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A STEADY STATE APPROXIMATION OF POPULATION DENSITY DISTRIBUTIONS OF ARGON ATOMS IN AN INDUCTIVELY COUPLED PLASMA AS AN EXCITATION SOURCE FOR ATOMIC SPECTROMETRY

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The population density distributions of argon atoms in an inductively coupled plasma (ICP) are calculated based on the collisional-radiative model under a steady state approximation. The results obtained help to interpret the physical states of the argon plasma and to elucidate the characteristics of the ICP as an excitation source for spectrochemical analysis.

An inductively coupled plasma (ICP) has been widely used as an excitation source for atomic emission spectrometry,[1-3] and recently it is also used as an atomization source for atomic fluorescence spectrometry[4] and as an ionization source for mass spectrometry.[5] The ICP sustained with argon gas can be usually characterized with high excitation temperature, significantly large electron number density, and high excitation efficiency.[5] Furthermore, the ICP shows unique spatial structures of such plasma parameters, so-called "doughnut structure", which allows efficient nebulization of the solution samples into the plasma.

Since the pioneer works of Fassel[6] and Greenfield,[7] inductively coupled plasma atomic emission spectrometry (ICP-AES) has been investigated in terms of fundamental properties as well as applicability to trace analysis. The excitation mechanisms are one of the important subjects to be explored, and have been proposed by many workers.[8-13] The Penning ionization processes proposed by Mermet,[8] the concepts of soft and hard lines by Boumans,[9] the norm temperature correlation of soft lines in the thermal region by Horlick et al.,[10,11] the radiation trapping model by Blades and Hieftje,[12] and the recombination plasma model by Boumans[13] have been applied to the interpretation of the excitation mechanisms and spectroscopic behaviors of emission lines in the ICP. The present authors estimated absolute number densities of metastable argon atoms, calcium atoms and ions, and their spatial distributions in the ICP.[14] The results obtained in these works can interprete some characteristics of the ICP as an excitation source, but not all of them. Therefore, further study on the plasma diagnostics is required to characterize the argon ICP. Hence, in the present paper, the population density distributions of argon atoms in the atomic energy states have been calculated theoretically based upon a steady state approximation using a collisional-radiative model.[15)]

The collisional and radiative processes which are taken into consideration are as follows:

i) Electron impact excitation and deexcitation

$$Ar(p) + e^- \underset{K(q,p)}{\overset{K(p,q)}{\rightleftharpoons}} Ar(q) + e^- \qquad (1)$$

ii) Electron impact ionization and three-body recombination

$$Ar(p) + e^- \underset{\alpha(p)}{\overset{S(p)}{\rightleftharpoons}} Ar^+ + e^- + e^- \qquad (2)$$

iii) Spontaneous emission

$$Ar(p) \xrightarrow{A(p,q)} Ar(q) + h\nu_{line} \qquad (3)$$

iv) Radiative recombination

$$Ar^+ + e^- \xrightarrow{\beta(p)} Ar(p) + h\nu_{cont} \qquad (4)$$

where Ar(p) : argon atom in the level p,

K(p,q) : rate coefficient for excitation (p<q) or deexcitation (p>q),

S(p) : ionization rate coefficient of argon atom in the level p,

α(p) : rate coefficient for three-body recombination of argon atom in the level p,

A(p,q) : Einstein's spontaneous transition probability,

β(p) : radiative recombination rate coefficient of argon atom in the level p,

$h\nu_{line}$: radiation of line emission,

$h\nu_{cont}$: radiation of continuum band.

In addition to the processes shown in Eqs. 1-4, the following rate processes may take place in the plasma :

$$Ar + Ar^* \rightleftharpoons Ar^* + Ar \qquad (5)$$

$$Ar + Ar \rightleftharpoons Ar^+ + Ar + e^- \qquad (6)$$

$$Ar + Ar^m \rightleftharpoons Ar^+ + Ar + e^- \qquad (7)$$

where Ar, Ar*, Ar^m, and Ar^+ are ground state atom, excited state atom, metastable atom, and ion of argon, respectively. However, since the translational motions of such atoms and ions are very small compared to electrons at plasma temperature below 10000 K, such processes shown in Eqs. 5-7 may be neglected.

In order to estimate the number density n(p) of argon atom in the level p, the following rate equation was calculated under the steady state approximation.

$$\frac{dn(p)}{dt} = \sum_{q<p} K(q,p)n_e n(q) - [(\sum_{q\neq p} K(p,q) + S(p))n_e + \sum_{q<p} A(p,q)]n(p) + \sum_{q>p} [K(q,p)n_e + A(q,p)]n(q) + \alpha(p)n_e^3 + \beta(p)n_e^2 = 0 \qquad (8)$$

In Eq. 8, p=1, 2, 3, ..., where p=1 corresponds to the ground state, and n_e electron number density. Among the parameters in Eq. 8, K, S, α, and β are the functions of electron temperature. The values of K, S, α, β, and A are obtained from the literature values for collisional cross sections.[16)]

According to our survey, only one experimental value of electron temperature T_e in the argon ICP is available along with electron number density in the literature.[17)] Batal et al. obtained T_e=9000 K and n_e=5x10^{14} cm^{-3} for a 40 MHz ICP, where excitation temperature T_{exc} was 5000 K when measured at the observation height 15 mm above the load coil. Although it seems that the values of n_e and T_{exc} for the 40 MHz ICP are slightly low compared to those for the usual 27 MHz ICP, T_e=9000 K and n_e=5x10^{14} cm^{-3} were used in the estimation of the rate coefficients and calculation of the number densities.

The calculated results for the number densities of argon atom in the 26 energy levels including the ground state $(3p)^6$ are summarized in Table 1. As is well known, the electron configurations of $^2P^\circ_{3/2}$ and $^2P^\circ_{1/2}$ exist in argon atom, and they are shown, for example, as 4p and 4p', respectively. It should be noted here that no energy crossing between the two different electron configurations was assumed for convenience in calculation. Furthermore, it was assumed that the plasma was an optically thin and homogeneous plasma. This assumption was made to neglect the self-absorption processes. In Table 1, $4s[3/2]^\circ_2$ and $4s'[1/2]^\circ_0$ are the metastable states of argon atom. The ionization energies of argon atom are 15.76 for $^2P^\circ_{3/2}$ and 15.94 eV for $^2P^\circ_{1/2}$.

Table 1. Population densities of argon atom calculated based on a collisional and radiative model under a steady state approximation[a)]

Term	Energy/eV	g	n(p)/cm^{-3}	(n(p)/g)/cm^{-3}
$(3p)^6$	0	1	5.6x10^{18}	5.6x10^{18}
$4s[3/2]^\circ_2$	11.548	5	5.8x10^{10}	1.2x10^{10}
$4s[3/2]^\circ_1$	11.624	3	2.2x10^{10}	7.4x10^{9}
$4s'[1/2]^\circ_0$	11.723	1	6.4x10^{9}	6.4x10^{9}
$4s'[1/2]^\circ_1$	11.828	3	8.8x10^{9}	3.0x10^{9}
4p	13.097	24	1.0x10^{10}	4.3x10^{8}
4p'	13.319	12	3.9x10^{9}	3.2x10^{8}
3d	14.008	40	1.7x10^{10}	4.2x10^{8}
5s	14.077	8	1.2x10^{9}	1.5x10^{8}
3d'	14.240	20	1.2x10^{9}	5.9x10^{7}
5s'	14.252	4	1.5x10^{8}	3.7x10^{7}
5p	14.509	24	2.5x10^{9}	1.1x10^{8}
5p'	14.690	12	2.9x10^{8}	2.4x10^{7}
4d	14.780	40	1.3x10^{9}	3.3x10^{7}
6s	14.843	8	3.5x10^{8}	4.3x10^{7}
4f	14.906	56	1.3x10^{9}	2.3x10^{7}
4d'	14.968	20	2.6x10^{8}	1.3x10^{7}
6s'	15.020	4	3.3x10^{7}	8.3x10^{6}
6p	15.028	24	8.6x10^{8}	3.6x10^{7}
4f'	15.083	28	2.3x10^{8}	8.3x10^{6}
5d	15.147	40	6.8x10^{8}	1.7x10^{7}
7s	15.183	8	2.0x10^{8}	2.5x10^{7}
6p'	15.205	12	1.4x10^{8}	1.2x10^{7}
5d'	15.317	20	1.7x10^{8}	8.4x10^{6}
7s'	15.359	4	3.9x10^{7}	9.8x10^{6}

a) The values of T_e=9000 K and n_e=5x10^{14} cm^{-3} were used in the calculation (Ref.17).

The number density n(p) and normalized number density n(p)/g, where g is a statistical weight, are shown in Table 1. From these results, we can interpret some interesting characteristics of the argon ICP, and lead some important conclusions. In the previous paper,[14)] the present authors reported that the number density of metastable argon atom was 1.2x10^{11} cm^{-3}, which was obtained experimentally by an atomic absorption technique using the transition between $4s[3/2]^\circ_2$ and $4p[5/2]^\circ_3$. The present calculated result for the number density of metastable argon atom is about 0.6x10^{11} cm^{-3}, which is almost consistent with the experimental value(1.2×10^{11} cm^{-3}). This fact suggests that the present calculation is quite reliable for the estimation of the population density distributions. When the Penning ionization processes were proposed as the excitation mechanisms, the overpopulation of the metastable argon atoms was assumed because of their long lifetimes in the metastable states due to the forbidden transitions to the ground state. From the results in Table 1, it should be stressed here that metastable states are not overpopulated in the argon ICP, and also that the population of metastable argon atom may not be enough to interpret the excitation mechanism through the Penning ionization processes, as in similarity to the conclusion led in the previous paper.[14] On the other hand, the results in Table 1 indicate that argon atoms distribute in all the energy levels following the Boltzmann distribution. Total number density of excited argon atom is approximately 1.37×10^{11} cm^{-3}, while the number density of argon ion or electron is 5×10^{14} cm^{-3}. From this fact, i. e., the difference between the number densities of excited argon atom and electron (equal to argon ion) is about 3 orders of magnitude, it is difficult to assume the Penning ionization processes as the main excitation mechanisms. Another important point deduced from the results in Table 1 is that rapid interconversions between argon energy states occur through electron collisions. This can be supported by the fact that the argon populations in the upper energy states follow the Boltzmann distribution. Such an interconversion process may intepret close population of argon atom in the $4s[3/2]^{\circ}_{2}$ (metastable) and $4s[3/2]^{\circ}_{1}$ (normal) levels and non-overpopulation of metastable states. It may be concluded that the present collisional-radiative model is useful for the estimation of the population density distributions of argon atoms in the argon plasma. In the present paper, however, the plasma was assumed to be thin and homogeneous or uniform (not-structured). Therefore, the collisional-radiative model should be extended to the thick (or large) and inhomogeneous (structured) plasma with further modification to discuss the excitation mechanisms and physical properties of the real argon ICP.

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