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Absorption spectroscopy on an expanding argon arc plasma

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Résumé – Nous avons utilisé la spectroscopie d'absorption pour déterminer les densitées des niveaux 4s, résonnantes et métastables, dans un plasma d'argon en expandant d'un arc à cascade. Une technique avec une détection optique par un réseau de diodes est presentée. On a mesuré aux lignes spectrales fortes en la région de 790 à 860 nm. Ensuite on obtient une relation non–linéaire entre les valeurs d'absorptions mesurées et les densitées à déterminer. Une procédure mathematique pour évaluer cette relation est presenté. C'est demonstré qu'on peut obtenir des résultats satisfaisants, sans mésurer exactement le profil de la ligne spectrale. Les valeurs des densitées des niveaux 4s sont de l'ordre de $10^{17}/m^3$, à une pression dans le récipient de 40 Pa.

Abstract – Absorption spectroscopy has been used to determine the population densities of the resonant and metastable 4s levels in an expanding cascaded arc argon plasma. An experimental method using optical multichannel analysis is presented.
Measurements have been done on the argon lines between 790 and 860 nm. The use of these strong lines necessitates a correction procedure for the non–linear relation between the measured absorption values and population densities. It is demonstrated that, to this end, in the present method an exact line shape analysis is not necessary. Ar 4s densities have been determined in the order of $10^{17}/m^3$ at a background pressure of 40 Pa.

1 – INTRODUCTION

There is considerable interest in non–equilibrium phenomena in a supersonically expanding argon plasma /1–2/. By emission spectroscopy and Thomson scattering experiments it has been established that the higher excited states are approximately in equilibrium with the continuum /2/. The lower excited states are underpopulated, indicating the recombining character of the plasma (see for instance /2–6/). In other work /7/ the densities of the 4s excited states are shown to be higher than those predicted by the Saha equation.

In our group expanding cascaded arc plasma's are used for deposition purposes. By admixing gases like hydrocarbons or silane, and hydrogen or oxygen amorphous and crystalline carbon and silicon layers have been deposited /8–10/. Generally the growth rates of these layers (tens of nm/s) are an order of magnitude higher than with conventional methods like PECVD (Plasma Enhanced Chemical Vapour Deposition). In these specific plasma's the abundance of the argon 4s–metastables is of interest as they may play an important role by exchange mechanisms like Penning ionisation.

2 – ABSORPTION THEORY

The argon $(3p^5)$ 4s states can be distinguished into two metastable states ($^3P_0$ and $^3P_2$, or in other notation, s_3 and s_5) and two resonant states ($^1P_1$ and $^3P_1$, s_2 and s_4).
We will briefly discuss the theory for the case of a light source with continuum emission (intensity I_0) on all frequencies
For the absorption coefficient k_ν on an atomic level with a population density N_i the following relationship can be derived:

$$\int_0^\infty k_\nu d\nu = \lambda_0^2 g_k.N_i.A_{ki}/8_\Pi.g_i \tag{1}$$

k_ν depends on frequency ν because line absorption is a typical resonance phenomenon.

λ_0 is the wavelength, g_i and g_k are the statistical weights of the lower and upper quantum levels of the transition, respectively. A_{ki} is the transition probability (Einstein coefficient).

It appears that for determining N_i one is more interested in the total line intensity and in the total line absorption, than in spectral intensity I_ν. The total absorption A_g is defined as ratio of the absorbed energy to the incident intensity /11/. If the incident intensity is I_0, the absorbed energy will be $I_0 \int_0^\infty [1 - \exp(-k_\nu l)]d\nu$, and:

$$A_g = \int_0^\infty [1 - \exp(-k_\nu l)]d\nu = \Delta\nu_c \frac{I_0 - I_\nu}{I_0} \tag{2}$$

where $\Delta\nu_c$ is the spectral width of the section of the continuum spectrum which is admitted through the spectral device, l is the optical pathlength.

For the case of weak absorption, when $k_\nu l << 1$, expression (2) can be simplified to:

$$A_g = \int_0^\infty [1 - \exp(-k_\nu l)]d\nu \cong l \int_0^\infty k_\nu d\nu. \tag{3}$$

Using (2) and (3) one can directly obtain a relationship between the measured total absorption and the population density N_i:

$$\Delta\nu_c \frac{I_0 - I_\nu}{I_0} = \lambda_0^2 g_k.N_i.A_{ki}.l/8_\Pi.g_i \tag{4}$$

It suffices to measure only the value of the relative absorption $(I_0 - I_\nu)/I_0$, and the spectral width of the light source $\Delta\nu_c$. In this case it is not necessary to carry out detailed measurements of the spectral line shapes.
In practice the measuring of weak absorption puts high demands on the optical system (e.g. multipass methods), the stability of the light source and the sensitivity of detection.
In the case of strong absorption the integral in the left part of equation (3) can be calculated by numerical methods. The total absorption on a 'strong' line, governed by the exponent, depends severely on the function $k(\nu)$, i.e. the ratio between Lorentz and Gauss fraction of the line. In the case of a pure Lorentzian profile radiation can still escape through the wings of the line. The escaping radiation intensity again yields an approximately linear relationship to the incident intensity. In the general case of a considerable Gaussian broadening a non–linear relationship arises: saturation of the measured absorption may arise in the top of the profile. An

extensive treatment of this problem has been given by van der Held /12/.
The particular shape of the profile of the absorption coefficient depends on the mechanisms of spectral line broadening in the plasma. For a typical expanding plasma (at a distance of > 2 cm from the nozzle), with a typical temperature of 3000 K and an electron density of $<10^{19}$ m^{-3}, the ratio between Lorentz and Gauss width is in the order of 0.01 or less. For convenience, in the present study we will assume a pure Gaussian line profile:

$$k_\nu = k_0 \exp\left\{-\left[2\sqrt{\ln 2}\,\frac{(\nu - \nu_0)}{\Delta\nu_d}\right]^2\right\}, \qquad (5)$$

where $\Delta\nu_d$ is the full width at half–height. For Doppler broadening the value of $\Delta\nu_d$ depends only on the temperature T, and on the molecular weight M of the absorbing (emitting) particles:

$$\Delta\nu_d = 2\sqrt{2R\ \ln 2}\,\frac{\nu_0}{c}\sqrt{T/M}, \qquad (6)$$

M in molar mass of the gas, R is the gas constant.
Combining equation (1), (2) and (5) one can calculate the curve shown in fig. 1 between measured total absorption A_g and the optical depth k_0l, which directly yields the density N_i.

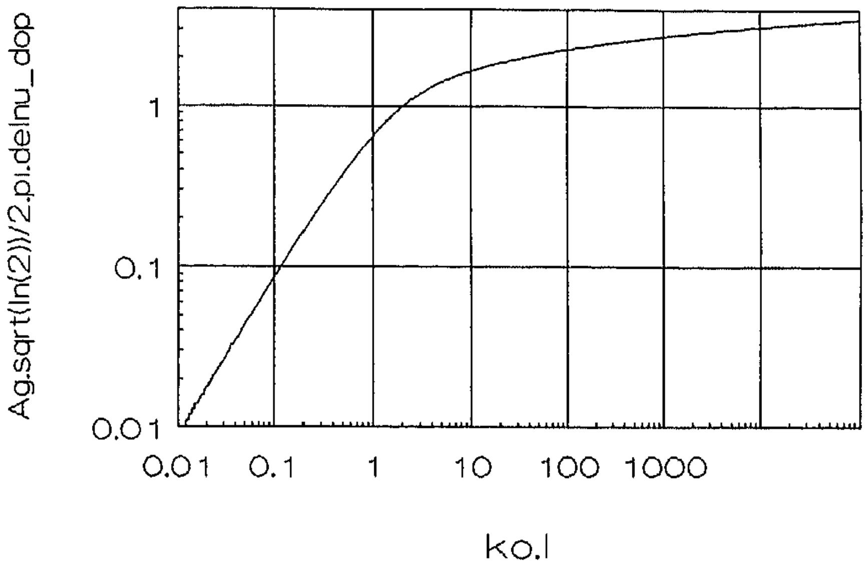

Fig. 1 The van der Held curve for the case of a pure Gaussian absorption profile

3 – THE EXPANDING CASCADED ARC AND THE ABSORPTION SPECTROSCOPY SET UP

In figure 2 an outline of the expanding cascaded arc up with the absorption spectroscopy arrangement is shown. A cascaded arc plasma (4 mm diameter, 6 cm length), expands in a vacuum chamber. Specific features of the source are a high power dissipation (current 45 A, power ~4 kW), a thermal plasma (temperatures ~1 eV) and a high ionization degree (about 10%). The argon is injected at the beginning of the arc channel at a flow rate of 3.5 standard liter per minute (normalized on a pressure of 10^5 Pa). The inlet pressure is in the order of 5.10^4 Pa. The electron density is in the order of 10^{22}/m^3. In the arc, the plasma is close to LTE (Local Thermal Equilibrium). The particles are accelerated, pass through a nozzle and reach supersonic velocities up to ∼4000 m/s. After passing through a shock they expand further in the chamber at subsonic velocities, decreasing down to a few hundreds of m/s. The typical value for the chamber pressure is in this case 40 Pa; in this case the shock can be observed at about 6 cm from the nozzle. Beyond the shock, the total energy of the species decreases to typically about 0.5 eV. The total transport time of all particles is relatively small (in the order of 10^{-4} to 10^{-3} s), the radiative recombination is neglegible, the loss of ionization by three particle recombination is less than 1% /2/. More details on the reactor and the cascaded arc can be found elsewhere /2, 8–10/.

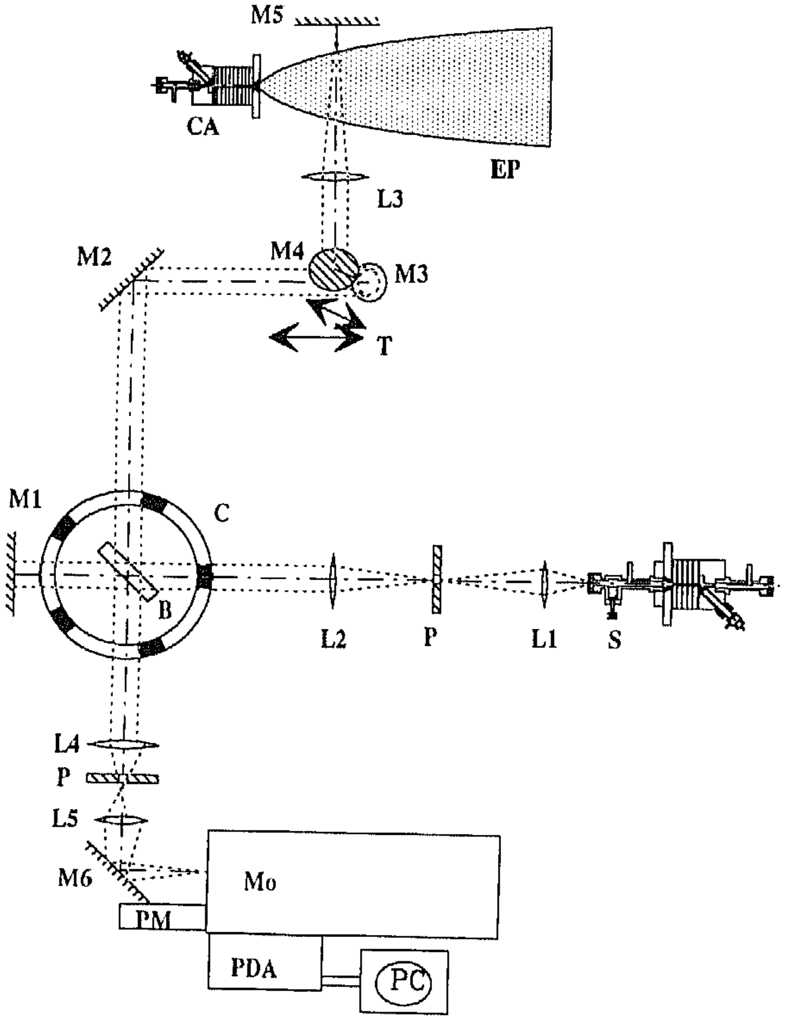

Fig. 2 The expanding cascaded arc plasma and the absorption spectroscopy set up. L1–5 are lenses, M1–6 mirrors; the characters P indicate diaphragmas.

The light source (S) for the absorption spectroscopy is a stagnation cascaded arc /13/ with a high pressure of 4 bar and a temperature of 1.5 eV. The emission profile follows Planck and approaches it in its line intensities. The stability is better than 1%. By using argon in this arc too, one can make use of these high line intensities. The Stark broadening is so large (some ångströms) that we can consider this as a continuum source. The light is transmitted via a rotatable chopper (C) with a beam splitter (B), and the optical system through the expanding plasma (EP). The light is reflected focused on a mirror (M5) at the back of the chamber and reflected back through the optical system to the detection. With the translation (T), axial and lateral scans can be made. By rotating the chopper one can alternately pass the intensities to be measured to the monochromator (Mo) and with the diode array (PDA), or block them. The use of a diode array coupled to a personal computer (PC) makes very fast data acquisition for more lines simultaneously possible. (A photo multiplier PM can also be used). It can be deduced that in formula (2) for the spectral slit width, the spectral width of one pixel has to be used. One can easily understand this by considering each pixel as a very small slit of 25 μm. The spectral width per pixel is 17 picometer. Intensities are measured, integrated over a line of sight, so Abel inversion has to be applied. We can suppose that the analysed absorbing medium has cylindrical symmetry. The observation occurs perpendicular to the axis of symmetry.

A severe restriction of the method appears here: We have to assume that along the observation path the profiles of the spectral lines do not change. Otherwise the contributions of the variations of k_0 and the non–linearity cannot not be resolved.

This requirement will be fullfilled if the radial gradients of electron density and the temperatures are small. In the present case of pure Gaussian broadening the radial gradient of the heavy particles temperature is small enough, not to close to the nozzle ($\succeq$ 2 cm).

The measured A_g can then directly be related to $k_0 l$ according to fig. 1. However in this case this means $\int k_0 dx$, which means that we do not know the length l exactly. It is approximated in the Abel inversion procedure. k_0 is coming in the familiar Abel inversion formulas in the place of emissivity (in the case of emission), and has been computed by a tomographic Abel inversion numerical method /14, 15/.

4 – RESULTS AND DISCUSSION

In figures 4.a through h, the results, obtained for various strong and weak transitions are given. As explained in section 2, the heavy particle temperature has to be taken constant over a radial crossover of the plasma. On a similar cascaded arc set up, with the same standard conditions, the axial values for the temperature have been determined by Fabry–Perot line profile measurements/3/. They are shown in figure 3. The shock can clearly be distinguished by the temperature increase at about 40 mm from the nozzle. For our case these values appear to be not suited. The densities obtained for lines of various transition probabilities varied widely. The temperatures which gave the best over–all results for the densities determination, using different lines, are depicted in the figure by the symbol ▾. The values are mostly shifted in axial direction by about 20 mm, which means that in our case the shock occurs at about 60 mm from

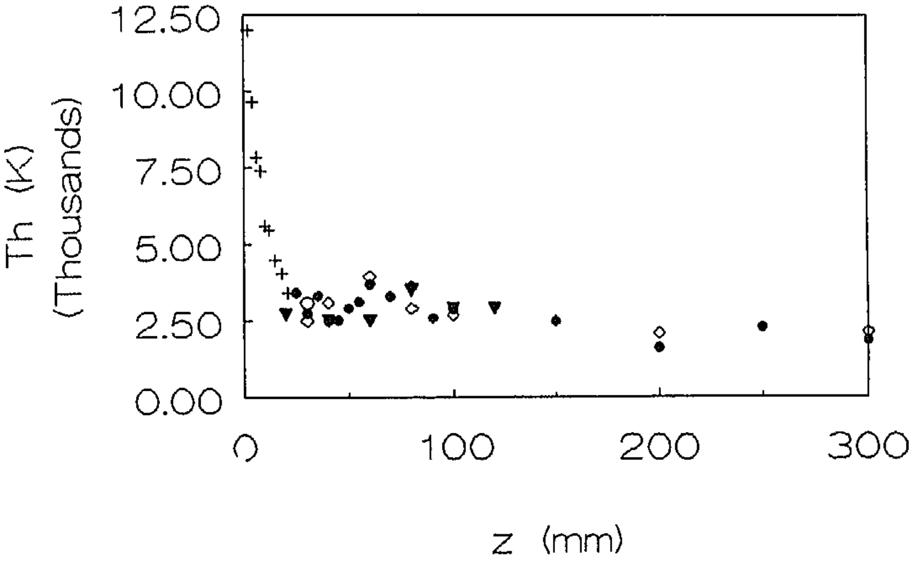

Fig. 3 Heavy particle temperature T_h on the axis of the expansion for the actual standard arc conditions (from /3/). z is the distance from the nozzle. Spectral lines used: o, •, ◇ 696.5 nm, + 415.9 nm The symbols ▾ indicate the estimated averaged temperatures in our case.

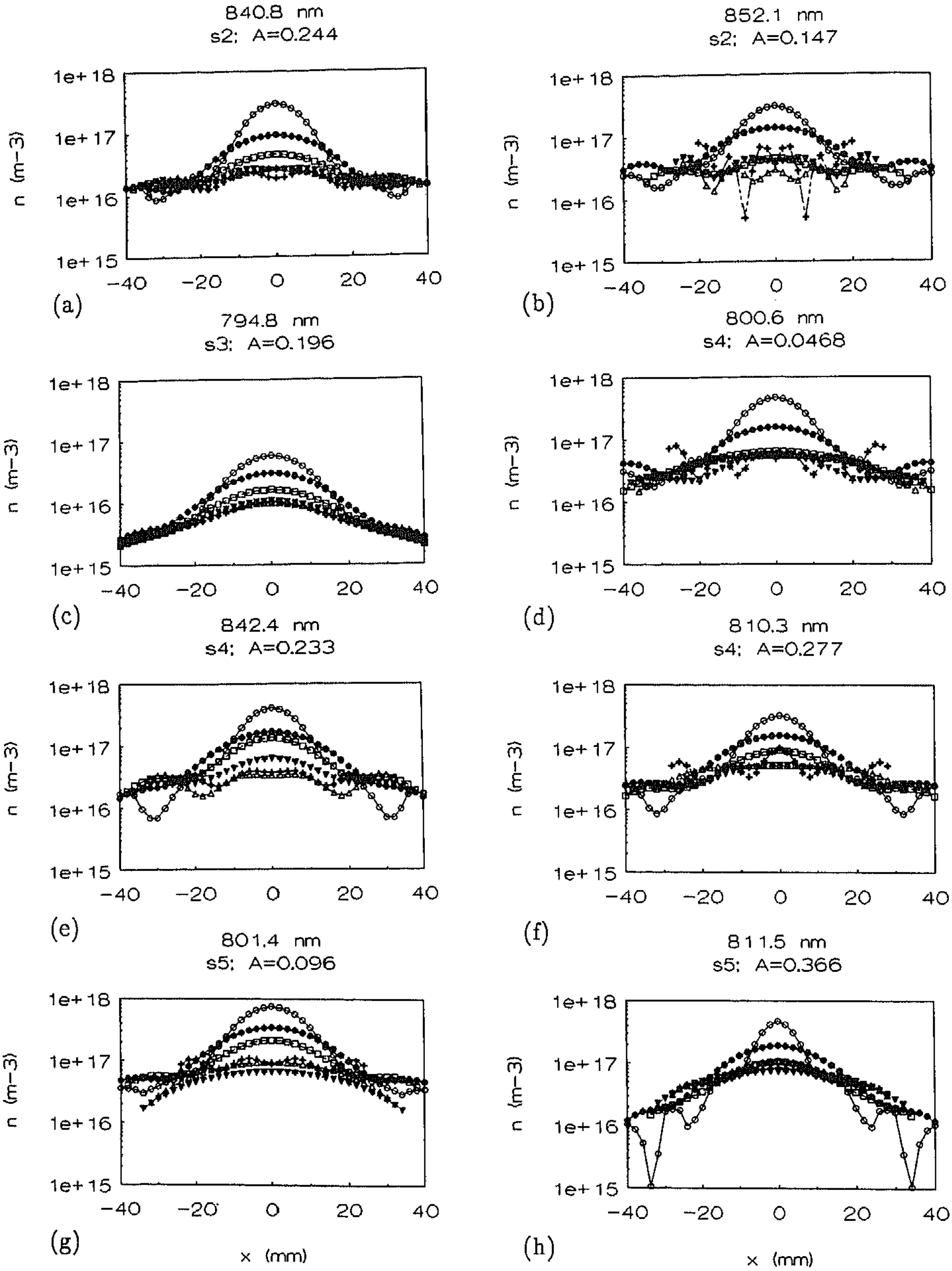

Fig. 4 (a)–(h) Population densities of the four Argon 4s–states, using various lines. x is the lateral coordinate, z the distance from the nozzle, o, •, □, ▼, △, + 20, 40, 60, 80, 100 and 120 mm respectively.

the nozzle. This implies that in principle this method also supplies a way to determine temperatures. Furthermore, an effect of averaging the temperature over the optical path has to be taken into account.

An example of the reproducibility of the obtained densities is given in figs. 4 (d) through (f), for 3 lines coming from the same state s_4. For most axial positions the values vary within 20%. The absolute values of the densities are in the same order as the ones obtained in /3/. In the values for the four states their statistical weights g_i (3, 1, 3, 5 resp.) are reflected. This means that n_i/g_i is about the same, indicating a kind of equilibrium between the four states. With respect to the argon ion level, these 4s densities imply an underpopulation factor of about $3.5.10^{-4}$ /2/, indicating the recombining character of the plasma. As concerns the processes in the shock, the actual density measurements are not sufficiently accurate to analyze these.

5 – CONCLUSIONS

1 The measurement of the population densities of the Ar 4s levels is very well possible. For this purpose it is not necessary to resolve the shape of the absorption profile.

2 For high values of k_0l complications arise, because of the non–linearity of the formulas. However, in order to determine accurate lateral values the use of these lines is preferable. Accurate determination of radially resolved values becomes a complicated question, and is probably only possible for the linear case of weak absorptions.

3 Densities of the levels varying from values in the order of $10^{18}/m^3$ near the nozzle to values in the order of $10^{16}/m^3$ at off–axis values and further from the nozzle. The concentration of the 4s metastables near the nozzle would imply an underpopulation factor of about $3.5.10^{-4}$.

4 The method offers a way for determining (averaged) temperatures.

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