Atomic hydrogen and argon ground state density determination in a recombining plasma using visible light absorption spectroscopy

Citation for published version (APA):

DOI:
10.1088/0022-3727/28/7/013

Document status and date:
Published: 01/01/1995

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 23. Apr. 2019
Atomic hydrogen and argon ground state density determination in a recombining plasma using visible light absorption spectroscopy

D K Otorbaev, A J M Buuron, M C M van de Sanden, R F G Meulenbroeks and D C Schram

Department of Physics, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Received 9 February 1995, in final form 5 April 1995

Abstract. The atomic radical density in the first excited state, obtained by the technique of optical absorption spectroscopy, and a simple kinetic model are used to determine the radical ground state density in a recombining expanding plasma. The kinetic model used does not require knowledge of the shape of the electron energy distribution function. The information on electron density and electron temperature has been derived from the Thomson-Rayleigh scattering diagnostic. The method is demonstrated for the determination of the absolute ground state densities of atomic hydrogen H($n=1$) and argon Ar(3p$^6$) in a freely expanding plasma jet.

1. Introduction

Development and characterization of high-intensity sources of reactive short-lived radicals are of great interest to the surface physics, fusion and low-temperature plasma physics community. As a rule, the kinetics of the radicals in the plasma is difficult to simulate since it requires accurate knowledge of all the relevant kinetic processes, including heterogeneous phenomena on the walls [1]. Therefore, experimental methods have to be employed to characterize the radical properties in the plasma.

Optical emission spectroscopy (OES) is the main technique used to measure the radicals' excited states' population densities, since it is easy to realize this method in practice. More complicated problems arise when OES is used to derive the radical ground state density, which is the main quantity of interest for plasma characterization. Detailed kinetic modelling, including accurate information about the electron energy distribution function (EEDF) is usually required in order to find a correlation between the radicals excited and ground state densities [1].

Using optical absorption spectroscopy (OAS), information on the density of the lower quantum state of the radiative transition can be obtained. However, for many of the practically important atomic radicals, such as H, O, C, N, F and Cl, the resonant radiative transitions belong to the vacuum ultraviolet (VUV) part of the spectrum. Therefore, for radical characterization in the general case, a complicated technique involving the VUV coherent and non-coherent OAS must be used to get quantitative information on the radical ground state (see for example [2,3]).

The aim of this paper is to present a method for radical ground state density determination using experimental data on the radical density in the first excited state. The technique presented is applicable to recombining plasmas. The radical density in the ground state is derived from visible light OAS and a simple kinetic scheme, which does not require knowledge of the shape of the EEDF in the plasma. The information about electron density and electron temperature has been obtained from a spatially resolved Thomson-Rayleigh scattering diagnostic.

2. Methods

In recombining plasmas, the excited states of atoms and molecules are populated by the flux going from the recombination of ions and electrons to the ground state. It is important that, even at the very beginning of the recombination, a rapid drop of the electron and heavy particle temperature takes place in the expansion [4,5]. For the transitions between the ground and excited electronic quantum states, only the radiative processes remain important, because the energy gaps between the levels $\Delta E_{ph}$ are much larger than the electron and heavy particle kinetic energies $kT_e$ and $kT_0$. At the same time collisional processes are still important for the high-lying states, $\Delta E_{ph} \leq kT_0$. For a plasma with 'cold' electrons, the reactions of direct electronic excitation, dissociation and
ionization of the atoms and molecules in inelastic collisions with electrons and heavy particles become ineffective and can be totally ignored.

It is well known that, for charged particle recombination, low-energy collisions are most effective [6]. Therefore, for the kinetics of recombination it is not necessary to have detailed information on the EEDF over a broad energy range (which is a complicated problem for ionizing plasmas). Usually information on the mean electron energy (namely the electron temperature) is sufficient.

A particularly simple kinetic scheme can be realized for the first excited quantum state for recombining expanding plasmas. For example, in the subsonic region of the expanding cascaded arc plasma [5], it follows from a kinetic analysis of the elementary processes, both in pure argon and in an argon–hydrogen gas mixture [7, 8], that the stationary density of the first excited state \( n_p^1 \) can be determined simply from the balance between the recombination flux \( \Phi \) to this level and radiative decay from this level:

\[
\Phi - n_p^1 A_{21} \Lambda_{21} = 0. \tag{1}
\]

Here \( A_{21} \) is the resonance radiative transition probability, and \( \Lambda_{21}(kR) \) is the escape factor for the emission of resonance radiation. Particle kinetics in the supersonic expansion and inside the shock front are more complicated, especially in a mixture of gases. Since the dynamics of an argon–hydrogen expanding plasma has been extensively discussed in our previous publications (see, for example, [9–12]), we will analyse here only plasma properties in the subsonic expansion.

The transport of resonance radiation in the limiting cases of pure Doppler and pure pressure-broadened absorption profiles was first quantitatively investigated by Holstein [13] and Biberman [14]. Detailed experimental and theoretical studies of the transport of resonance radiation at low and intermediate pressures have been reported in [15] to describe energy pathways in helium and argon excited by electrons and protons. In [16] the authors investigated the problem of absorption of transport radiation in sodium. One of the principal conclusions with respect to the low-density media was derived in [15]. It was illustrated that, for gas density in the pressure region \( p \leq 67 \text{ Pa} \), and with \( T = 300 \text{ K} \), there is substantial disagreement between the theory, which assumes complete redistribution of frequency (that is, which takes the emission and absorption profiles to be equal), and the real situation.

It was shown that the escape factor is directly connected with the effective optical depth for the transmission of radiation \( kR \) (for optically transparent media \( \Lambda = 1 \) and \( kR = 0 \)). The functional dependence of \( \Lambda(kR) \) depends on the emission and absorption line profiles [13, 15]. The dependence of \( \Lambda(kR) \) as a function of the Voigt parameter for the emission profile \( a = (\ln 2)^{1/2}(\Delta \lambda_L / \Delta \lambda_D) \) has been tabulated, for example in [17]. In the general case the escape factor \( \Lambda \) is a complicated function of the effective Voigt optical depth \( k_{V}R \). For large optical depths (that is, the case of the resonance transition of argon) the escape factor is mainly determined by the Lorentzian line wings. It is easy to derive quantitatively, and it has been shown in [13, 17, 18], that, for \( (k_{V}R)^{-1} \ll \Delta \lambda_L / \Delta \lambda_D \leq 100(k_{V}R)^{-1} \), the dependence of \( \Lambda \) is only through the Lorentz fraction of the line width:

\[
\Lambda(k_{V}R) = \left( \frac{4\pi c g_q \Delta \lambda_L}{8 \rho A_{pq} n_q \mu R} \right)^{1/2}. \tag{2}
\]

Here \( \lambda_{pq} \) is the wavelength of the radiative transition, \( c \) is the velocity of light, \( g_q \) and \( \Delta \lambda_D \) are the statistical weights, \( n_q \) is the density of the lower state of the transition, \( \mu \) is a geometrical factor [17, 19] and \( R \) is the mean radius of the plasma beam. For resonance lines the Doppler broadening \( \Delta \lambda_D \) is of the order of \( 10^{-3} \text{ nm} \) [20]. The Lorentzian broadening mechanisms in the expansion that we should consider are natural, Stark and resonance broadening. The first has values of \( 5 \times 10^{-7} \text{ and } 2.5 \times 10^{-6} \text{ nm respectively for the two resonance lines of argon} \). The Stark broadening is given by \( \Delta \lambda_{\text{Stark}} \leq 10^{-7} \text{ nm} \) [20] and we may neglect it. Resonance broadening can be estimated as \( \Delta \lambda_{\text{Res}} \leq 10^{-8} \text{ nm} \) and can also be neglected [20]. So, in the subsonic part of the expansion, natural broadening is the most important Lorentzian broadening mechanism; \( k_{V}R \) is of the order \( (1.5 \sim 10^{5}) \), and thus equation (2) can be applied for approximating the escape factor [20]. Since for a resonance line \( \Delta \nu = A/2\pi \), equation (2) becomes

\[
\Lambda(k_{V}R) = \left( \frac{2g_q}{g_p n_q \lambda_{pq} \rho \mu R} \right)^{1/2}. \tag{3}
\]

It appears that the escape factor for the resonance lines is independent of the radiative transition probability \( A_{pq} \). Furthermore, it implies that the effective transition probabilities \( A_{21} \Lambda_{21} \) remain linear in \( A_{1} \), and that the level with the largest transition probability represents the most important loss channel for the Ar*+(3p^5 4s) states. Because of the strong coupling between the four Ar*+(3p^5 4s) sub-levels (see later), an average effective transition probability of \( A_{21} \sim 1.5 \times 10^{-8} \text{ s}^{-1} \) has to be used [18, 21].

The condition \( (k_{V}R)^{-1} \leq a \leq 100(k_{V}R)^{-1} \) under which equation (2) is valid determines the range of experimental parameters (ground state density, temperature and effective radius of the plasma beam) within which one can use the present approach.

In the general case, the effective optical depth for the transmission of radiation is defined as [17, 19]

\[
k_{V}R = \frac{(\ln 2)^{1/2} \lambda_{pq}^4 g_q}{4\pi \sqrt{\pi} c \Delta \lambda_{pq} n_q \rho \mu R} \tag{4}
\]

where \( \Delta \lambda_{pq} \) is the FWHM of the emission profile. If the information on the recombination flux to the first excited state and absolute density of this state is available, and if the spectral line shape for the resonance transition is known, then, from equation (1), one can determine the escape factor \( A_{21} \) and effective optical depth \( k_{V}R \) [17] for the resonance radiative transition from equation (2). Finally, from equations (3) or (4), the absolute density of the radicals in the ground electronic state can be derived.

For the current experimental situation, the radiation of argon resonance spectral lines has been significantly

1363
trapped. That is the effective optical depth $\bar{e}$ was of the order of $(1-5) \times 10^3$. In this case equations (2) and (3) have been applied for approximating the escape factor [20]. However, for the Doppler-dominated case of resonance radiation of hydrogen, the escape factor was of the order of $0.2-1$, that is, the plasma was optically almost transparent for the hydrogen resonance spectral lines [8]. The effective optical depth was of the order of (0.1-3, and general correlations $\Lambda(\bar{e})$ (see [13, 17, 18]) were used to calculate $\bar{e}$.

The proposed method has been applied to the determination of the absolute ground state density of atomic hydrogen $H(n = 1)$ and argon Ar$(3p^6)$ in a freely expanding plasma jet. The pure argon case has been studied in order to check the validity of the method, since the argon ground state density under similar experimental conditions has accurately been determined by Thomson–Rayleigh scattering [5, 7].

3. Experimental

The argon density in the first excited state Ar$(3p^54s)$ has been measured in a pure argon plasma by the absorption of eight argon spectral lines, belonging to the transition Ar$(3p^44p \rightarrow 3p^54s)$. The hydrogen density in the first excited state $H^*(n = 2)$ has been determined in an argon–hydrogen plasma by hydrogen Balmer-$\alpha$ spectral line absorption.

In figure 1 the outline of the expanding cascaded arc, with the optimal set-up for performing emission and absorption spectroscopy, is shown. A pure argon or argon–hydrogen gas mixture in various proportions can be introduced directly into the beginning of the cylindrical channel (diameter 4 mm) of the cascaded arc with a flow rate of 10–100 cm$^3$ s$^{-1}$, at a pressure of about 0.5 bar in the cathode space. The hydrogen percentage in the total gas flow was varied in the range 0.7–10%. The plasma generated by the arc is under close to partial local thermal equilibrium (PLTE) conditions with temperatures of the order of 1 eV, an electron density of the order of $10^{22}$ m$^{-3}$ and a degree of ionization of about 10% [22]. A fully dissociated and highly ionized thermal plasma flows through the channel, is accelerated and expands supersonically through a conically shaped nozzle into a vessel at low background pressure. This plasma source has been described in detail elsewhere [7, 23]. The plasma conditions under which the experiments were performed are the following: background pressure 40 Pa, flow rate $58$ cm$^3$ s$^{-1}$, arc current 45 A and arc voltage 80–115 V.

The optical set-up used for the absorption spectroscopy experiments is also shown in figure 1. As a light source, another cascaded arc, specially designed for the purpose of emitting high-intensity radiation, is employed [23]. The arc has almost the same construction as the cascaded arc used as a plasma source. The mirrors M3 and M4 together with lens L3 can be translated, which enables both an axial and a lateral scan of the plasma. The detection system consists of a monochromator with a focal length of 1 m, and a Peltier cooled photodiode array. After AD conversion the signal of the photodiode array is recorded by a personal computer.

| Table 1. Typical plasma parameters on the axis of the expanding cascaded arc for the case of 1.4% hydrogen admixture in the total gas flow at an axial position $z = 70$ mm in the expansion. |
|---------------------------------|----------------|----------------|
| **z = 70 mm**                   |                |                |
| Electron density, $n_e$ (m$^{-3}$) | 3.0 x 10$^{16}$ | 2500           |
| Electron temperature, $T_e$ (K)  |                |                |
| Argon ion density, $n_{Ar^+}$ (m$^{-3}$) | 2.9 x 10$^{18}$ | 0.8 x 10$^{16}$ |
| Proton density, $n_p$ (m$^{-3}$)  | 1.0 x 10$^{21}$ | 3000          |
| Neutral particles density, $n_n$ (m$^{-3}$) | 2.4 x 10$^{15}$ | 2.2 x 10$^{13}$ |
| Measured H$(n = 2)$ density, $n_{H^*(n=2)}$ (m$^{-3}$) | 2.2 x 10$^{13}$ | 1.0 x 10$^{13}$ |
| Measured H$(n = 3)$ density, $n_{H^*(n=3)}$ (m$^{-3}$) | 0.5 x 10$^{13}$ |                |
| Measured H$^*(n = 4)$ density, $n_{H^*(n=4)}$ (m$^{-3}$) | 2.4 x 10$^{17}$ |                |
| Estimated radius of the plasma, $R$ (m) | 0.035 | |

For typical parameters of the expanding cascaded arc plasma at a distance of $z = 70$ mm from the exit of the cascaded arc (see table 1), the estimated ratio of the Lorentzian to Gaussian width of the Ar and H spectral lines is less than 0.01. Therefore, for the calculation of the absorption coefficient $k_0$ of transitions whose lower level is the first excited state, it was accurate enough to assume a purely Gaussian line profile.

The measured values of the total absorption can be related directly to an integral absorption coefficient in accordance with [24], and then to the absolute density of absorbing particles. The absorption length $l$ is determined by the widths of Gaussian beam profiles, which are used to fit the measured absorption data (using an Abel integration procedure [20]).

4. Results and discussion

The radial dependencies of the total density of the first excited state of argon, Ar$^+(3p^54s)$, summed over the quantum states $3p^44s(3P_0, 3P_1, 3P_2$ and $1P_1)$, for various axial positions in the expansion of a pure argon arc, are presented in figure 2. Similar dependencies for the density of the first excited state of hydrogen $H^*(n = 2)$ obtained for the different axial positions in the expansion were presented in our previous paper [8].

In [5, 10] a similar expanding argon cascaded arc plasma in pure argon and with different amounts of hydrogen added was studied using the technique of Thomson–Rayleigh scattering and optical emission spectroscopy. The electron density and temperature, neutral species density and excited hydrogen atom $H^*(n \geq 3)$ absolute population density were determined as functions of the axial position in the expansion.

Values of the plasma parameters on the axis of the expanding cascaded arc at axial positions $z = 70$ mm in the vessel are given in table 1, using the data for 1.4% hydrogen in the gas flow as an example. The data on electron density and temperature, neutral species density and temperature, and population density of excited hydrogen atoms $H^*(n \geq 3)$ are taken from [10].
the first excited state \( H^*(n = 2) \) determined in the present work is listed as well. Detailed kinetic analysis carried out for typical conditions of expanding plasmas with the atomic, molecular, ionic and electronic parameters as presented in table 1 shows that the following recombination processes are responsible for the population of the argon and hydrogen first excited states [8, 20].

(i) For pure argon plasma, the three-particle recombination reaction [4, 5] is

\[
\text{Ar}^* + e + e \rightarrow \text{Ar}^* (3p^5 4s) + e \tag{5}
\]

where it is assumed that the majority of the recombination flux is caused by three-particle recombination to high-lying excited levels, which all cascade down to the \( \text{Ar}^* (3p^5 4s) \) state [25]. Therefore, for pure argon plasmas, the recombination flux to the first excited argon state \( \text{Ar}^* (3p^5 4s) \) is equal to \( \Phi_1 = k_1 n_e^2 \).

(ii) For the considered recombining argon–hydrogen plasmas the population kinetics of the first excited state of hydrogen are dominated by molecular processes even for very low \( \text{H}_2 \) admixtures. The most important is the charge exchange reaction [8]

\[
\text{Ar}^* + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \tag{6}
\]

followed by dissociative recombination of the \( \text{ArH}^+ \):

\[
\text{ArH}^+ + e \rightarrow \text{Ar} + \text{H}^*(n = 2). \tag{7}
\]

Thus, for the argon–hydrogen plasmas, the recombination flux to the first excited state of atomic hydrogen (1) \( \text{H}^*(n = 2) \) is equal to \( \Phi_2 = n_{\text{H}_2} n_e k_2 \).

It is well known that the first excited states of argon \( \text{Ar}^* (3p^5 4s) \) and hydrogen \( \text{H}^*(n = 2) \) consist of four and two sub-levels, respectively. Half of them are metastable and half are connected to the ground state by ordinary dipole selection rules. Our experiments show that, on the axis, the densities per statistical weight for all the four argon sub-levels are approximately the same. One possible
expansion total density obtained between the sub-levels, since the energy gap between the sub-levels in comparison with the kinetic temperature of particles is small (less than 0.1 eV for argon and about $10^{-4}$ eV for hydrogen). Another explanation is collisionally induced radiation to the ground atomic states, as proposed for this reaction is exothermic: the positive excess of energy in those cases are approximately 1.2 eV. The dissociative recombination reactions of vibrationally non-excited molecular ions $H^+(n=2)$ must be negligibly small in comparison with the recombination flux directly to $H^+(n=2)$.

Finally, to calculate the absolute density of the atoms from equation (4) one has to know the radius of the plasma beam $R$. As an effective radius of the plasma one could choose either the width of the radial distribution of $\text{Ar}^+(3p^5 4s)$ and $H^+(n=2)$ (known from the absorption spectroscopy measurements (see figures 2 and 3)), or the width of the radial distribution of the electron density $n_e$ (known from the Thomson–Rayleigh scattering measurements [7,10]), since the corresponding widths are approximately equal to each other. Experimentally determined values of the radius of the plasma beam for various conditions are also presented in table 1.

In the framework of the validity of the kinetic equation (1), the plasma parameters have been measured (see table 1), and with known values of the rate constants $k_1$, $k_2$, and $A_{21}$, one can determine the escape factors and the effective optical depths [17] as a function of the percentage of hydrogen in the plasma. Finally, from equation (4) one can readily determine the hydrogen $H(n = 1)$ and the argon $\text{Ar}^+(3p^5)$ atom ground state densities.

Figure 3 illustrates the axial dependence of the $\text{Ar}^+(3p^5)$ ground state density, determined both from the Thomson–Rayleigh scattering [7] and by the method discussed. The escape factor and effective optical depth for the resonance radiative transition of argon were of the order of $10^{-3}$.
and $10^5$ respectively. Since the dynamic behaviour of heavy particles in an expanding pure argon plasma has been recently analysed in detail by van de Sanden et al [9], we will limit the discussion to presentation of the figure. From figure 3 one can see that the agreement between the two methods is quite good. Hence it seems that the assumptions upon which the discussed method is based are correct, and for the recombining expanding plasma the method can also be applied to ground state density determination of short-lived radicals.

Absolute population densities of atomic hydrogen, which have been calculated using equation (1) are presented in table 2, as a function of plasma parameters in the subsonic expansion. The escape factor for the resonance radiative transition of hydrogen is in the range 1–0.1, so the corresponding effective optical depth varied in the range 0.1–1 [17]. Here we have to admit that the accuracy of the discussed method drops dramatically at low effective optical depths, and depends linearly on the accuracy in the collisional rate constants.

The presented data clearly indicate a moderately low H atom density ($\leq 9 \times 10^{16}$ m$^{-3}$), which drops with distance from the exit of the cascaded arc and with increasing hydrogen concentration in the plasma. The reasons for the decrease in the atomic hydrogen density in the subsonic part of an expanding plasma may be fast diffusion of H out of the plasma and effective admixture of molecular hydrogen, freely re-circulating in the vacuum vessel into the expanding plasma [30]. If the partial H$_2$ pressure were equal to the seed fraction times the total pressure, then the associated degree of dissociation would be 22% at its maximum. However, one must expect that, in the expanding plasma, the H$_2$ density is low because of dissociation (see reaction (6)), that is, it burns out.

5. Conclusion

The densities of argon and hydrogen atoms in the first excited states, determined by the ordinary technique of optical absorption spectroscopy, and a simple kinetic model can be used to determine absolute ground state densities of the Ar and H atoms in the recombining plasmas. It is important that the kinetic model employed does not require information on the shape of the BEDF in the plasma due to the recombining character of the plasma.

The accuracy of this indirect method of ground state density determination is limited by the error both in the recombination coefficients and in the experimental signal-to-noise ratio. Without any special amplification of the light signal, for the effective optical length of only about 2–6 cm, the minimum detected local density of excited atoms was about $10^{14}$ m$^{-3}$, to within an accuracy of 20%.

The proposed technique can be used as well for characterization of other kinds of radicals in non-equilibrium recombining plasmas of various chemical compositions, which information is difficult to obtain by other means. We do not see any obstacles in principle preventing employment of the same technique to measure the density of such radicals as O, C, N or F. Only in two extreme cases, when the plasma is either fully optically opaque for the resonance radiation (the escape factor is equal to zero), or completely optically transparent for the resonance radiation (the escape factor is equal to unity), can the proposed procedure no longer be used. Besides, as has been mentioned already, the accuracy of the method is very low for escape factors close to unity.

Acknowledgments

This work was supported by the Netherlands Foundation for Fundamental Research (FOM). DK Otorbaev acknowledges support from the Eindhoven University of Technology. The work of MCM van de Sanden was made possible by the Royal Netherlands Academy of Arts and Sciences. The authors wish to thank MJF van de Sande, ABM Hüsken and HMM de Jong for their skilful technical assistance.

References

D K Otorbaev et al.