Determination of the neutral gas density by VUV absorption measurements

IEPC-2024-373

Presented at the 38th International Electric Propulsion Conference, Toulouse, France
June 23-28, 2024

Ruslan Kozakov*, Mischa M. Bär†,
Colum Walter‡
and Jochen Schein§
University of the Bundeswehr Munich, Neubiberg, 85579, Germany

The method of the neutral gas density measurements by absorption of the vacuum ultra-violet radiation (VUV) is presented. The absorption of plasma for different types of spectroscopic profiles is calculated. The results of experiments in model plasma source in Krypton plasma are presented. The discrepancy between experiment and theoretical values are found. The reasons of discrepancy are discussed. Possible improvements of the method are indicated.

Nomenclature

I_λ	= spectral density of radiation intensity
I	= radiation intensity integrated over the line profile
$\Delta\lambda$	= width of a spectroscopic line in wavelength domain
$\Delta\nu$	= width of a spectroscopic line in frequency domain
k_λ	= spectral density of the absorption coefficient
k_0	= value of the absorption coefficient in the center of the line profile
τ	= $k_0 d$ optical density in the center of the line profile for absorption length d
A_L	= absorption function of the plasma for the case of line radiation
N_l	= density of the absorbing atoms, the lower state of spectroscopic transition
f_{lu}	= oscillator strength of spectroscopic line in absorption
A_{ul}	= transition probability of spectroscopic line
ε_0	= electric permitivity of vacuum $8.854 \cdot 10^{-12}$ F/m
c	= speed of light $2.98 \cdot 10^8$ m/s
e	= electric charge of electron $1.6 \cdot 10^{-19}$ C
R	= reflection coefficient of a mirror
K	= geometric correction factor

*Dr. rer. nat, Institute of Plasma Technology and Basics of Electrical Engineering, ruslan.kozakov@unibw.de.
†B.Sc., Institute of Thermodynamics, mischa.baer@unibw.de.
‡M.Sc., Institute of Thermodynamics, colum.walter@unibw.de.
§Professor, Institute of Plasma Technology and Basics of Electrical Engineering, js@unibw.de.

I. Introduction

The density of the neutral species in the plume of the electric propulsion devices is a quantity of interest for several reasons. On the one hand, it is a lifetime limiting factor of the gridded ion thrusters due to the grid erosion by the CEX ions. On the other hand, it allows for direct determination of the propellant utilization efficiency.

The direct measurement of the neutral gas densities in the plume is a challenging task due to the low gas pressure. The sensitivity of the usual, density gradient based techniques like Schlieren and interferometry is not sufficient to detect these values. The Rayleigh laser scattering technique requires careful discrimination of the stray light. The measurements by the ionization vacuum gauges[1] introduces a significant disturbance due to the size of the gauge. The two-photon absorption laser induced fluorescence (TALIF)[2,3] requires intensive tunable lasers of high quality beam which is not readily available. The optical emission spectroscopy (OES) is not the direct method of measurement, as it requires a valid collisional radiative model,[4] which connects the measured values with the desired plasma parameters.

Another possibility of the direct measurement of the neutral gas density is the absorption measurement on spectroscopic lines of the resonant transitions of the propellant gas. The absorption measurements deliver the density of the lower state of a spectroscopic line. For the resonant transitions the lower state is the ground state of the atom and gives thus the access to the direct measurement of the neutral gas density. Since the noble gases Ar, Kr and Xe are often used in the field of electric satellite propulsion and their transitions from the ground state usually have high energy differences of up to $14eV$, the emission lines of these plasmas are often situated in the ultra-violet (UV) or vacuum ultra-violet (VUV) range between 100 and 150 nm. Another advantage of absorption measurements is its non-intrusiveness and being a relative measurement method which does not require absolute calibration.

This paper presents the results of the applicability tests of VUV absorption spectroscopy for determination of neutral gas pressure of Krypton plasmas. The measurement technique is based on the detection of the plasma emission with and without a mirror placed behind the plasma. The partial absorption of the reflected radiation allows the determination of the particle density within the plasma. The tests were conducted on the dedicated hollow cathode discharge.

This paper is structured as follows: first the theoretical background is discussed. Secondly the description of the experimental setup is given. In the last chapter of this paper the overview and discussion of the experimental results is provided.

II. Theoretical Background

The absorption of radiation $I_{0\lambda}$ of wavelength λ passed through a layer of width d of absorbing medium can be described by the exponential relation

$$I_\lambda(d) = I_{0\lambda} e^{-\int_0^d k_\lambda dx}, \tag{1}$$

where $k_\lambda = k_0 \varphi(\lambda)$ is the absorption coefficient at the radiation wavelength, $\varphi(\lambda)$ is the spectral profile of the absorption line, k_0 is the absorption coefficient in its center and $I_\lambda(d)$ is the intensity of the radiation after the absorption. After integrating over the spectroscopic line profile the total intensity of the transmitted radiation is

$$I(d) = \int_0^\infty I_{0\lambda} e^{-\int_0^d k_\lambda(x) dx} d\lambda. \tag{2}$$

Measuring the intensity with and without the absorbing medium the absorption function of the medium can be calculated:

$$A_L = \frac{I_0 - I}{I_0} = 1 - \frac{\int_0^\infty I_{0\lambda} e^{-\int_0^d k_\lambda(x) dx} d\lambda}{\int_0^\infty I_{0\lambda} d\lambda}. \tag{3}$$

The value of A_L is accessible experimentally by the lhs of Eq. 3 from the measurements of the plasma radiation intensity with and without the mirror placed behind the plasma, see section III. On the other hand the quantity A_L can be calculated from the rhs of Eq. 3 for different values of optical density $\tau = k_0 \cdot d$ and the curve $A_L(\tau)$ can be tabulated. The optical density can be determined from this curve by finding the value τ which delivers the experimental A_L value. After the optical density is determined, the absorption coefficient in line center can be found as $k_0 = \tau/d$.

Neglecting the influence of stimulated emission processes the absorption coefficient of the medium depends on number density of the absorbing atoms N_l and can be written as[8]

$$\int k_\lambda d\lambda = \frac{e^2\lambda^2}{4\varepsilon_0 m_e c^2} N_l f_{lu}, \tag{4}$$

where f_{lu} is the oscillator strength which is proportional to the transition probability A_{ul} of the spectroscopic line. The integral on the lhs of Eq. (4) can be evaluated as $ak_0\Delta\lambda$, where $\Delta\lambda$ is the full width half maximum (FWHM) of the spectral line profile and a is coefficient which depends on its form - Doppler, Lorentz or Voigt.

Finally, the value of the absorbing atoms density can be calculated as

$$N_l = \frac{4\varepsilon_0 m_e c^2}{e^2\lambda^2 f_{lu}} ak_0\Delta\lambda. \tag{5}$$

The line profile plays an important role in the determination of the absorbing atoms density. The value of the integral in Eq. 3 depends on the form of the line and is important for the correct determination of the optical density of the medium. The information of the line profile is also used in Eq. 5 for the calculation of the number density. The line profile of a spectroscopic line is determined by different broadening processes like Doppler, natural, pressure broadening and Stark-effect. The Doppler broadening can be written as

$$\Delta\nu_D = \frac{2\nu_0\sqrt{2R_m ln(2)}}{c} \cdot \sqrt{\frac{T}{M}} \tag{6}$$

where T is the temperature of the medium, M is the atomic mass and R_m is the universal gas constant. The line broadening due to limited lifetimes of the excited states is referred to as natural broadening and the corresponding full width at half maximum of the spectral line in frequency domain ($\Delta\nu_N$) is determined by the following equation:[6]

$$\Delta\nu_N = \frac{A_{ul}}{2\pi}. \tag{7}$$

The broadening due to the collisions with the particles of the same species is known as resonant or Holtsmark broadening and can be calculated in frequency domain as[7]

$$\Delta\nu_H = \frac{cr_e}{8} k_{jj'} f_{lu}\lambda_0 N_l. \tag{8}$$

where r_e is the classical radius of electron and the coefficient $k_{jj'}$ depends on quantum numbers of upper and lower states, for noble gases $k_{jj'} = 1.53$. The comparison of the relative importance of the different broadening mechanisms is given in Table 1. The temperature value of 300K was used for estimation of Doppler width. The number density $10^{20}m^{-3}$ was used for estimation of resonant broadening. The width are given in wavelength domain and the values are shown in picometers.

Table 1: Comparison of the different broadening mechanisms. Calculated for temperature 300K and number density $N_l = 10^{20}m^{-3}$

line, nm	$\Delta\lambda_D$, pm	$\Delta\lambda_N$, pm	$\Delta\lambda_H$, pm
Xe 129.56	$1.40\cdot10^{-1}$	$2.25\cdot10^{-3}$	$2.23\cdot10^{-5}$
Xe 146.96	$1.59\cdot10^{-1}$	$3.13\cdot10^{-3}$	$4.52\cdot10^{-5}$
Kr 116.49	$1.58\cdot10^{-1}$	$2.22\cdot10^{-3}$	$1.59\cdot10^{-5}$
Kr 123.58	$1.67\cdot10^{-1}$	$2.42\cdot10^{-3}$	$2.07\cdot10^{-5}$

The comparison of the data from Table 1 shows that the natural broadening constitutes less than 1 percent of the Doppler broadening. For the conditions of plasma plumes of the EP thrusters where the neutral particle density is expected to be $< 10^{20}m^{-3}$ the resonant pressure broadening can be neglected.

Although the natural broadening is two orders of magnitude smaller than the Doppler broadening it can not be neglected for the absorption measurements. For the correct determination of the absorbing atoms density care should be taken when calculating the integral on the rhs of Eq. (3). The line profile due to combined broadening mechanisms represents the Voigt profile which for the values of Table 1 represents the Gaussian core with the Lorentzian wings. For the expected very high optical densities $\tau > 10$ the Gaussian core is completely absorbed and the absorption in the Lorentzain wings starts to play the role. The absorption function $A_L(\tau)$ is a dimensionless quantity between 0 and 1 which represents the relative amount of the radiation absorbed by a spectroscopic line within the spectral range recorded by the measuring device. The ultimate value of the absorption depends not only on the form of the absorbing profile, but also on the spectral form of the incident radiation. The cases of continuous and line-type spectral distributions of incident radiation should be treated separately. In our case the spectral distribution of the incident radiation equals that of the radiation emitted by plasma. The spectral distribution of the radiation exiting the plasma is modified by the re-absorption processes which result in the Voigt profile with a flattened central part. The absorption profile is identical with optically thin emission profile and represents the undisturbed Voigt profile.

The calculated absorption functions for the different types of spectral profiles are shown in Fig. 1. The curves for Lorentz and Doppler profiles define the range where all possible absorption function can be found. For the pure Doppler profile the absorption function tends to 100 percents at extremely high optical densities. For the pure Lorentzian profile the maximal achievable absorption lies at approx 60 percents. The Voigt profiles deliver absorption functions which start as Doppler at low and transform to Lorentzian at very high optical densities.

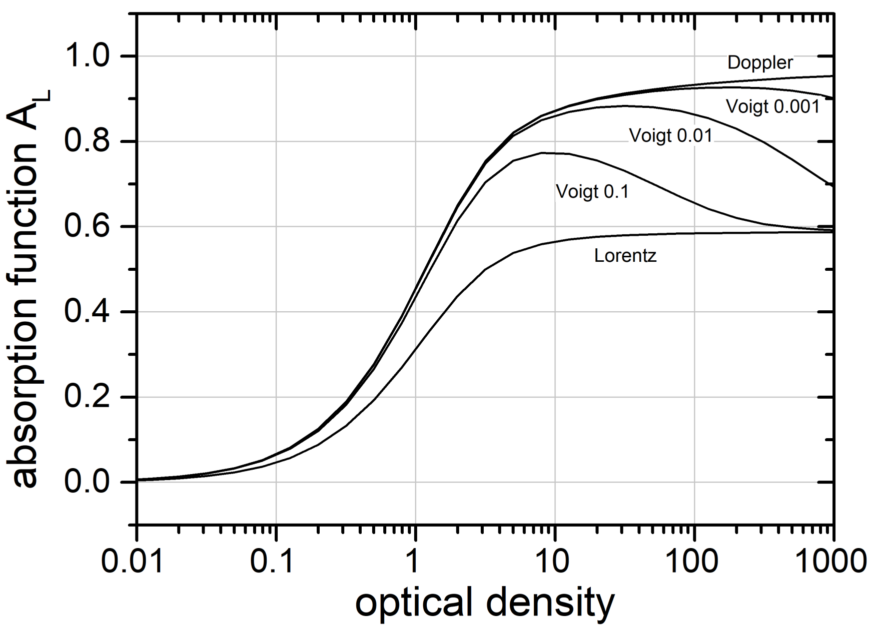

Figure 1: Absorption functions A_L calculated according to Eq. (3) for different types of spectral line profile. The parameter of the Voigt profile represents the ratio of Lorentzian and Doppler widths. The curves for pure Lorentz profile, pure Doppler profile and Voigt profile with parameter 0.1, 0.01 and 0.001 are shown.

For our experimental conditions the Voigt parameter has value 0.0145 for Krypton line 123.5838 nm and 0.0197 for Xenon line 146.961 nm. For this specific case the values of A_L as a function of optical density τ are shown in fig. 2. It can be seen that the maximal absorption which can be expected lies by approximately 87 percents.

III. Experimental results

As stated previously the degree of absorption A_L is the ratio of absorbed radiation to radiation incident onto the plasma. In our experiments the measured radiation consists of two components: the radiation I_0 emitted by the plasma both towards the spectrograph and towards the mirror. This radiation can be measured when the mirror is removed from the optical path. When the mirror is inserted into the optical path the additional radiation ΔI adds to the signal. It is created by the mirror reflecting a portion of I_0

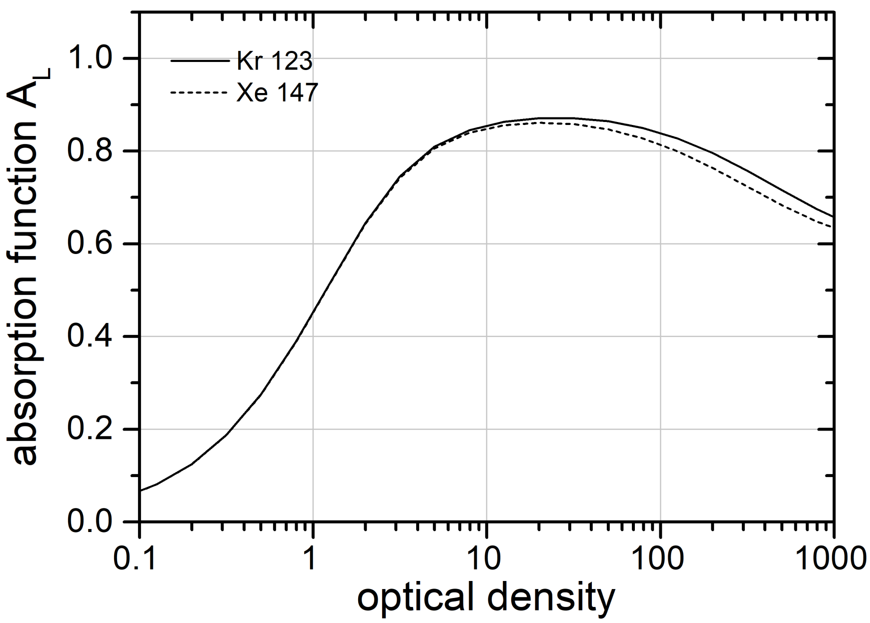

Figure 2: Absorption functions A_L as function of the optical thickness τ of Kr at $\lambda = 123.5838$ nm and Xe at $\lambda = 146.961$ nm and $T = 300K$

back into the plasma through which the amount $(1 - A_L)$ is transmitted . However, even without absorption the ΔI will always be less than I_0 for two reasons:(i) the mirror has a reflectivity R which is less than 1 and (ii) due to the adjustment of the mirror as well as the unavoidable expansion of the beam only a portion of I_0 exiting the plasma is reflected back into it. This can be written as

$$\Delta I = R \cdot K \cdot I_0 \cdot (1 - A_L),$$

where $K < 1.0$ is the geometric correction factor. The signal with mirror I_M can be written as:

$$I_M = I_0 + \Delta I.$$

Using the ratio

$$\frac{I_M - I_0}{I_0} = \frac{\Delta I}{I_0} = R \cdot K \cdot (1 - A_L),$$

we can find

$$1 - A_L = \frac{\Delta I}{R \cdot K \cdot I_0} \tag{9}$$

The factor K can be determined from the measurements of optically thin spectroscopic line for which absorption A_L equals zero. It follows from Eq. (9) that for this case

$$K = \Delta I/(RI_0) \tag{10}$$

The absorption signal is recorded by monitoring the intensity of the certain spectroscopic line. The mirror behind the plasma source is continuously rotated back and forth with the frequency of 0.5 Hz. Almost all of the time the signal from the mirror is reflected away from the optical axis and the recorded signal corresponds to the plasma radiation I_0. In certain time instances the mirror gets aligned with the optical axis and the combined signal I_M is recorded. The reference signal of mirror positioning system allows for averaging over many rotation periods.

A. Setup

The experimental setup is schematically shown in fig. 3 and mainly consists of two assemblys: the vacuum chamber - housing the plasma source and the mirror - and the spectrometer. The vacuum chamber consists of a steel cylinder with an inner diameter of $30cm$, which is welded onto a steel plate on one end. The other end of the cylinder is sealed of from the outside air using a glass bell with a rubber sealing at its bottom. The chamber's vacuum system consists of a fore-vacuum pump and a turbomolecular pump. The pressures as low as $6 \cdot 10^{-6} mbar$ without and in the range from $10^{-4} - 10^{-3} mbar$ with the gas flow can be achieved.

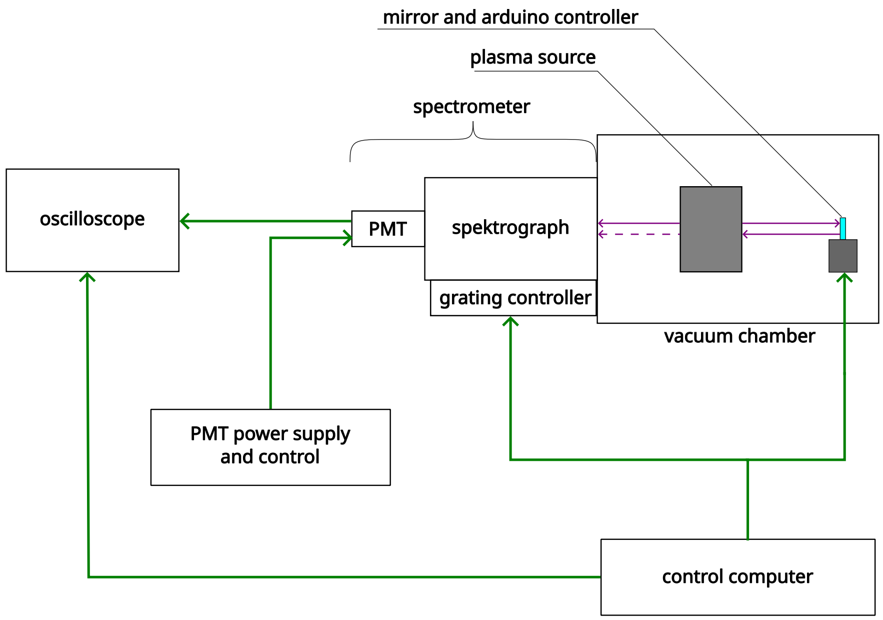

Figure 3: Schematic overview of the setup

The plasma source is mounted along the optical axis about $7cm$ away from the cylinder wall. The mirror is also mounted on the optical axis approximately $7cm$ behind the plasma source. The plasma source is made of two aluminum caps with an inner diameter of $20.5mm$ and an height of $22.5mm$ each. The lower half has two slits milled on its opposite sides with a width of $1mm$ and height of $3mm$. These slits are aligned along the optical axis and allow the emission of light towards the spectrometer and the mirror. The gas supply and the anode are fed through the top half. The plasma used in our experiments represents a hollow cathode discharge. A voltage is applied to the internal anode electrode so that the outer cylinder serves as the cathode. The high voltage power supply along with the series resistor of 18 kOhm allows the electric current to be set in the range $10mA - 50mA$. The plasma source was supplied with Kr during the experiments.

The VUV enhanced mirror made from aluminum coated with MgF_2 allows its use in the wavelength range around $100nm - 200nm$. It is mounted on a rotating platform attached to a stepper motor.

The "easyLIGHT plus" spectrometer (hp spectroscopy GmbH) is particularly suited for VUV measurements due to the toroidal diffraction grating used for focusing and dispersing of VUV radiation. The spectrograph is attached directly to the vacuum chamber. The signal is registered with the PMT (Hamamatsu Photonics R8486). The diffraction grating with 300 lines/mm can be rotated to select the required wavelength. The accessible spectral range lies within 120 nm - 320 nm and is mainly determined by the sensitivity of the photomultiplier. For the assessment of the correction factor K the photomultiplier was temporary replaced by the one sensitive in the visual range (9781B by EMI Electronics Ltd). It was used for the recording of the signal from the optically thin line of Krypton at 437.612 nm. The PMT signal is recorded by an oscilloscope (RTO4 by Rhode & Schwarz GmbH).

B. Measurements of absorption

The example of the Krypton spectrum is shown in fig. 4. The two resonant lines at 116.5 and 123.6 nm can be identified. Although the intensity of both lines should be approximately the same, the recorded intensity of 116 nm line is smaller due to the limited transparency of MgF_2 window of the PMT. The signal in the range of the second and the third diffraction orders at the apparent wavelengths of 240 and 360 nm can also be observed.

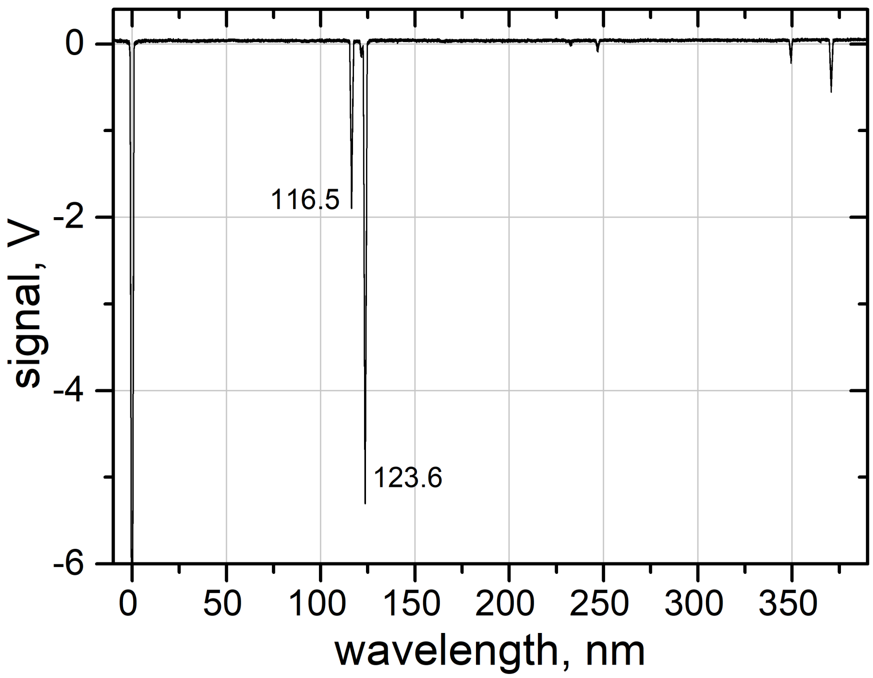

Figure 4: Example of the measured Krypton spectrum.

For the determination of the unknown geometric correction factor the measurement on the optically thin transition of Krypton at 437.612 nm was performed. The lower level of this line is at the energy of approx 10 eV which makes its number density many orders of magnitude smaller than that of the ground state. The optical density of plasma for this transition is negligible. According to Eq. (10) the correction factor K can be determined with the help of this spectroscopic line. The results of the measurement are shown in fig. 5. The constant intensity of the plasma radiation is overlaid with additional signal reflected by the mirror. In the case of the ideal mirror and perfectly parallel rays the signal should increase by factor 2. The observed increase of approx 30% quantifies the radiation losses on the way to spectrometer. According to the datasheet of the manufacturer the reflection coefficient of the mirror equals 0.93 at the wavelength 438 nm. Together with the data in fig. 5 the correction factor can be estimated to have the value $K = 0.3$.

After the determination of the geometric correction factor K the measurements of the gas density can be performed with the help of the resonance transition line 123.6 nm. The values of plasma transmission $1 - A_L$ after correction for geometric factor and mirror reflectivity are plotted in fig. 6. The transmission 0.05 (absorption 0.95) can be observed.

This result indicates, that no neutral gas density can be determined with the calculated absorption function shown in figure 2. The maximal theoretical absorption for this line lies at 0.87.

IV. Discussion and outlook

The discrepancy between the measured absorption of 0.95 and maximal possible of 0.87 can have several reasons. One reason is the assumption on the temperature which was used for the calculation of the Doppler width. The assumed room temperature is the lower limit for the real experimental conditions and delivers the maximal value of the Voigt parameter. With increasing temperatures the Voigt parameter tends to the

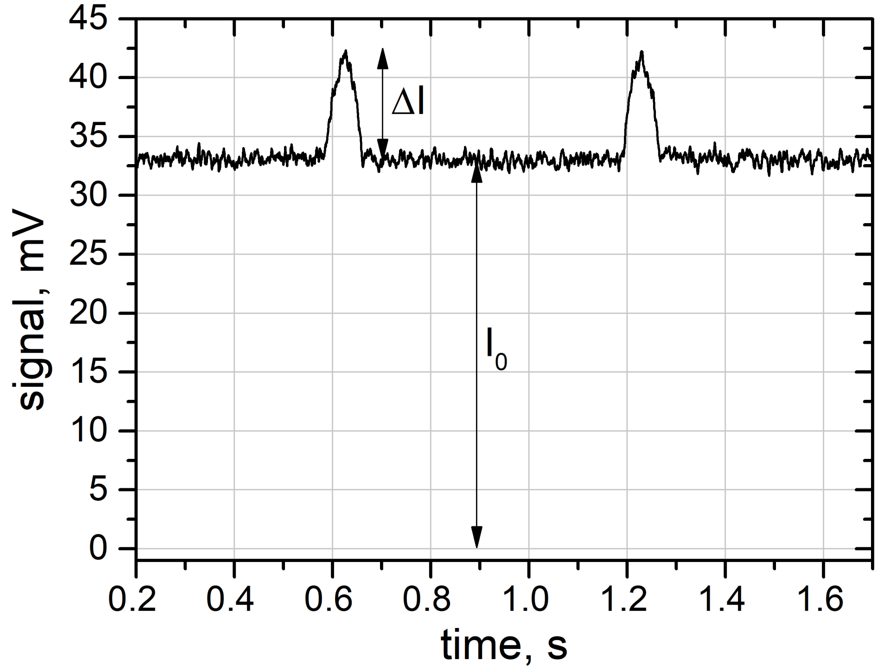

Figure 5: Results of the measurements for optically thin Kr line 437.612 nm. Signal without mirror I_0 and difference due to mirror ΔI are indicated.

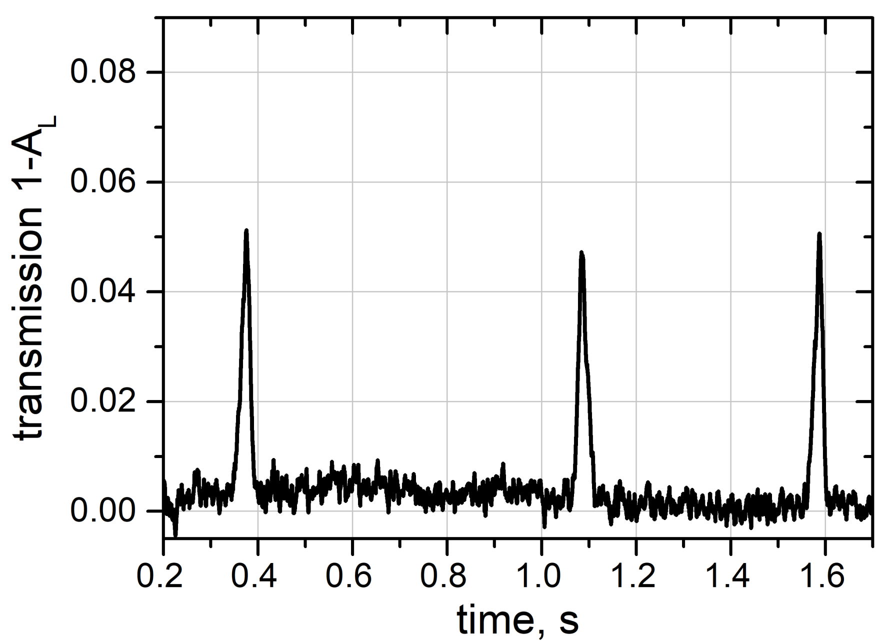

Figure 6: Transmission $1 - A_L$ according to Eq. (9) for optically thick line 123.6 nm of Krypton. The reflection coefficient of the mirror 0.83 and geometric correction factor 0.3 were used.

smaller values. This results in more Doppler like profile which allows for higher theoretical absorption values to be achieved, see figure 1.

Another reason lies in the action of the plasma source as a sputtering device. After the opening of the vacuum chamber is was noted that the mirror was covered with a thin film of the material presumably sputtered from the plasma source. This film would affect the actual reflection coefficient of the mirror. The lower values of the reflection coefficient would yield the lower values of the measured absorption according to Eq. 9.

The mentioned difficulties can be avoided in the case of Xenon plasma. The list of lines[9] in the range 120-200 nm is given in Table 2. The two atomic lines at 125.0210 and 129.5588 have oscillator strengths f_{lu} and hence optical thickness which differ by factor 19. Their corresponding absorption values should differ by the known factor. The reflection coefficient of the mirror should be equal for these near lying two lines.

Table 2: List of the Xenon lines in the wavelength range between 120 and 200 nm.

species	λ_0, nm	f_{lu}
Xe II	124.4756	
Xe I	125.0210	0.01
Xe I	129.5588	0.19
Xe I	146.9610	0.265
Xe II	188.1485	
Xe II	197.2673	

The ratio of the measured signals according to Eq. (9) can be written as

$$\frac{1 - A_L(\tau)}{1 - A_L(\tau/19)} = \frac{\Delta I_{129}}{I_{129}} \frac{I_{125}}{\Delta I_{125}}. \tag{11}$$

The lhs can be calculated from the corresponding absorption functions A_L. The rhs of this equation is given from experiment. This allows the determination of the τ and eliminates the uncertainty connected to the reflection coefficient of the mirror.

The experiments on Xenon plasma are planned in the near future.

V. Conclusion

This paper investigates a method for measuring the neutral particle density in plasmas using VUV absorption spectroscopy. For this purpose, an evaluation method was developed which allows the neutral state density N_l to be inferred from the degree of absorption A_L. The theoretical values of the plasma absorption at high optical densities are considered. It is shown that the line profile of the spectroscopic line plays crucial role in the determination of the optical density of the plasma.

The experiments conducted on model plasma source in Krypton plasma revealed the difficulties in the application of the method. The important factors like reflection coefficient of the mirror and the temperature of the gas are identified. The possible way to avoid those difficulties is shown.

References

[1]M. Walker, 2005 *Effects of facility backpressure on the performance and plume of a hall thruster*, University of Michigan

[2]C. Eichhorn et al *Two-Photon Spectroscopy on Neutral Xenon in the Plume of the Radio-Frequency Ion Thruster RIT-10*, IEPC-2011-302, The 32nd International Electric Propulsion Conference, Wiesbaden, Germany September 11–15, 2011

[3]S. Mazouffre et al "Two-photon laser induced fluorescence spectroscopy performed on free nitrogen plasma jets" *Plasma Sources Sci. Technol.*, Vol. 11, 2002, 439.

[4]J. Yang, S. Yokota, R. Kaneko, and K. Komurasaki, "Diagnosing on plasma plume from xenon Hall thruster with collisional-radiative model", *Phys. Plasmas* , Vol. 17, 2010, 103504

[5]Stroth, U., *Plasmaphysik - Phänomene, Anwendungen und Grundlagen*, 2nd vol., Springer-Verlag, Berlin, 2018, pp. 301

[6]Demtröder, W., *Laserspektroskopie 1 - Grundlagen*, 6th ed., Springer-Verlag, Berlin, 2011

[7]R. J. Cedolin, R. K. Hanson, and M. A. Cappelli, "Laser-induced fluorescence measurements of resonance broadening in xenon", *Rhysical Review A*, Vol. 54, 1996, pp. 335-342

[8]Mitchell, A. C. G. and Zemansky, M. W., *Resonance radiation and excited atoms*, 2nd ed., Cambridge University Press, New York, 1961, Chap. 3

[9]National Institute of Standards and Technology, "NIST Atomic spectra database," *A spectral line database* [online database], URL: https://physics.nist.gov/PhysRefData/ASD/lines_form.html [cited 27 May 2024]

[10]Kunze, H. J., *Introduction to plasma spectroscopy*, Springer-Verlag, Berlin, 2009, Chap. 2