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Dedicated to Acad. Prof. Dr. Margareta Giurgea with the occasion of her 90-th anniversary

ABSORPTION SPECTROSCOPY WITH INTENSE PULSED CALIBRATED SOURCE

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An intense calibrated pulsed spectral source was used to determine the density of neon metastable atoms in the negative glow of a hollow cathode discharge by optical absorption technique.

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1. Introduction

The ability to measure the concentrations of molecular species is important in many areas of science and technology. The challenges are enormous and it is unlikely that any of the techniques will be universally applicable.

In this paper, we propose an optical absorption technique with an intense pulsed calibrated lamp. The absorption measurements require the knowledge of the line profile of the lamp, namely the gas temperature of the pulsed discharge. The analysis of the standing waves frequencies which are produced during the breakdown of a high voltage pulsed discharge allows the determination of gas temperature and then the line Doppler profiles of the lamp.

This optical absorption method was used for the determination of the neon metastable density in the negative glow of a hollow cathode discharge. Particularly, the glow discharge has numerous applications in industry such as plasma assisted integrated circuit fabrication and various other chemical deposition and etching processes. The densities of metastable atoms in these plasmas are of major importance for the chemistry of the discharge, because they are involved in many chemical reactions such as Penning ionization, as well as various other energy transfer processes.

2. Experimental set-up

The experimental set-up is presented in Fig. 1.

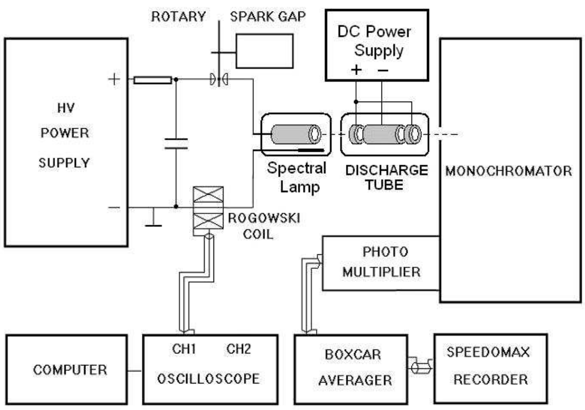

Fig. 1. Experimental set-up.

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The intense calibrated pulse lamp consists of a glass chamber containing a titanium cylindrical hollow cathode (15 mm length and 3 mm diameter) and a stainless steel wire anode. High current pulses of short duration were obtained by repetitively discharging a storage capacitor C through a rotary spark gap with a commutation time below 10 ns [1]. Working at 1-5 torr neon gas pressure, peak current pulses in the range of 20 - 100 A with duration of 60 ns (at half-width) were obtained (depending on the charging voltage of the main capacitor). This pulsed high current density provides a large amount of excited atoms and ions of both, the filling gas and the sputtered cathodic metal with intense emission lines.

The profile of the spectral lines emitted by this lamp is of a Doppler type and it was determined by measuring the gas temperature of the pulsed plasma from the standing waves frequencies produced during the breakdown of a high voltage pulsed discharge [2].

Fig. 2 presents the acoustic modulation of the H_α line afterglow of the hydrogen impurity in neon (5 torr) afterglow. In order to determine the gas temperature, the modulation of the Balmer line has been processed by a mathematical artifice. Thus, the undulations were better revealed when the light signal was fitted by a 9-th order polynomial (dashed curve), which has been extracted from the experimental signal. The frequency of the standing wave in neon has been obtained from the Fourier spectrum of these clean oscillations.

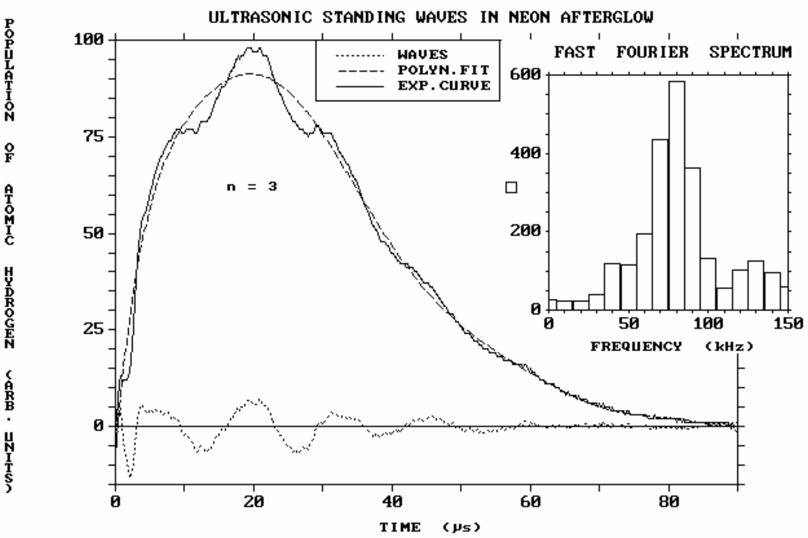

Fig. 2. The modulations of the H_α line of hydrogen in the neon afterglow, the fitted curve, the clean oscillations and the Fourier analysis.

The gas temperature was evaluated using the Rayleigh formula for the sound velocity: $v_s = 2\pi\nu_s / k_s = (\gamma kT / m)^{1/2}$ 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 Boltzmann constant, T is gas temperature, and m is the mass of the gas atom.

The evaluation of the gas temperature allows the determination of the Doppler profile of the neon spectral lines of the lamp. Depending on the peak current value, the standing wave frequency changes and consequently the gas temperature and the line profile. Under the experimental conditions of 5 torr neon pressure and 30 A peak current, the measured frequency was about 80 kHz, v_s = 1200 m/s and T = 2100 K.

The absorption species of interest are neon metastable atoms produced in the negative glow of a dc hollow cathode discharge. The discharge cell used contains a cylindrical hollow cathode of Titanium (20 mm length and 4 mm diameter) and an anode consisting of two stainless steel rings (4 mm diameter) placed symmetrically at the two ends of the cathode. Working at 5 torr neon, 20 mA dc current and 350 V applied voltage, the external temperature of the cathode did not exceed 310 K.

The light emission of the lamp was filtered with a 1 m Jarrell-Ash grating monochromator, detected with an EMI photomultiplier tube and recorded with a box-car averager with a variable temporal electronic gate which may be opened at certain times after the start of the current pulse. By adjusting the position and the duration of the electronic gate, it is possible to choose the time when the intensity of the emission light does not exceed the threshold of a significant self-absorption of the spectral lines.

3. Results and discussion

The experimental set-up presented above allows recording the emission light of the pulsed lamp, Fig. 3a, and the transmission light through the negative glow of the dc hollow cathode discharge, Fig. 3b in the wavelength range of 5875- 6340 Å. The spectra are recorded with the electronic gate positioned on the current period, the peak current being 30 A.

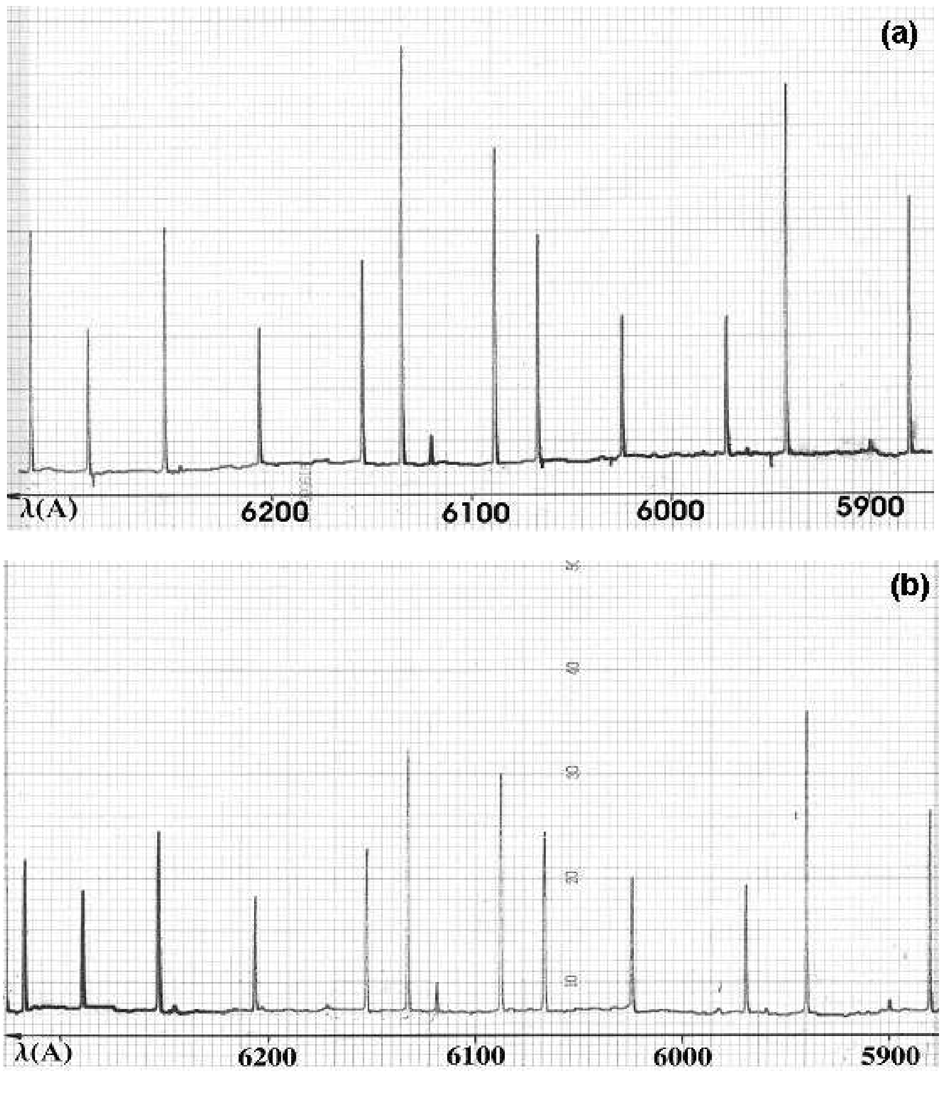

Fig. 3. (a) The emission light of the pulsed lamp, (b) The transmission light through the negative glow of the dc hollow cathode discharge.

Table 1 presents the wavelengths of the recorded spectral lines, the transitions, the oscillator strengths *f*, [3], halfwidth of the Doppler profile and the measured relative absorption $A = 1 - I_t/I_0$ in percents. I_0 is the intensity of the emitted light of the lamp and I_t the transmitted light, which is obtained by subtracting the emitted light of the plasma from the light emitted simultaneously by the plasma and the lamp ($I_t = I_{plasma + lamp} - I_{plasma}$). The plasma intensity I_{plasma} can be neglected when the light recording is triggered by the pulsed lamp.

Table 1.

λ [Å]	Transition	*f* [3]	$\Delta\vartheta_D$ [cm^{-1}]	*A* [%]
5881	$^3P_2 - 2p_2$	0.0398	0.0471	21.6
5944	$^3P_2 - 2p_4$	0.0556	0.0466	18.6
5975	$^3P_2 - 2p_5$	0.0139	0.0464	6.1
6029	$^3P_1 - 2p_2$	0.0342	0.0460	3.9
6074	$^3P_1 - 2p_3$	0.114	0.0457	18.5
6096	$^3P_1 - 2p_4$	0.157	0.0455	24
6143	$^3P_2 - 2p_5$	0.122	0.0452	40.7
6163	$^3P_0 - 2p_2$	0.273	0.0450	19.6
6217	$^3P_2 - 2p_7$	0.027	0.0446	14.6
6266	$^3P_0 - 2p_5$	0.394	0.0442	25.9
6334	$^3P_2 - 2p_8$	0.0818	0.0438	37.9

According to Mitchell and Zemanski [4] the absorption is given by

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

where k_0 is the maximum absorption coefficient of the line, L the absorption length (2 cm) and

$$\alpha = \frac{Doppler\ lamp\ line\ broadening}{Doppler\ species\ line\ broadening}$$

where the *Doppler line broadening* is given by the formula $\Delta\vartheta_D(cm^{-1}) = \frac{7.16\times10^{-7}}{\lambda(cm)}\sqrt{\frac{T}{M}}$. Thus, $\alpha = (T_l / T_s)^{1/2}$ with T_l standing for the gas temperature of the lamp (2100 K), and T_s for the absorbing species temperature (310 K).

The neon metastable density N (atoms/cm^3) has been computed with the Ladenburg's formula for k_0,

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

where $\Delta\vartheta_D$ is the Doppler broadening, e and m are the electron charge and mass, c is the light velocity and f is the oscillator strength of the transition.

Under the conditions of the dc glow discharge mentioned above (p_{Ne} = 5 torr, applied voltage ~ 350V,) the average value of the $^3P_2$ (16.62 eV) neon metastable level density as calculated for all the recorded transitions is about 3.31×10^{11} atoms/cm^3; in the same way, for the $^3P_0$ (16.71 eV) metastable level a density of about 5.3×10^{10} atoms/cm^3 is obtained.

The applicability of this optical absorption technique with a conventional calibrated pulsed source was tested in the neon – hydrogen mixture where the Penning ionization occurs via the reaction $Ne^m + H_2 \rightarrow Ne + H_2^+ + e$ and the neon metastable density is altered.

Fig. 4 presents the emission and the transmission light by the transition $^3P_2 - 2p_5$ at 6143 Å for two different partial pressures of hydrogen impurities: (a) 3.7×10^{-2} torr and (b) 5.4×10^{-2} torr.

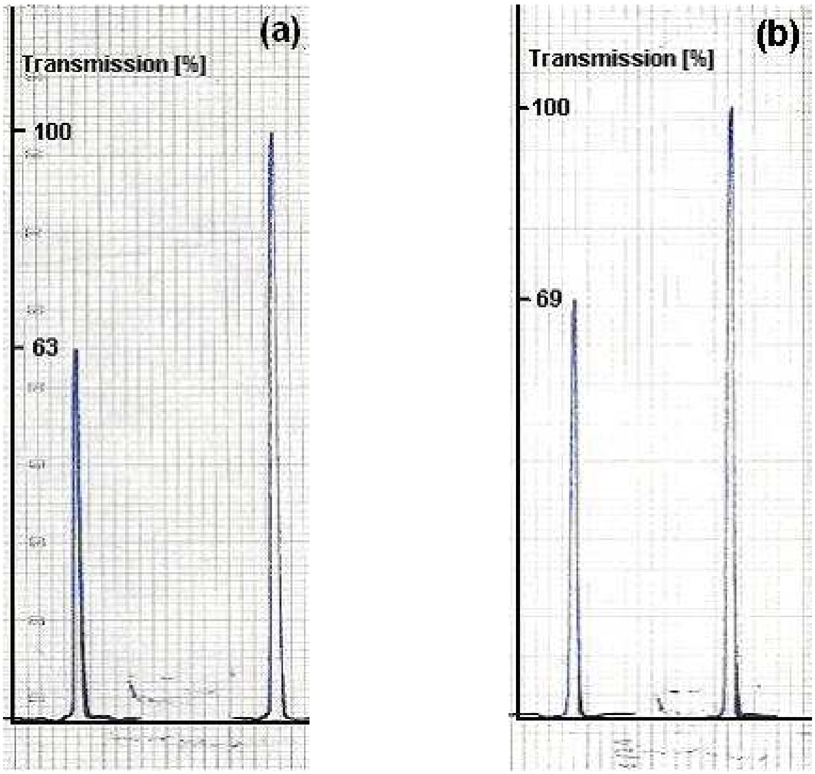

Fig. 4. The transmission light of the lamp at 6143 Å with and without absorbing species when hydrogen impurities had been added in the discharge at: (a) 3.7×10^{-2} torr partial pressure and (b) 5.4×10^{-2} torr partial pressure.

The calculated neon metastable density is about 2.34×10^{11} atoms/cm^3 for a partial hydrogen pressure of 3.7×10^{-2} torr; similarly, we get 1.99×10^{11} atoms/cm^3 for 5.4×10^{-2} torr. The measurements of neon metastable density when controllable hydrogen impurities are added allow estimating the Penning ionization cross section of the $^3P_2$ level of about 1.3×10^{-16} cm^2.

4. Conclusions

The intense pulsed calibrated source presented in this paper is revealed as a convenient tool for optical absorption spectroscopy. The pulsed high current density of the discharge leads to the emission of intense spectral lines ensuring an appropriate signal/noise ratio of the absorption measurements. The analysis of the standing waves frequencies produced during the breakdown of a high voltage pulsed discharge allows evaluating and controlling the gas temperature and consequently the Doppler line profile in accordance to the discharge parameters. The detection chain with variable temporal electronic gate avoids any significant self-absorption effect of the spectral lines.

A satisfactory agreement of the Penning ionization cross-section value obtained from absorption measurements in neon-hydrogen mixture with the value obtained by other methods [5] represents an argument for the use of this method in quantitative analysis of atomic and ionic species.

As compared to other techniques, such as laser-induced fluorescence (LIF) and mass spectrometry, the optical absorption spectroscopy method presented in this paper appears to be more convenient in many ways, not expensive and easy to use in laboratory discharges [6] and in deposition reactors [7].

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