MONITORING THE EVOLUTION OF THE $^3P_2$ NEON METASTABLE LEVEL DENSITY IN TEMPORAL AFTERGLOW PLASMA BY ABSORPTION SPECTROSCOPY USING A PULSED HOLLOW CATHODE SPECTRAL SOURCE

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The temporal evolution of the $^3P_2$ Neon metastable level density during the afterglow plasma of a high current pulsed hollow cathode discharge has been determined by an absorption spectroscopy technique using a pulsed hollow cathode spectral source. The measured values of the Neon 2^3P_2 state density in the 5–60 μs temporal afterglow range are found to vary from $3 \times 10^{12} \pm 20\%$ cm^{-3} to $1.7 \times 10^{11} \pm 20\%$ cm^{-3} following an exponential decay curve. The absorption measurements have been performed on the $^3P_2 - 2p^4$ Neon transition at 633.4 nm. It was shown that using a pulsed spectral source with variable line emission broadening the best absorption sensibility was obtained when the line broadening of the spectral source is closed to the broadening of the emission line of absorbing species from the temporal afterglow plasma.

Key words: absorption spectroscopy, metastable atoms, pulsed discharge

1. INTRODUCTION

In this paper an absorption spectroscopy technique for the diagnostics of the temporal afterglow plasma of high current pulsed discharge [1, 2] has been developed using a pulsed spectral source with variable line emission broadening [3, 4].

The study of the temporal afterglow plasma of a pulsed gas discharge is of great scientific interest, because after switching off the electromagnetic field, various relaxation phenomena governed by collisions, radiation, recombination, etc. proceed during the spatial or temporal decaying plasma, being unobserved in the active phase. Temporal afterglow plasmas are used successfully for measurements of the rate coefficients of elementary processes and effective lifetimes of various excited states [5, 6].

Depending on the gas composition, superelastic collisions may continue to sustain the plasma in the afterglow for a while by releasing the energy stored in metastable atoms and molecules. Excited metastable atoms play a key role in plasma ionization and sustainment mechanisms. The excitation energy of noble gases metastable states is significantly lower than their ionization energy. Consequently, during the pulse current, noble gas metastable atoms are produced by electron impact excitation from the ground state and loosed by electron impact quenching, quenching by collision with noble gas neutral atoms and by diffusion to the walls. In the analytical systems like pulsed *Glow Discharge Mass Spectrometry* (GDMS) or pulsed *Glow Discharge Optical Emission Spectroscopy* (GDOES) noble gas metastable atoms are produced more efficiently and can act as an important energy reservoir for subsequent Penning ionization of analyts, gas impurities or minority admixtures.

The current article presents the determination of the temporal evolution of the density of Neon metastable atoms in a temporal afterglow of a high current pulsed discharge (HCPD) by optical absorption spectroscopy using a high voltage pulsed hollow cathode spectral lamp (HVPSL) with intense atomic and ionic emission lines and controllable spectral line profile [3, 4]. The experimental set-up is featured with an original time synchronized system. Until now, the reported data on the density of metastable atoms existing in different configurations of pulsed discharges have been obtained using laser absorption or laser induced fluorescence techniques [7–9] only.

The temporal evolution of metastable atoms density in the temporal afterglow plasma, achieved in this work, is useful in transient plasmas processing [10, 11] and especially in analytical investigations with systems like GDOES, GDMS [12–18] and Direct Analysis in Real Time Mass Spectrometry (DARTMS) [19, 20], in which the energy transfers of the metastable atoms, are central for the excitation and ionization of the analyte species.

2. EXPERIMENTAL AND THEORETICAL METHODS

The experimental set up is presented in Figure 1.

The spectral source is a high voltage pulsed hollow cathode spectral lamp (HVPSL) consisting of a glass chamber which contains a titanium cylindrical hollow cathode (15 mm length and 3 mm diameter) and a stainless steel wire anode. A HV pulser is used to generate high current pulses in Neon at 5 torr pressure. The peak current is about 10-30 A with a duration of 150 ns (half-width) and repetition rate of 30 Hz. This high density pulsed plasma provides plenty of excited atoms and ions of neon which emit intense atomic and ionic spectral lines.

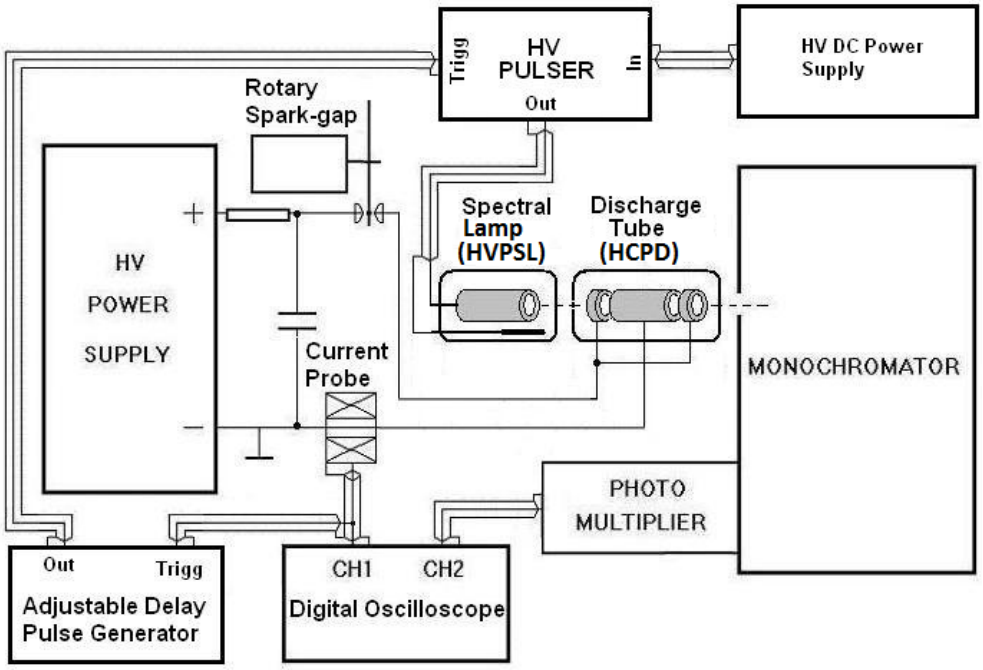

Fig. 1 – Experimental set-up for optical absorption measurements with temporal resolution using a pulsed hollow cathode spectral source.

The line profile of the HVPSL is of Doppler type and its broadening $\Delta\vartheta_D$ was determined by the absorption spectroscopy method presented in [4]. In short, we used the absorption measurements performed with a spectral source with a known line profile, namely a diode laser tuned to the $^3P_2 - 2p^4$ Neon transition at 633.4 nm, to determine the unknown line profile emitted by our spectral lamp HVPSL, presented above. The absorption measurements were performed with each of the two spectral sources on a same absorbing system with exactly the same parameters: Ne metastable atoms excited on $^3P_2$ energy level produced in a hollow cathode dc discharge. The measured absorption parameters were compared as explained below.

We started from Mitchell and Zemanski [21] absorption formula

$$A = \sum_{m=1}^{\infty} \frac{(-1)^{m+1}(k_0 L)^m}{m!\sqrt{1+m\alpha^2}} = \frac{k_0 L}{\sqrt{1+\alpha^2}} - \frac{(k_0 L)^2}{2!\sqrt{1+2\alpha^2}} + \ldots, \tag{1}$$

where k_0 is the maximum absorption coefficient defined as $k_0 = \frac{2}{\Delta\vartheta_D}\sqrt{\frac{\ln 2}{\pi}}\frac{\pi e^2}{mc}Nf$, with $\Delta\vartheta_D$ the Doppler species line broadening, e and

m are the electron charge and mass, *c* the light velocity, *f* is the oscillator strength of the transition of the spectral line, *L* is the optical length and

$$\alpha = \frac{Broadening\ \ of\ \ spectral\ \ source\ \ line}{Doppler\ \ line\ \ broadening\ \ \ of\ \ absorbing\ \ species}. \tag{2}$$

Thus, we find the roots for the scenarios

$$\text{I. } f(x) = \sum_{m=1}^{\infty} \frac{(-1)^{m+1} x^m}{m!\sqrt{1+m\alpha^2}} - A = 0, \quad \text{with } x = (k_0 L),$$

using the experimental absorption data obtained with the diode laser tuned on 633.4 nm as spectral source.
With the previously obtained k_0L value we started to find the roots of the second scenario

$$\text{II. } f(x) = \sum_{m=1}^{\infty} \frac{(-1)^{m+1} (k_0 L)^m}{m!\sqrt{1+mx^2}} - A = 0, \text{ with } x = \alpha,$$

using the measured absorptions *A* recorded with the pulsed spectral lamp HVPSL on the same absorbing system, *i.e.* the Neon metastable atoms produced in a hollow cathode dc discharge.

The derivative of *f(x)* can be defined analytically (*i.e.*, *f(x)* is differentiable on our interval of interest and with values in the real numbers); therefore, for both cases we have used a New-Raphson method with derivative to find the roots. Because the global convergence properties of this algorithm are known to be poor, we have used a combination of bisection and Newton-Raphson methods. Calculations have been performed for any *m* in a few numbers of iterations and with very high accuracy. This procedure allowed us to determine the line profile of the high voltage pulsed spectral lamp (HVPSL) at different peak currents, as presented in Table 1. As the line profile is Doppler type we were able to calculate the gas temperature of the pulsed lamp (HVPSL) for different peak currents [5]. The results are also presented in Table 1.

Table 1

The Doppler line broadening of the Neon at 633.4 nm emitted by the high voltage pulsed spectral lamp HVPSL and the corresponding gas temperature of the discharge at different working peak current values

Peak current of the pulsed source <A>	$\Delta\lambda_D$ *10^{-3} <nm>	T_{gas} of the pulsed source <K>
16	4.70	2154
20	5.37	2808
26	6.21	3759

In our experiment we have monitored the evolution of the neon metastable atoms density existing in the temporal afterglow plasma of a high current pulsed hollow cathode discharge tube HCPD. The discharge tube consists of a cylindrical hollow cathode of Titanium (20 mm length and 4 mm diameter) and two stainless steel anode rings (4 mm internal diameter) placed symmetrically at the two ends of the cathode. It operates at a pressure of 5 torr neon, 60 A peak current and 5 kV voltages applied by using a rotary spark-gap [22]. High current pulses of short duration in the hollow cathode discharge tube were obtained by repetitive discharges (at frequency of 30 Hz) of a storage capacitor C through a rotary spark gap with a commutation time below 10 ns. The geometrical configuration of the discharge tube [23] provides a good stability of the pulsed discharge. The high current pulsed discharge is followed by a long afterglow plasma (> 100 μs) sustained by the large amount of metastable atoms produced during the current pulse. The spectral profile of the light emitted by the species existing in the discharge tube during the temporal afterglow plasma is of Doppler type. The gas temperature of this plasma was deduced by processing the signals of shock waves produced in the high voltage discharges. These shock waves were observed in the temporal afterglow of the emission spectral lines [24]. Figure 2 resumes the procedure used in Ref. [24] to determine the frequency of the shock waves in the afterglow plasma of the hollow cathode pulsed discharge (60 A peak current at 5 kV applied voltage), 5 torr Neon and 10^{-2} torr Hydrogen. The observed acoustic modulation of the hydrogen H_α Balmer line (the black line in Figure 2a) has been processed by a mathematical treatment. Undulations were revealed when the light signal was fitted by a 9-th order polynomial (red curve in Figure 2a) and extracted from the experimental signal (curve from the bottom of Figure 2b). From the Fourier spectrum of these oscillations (curve from the top of Figure 2b) we have determined the frequency of the shock waves in the discharge tube during the afterglow. Its value is 78 kHz.

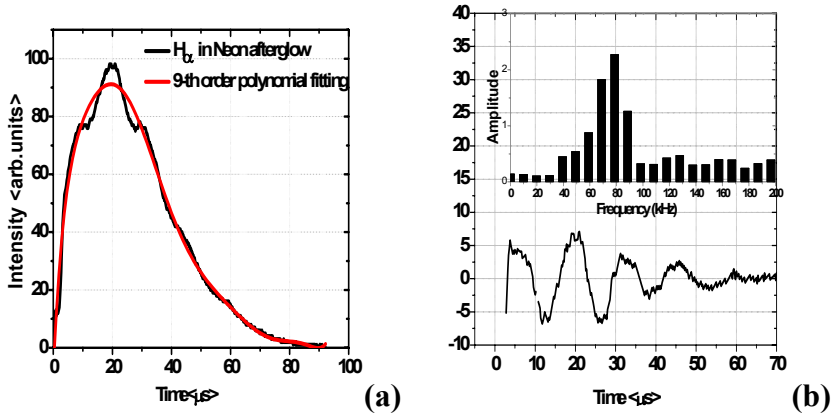

Fig. 2 – (a) The modulations of the H_α line of hydrogen in the neon and the fitted curve, (b) the clean oscillations, and the Fourier spectrum of the oscillations.

The gas temperature was evaluated using the Rayleigh formula for the sound velocity for isotropic linear media: $\upsilon_S = 2\pi\nu_s / k_s = (\gamma kT/m)^{1/2}$ where ν_s. and k_s are the frequency and the corresponding wave number of the sound, $\gamma = c_p / c_v$ is the ratio of specific heats, k stands for the Boltzmann constant, T is the gas temperature, and m is the mass of the gas atom. Thus, the calculated gas temperature for the afterglow plasma in the discharge tube is T_s = 2100 K. In this case, the line broadening is 4.6 10^{-3} nm.

As it can be seen in the Fig. 1, the spectral lamp is aligned optically with the hollow cathode pulsed discharge tube**.** In this way, both, the light emitted by the discharge tube and that emitted by spectral lamp and transmitted through the discharge tube are filtered with a 1 m Jarrell-Ash grating (1200 lines mm^{-1}) monochromator, detected with an EMI photomultiplier tube and recorded with a Tektronix oscilloscope.

A specific original electronic arrangement has been used for temporal synchronization of the HVPSL pulses with those of the HCPD. As shown in Fig. 1, the HV Pulser, which supplies the HVPSL, was triggered using the signals collected with a current probe from the HCPD circuit. The signal was temporally delayed in a controllable manner by an adjustable pulse generator from the discharge tube current pulse. This electronic arrangement allow us to detect simultaneously the emission light of the high current discharge tube and that of the spectral lamp transmitted through the discharge tube as it can be seen in the oscilloscope image in Fig. 3.

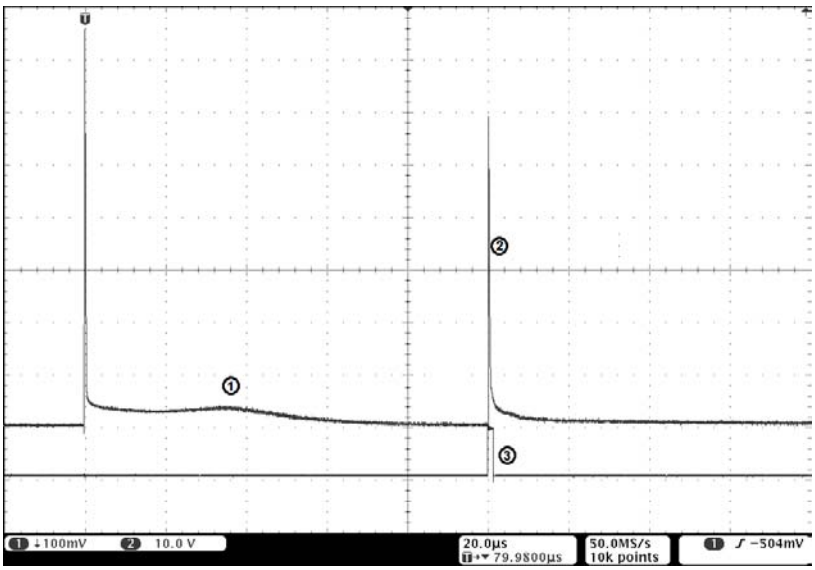

Fig. 3 – The Ne light signal at 633.4 nm; (1) Light emitted by the afterglow plasma of HCPD; (2) Light emitted by HVPSL and passing through HCPD; (3) Trigger signal from Adjustable Pulse Generator.

Positioning the trigger signal of the spectral lamp with different time delays with respect to the discharge tube current pulse, the transmitted light of the spectral source through the discharge tube may be monitored at different temporal moments in the afterglow of the HCPD, as presented in Fig. 4.

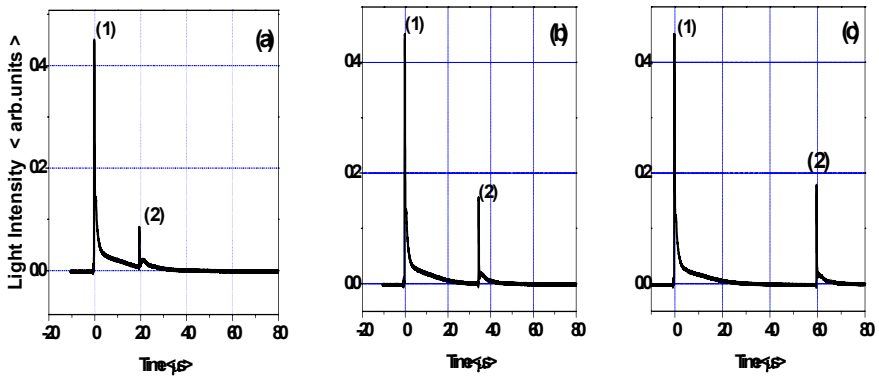

Fig. 4 – The Ne light signal at 633.4 nm; (1) Light emitted by the afterglow plasma of HCPD; (2) Light emitted by HVPSL and passing through HCPD at various temporal position; (a) 20μs, (b) 35μs and (c) 60μs.

By adjusting the delay of the trigger signal continuously, so that the light pulse emitted by HVPSL sweeps the entire afterglow range of HCPD, we have obtained the envelope of the temporal evolution of the intensity of the light emitted by the spectral lamp and transmitted through the discharge tube (see the photo in Fig. 5). This photo is taken with a long exposure time, equal with the sweeping duration.

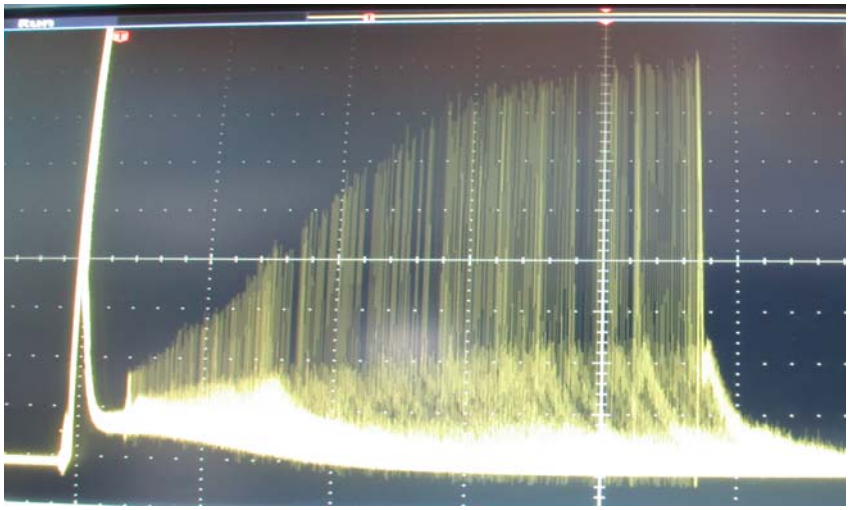

Fig. 5 – Photo representing the temporal evolution of the intensity of the light pulse emitted by the spectral lamp at 633.4 nm and passing through the temporal afterglow plasma of the discharge tube.

As known from absorption spectroscopy theory, the measured relative absorption is given by the formula $A = 1 - I_t/I_{lamp}$, where I_{lamp} is the intensity of the emitted light of the spectral lamp while I_t is the total transmitted light. I_t is obtained by subtracting the emitted light of the pulsed discharge tube plasma I_{plasma} from the light emitted simultaneously by the plasma and the spectral lamp I_{lamp} ($I_t = I_{plasma + lamp} - I_{plasma}$).

The measured absorptions using the high voltage pulsed spectral lamp for different values of the current peaks are presented in Fig. 6. The attached medallion of Fig. 5 presents the Doppler profiles of both, the Neon line at 633.4 nm emitted by HVPSL at various peak currents (16 A, 20 A and 26 A respectively, as shown in Table 1), and by the species existing in HCPD. In the three cases of the working peak currents of HVPSL, α given by Eq. (2) is α = 0.97 when HVPSL is working at 16 A current peak. α = 1.1 when HVPSL is working at 20 A peak current and α = 1.29 when HVPSL is working at 26 A peak current. From Fig. 5 it can be seen that the measured absorption is dependent on α: the closer is α to 1, the greater is the measured absorption. Thus, we appreciate that using a spectral source with a spectral line profile (broadening) close to that of the emission line of absorbing species, the sensibility of the absorption measurements can be improved.

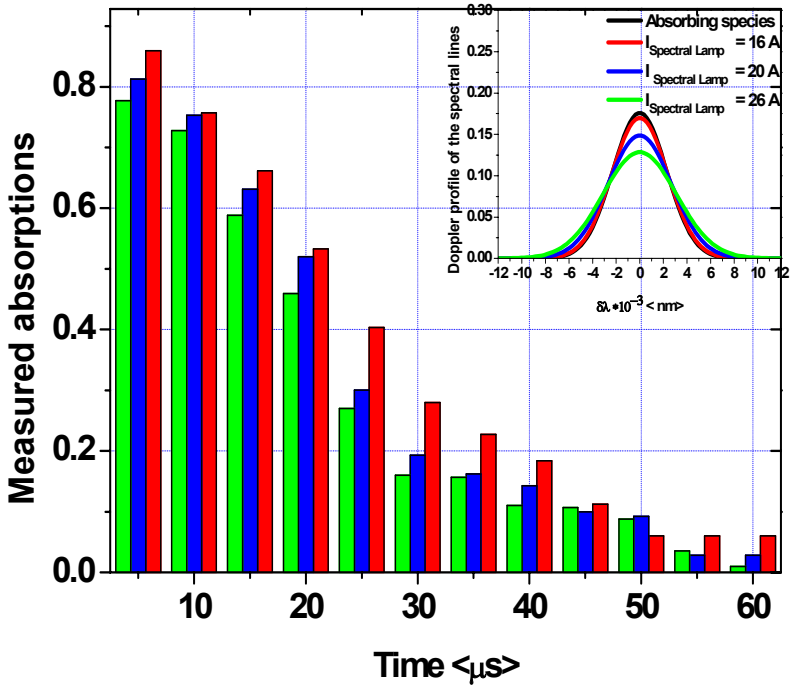

Fig. 6 – Temporal evolution of the absorption of the Neon line at 633.4 nm obtained during the temporal afterglow plasma of HCPD, measured using the pulsed spectral lamp at different peak currents (16 A – red, 20 A – blue, 26 A – green) (color online).

3. RESULTS AND DISCUSSIONS

The neon metastable density N (atoms/cm^3) was computed with the Ladenburg's formula:

$$k_0 = \frac{2}{\Delta\vartheta_D}\sqrt{\frac{\ln 2}{\pi}}\frac{\pi e^2}{mc}Nf \tag{3}$$

where $\Delta\vartheta_D$ is the Doppler species line broadening, e and m are the electron charge and mass, c is the light velocity and f is the oscillator strength of the Neon transition $^3P_2 - 2p^4$ at 633.4 nm.

The roots x of the scenario I

$$f(x) = \sum_{m=1}^{\infty}\frac{(-1)^{m+1}x^m}{m!\sqrt{1+m\alpha^2}} - A = 0, \quad \text{with} \quad x = k_0 L$$

were obtained by the method described above for α = 0.97, α = 1.1 and α = 1.29. The dependence of k_0L on the absorptions in the range of 0.01–0.9, as results from numerical calculations, is presented in Fig. 7.

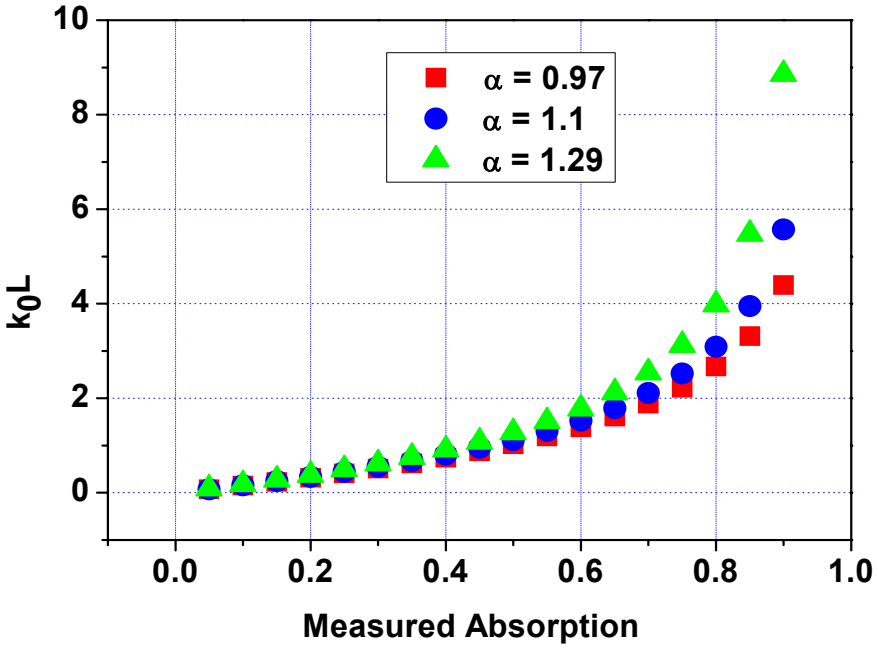

Fig. 7 – The theoretical dependence of the k_0L on the measured absorptions.

Considering the optical length of our experiment L = 2 cm and using the measured absorption data obtained at different moments of time during the temporal afterglow plasma (Fig. 5) we have calculated the $^3P_2$ Neon metastable level density with the relation

$$N[\mathrm{cm}^{-3}] = \frac{k_0 * \Delta\lambda_D}{8.25 * 10^{-13} * f * \lambda^2} \tag{4}$$

where f = 0.0818 and λ = 633.4 nm. The Doppler width of the emission line of absorbing species is $\Delta\lambda_D = 4.6*10^{-3}$ nm which corresponds to the 2100 K the gas temperature of the afterglow plasma.
The evolution of the Neon metastable density in the temporal afterglow plasma in the range of 0–60 μs of the temporal afterglow plasma of the high current pulsed discharge is presented in Fig. 8.

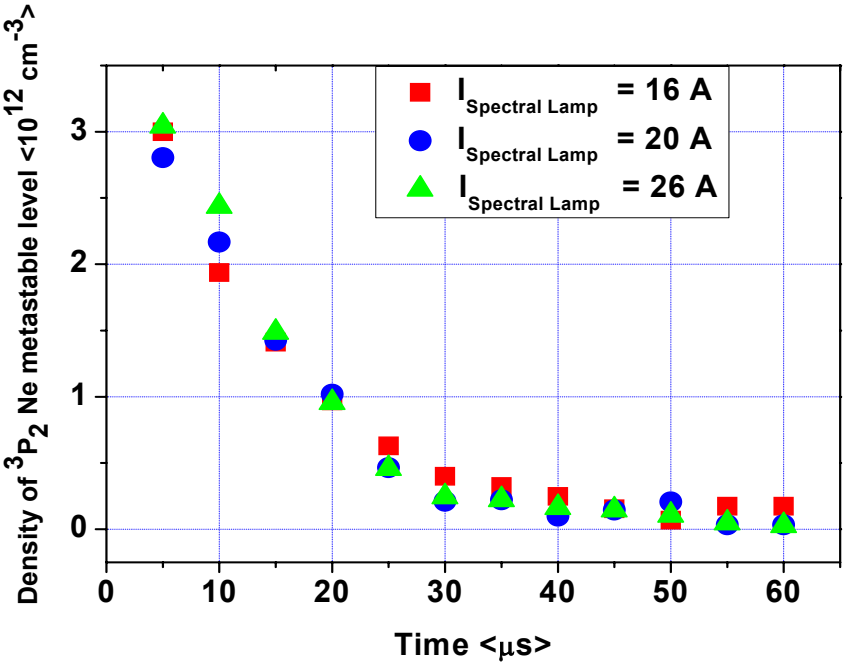

Fig. 8 – The temporal evolution of $^3P_2$ Neon metastable level density in the temporal afterglow plasma according to the absorption measurements on $^3P_2 - 2p^4$ transition at 633.4 nm.

On the same graph we have plotted the calculated values obtained using the pulsed spectral lamp working at 16, 20 and 26 A peak current. The measured values for Neon 2^3P_2 state density in the 5–60 μs temporal afterglow range are found to vary from $3 \times 10^{12} \pm 20\%$ cm^{-3} to $1.7 \times 10^{11} \pm 20\%$ cm^{-3} following an exponential decay curve, as it can be seen in Fig. 8. We suppose that this temporal evolution is due to

loss processes including diffusion, Penning transfer to hydrogen traces coming from the discharge tube walls ($\sigma = 2.65\times10^{-16}$ cm^2 [25]), Penning transfer to titanium sputtered from the cathode and processes leading to amplification of the ionic lines [13].

4. CONCLUSIONS

In this paper we developed the technique of absorption spectroscopy with temporal resolution [1, 2], using a classical pulsed spectral source with controllable profile of the emission spectral lines [3, 4]. The obtained results demonstrate that this absorption technique is appropriate for absorption measurements in the pulsed and temporal afterglow plasma, namely the evolution of the $^3P_2$ Neon metastable level density during the temporal afterglow plasma of a high current pulsed hollow cathode discharge.

The absorption measurements performed by using a pulsed spectral lamp with different emission line profiles corresponding to various working peak currents, demonstrate that the measured absorption sensibility is improved when the line profile of the spectral source emission lines is closed to the profile of the emission lines of absorbing species. We demonstrate that the use of an original electronic arrangement for time synchronization of pulses and of a classical pulsed spectral source with controllable line profile is beneficial for the absorption spectroscopy with temporal resolution.

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