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NON-BOLTZMANN ENERGY LEVEL DISTRIBUTIONS OF ARGON ATOMS IN THE INDUCTIVELY COUPLED ARGON PLASMA

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Based on collisional and radiative processes occurring in the inductively coupled plasma, non-Boltzmann energy level distributions of argon atoms are calculated under various conditions, by using ideal gas law and solving rate equations.

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I. INTRODUCTION

During the past two decades, inductively coupled argon plasma (ICAP) has been rapidly developed. It has not only progressively become the most widely used excitation source in analytical spectroscopy, but also begun to show a great potential in mass spectrographic analysis[1]. Although it has many advantages, ICAP is by no means perfect[2, 3]. In order to further improve its performance, one has to get a thorough understanding of the fundamental physical processes which occur in the plasma. As an excitation source, ICAP is a steady-state discharge sustained at atmospheric pressure, with argon as the working gas. The ionization degree in such a discharge is generally less than 1%; in normal spectroscopic observation region the ionization degree is usually of the order of 0.1%. Apparently, the vast majority of the particles in an ICAP are argon atoms which collide with electrons, argon ions, as well as photons in the plasma, resulting in a certain energy level distribution of argon atoms under steady-state conditions. In turn, this energy level distribution will not only directly determine the spectroscopic characteristics of the plasma itself, but also influence the excitation features of other elements introduced into the plasma. Since ICAP is not in local thermodynamic equilibrium (LTE), argon atoms in the plasma do not necessarily obey the Boltzmann law, i.e. the real argon atom energy level distribution cannot be determined by a single physical parameter only. In the present paper, several non-Boltzmann energy level distributions of argon atoms in the ICAP are calculated by solving rate equations under different conditions, assuming that the measurable fundamental physical parameters[4], i.e. electron temperature T_e, electron density n_e and gas temperature T_g, are known. During the calculations the peculiarity of atmos-

pheric pressure discharge was considered, and the number density of ground level argon atoms was determined by using the ideal gas law. Finally the effects of electron density, resonance absorption and gas temperature on argon atom energy level distributions are discussed.

II. PRINCIPAL PROCESSES AFFECTING ARGON ATOM ENERGY LEVEL DISTRIBUTIONS

The interactions among electrons, ions, photons and neutral atoms in the ICAP are complicated, and it is these interactions that dictate various properties of the plasma[5]. The major physical processes that greatly affect argon atom energy level distributions are listed as follows.

A. Electron collision excitation

Because of the direct collision by electrons, argon atoms at lower energy levels will gain energy from them and transit to higher energy levels. The rate of this process depends mainly on T_e and is proportional to n_e.

B. Electron collision de-excitation

This is the reversal of the above mentioned process, and again the rate is mainly determined by T_e and proportional to n_e.

C. Electron collision ionization

Argon atoms at certain energy levels are ionized by direct electron collision. The rate of ionization in this process is T_e-dependent, and is also proportional to n_e.

D. Three-body recombination

This is the reversal process of electron collision ionization, and its rate depends on T_e, but is proportional to n_e^2.

E. Radiative recombination

Argon ions can be recombined with free electrons via collision with the release of photons. The recombination rate in this process is dependent on T_e and proportional to n_e.

F. Spontaneous radiation

Argon atoms will transit spontaneously from higher to lower energy levels, while photons are released. The rate of this process is determined by Einstein's coefficient of spontaneous radiation.

Photo-excitation and photo-ionization have not been taken into consideration, since ICAP is an optically thin plasma, and all the absorption processes, except those for argon resonance lines, can be neglected. As for the effect of resonance absorption, detailed discussions will be given in the following calculations.

III. THE CALCULATIONS OF ARGON ATOM ENERGY LEVEL DISTRIBUTIONS

A. Rate equations

Since ICAP is a steady-state discharge sustained at atmospheric pressure, it will be in a dynamic equilibrium, i.e. argon atoms in unit volume which are originally at energy level P but removed in unit time via the above-mentioned processes, should equal in number the atoms in unit volume which are originally at other energy levels q but transferred in unit time to energy level p via similar processes. This can be expressed by

$$
\begin{aligned}
&- \sum_{q>p} K_{ce}(q,p) n_e n_p - \sum_{q<p} K_{cd}(q,p) n_e n_p - K_{ci}(c,p) n_e n_p \\
&- \sum_{q<p} K_{rd}(q,p) n_p + \sum_{q<p} K_{ce}(p,q) n_e n_q + \sum_{q>p} K_{cd}(p,q) n_e n_q \\
&+ K_{3b}(p,c) n_e^2 n_i + \sum_{q>p} K_{rd}(p,q) n_q + K_{rr}(p,c) n_e n_i = 0 \ , \qquad (1)
\end{aligned}
$$

where the symbols used are similar to those in Lovett's paper[6]. The first four terms on the left hand side of Eq. (1) represent the loss rates of argon atoms in unit volume for energy level p caused by electron collision excitation, electron collision deexcitation, electron collision ionization and spontaneous radiation, respectively. The next four terms are the gain rates of argon atoms for energy level p through the reversal of the processes mentioned for the first four terms, and the last term is the gain rate of argon atoms for energy level p due to radiative recombination. In Eq. (1), K_{xy} in each term is the rate constant of the process specified by the subscripts x and y. n_p, n_q and n_i denote the number densities of argon atoms at energy levels p and q, and that of the argon ions, respectively.

Note that the values of n_i and n_e are almost the same. For given electron density n_e and electron temperature T_e, the 7th and 9th terms on the left hand side of Eq. (1) are constant. Therefore, Eq. (1) is a linear equation concerning the number densities of argon atoms at different energy levels. For each energy level considered, a corresponding equation of the kind of Eq. (1) can be established, and the resulting complete set of linear equations are then solvable.

B. Number density of ground level argon atoms

Since ICAP is an atmospheric-pressure argon plasma, and its total pressure consists of the fractional pressures contributed by neutral atoms, ions and electrons, we have, using the ideal gas equation,

$$
P = n_a K T_g + n_i K T_g + n_e K T_e \ , \qquad (2)
$$

where P is a constant (i.e. 1 atm), k the Boltzmann constant, n_a the neutral atom number density, and both the neutral atom temperature and the ion temperature are considered equal to the gas temperature T_g. Note that n_i is equal to n_e, from Eq. (2) the neutral atom number

density n_a can be determined by

$$n_a = \frac{P - n_e K(T_g + T_e)}{K T_g} \quad (3)$$

Actually Eq. (3) can be used to express the number density of ground level argon atoms n_1, because the number density of all neutral argon atoms at excited states is much less than the total number density of argon atoms in the ICAP. Clearly, given T_e, n_e and T_g, the value of n_1 is simply determined by Eq. (3). In addition, the number density of charged particles in the ICAP is at least two orders of magnitude lower than that of neutral argon atoms; therefore, the 2nd and 3rd terms on the right hand side of Eq. (2) are much less than the 1st term. If the last two terms are neglected, then the value of n_1 is dependent only upon T_g. Calculation in such a way will cause just a small error in the result, which is generally much less than 1%.

C. Excitation levels of argon atoms

For simplicity and easy comparison, we follow the treatment of Hasegawa *et al.*[7], and accordingly the energy levels of the fine structure are grouped together as one level, and only those levels that are lower than 7s in state $^2P_{3/2}$ and 7s′ in state $^2P_{1/2}$, including 7s and 7s′, will be taken into account. Thus 12 levels in state $^2P_{3/2}$ and another 12 levels in state $^2P_{1/2}$ will be considered respectively in the following calculations, resulting in a total of 24 excitation levels of argon atoms, among which both $4s[3/2]_2^0$ in state $^2P_{3/2}$ and $4s[1/2]_0^0$ in state $^2P_{1/2}$ are metastable, whose density will decide the role the Penning effect will play in the excitation processes of analyte elements[8].

D. The calculation of number density distributions of excitation-level argon atoms

As stated earlier, if given T_e, n_e and T_g, the number density of ground level argon atoms is simply determined by Eq. (3). Thus, to obtain number density distributions of excitation-level argon atoms $n_p(p=2,3,...,25)$, it is only necessary to solve a set of 24 linear equations of the form of Eq. (1).

The rate constants for an ICAP with $T_e = 9000$ K(Ref.[7]) will be taken for comparison, and with given values of n_e and T_g, the coefficient $a_{p,q}$ in each term of Eq. (1), as well as other constant terms b_p, can be calculated. The set of 24 linear equations can then be simplified to the form of a matrix equation with respect to a 24-dimension vector $n_p(p=2,3,...,25)$

$$\begin{bmatrix} a_{2,2} & a_{2,3} & \cdots & a_{2,25} \\ a_{3,2} & a_{3,3} & \cdots & a_{3,25} \\ & & & \\ a_{25,2} & a_{25,3} & \cdots & a_{25,25} \end{bmatrix} \begin{bmatrix} n_2 \\ n_3 \\ \\ n_{25} \end{bmatrix} = \begin{bmatrix} b_2 \\ b_3 \\ \\ b_{25} \end{bmatrix}, \quad (4)$$

where $a_{p,q}(p \neq q)$ denotes the transition rate of argon atoms from excitation level q to excitation level p via collisional and radiative processes; $a_{p,q}(p=q)$ stands for the rate at which argon atoms are transferred from excitation level p to all the other states (including other excitation levels, the ground-level and ionization states) due to collisional and radiative

processes, and b_p is the total number of particles in unit volume that transfer from argon atom ground level to excitation level p through electron collision excitation or from ionized states to argon atom excitation level p through three-body recombination and radiative recombination in unit time. It should be noted that Eq. (4) describes a dynamic equilibrium process, so both $a_{p,q}(p=q)$ and b_p are negative, but $a_{p,q}(p\neq q)$ are positive.

IV. RESULTS AND DISCUSSION

For different electron densities and gas temperatures and in the presence or absence of resonanse absorption, the number densities of ground-level argon atoms are calculated by using Eq. (3). These in turn allow the determination of all the rate coefficients. Finally the number density distributions of excitation-level argon atoms under different conditions are obtained by solving Eq. (4). In the following the effects of several factors on energy level distributions are discussed.

A. The effect of electron density n_e

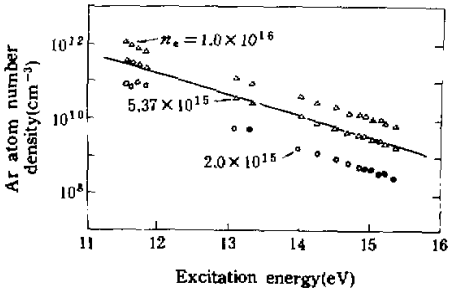

Fig.1. Energy level distributions of excited Ar atoms with different electron density n_e.

Figure 1 shows the relation between the number density of excitation level argon atoms and the corresponding excitation energy. The solid line indicates the Boltzmann distribution (the same is true in figures that follow), assuming the plasma is in LTE, with T_e as a determining parameter. In this case the LTE value of electron density has been calculated to be $n_e=5.37\times10^{15}\text{cm}^{-3}$, using the Saha equation. In Fig.1 the circles, filled triangles and open triangles represent the number densities of excitation levels calculated through the above-mentioned approach for $n_e=2.0\times10^{15}$, 5.37×10^{15} and $1.0\times10^{16}\text{cm}^{-3}$, respectively. For the sake of clarity, only 16 excitation levels are presented, as the higher levels are crowded together. In the sequence of increasing excitation energy, the levels shown in the figure are $4s[3/2]^0_2$, $4s[3/2]^0_1$, $4s'[1/2]^0_0$, $4s'[1/2]^0_1$, 4p, 4p′, 3d, 3d′, 5p, 5p′, 6s, 4f, 6s′, 5d, 6p′, 7s′, among which the symbols with a prime belong to the state $^2P_{1/2}$, and others belong to the state $^2P_{3/2}$.

Obviously, the number densities of argon atoms at all excitation levels are very sensitive to n_e, and usually increase with n_e even more rapidly than a linear relation. Interestingly, when the LTE value for n_e is used, the argon atom energy level distribution obtained by solving the rate equations is almost in perfect agreement with the Boltzmann distribution (compare the filled triangles and the solid line in Fig.1). No doubt, this consistency can be regarded

as a verification of the rationalities of setting up the equations as well as the calculation of rate coefficients.

In the above calculations it has been assumed that T_g is the same as T_e, and that the resonance radiation is completely absorbed.

B. The effect of gas temperature T_g

The calculations with different values of T_g indicate that the effect of T_g on the number density distributions of excitation-level argon atoms is negligible, provided n_e is larger than or equal to its LTE value. However, with lower n_e, e.g. $n_e = 1.0 \times 10^{15}\text{cm}^{-3}$, the number densities of argon atoms at excitation levels increase with decreasing T_g. This can be seen in Fig. 2, where the filled and open triangles denote the number densities of excitation-level argon atoms with $T_g = 6000$ and 9000 K, respectively.

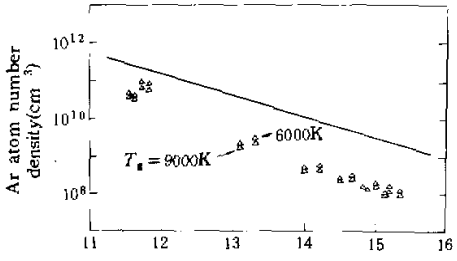

Fig.2. Effect of gas temperature T_g on energy level distributions of excited Ar atoms ($n_e = 1.0 \times 10^{15}$ cm^{-3}).

In fact, the gas temperature directly influences the number density of ground level argon atoms n_1. However, when n_e is relatively high, ICAP appears to be a recombining plasma[4], the number densities of excitation-level argon atoms are controlled mainly by T_e and n_e, and therefore should not be affected by n_1. On the contrary, when n_e is relatively low, the ICAP will behave as an ionizing plasma, and its energy level distribution should, of course, depend on its ground level number density. Such features of the ICAP are exactly reflected by the results of our calculations.

C. The effect of resonance absorption

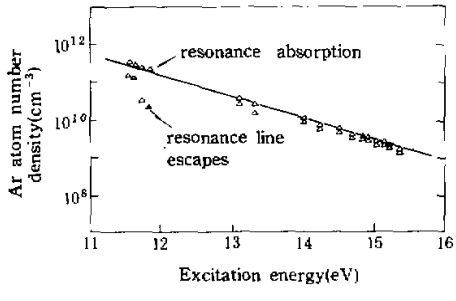

Fig.3. Effect of resonance absorption on energy level distributions of excited Ar atoms ($n_e = 5.37 \times 10^{15}\text{cm}^{-3}$).

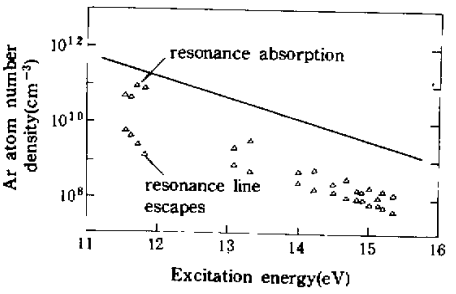

Fig.4. Effect of resonance absorption on energy level distributions of excited Ar atoms ($n_e = 1.0 \times 10^{15} cm^{-3}$).

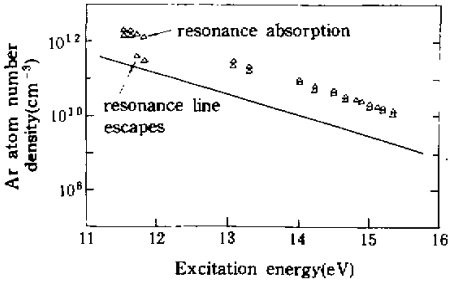

Fig.5. Effect of resonance absorption on energy level distributions of excited Ar atoms ($n_e = 1.5 \times 10^{16}$ cm^{-3}).

Figures 3–5 show the effects of resonance absorption on the number density distributions of excitation-level argon atoms with $n_e = 5.37 \times 10^{15}$, 1.0×10^{15} and 1.5×10^{16} cm^{-3}, respectively. The filled and open triangles in the figures denote the number densities of excitation-level argon atoms when the resonance line is fully absorbed by or completely escapes from the plasma, respectively. Apparently, strong resonance absorption leads to an increase in the number densities of argon atoms at all excitation levels; moreover, the lower the electron density, the more significant this effect would be. In addition, resonance absorption has even greater impact on energy levels in state $^2P_{1/2}$ than in state $^2P_{3/2}$, partcularly for 4s levels.

To calculate the energy level distributions of argon atoms, mathematically the number density of ground level argon atoms n_1 can also be considered as a variable, and a set of 25 linear equations are to be solved. Unfortunately, this approach will lead to a calculated n_1 that is extremely sensitive to both n_e and T_e, resulting in a value of n_1 which fluctuates in a range of several orders of magnitude[7]. This implies that the plasma pressure could be several orders of magnitude higher or lower than the atmospheric pressure, and therefore is not consistent with the fact that the pressure in the ICAP should be equal or close to 1 atm.

In fact, the normal spectroscopic observation region in the ICAP is a recombining plasma[4, 9], whose electron density is obviously higher than the LTE value. This case is shown by the open triangles in Fig.1. Consequently, the number densities of argon atoms at all excitition levels, including the metastable ones, are definitely much higher than the Boltzmann distribution (by a factor of about 4 on average, as can be seen from comparing the open tri-

angles with the solid line in Fig.1), which will certainly enhance the role of Penning effect in excitation mechanism[8]. On the other hand, ICAP is an optically thin plasma and absorbs only a negligible amount of light at any wavelengths except the argon atom resonance line, which is, however, almost completely absorbed [5, 10]. The strong absorption of resonance radiation not only leads to a high number density of the resonance excitation level itself, but also plays a significant role in maintaining relatively high population of the metastable and other excitation levels (see Figs.3–5). Finally, it should be pointed out that as far as ground level argon atoms are concerned, the correct number density n_1 cannot be obtained by solving the rate equations. Instead, it should be calculated by using the ideal gas law with gas temperature as the determining parameter.

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