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A new absorption spectroscopy setup for the sensitive monitoring of atomic and molecular densities

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This paper deals with the specifications and the possibilities of a novel highly sensitive optical absorption spectroscopy method. It consists of a cascaded arc as an extremely bright broadband light source with a high resolution spectrometer as a detector. Its interest for a continuous quantitative monitoring of the densities of waste atoms and molecules in the atmosphere is investigated. To this end, theoretical considerations are given with respect to the detection limits and the resolution necessary for selective spectrochemical analysis. In the first measurements with the setup, on a laboratory argon-hydrogen plasma, the versatility and sensitivity of the technique for measuring low density species is demonstrated. Densities of the sublevels of the argon first excited state, the four Ar(3p^4 4s) metastable and resonant substates, were measured simultaneously in one measuring sequence. The data were analyzed using an efficient line of sight integration technique. The densities of these substates are of the order of 10^{17} m^{-3} in a plasma with a pressure of 40 Pa. For the atomic hydrogen H(n = 2) state, densities of the order of 10^{14} m^{-3} over a length of about 2 cm could be measured, representing a detection limit of approximately 2 \times 10^{12} m^{-2}.

I. INTRODUCTION

In recent years, at the Eindhoven University of Technology (EUT) a high-intensity broadband continuum light source has been developed\(^2\) which serves as a light source for various analytical techniques such as ellipsometry\(^3\) and infrared absorption measurements on thin solid films, and Fourier transform infrared spectroscopy (FTIR) on plasmas.\(^4\) Recently, the source was also applied in a setup for optical absorption spectroscopy (OAS) on low-pressure laboratory plasma. As a detection device a photodiode array was used. This device covers a range of about 200 nm around a wavelength position which is selected by a monochromator in the range of 200–900 nm and enables fast recording of multiple atomic spectral lines or complete molecular bands. The aim of this paper is to demonstrate the possible merits of this novel absorption spectroscopy setup for a continuous, simultaneous and sensitive detection of waste-atmospheric particles. To this end, first a brief review is given of the requirements and the characteristics of the various methods currently employed for the monitoring of species in gases and plasmas. Subsequently, the method of optical absorption spectroscopy is addressed in more detail. In the analysis, the specifications of the experimental setup are presented. Its possibilities are illustrated by the results of the first experiments on an expanding cascaded arc plasma, a low-pressure laboratory plasma.

II. METHODS FOR THE MONITORING OF LOW-DENSITY SPECIES

Currently the methods of analytical chemistry are sensitive enough to permit the detection and identification of almost any waste atoms and molecules in the Earth's atmosphere. Growing concern with the pollution of the atmosphere has lead to an explosive increase in the research on various methods for the determination of its composition. The central point in the problem of control and treatment of waste atoms and molecules is the quantitative monitoring of the densities of these particles. Global tasks such as understanding chemical pathways of a given pollutant, estimating the efficiency of a destruction process, evaluating the potential chemical hazard, surveying the compliance of the emissions of a plant with the regulations, etc., require application of sophisticated methods of various absolute concentration measurements. The selection of a particular analytical method depends on a number of criteria: (a) which and how many species are to be measured and over which concentration ranges; (b) what precision and/or accuracy are required; (c) what temporal and spatial resolution is required; (d) how complex is the instrument to operate; is it commercially available.

Among the various methods of analytical chemistry the spectroscopic ones have a high potential to satisfy many of the requirements to resolution, accuracy, and simplicity of the analysis; since all the species have unique spectral characteristics, spectroscopy affords a universal identification in principle, provided that the spectral resolution is sufficient.\(^5\) It is a passive (nonperturbative) technique, which is capable of making real time, in situ measurements. Currently, several spectroscopic methods offer perspectives for the monitoring of waste-atmospheric particles.\(^6\) Among them: (1) Fourier transform infrared spectroscopy (FTIR), (2) tunable diode laser absorption spectroscopy (TDLAS); (3) laser induced fluorescence (LIF); (4) photoacoustic absorption spectroscopy (PAS); (5) optical absorption spectroscopy (OAS). All of the above-mentioned methods have their own advantages and disadvantages. FTIR has the greatest universality and can simultaneously measure a large number of species. Its
main advantage is its ability to measure and identify relatively complex molecules but, its spectral resolution is often insufficient to deal with interferences of rovibrational bands, for example, from CO₂ and H₂O. Temporal and spatial resolution are also often insufficient. It is fairly demanding on operational skill and computational analysis. The basic spectrometer is commercially available, but requires adaptations for field measurements.

TDLAS has the highest spectral resolution and therefore represents the most adequate method of identification. Operating in the infrared spectral region, TDLAS is a universal method although its advantages are restricted to molecules which have resolved rovibrational lines. Its main limitation is the number of species that can be measured simultaneously. One of the large disadvantages of TDLAS is the need for a number of laser diodes to cover a wide spectral range. Complete systems suitable for the measurements are commercially available, but relatively expensive.

LIF has a very high sensitivity and selectivity. This method is not as universal as the others since different excitation mechanisms have to be used for different species. It is an in situ method with a good temporal and spatial resolution, but LIF systems are relatively complex and require a high degree of operator skill. No commercial system is currently available.

PAS is, in principle, a sufficiently simple method and it enables simultaneous measurements. In addition, since the signal is also proportional to the power of the light source, high sensitivity is also potentially attainable. In practice however, it suffers from lack of resolution and from serious interferences, for example, of CO₂ and H₂O. At present, the PAS technique has not been able to reach the same degrees of universality and sensitivity achieved by other spectroscopic methods.

OAS is a technique which is relatively simple to operate. Because most of the commonly used external light sources have limited emission in the infrared, OAS is mainly applied to measurements on the electronic transitions in the visible and ultraviolet. This has the advantage that the molecular bands of various species are clearly separated from each other and that the concentrations of both atomic and molecular reactive species, such as free radicals can be measured with good accuracy, because of the relatively high absorption coefficients in this frequency range. For an adequate quantitative analysis of atomic and molecular spectra it is necessary to use spectrometers with a high sensitivity and a good spectral resolution. Otherwise, in the case of overlapping molecular rovibrational bands, a complicated deconvolution procedure may have to be adopted. Commercial instruments are available, but often the spectral, temporal, and spatial resolution are limited.

From this short review, one can conclude that, if it is not necessary to measure the absolute densities of complex molecules, the method of OAS has the advantages of simplicity of experimental realization and accuracy of the obtained data, and requires limited financial investments. The performance of the OAS methods can be optimized if a stable, high intensity external light source is used which emits broadband continuum radiation combined with an optical multichannel analysis (OMA) device. In this way one can monitor simultaneously and continuously the absolute concentrations of a number of species.

III. OPTICAL ABSORPTION SPECTROSCOPY

Normally OAS is used for absorption measurements in the spectral range from about 200 to 2000 nm. This is determined by the spectral range of the radiation of the commonly used external light sources such as high pressure Xe or Hg lamps and of the detector. In the typical OAS arrangement, a broadband light source is placed at the focus of a spherical or parabolic mirror, the collimated light is received by a similar mirror and focused on the entrance slit of spectrometer. In the space between the mirrors the absorption of radiation occurs. In this way, total or spectral absorption can be measured.

The principal of all OAS methods consists of the experimental determination of the frequency integrated absorption coefficient \( \int_0^\omega k_\nu \, d\nu \), which for homogeneous media is equivalent to\(^7\text{--}\text{9}\)

\[
\int_0^\infty k_\nu \, d\nu = \frac{\lambda_0^2}{8\pi} \frac{g_k}{g_i} \Omega_{k\nu} \left( 1 - \frac{g_i n_i}{g_k n_k} \right),
\]

(1)

where \( k_\nu \) is the spectral absorption coefficient, \( n_i \) and \( n_k \) are the population densities of the lower and upper quantum levels of the radiative transition, \( g_i \) and \( g_k \) are the statistical weights, \( \lambda_0 \) is the wavelength, \( \Omega_{k\nu} \) is the Einstein transition probability. It appears that for determining \( n_i \) one is more interested in the frequency integrated absorption than in the spectral absorption. The total absorption \( \int_0^\infty k_\nu \, d\nu \) is defined as the ratio of the absorbed energy to the incident intensity.\(^8\text{--}\text{9}\) If the incident light is a continuum with spectral intensity \( I_0 \) then

\[
\int_0^\infty k_\nu \, d\nu = \Delta \nu_c \int_0^\omega \frac{\Omega_{k\nu} (I_0 - I_\nu) \, d\nu}{I_0 \, d\nu}.
\]

(2)

with \( \Delta \nu_c \) the optical pathlength and with \( \Delta \nu_c \) the spectral width of the spectrometer. \( f_{app} \, d\nu \) denotes convolution of the intensities with the apparatus profile of the monochromator. Hence, after the measurements of \( \Delta \nu_c \) and \( \int_0^\omega (I_0 - I_\nu) \, d\nu / I_0 \, d\nu \), with known values of \( \Omega_{k\nu} \), \( g_i \) and \( g_k \), and \( \nu \), from Eqs. (1) and (2) one can determine the absolute concentration of the absorbing particles \( n_j \) (of course, if \( n_j \approx n_k \), which is true for most gases and plasmas).

One of the major advantages of OAS is the possibility to measure in situ absolute concentrations of short-living radicals. The determination of radicals such as OH, CH₃, CH₂, NO₃, NH₃, HNO₂, BrO, IO, ClO in the atmosphere, in the exhausts of cars, during waste molecules treatment, in plasmas, etc., is already a common practice. Another advantage of OAS is its ability to measure a number of species simultaneously. In addition to the reactive species mentioned above, OAS can be used to measure the concentrations of O₃, NO₂, NO, SO₂, CH₂O, Ar, Hg, and aromatics, such as naphthalene, xylene, benzene, and toluene.

From Eqs. (1) and (2) one can easily find, that for the chosen atomic/molecular system, there are two parameters which are mainly determining temporal, spatial, and spectral...
FIG. 1. The expanding cascaded arc plasma and the spectroscopy setup: CAS, cascaded arc light source; M: mirrors; L: quartz lenses; P: pinholes; B: beam splitter; C: chopper; T: translator; CASp, cascaded arc particles source; EP: expanding plasma; SS: movable substrate support; W: quartz window; F: order filter; MC: monochromator; PDA: photodiode array; PM: photomultiplier; PC: personal computer.

resolution of the OAS method: (1) radiative power of the external light source, (2) spectral resolution of the spectrometer.

In addition there are two parameters which are mainly determining the sensitivity: (1) the stability of the external light source, (2) the noise of the detection device.

Recently, at the EUT an absorption spectroscopy setup has been developed with excellent qualifications with respect to the requirements above. The system employs a cascaded arc as a bright external light source and, for the detection a high resolution monochromator combined with photodiode array. All of these components are commercially available at limited costs. In the next section these components are addressed in more detail.

IV. EXPERIMENTAL SETUP

A. The light source

In Fig. 1 the optical setup for performing absorption spectroscopy measurements on a low pressure plasma is shown. As a light source, a stagnant cascaded arc, especially designed for the purpose of emitting high intensity radiation, is employed. The arc consists of three tungsten thorium cathodes, with a diameter of 1 mm, a stack of four insulated copper plates, and an annular copper anode. The length of the arc is 42 mm, the diameter of the channel 2 mm. The arc operates on argon with a low flow rate of only 0.05 scc/s (standard cubic centimeter per second), at a pressure between 1 and 10 bar. The current can be adjusted from 20 to 70 A, at a voltage ranging from 85 to 120 V. The temperature in the arc is in order of 12 000-14 500 K. In Fig. 2 the spectral intensity of this arc is shown (adopted from Ref. 1), compared to that of various conventional continuum light sources, such as a commercial 1000 W xenon lamp, and a globar of 1600 K. Compared to these light sources which radiate continuum in a limited region of the ultraviolet/visible, or infrared spectrum, the arc emits a higher intensity radiation over a broader spectral range, extending from the infrared all the way into the ultraviolet region. The intensity of the continuum radiation is only a factor ~10 lower than according to Planck's law. For the spectral lines in the 700-800 nm range, the intensity approaches the value according to Planck and has a value of the order of $2 \times 10^{14} \text{W m}^{-2} \text{m}^{-1} \text{sr}^{-1}$ (again approximately a factor of 10 lower than blackbody radiation). For an application of the source in an OAS technique the high intensity is a major advantage. The accuracy of the absorption data is dependent on the intensity of the external light source as can be seen from Eq. (2), and on the stability of the light source. The variations in the spectral intensity of the source are mainly determined by the statistical noise, which is lower than 1%. The Stark broadening of the argon lines is very large (several tenths of nanometers), and so for absorption measurements on narrow spectral lines, in the direct vicinity of these lines one can consider the source as emitting approximately uniform continuum radiation, with an intensity according to Planck. In previous applications of the cascaded arc its excellent qualities as an external light source have already been proven. For example, in the case of the spectroscopic ellipsometer an extended wavelength range from about 200 nm to 8.5 μm was attained, with the change of a few optical components. In the case of FTIR the improvement of a factor 20-200 (wavelength dependent) in signal-to-noise ratio has been obtained in the infrared in comparison with globars. Summarizing, the application of a cascaded arc as an external light source for optical absorption spectroscopy
(OAS) significantly improves both sensitivity and detection range of the method.

B. The optical system

The light from the source CAS is transferred to the studied medium of the expanding EP cascaded arc plasma CAS, in the following way: By the lenses L1 and L2 (focal lengths 75 and 400 mm, respectively) and pinhole P1 a beam of parallel light is created, and passed on by the beam splitter (B). Rotating the chopper C makes it possible to image a selected signal on the detection system. By using mirror M1 a reference measurement of the external light source intensity Ie can be obtained. If the source is closed, only the emission Ie from the absorbing medium (in this particular case—the low pressure expanding arc plasma) is transmitted to the detection system. In a similar way the dark current of these lenses are 400 and 75 mm, respectively. On the plasma the light beam through the plasma I, is measured in the following way: While mirror M1 is blocked by the chopper, the beam is passed on by the mirror M2, M3, and M4 and focused by a lens L3 (focal length 780 mm), through the plasma, on the mirror M5. The mirror M3, and mirror M4 together with lens L3 are transferable, which enables axial and lateral scanning. The light is reflected, passes the plasma once again, and is transmitted, through the order filter F, to the detection section. The beam is focused on the entrance slit of the monochromator by the optical system, consisting of the lenses L4 and L5 and pinhole P2; the focal lengths of these lenses are 400 and 75 mm, respectively. On the plasma axis the diameter of the detection volume is ~1 cm. A calibration factor for the attenuation through the two branches of the optical system was obtained by taking the intensity ratio of the continuum radiation in the vicinity of the lines under study. The rotation of the chopper C and the translation of the translator T are controlled by the personal computer. In this way, fast and continuous, fully automatic data acquisition has been realized on several spectral lines simultaneously, subsequently on various axial and lateral positions.

C. Influence of the incident light on the medium under investigation

It should be established whether or not the high intensity of the light source perturbs the medium under investigation significantly, for example by photoexcitation or photodissociation. One can estimate the number of atoms, photoexcited per unit of volume and per unit of time, \( \Delta n_{\text{exc}} \) as a consequence of light absorption. For the spectral lines the light source plasma is optically thick and we can consider the radiation emitted by the end of the arc channel as approximately isotropic. This source, with an emissivity according to Planck and an area of \( S_v \), is radiating on a lens with a collection solid angle of \( \Delta \Omega_v \). The acceptance solid angle of the detection volume is \( \Delta \Omega_d \) and its average cross-section area \( S_d \). Now using the concept of radiation density and the Einstein relations it can easily be deduced that in the detection volume

\[
\Delta n_{\text{exc}} = n_i A_{ki} \left( \frac{1}{h \nu} \right) \frac{1}{4 \pi} S_v \Delta \Omega_v \frac{S_d}{S_v} \Delta \Omega_d,
\]

with \( n_i \) the concentration of the absorbing atoms, \( A_{ki} \) is emission transition probability, and \( T \) the radiation temperature of the source. \( S_d = L^2 \Delta \Omega_d \) with \( L \) the distance to the focal plane on mirror M5. In the present experimental situation \( S_d/S_v = 4 \times 10^{-2} \), \( \Delta \Omega_v = 1.4 \times 10^{-5} \) sr, \( h \nu/kT = 1 \), \( g_b/g_i \) is maximally 5/3. For the attenuation factor through the optical system and the windows a lower limit of at least 5 can be taken into account. So, in a transition with a probability \( A_{ki} = 10^6 \) s\(^{-1}\), we find \( \Delta n_{\text{exc}} < 10^5 n_i \).

This photoexcitation rate should be compared with the excitation rates by collisional processes in the plasma. For the typical conditions in an expanding cascaded argon arc plasma: the electron density \( n_e \approx 10^{10} \) m\(^{-3}\), the electron temperature \( T_e \approx 2-3 \times 10^3 \) K, \( ^{10} \) and for the rate constants \( \langle \sigma v \rangle \) of direct electron excitation of argon atoms \( \text{Ar}(4s \rightarrow 4p) \), \(^{11} \) it is easily established that \( \Delta n_{\text{exc}} = n_e \langle \sigma v \rangle \approx 10^{-5} n_i \). This estimate shows that the photoexcitation rate of the argon atoms in an expanding arc plasma is of much lower order than the electron excitation rate so, in this case the influence of the external source radiation on the properties of the plasma under investigation can be neglected and the use of attenuation filters is not necessary.

D. The detection system

The detection system consists of a Czerny–Turner monochromator (THR-1000 of Jobin–Yvon), with a focal length of 1 m. The entrance slit width was set at 25 \( \mu \)m. The entrance angle of the light beam was approximately 1/10 rad, and optimum filling of the diffraction grating was obtained. For a 1200 grooves/mm grating the dispersion of the monochromator is 0.8 nm/mm (at a wavelength of 5000 nm). On the exit plane of the monochromator a photodiode array (Reticon RL 1024 S) is placed. The array is Peltier cooled (to \(-14^\circ \)C) in order to reduce the thermal noise of the device. It consists of 1024 elements (pixels) with a width of 25 \( \mu \)m per diode, and a height of 2.5 mm. With this element a spectral range of about 20 nm can be recorded at one time. After AD conversion by a PCL-718 lab card (4096 bits), the signal of the photodiode array is recorded by a personal computer.

E. The spectral resolution

The application of a photodiode array in absorption spectroscopy experiments requires a careful analysis of the measured data. The measured integrated relative absorption \( A_m \) is given by

\[
A_m = 1 - \int_{\text{app}} (I_i + I_e) d\nu - \int_{\text{app}} I_e d\nu - \frac{S_d}{S_v} \int_{\text{app}} \frac{S_v}{S_d} I_d d\nu.
\]

\( f_{\text{app}} d\nu \) denotes convolution of the intensities with the apparatus profile of the detection system, that is the monochromator and the diode array. The measured source intensity per pixel can be written as
\[ I_{\text{pixel}} \left( \int \frac{M(v')I_0}{\Delta \nu_{\text{pixel}}} dv' \right) dv = \int \frac{I_0 \Delta \nu_{\text{pixel}}}{I_0} = I_0 \Delta \nu_{\text{pixel}}, \]

in which \( M(v) \) expresses the apparatus profile, which is normalized to unity as usual: \( \int M(v)dv = 1 \). As the source is a continuum source, \( \text{Eq. (5)} \) is true for every pixel in the array. Considering that the width of the absorption line (\( \sim 4 \) pm) is much smaller than the spectral width of one pixel (\( \sim 17 \) pm), the maximum measured absorbed source intensity in one pixel is the integrated absorption area \( \int I_{\text{abs}}(v)dv \).

For broader lines and/or a broad apparatus profile we can write the measured absorbed source intensity per pixel \( I_p \), more generally as:

\[ I_p = \int \frac{I_{\text{pixel}} M(v')I_{\text{abs}}(v-v')dv'}{\Sigma_{\text{app}} \Delta \nu_{\text{pixel}}} = \int \frac{I_{\text{pixel}} M(v')I_{\text{abs}}(v-v')dv'}{\Delta \nu_{\text{pixel}}}. \]

Some care should be taken in applying \( \text{Eq. (4)} \). In general, it is not possible to apply this equation for each pixel separately; except for the case of a large entrance slit width and a rectangular apparatus profile. The equation for the general case of an arbitrary apparatus profile is obtained by integrating the intensities over the entire apparatus profile (\( N \) pixels). Now, by using the expression for \( I_p \) for the numerator and \( \text{Eq. (5)} \) for the denominator, we can write \( \text{Eq. (4)} \) as:

\[ A_m = \int \frac{I_{\text{app}} M(v')I_{\text{abs}}(v-v')dv'}{\Sigma_{\text{app}} \Delta \nu_{\text{pixel}}} = \frac{1}{N \Delta \nu_{\text{pixel}}} \int I_{\text{abs}}(v)dv \]

\[ = \frac{1}{N \Delta \nu_{\text{pixel}}} A_{bg}, \]

with \( A_{bg} \) the total absorption as defined by \( \text{Eq. (2)} \). With \( N \Delta \nu_{\text{pixel}} = \Delta \nu_v \), \( \text{Eq. (6)} \) is equivalent to \( \text{Eq. (2)} \). Of course, increasing the entrance slit width of the monochromator does not change the value of the total absorption at all. The slit width enters the equation only because the measured total source intensity is proportional to the square of it and the measured total absorption only linearly proportional to it. Furthermore, it should be stressed that \( N \) is the number of pixels over which the apparatus profile spreads the absorption, and it is clear that this number should not be too small in the calculation. Note, however, that the exact value of \( N \) is not an integer. Fortunately, \( \text{Eq. (6)} \) remains valid if the number of pixels \( N \) is taken larger than the number over which the apparatus profile is spread, and this supplies us with the following method of determining \( A_{bg} \) without determining the apparatus profile (the number of pixels \( N \)) exactly. By integrating the last term of \( \text{Eq. (6)} \) over a variety of values \( N \), \( A_{bg} \) can be determined from the slope in a graph of measured absorption \( A_m = N \Delta \nu_{\text{pixel}} \) vs \( 1/N \). This procedure was applied on every measured absorption value.

In the current experiments on the expanding argon plasma the spectral width of the atomic absorption lines was much smaller than the spectral width of one pixel. As one is mainly interested in the total absorption, this is no objection. In the case of the quantitative monitoring of the densities of molecules, however, the rotational structure may have to be resolved. If the main broadening mechanism is Doppler broadening (e.g., in atmospheric gases and low-density plasmas), in general, the spectral resolution has to be in the range \( \sim 1-10 \) pm.\(^5\) In the case of the absorption of radiation in a plasma, additional mechanisms of spectral line broadening may be present and a higher resolution may be necessary to determine the total absorption of a separate rotational line. It is evident that a reduced width of the pixels and/or an increased dispersion of the monochromator will improve not only the spectral resolution of a system, but also the signal-to-noise ratio [cf. \( \text{Eq. (6)} \)].

\[ A_m = 6.4 \times 10^{-1} \frac{g_k}{g_i} \frac{\tilde{n}_i \Lambda_{kl} I}{\tilde{n}_i \Lambda_{kl} I}, \]

with \( \tilde{n}_i \) expressed in units of \( 10^{15} \text{m}^{-3} \), \( \Lambda_{kl} \) in units of \( 10^8 \text{s}^{-1} \), \( I \) in m (the coefficient is already multiplied by 2 for the double pass). As an example, taking for the density a value \( \rho_{p1} \leq 1 \) in \( \text{Eq. (2)} \) for weak absorptions [and applying \( \text{Eq. (6)} \)]. For the measured integrated relative absorption \( A_m \) we find, with \( \Delta \nu_v = 8 \times 10^9 \text{s}^{-1} \)

\[ A_m = 6.4 \times 10^{-1} \frac{g_k}{g_i} \frac{\tilde{n}_i \Lambda_{kl} I}{\tilde{n}_i \Lambda_{kl} I}, \]

with \( \tilde{n}_i \) expressed in units of \( 10^{15} \text{m}^{-3} \), \( \Lambda_{kl} \) in units of \( 10^8 \text{s}^{-1} \), \( I \) in m (the coefficient is already multiplied by 2 for the double pass). As an example, taking for the density a value of \( 10^{-15} \text{m}^{-3} \) and for the length \( l \) the diameter of the chamber (50 cm), for the three transitions coming from the argon \( 2p_1 \) substrate, 800.6, 810.3, and 842.4 nm, we will find measured absorptions of 0.025, 0.089, and 0.124, respectively. An analytical expression for the inaccuracy in the density determination, based on the absolute or relative measurement error.
cannot be deduced, because the total absorption depends nonlinearly on the density of the absorbing species.

The absolute inaccuracy in the measured relative absorption value is maximally -0.05. By the integration fit procedure the inaccuracy is reduced by a factor of $\sqrt{N_m}$, with $N_m$ the number of lateral measuring positions, and becomes -0.01. This implies that for the strong argon lines, the lower limit of the detection is of the order of a density of $10^{15} \text{ m}^{-3}$ over a length of 5 cm, that is the plasma core. This also means that lower densities will give significant absorption data when the optical pathlength is longer, e.g., for the background gas in the vessel. For the strong 656.3 nm $\text{H}_\alpha$ line the sensitivity of detection is even better as it is illustrated in the next section.

V. DISCUSSION

The first experiments with the experimental setup have been carried out on the determination of the population densities of the resonant and metastable substates of the argon $\text{Ar}(3p^54s)$ state, and of the atomic hydrogen $\text{H}(n=2)$ state in an argon-hydrogen plasma jet, expanding from a cascaded arc plasma source into a vacuum chamber. This technique is used for the deposition of amorphous and crystalline carbon and silicon thin layers at very high growth rates. For this purpose, molecular gases like hydrocarbons or silane are admixed into the expanding plasma beam. In these specific plasmas the $\text{Ar}(3p^54s)$ and $\text{H}(n=2)$ metastables may play an important role in energy exchange processes to the admixed species by mechanisms like Penning ionization.

Preliminary experiments were performed to also measure the density of hydrogen metastables in an expanding argon-hydrogen plasmas. It appears that this species could only be detected in the case of specific reactor settings. The reactor parameters used were: arc current 45 A; argon flow rate 100 $\text{scm}$; molecular hydrogen flow rate 14 $\text{scm}$; chamber pressure 100 Pa.

In Fig. 3 the ability of the fit method to yield smooth density profiles is illustrated. A map of the total densities of the $\text{Ar} 3p^54s$ first excited state in an argon plasma jet expanding in the vacuum chamber (radius 25 cm) is shown, based on the radial density profiles obtained on six axial measurement positions. These profiles have been obtained by fitting the measured relative absorption values on the four substates with a combination of two Gaussian density profiles. The narrow profile represents the argon 4s first excited states in the core of the expanding plasma beam. The wide background profile represents argon 4s states in the background gas.

In Fig. 4 the axial decay of the densities of the four $3p^54s^2 P_{0,1,2,3}$ substates in an expanding plasma beam is shown. The values are given per statistical weight and corrected for the Boltzmann exponent. The inaccuracy in the density determinations is about 10%. It can be observed that the sublevels are approximately thermally populated, as they should be due to the strong coupling between the sublevels.

This result illustrates the ability of the experimental setup and the data analysis method to yield relatively accurate density determinations.

In Fig. 5(a) radial density profiles of the hydrogen $\text{H}(n = 2)$ states, obtained for two axial positions in an expanding argon-hydrogen plasma beam are shown, as obtained by absorption measurements on the strong $\text{H}_\alpha$ 656.3 nm transition. On axial position $z=127 \text{ mm}$, a local atomic density of the order of $2\times10^{14} \text{ m}^{-3}$, over a length of only ~2–4 cm in the plasma core has been detected. The broad background profile of the total density of the argon 4s first excited state in a cascaded arc plasma jet expanding in a vacuum chamber (radius 25 cm).

FIG. 3. Map of the total density of the argon 4s first excited state in a cascaded arc plasma jet expanding in a vacuum chamber (radius 25 cm).

FIG. 4. Argon 4s densities per statistical weight and corrected for the Boltzmann exponent as a function of axial position $z$ in an expanding plasma beam. (△), (○), (■), (●), $3p^54s(3P_0)$, $(3P_1)$, $(3P_2)$, and $(3P_3)$, respectively.
file, with a top density of $7 \times 10^{13} \text{ m}^{-3}$ and a $1/e$ width of $\sim 1.5 \text{ cm}$, represents hydrogen $H(n=2)$ atoms in the background gas. In Fig. 5(b) the power of the analysis method is illustrated. The actual measured relative absorption values and best-fit profiles through these points are shown. For $z=27 \text{ mm}$ the fitting with the two Gaussian density profiles yields an adequate fit to the measured relative absorption values. For the position $z=127 \text{ mm}$ the data are observed severely by the measurement noise. Nevertheless the fit procedure with the two Gaussian density profiles succeeds in obtaining a best-fit measurement profile which is positive on the average. It is obvious that in this case the uncertainty in the obtained density values is relatively high, of the order of 50%. Nevertheless, this example shows that in principle relative absorption values of the order of only 0.01 can be resolved. The uncertainty in the final result can be reduced by increasing the signal-to-noise ratio, e.g., by averaging over more measurements. Therefore, the detection limit for the atomic hydrogen $H(n=2)$ state is of the order of $2 \times 10^{12} \text{ m}^{-2}$ (see also Ref. 22).

Up to now, no absorption could be measured on molecular species in the expanding plasma beam. Recently, evidence has been obtained that this may be due to a population inversion in the expanding plasma beam.\(^\text{23}\)

In general, if densities are low and/or the signal is distributed over the rotational bands, the detection limit must be lowered by employing a multipass system.\(^\text{24}\) For a quasi-one-dimensional medium like the atmosphere, a construction with fixed mirrors is sufficient.

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