Influence of 4s levels (metastable and resonant) on thermodynamic equilibrium in argon microwave plasmas at atmospheric pressure

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1. Introduction

Microwave plasmas at atmospheric pressure have applications within different scientific and technological fields. In order to ensure that a specific discharge application is carried out with maximum efficiency it is necessary to be aware of all mechanisms (internal kinetics) taking place in the plasma. Plasma kinetics depends on the energy available in the discharge, together with the density of different plasma particles. Among them, metastable atoms, due to their long natural life time, play a fundamental role in the plasma processes and they are considered as an important energy reserve, which can be transmitted to the rest of plasma particles by means of collisions with them [1].

Laboratory surface wave discharges at atmospheric pressure (SWD) are in a partial local thermodynamic equilibrium (pLTE) state and show an axial variation in their degree of thermodynamic equilibrium [2]. Metastable and resonant atoms, both belonging to the 4s argon configuration, and the ground state might be the species with a greater deviation with respect to local thermodynamic equilibrium in this type of plasmas. In order to determine the population of 4s levels along the plasma column an easy self-absorption method was implemented an used in a previous work, obtaining that the densities of these levels also experience an axial modification [3]. Knowing the population of the argon metastable and resonant levels throughout the discharge has allowed us a more comprehensive study of the equilibrium degree and verifying the recombining or ionizing character of the discharge along the plasma column, which is the main objective of this study.

2. Experimental arrangement

The discharge was generated inside a dielectric tube open at one end (atmospheric pressure), which had an internal diameter of 1 mm and external one of 4 mm. The value of inner diameter of the discharge tube was chosen with chosen the aim to avoid radial contraction present in all discharges generated with pressures over 10 Torr. The gas was argon (pure 99.99%) with a flow of 0.25 slm. A *surfaguide* [4] has been used as excitation device to generate the plasma. The energy in continuous mode (250W) was supplied by a SAIREM generator (GMP12kT/t) producing a plasma length of 13.5 cm. Plasma diagnosis was done using spectroscopic techniques (non invasive measurements). The optical system for the detection and acquisition of data (4pm-practical resolution) was composed by a PCS 1000 optic fibre with a siliceous core, a Czerny-Turner type Jobin-Ybon THR-1000S monochromator (1 m-focal distance, 1200 lines/mm-holographic grating, 0.80nm/mm-typical reciprocal linear dispersion in the visible region), a Hamamatsu R636-10 photomultiplier used as a detector, and a Spectralink unit (interface between a computer and the monochromator, controlling the movement of the diffraction net, as a source of high tension for the photomultiplier and as a digital-analogical converter).

3. Results

Densities of the $^3P_2$ metastable and $^3P_1$ resonant levels were measured along the plasma column, obtaining that both populations increase as the value of *z* goes up, that is, for positions near the energy coupler device where the energy of the surface wave that creates the discharge is greatest [3]. For the experimental conditions used, the populations of metastable and resonant levels are within the same order of magnitude and both have the same tendency along the plasma column. At high pressure, due to collisions increase, the collisional coupling between these two types of levels is improved and a great interconnection between them takes place, being the interaction kinetics between 4s levels maintained along the plasma column.

To make a study of the type of thermodynamic equilibrium state which prevails in the plasma it is necessary to accurately know the *atomic-state distribution function* (ASDF). The ASDF can be represented using the so-called Boltzmann-plot for the excited level populations. Since the absolute densities of 4s levels have been measured experimentally, it is possible to represent the complete Boltzmann-plots for different z positions along the plasma column (Figure 1). In this figure, absolute population densities of 4p and superior atomic excited levels were determined from measurements of the intensity of spectral lines corresponding to atomic transitions starting at each specific level, calibrated or corrected for the spectral response of the optical system. Spectral lines corresponding to transitions from metastable levels are unlikely (optically forbidden) and outside the sensitive range of radiation detection system. These are the reasons why in the literature the populations of the 4s configuration levels, corresponding to the first excited levels above the ground state, do not appear in the experimental Boltzmann diagrams.

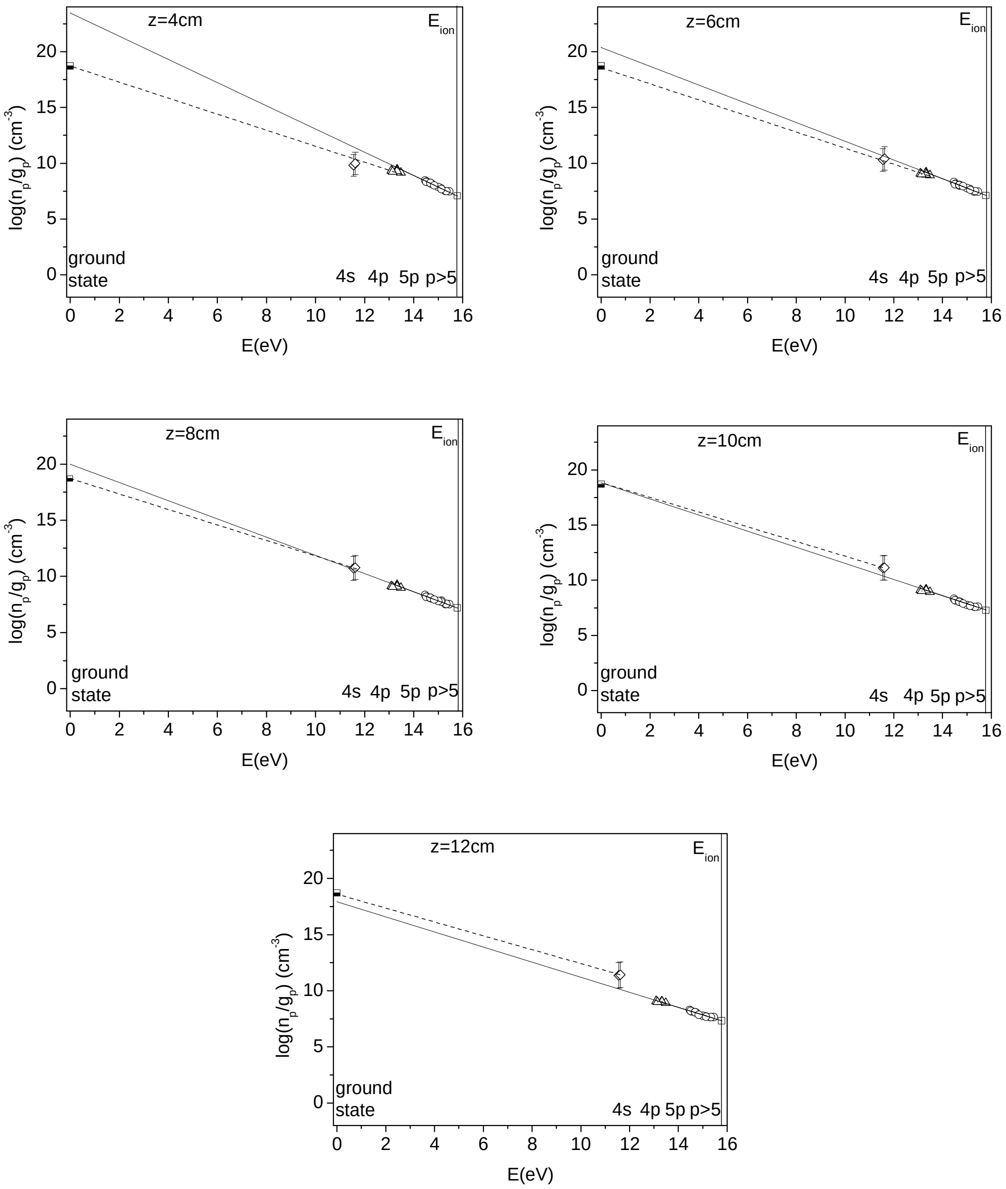

Figure 1. Bolztmann-plots for different positions along a plasma column (z = 0 correspond to the end of the plasma column) generated with an argon flow of 0.25 slm

In Figure1 it can be observed that along the plasma column, 4s configuration levels present a higher deviation from equilibrium distribution, being underpopulated with respect to the equilibrium density in positions far from the excitation energy device. Therefore the partial local Saha equilibrium (pLSE) state of the discharge and its recombining nature, previously reported [2], were found. However, it was also obtained that in the region closer to the excitation device the populations of 4s levels were exceptionally higher than those corresponding to equilibrium, overpopulation also found in the ground state. This last result seems to reflect an increase in excitation and ionization processes from 4s levels, being these who fundamentally contribute to the creation of the discharge in this region closer to the surfaguide (step-wise processes at atmospheric pressure). However, 5p and higher energy levels keep the Saha-Boltzmann equilibrium distribution regardless of the position along the plasma column, and the electrons are the particles that are controlling the excitation kinetics of these high-lying levels.

It can be observed that in all positions along the plasma column the ASDF in the argon plasma is described by two excitation temperatures, consequence of the pLSE state of the plasma, one temperature obtained from the slope of the straight line fitted to the atomic argon levels belonging to the "bottom" and the other from the slope corresponding to levels belonging to the "top" (result also obtained by Jonkers *et al*. [5]for both argon and helium discharges generated by a TIA). Last temperature can be considered as equal to the electron temperature (electrons belong to the bulk of the EEDF), since these levels verify Saha-Boltzmann balances [2]. Nevertheless the excitation temperature calculated with bottom levels can not be considered as equal to the electron temperature of the tail of the EEDF, electrons responsible for the direct excitation of 4s levels from the ground state, since they are not in pLSE and kinetic of these levels next to the ground state are not completely controlled by electrons, but other processes such as dissociative recombination being more important, playing a key role in the population of the 4s levels [6]. Therefore this temperature would be an underestimation of the electron temperature corresponding to the tail of the EEDF.

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References

[1] J. L. Delcroix, C. Matos-Ferreira, A. Ricard. *Atomes et Molécules Métastables dans les gaz ionisés*. Editions du Centre National de la Recherche Scientifique. Paris. (1975).

[2] M. D. Calzada, M. Moisan, A. Gamero and A. Sola. J. Appl. Phys. 80, (1996) 46-55

[3] I. Santiago and M.D. Calzada. IEEE Transactions on Plasma Science, 37, 6 (2009) 790-796

[4] M. Moisan, E. Etemandi and J.C. Rostaing, French Papent No. 2 762 748, European Patent No. EP 0 874 537 A1 (1998)

[5] J. Jonkers, H.P.C. Vos, J.A.M. van der Mullen, E.A.H. Timmermans. Spectrochim Acta B, 51 (1996) 457

[6] A. Sainz, J. Margot, M.C. García and M.D. Calzada, *J. Appl. Phys*. 97, 11 (2005) 113305-1 113305-7