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DEPARTURES FROM EQUILIBRIUM IN AN ARGON INDUCTIVELY COUPLED PLASMA[1]

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The extensive collisional-radiative model for an argon atom plasma is applied to an inductively coupled plasma system in order to investigate the population mechanisms and the departures from the local thermodynamic equilibrium in several selected locations. The computations are carried out for various sets of the input parameters T_e, T_a, n_e, n_1, R, Λ_{mn} and Λ_m, which were measured directly in the experiments or determined from the available experimental data.

I. INTRODUCTION

In our recent paper [1] a collisional-radiative (CR) model with an extended range of applicability was established for an argon atom plasma.

With the help of the numerical method developed, we can calculate the population coefficients determining the populations in all the excited effective levels considered. This enables us to study the mechanisms by which these levels are populated under various conditions in a nonequilibrium argon plasma characterized by a set of parameters such as the electron kinetic temperature T_e, the atom temperature T_a, the ion temperature T_i, the electron number density n_e, the ground-state atom population n_1, the plasma column radius R and the optical escape factors Λ_{mn} and Λ_m.

In this paper our model has been applied to the inductively coupled plasma (ICP) system investigated experimentally by Hasegawa and Haraguchi [2]. Our objective has been to study the departures from the local thermodynamic equilibrium (LTE) in this plasma, extensively used as an excitation source for atomic emission spectrometry [3], and to verify the so called " close-to-LTE concept "[4,5] which plays a key role in the plasma diagnostics and in the interpretation of analytical measurements.

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II. BASIC EQUATIONS

Assuming that the quasi-stationary quasi-homogeneous state model can be applied [6,7], we obtain [1] a set of coupled linear equations

$$\sum_{n=2}^{65} a_{mn} n_n = -\delta_m - a_{m1} n_1, \qquad (1)$$

where m=2,...,65, from which the unknown excited level populations n_n may be calculated, provided that the coefficients a_{mn} and δ_m are known and the ground -state atom population n_1 has been determined experimentally or calculated.

The coefficients a_{mn} and δ_m are related to the processes considered by the following expressions [1] :

$$\begin{aligned}
a_{mn} &= n_e C_{mn} + n_1 K_{mn}, \qquad m > n \\
a_{mn} &= n_e F_{mn} + n_1 L_{mn} + \Lambda_{mn} A_{mn}, \qquad m < n \\
a_{nn} &= -\,(n_e S_n + n_1 V_n + \sum_{\substack{m=1 \\ m \neq n}}^{65} a_{mn} + D_n/\Lambda^2 + n_1^2 B_n), \qquad m = n \\
\delta_m &= n_e n_+ (n_e O_m + n_1 W_m + \Lambda_m R_m).
\end{aligned}$$

Here C_{mn} and K_{mn} are the rate coefficients for collisional excitation by electrons and by ground-state atoms, respectively. F_{mn} and L_{mn} are respectively the rate coefficients for the inverse processes (collisional deexcitations). S_n and V_n are the corresponding collisional ionization rate coefficients, while O_m and W_m are the rate coefficients for the inverse three-body recombinations and R_m is the radiative recombination rate coefficient. A_{mn} is the transition probability, Λ_{mn} and Λ_m are the optical escape factors for bound-bound and bound-free transitions, respectively. D_n is the diffusion coefficient for metastable states and B_n is the rate constant for the three-body collisions of these states with the ground-state atoms.

In accordance with Caughlin and Blades [8], the electron energy distribution function is assumed to be Maxwellian in the general formulas used for the rate coefficients [1]. Then the ion temperature T_i does not appear among the input parameters.

The system (1) is solved in the standard form

$$n_n = n_n^{(0)} + G_n^{(1)} n_1, \qquad n = 2, \ldots, 65,$$

where the population coefficients $n_n^{(0)}$ and $G_n^{(1)}$ are obtained from equations (1) when we insert n_1=0 or n_1=1 and δ_m=0, respectively, in their right-hand sides.

The departures from the LTE state in the ICP considered are characterized by the so-called "Boltzmann decrements" defined by the relation

$$\frac{n_n}{n_1} = a_n \left(\frac{n_n}{n_1}\right)_{LTE},$$

which can be rewritten into the form

$$a_n = \frac{b_n}{b_1},$$

where $b_n = n_n/n_n^S$; n_n^S is the corresponding Saha population.

Note that the close-to-LTE concept [4,5] is based on the assumption that the departures from the Saha population densities occur only for the lower excited states and that $0.1 \leq b_1 \leq 10$. The parameter b_1 is related to transport phenomena in the corresponding plasma region. A value of $b_1 < 1$ describes a recombining plasma part, whereas for the ionizing plasma parts the relation $b_1 > 1$ holds.

III. RESULTS

Our numerical modelling of the population mechanisms in various spatial positions in the ICP discharge is based on the experimentally determined profiles of the electron temperature T_e and the electron number density n_e [2] and on realistic estimations of the atom temperature T_a [9,10]. The ground-state atom population n_1 has been determined from Dalton's law in the form

$$n_1 = \frac{p}{kT_a} - n_e\left(\frac{T_e}{T_a} + 1\right),$$

where p is the total pressure and k is the Boltzmann constant. The plasma column radius R is assumed to be equal to half the half-width of the n_e radial profile [11] and the local effect of radiation trapping has been described according to Mills and Hieftje [12].

The chosen values of T_e and n_e used as input parameters are listed in table 1. In table 2 we give the basic data [1] characterizing the excited effective levels studied in this paper.

The numerical results for the Boltzmann decrement a_n are shown in figure 1. Takin into account the relation $1.013 \leq b_n \leq 1.030$ valid for $n=37$ in all cases considered, we can use the results for a_n to verify the close-to-LTE concept and to characterize the plasma locally with respect to ionization and recombination.

Figure 2 shows the values of n_n/g_n, obtained for all the $4s$ and $4p$ states under the conditions at the observation height of 15 mm in the central channel, to illustrate the effect of the error of 10% in the experimental values of T_e and n_e,

Table 1

The local experimental values of the electron temperature and the electron number density determined (Hasegawa and Haraguchi [2]) in various spatial positions in the ICP system.

Local plasma parameters	Height above the load coil z = 5 mm			z = 15 mm			z = 25 mm		
	Radial distance from the plasma centre r (mm)								
	0	2	4	0	2	4	0	2	4
T_e (10^3K)	6.98	9.02	8.57	8.40	8.54	8.27	7.41	7.37	6.86
n_e (10^{15}cm^{-3})	0.98	2.10	2.82	1.41	1.64	1.28	0.92	0.72	0.31

Table 2

Data characterizing the excited effective levels considered in this paper.

Level number n	Designation $n_{pqnl}[K]_J$	Excitation energy ϵ_{1n}(eV)	Ionization energy ϵ_n(eV)	Statistical weight g_n
2	$4s\ [3/2]_2$	11.548	4.212	5
3	$4s\ [3/2]_1$	11.624	4.136	3
4	$4s'\ [1/2]_0$	11.723	4.214	1
5	$4s'\ [1/2]_1$	11.828	4.109	3
6	$4p\ [1/2]_1$	12.907	2.853	3
7	$4p\ [3/2]_{1,2}\ ,\ [5/2]_{2,3}$	13.116	2.643	20
8	$4p'\ [3/2]_{1,2}$	13.295	2.642	8
9	$4p'\ [1/2]_1$	13.328	2.609	3
10	$4p\ [1/2]_0$	13.273	2.487	1
11	$4p'\ [1/2]_0$	13.480	2.457	1
12	$3d\ [1/2]_{0,1}\ ,\ [3/2]_2$	13.884	1.876	9
16	$3d\ [3/2]_1\ ,\ [5/2]_{2,3} + 5s$	14.090	1.669	23
18	$5p$	14.509	1.251	24
20	$4d + 6s$	14.792	0.968	48
27	$5d + 7s$	15.153	0.607	48
37	$8p$	15.423	0.337	24
46	$n_{pqn} = 10$	15.801	0.136	400

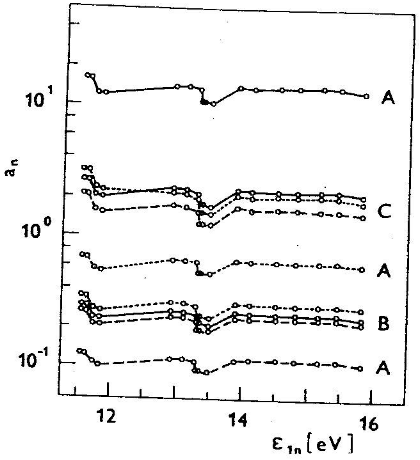

Fig. 1. The Boltzmann decrements obtained with the local values of T_e and n_e measured by Hasegawa and Haraguchi [2], see table 1: curves A, at $z = 5$ mm and with $T_a = 6500$ K; B, at $z = 15$ mm and with $T_a = 6500$ K; C, at $z = 25$ mm and with $T_a = 6000$ K. Full, broken and dotted curves represent the numerical results for the radial distances r=0, 2 and 4 mm, respectively.

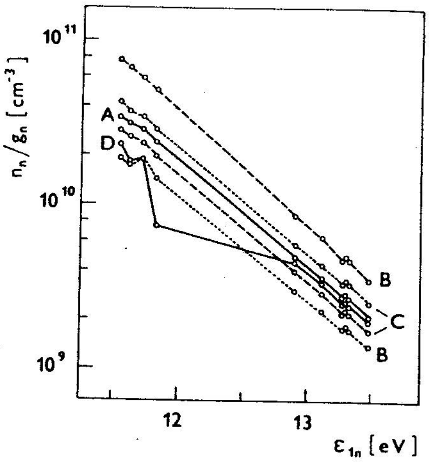

Fig. 2. The deviations in the numerical values of n_n/g_n for all the 4s and 4p states (see table 2) caused by the error of 10% in the experimental values of T_e and n_e, determined by Hasegawa and Haraguchi [2] in the central channel at the height $z = 15$ mm above the coil. Curve A, $T_e = 8400$ K, $n_e = 1.41 \times 10^{15}$ cm^{-3} and $T_a = 6500$ K; curves B, as for A but at $T_e = 7560$ K (broken curve) and at $T_e = 9240$ K (dotted curve); curves C, as for A but at $n_e = 1.27 \times 10^{15}$ cm^{-3} (broken curve) and at $n_e = 1.55 \times 10^{15}$ cm^{-3} (dotted curve); curve D, as for A but for a completely optically thin plasma.

and of resonance radiation trapping on the excited level populations.

In figure 3 we compare our result for a radial distribution of the argon atoms in the metastable state 4s $[3/2]_2$ at the height of 15 mm above the load coil in the ICP system of Hasegawa and Haraguchi [2], which used a rf generator with the output power of 1.1 kW and the carrier gas flow rate was 0.4 l min^{-1}, with the corresponding experimental values obtained by Nojiri et al. [13] under similar operating conditions when the rf power and the carrier gas flow rate were 1.5 kW and 0.65 l min^{-1}, respectively.

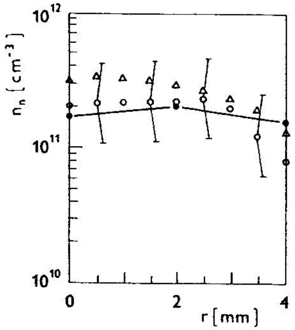

Fig. 3. The radial distributions of the argon atoms in the metastable state 4s $[3/2]_2$ at the height of 15 mm above the coil in the ICP discharge. Full curve denotes the numerical results obtained with the local values of T_e and n_e measured by Hasegawa and Haraguchi [2] and with T_a = 6500 K. Symbols o and △ represent the corresponding experimental results (Nojiri et al. [13]) determined under similar conditions at the carrier gas flow of 0.65 l min^{-1} and without it, respectively.

IV. CONCLUSIONS

From our results the following main conclusions can be drawn:

(i) Our model calculations may provide reliable information on the validity of the close-to-LTE assumption and the occurrence of an ionizing or a recombining regime in various parts of the ICP systems. In that studied by Hasegawa and Haraguchi [2] the close-to-LTE assumption proves to be well justified over the whole region investigated.

(ii) The metastable state 4s $[3/2]_2$ and the adjacent radiative state 4s $[3/2]_1$ have almost the same values of a_n and are overpopulated with respect to the corresponding Saha values in all cases considered. This is caused by resonance radiation trapping and by the collisions with electrons, which lead also to complete interconversion between the states 4s′ $[1/2]_0$ and 4s′ $[1/2]_1$ in all spatial positions selected.

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ОТКЛЮЧЕНИЕ ОТ РАВНОВЕСИЯ В ИНДУКТИВНО СВЯЗАННОЙ ПЛАЗМЕ АРГОНА

В работе показано применение расширеной модели соударений - радиации на атоме аргона и индуктивно связанной системе плазмы с целью исследовать механизмы популяции и нарушения детального термодинамического равновесия в разных выбранных областиях. Расчеты проведены с разными наборами входных параметров $T_e, T_a, n_e, n_1, R, \Lambda_{mn}, \Lambda_m$ которые измерены прямо в эксперименте, или определены на их основании.