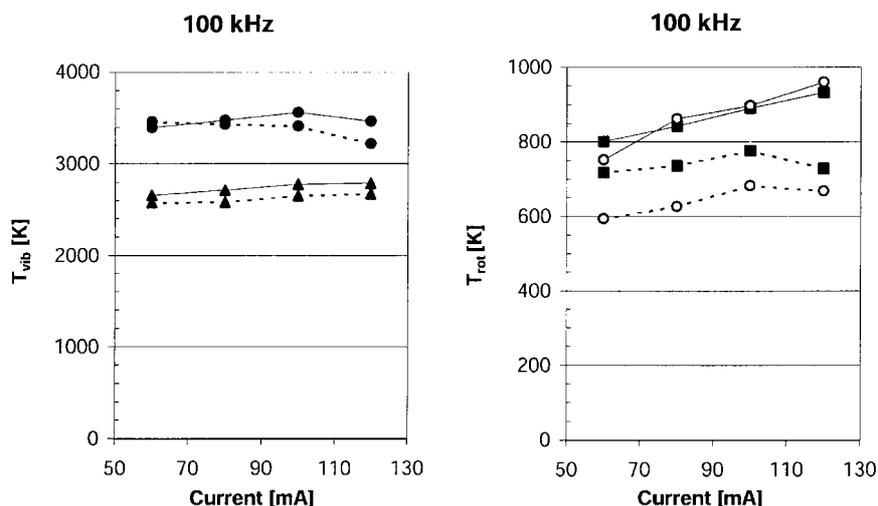


Fig. 10. The vibrational temperature (N_2 \blacktriangle , CN \bullet) and rotational temperature (N_2^+ \blacksquare , CN \circ) versus current - 2 torr (dashed line), 4 torr (solid line) in the $N_2/C_2H_2 = 1/1$ mixture.

of acetylene was higher in the dc discharge. Relative concentration of H and CN at pressure of 4 torr were the most significantly dependent on current while for at other species and other conditions the relations between the concentration and current were not so meaningful. Pressure was important parameter affecting plasma processes and concentration of plasma components.

The rotational temperatures determined from the CN $B^2\Sigma^+-X^2\Sigma^+$ (0-0) and $N_2^+ B^2\Sigma_u^+-X^2\Sigma_g^+$ (0-0) bands have been quite well consistent. Values of these temperatures are comparable to the plasma gas temperature *i.e.* kinetic temperature. The vibrational temperatures are dependent on experimental conditions and different for the N_2 and CN species. The vibrational temperatures are considerably higher than the rotational temperatures. The plasma generated in acetylene-nitrogen mixture by means of the dc and 100 kHz discharges is far from equilibrium state.

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