KINETICS OF EXCITED ATOMS
IN NON-STATIONARY NON-EQUILIBRIUM PLASMA OF INERT GASES
WITH ACCOUNT OF IONIC-MOLECULAR REACTIONS

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ABSTRACT

The expressions for the excited-state population densities and the recombination rate coefficients in an atomic gas plasma have been obtained taking into account the atomic-molecular ion conversion, the thermal dissociation of molecular ions, the associative ionization, the dissociative recombination and the complex of collisional radiative processes.

I. INTRODUCTION

Ionic-molecular reactions (IMR), such as atomic-molecular ion conversion (IC), thermal dissociation of molecular ions (TD), associative ionization (AI), dissociative recombination (DR) are characterized by large rate constants [I].

\[
\begin{align*}
A_1^+ + A_1 & \xrightarrow{AI} A_2^+ + e \\
A_2^+ + 2A_1 & \xrightarrow{IC} A_2^+ + A_1
\end{align*}
\] (1)

In the present paper we have analysed the influence of these reactions on the recombination coefficients and on the excited atom kinetics in the presence of the collisional radiative processes [2,3].

Numerous experiments show that one of the characteristic features of AI and DR is their selectivity. Thus, we may consider that only the atoms in the state with \( k=\alpha \) take part in the AI process and only the atoms in the state with \( k=\delta \) are formed in the DR process:

\[
\begin{align*}
A_\alpha + A_1 & \rightarrow A_2^+ + e \\
A_2^+ + e & \rightarrow A_\delta + A_1
\end{align*}
\]
2. EXPRESSIONS FOR THE EXCITED-STATE POPULATIONS

Consider a quasi-stationary plasma. It is well known that in the framework of the collisional radiative model in the case of \( \dot{N}_k / \dot{N}_k = 0 \) the excited level populations may be written as follows:

\[
y_k = \gamma_1(k) y_1 + \gamma_0(k) y_e^2
\]

(3)

Here \( y_k = N_k / N_k^0 \), \( y_e = N_e / N_e^0 \). \( N_k^0 \) and \( N_e^0 \) are the equilibrium concentrations of the electrons and of the atoms in the ground \((k=1)\) and excited \((k>2)\) states respectively, \( \gamma_0(k) \) and \( \gamma_1(k) \) the population coefficients. In the present paper we use the expressions for \( \gamma_0 \) and \( \gamma_1 \) obtained in [4, 5].

Taking into account the presence of the molecular ions we arrive at the following expression:

\[
y_k = y_1 \gamma_1'(k) + y_e^2 \gamma_0'(k) + y_e^2 \frac{N^+}{N^0} \left( p(k) - \frac{\gamma_1'(k)}{\gamma_0'(k)} \right)
\]

(4)

Here \( N^+ \) is the molecular ion concentration. The new population coefficients are given by the following expressions:

\[
\gamma_1'(k) = \begin{cases} \frac{\gamma_1(k) - \beta \gamma_0(k)}{1 + \gamma} & 2 \leq k \leq a \\ \frac{\gamma_1(k)}{1 + \gamma} & k > a \\
\end{cases}
\]

\[
\gamma_0'(k) = \begin{cases} \frac{\gamma_0(k)}{1 + \gamma} & 2 \leq k \leq a \\ \gamma_0(k) - c' \gamma_1'(k) & k > a \\
\end{cases}
\]

\[
p(k) = \begin{cases} q_d \gamma_0(k)(1 - \beta l) & 2 \leq k \leq d \\ q_d \gamma_1'(k) l & k > d \\
\end{cases}
\]

\[
\beta = \frac{r}{1 + \gamma} \frac{\gamma_1(a)}{\gamma_0(a)} ; \ c' = \frac{r}{1 + \gamma} \frac{\gamma_0(a)}{\gamma_1(a)} ; \ l = \frac{\gamma_0(d)}{\gamma_1(d)}
\]

\[
\gamma = \frac{R_{1a} R_{ae}}{R_{1e} \beta a} ; \ q_d = \alpha_d N_e^2 \times R_{de} ; \ \beta a = (N_k^0 N_a N_1 \beta a)^{-1}
\]

The level numeration corresponds to the well-known model [6]. The general expressions for \( R_{mk} \), \( R_{ke} \) and \( N_k \) are given in [7]. Here \( \alpha_d \) is the dissociative capture coefficient, \( \beta a \) the AI rate constant.
In this paper we express the $A_2^+$ concentration in terms of the plasma parameters ($N_1$ and $N_e$) and the rate constants for the reactions responsible for the balance of $N_2^+$.

It allows to obtain the expression for $y_k$ in the form analogous to (3):

$$y_k = \gamma_1(k) y_1^* + \gamma_0(k) y_e^*$$

$$y_1^* = \left\{ \begin{array}{ll}
y_1 & 2 \leq k \leq d \\
(A_{yd} l + 1) y_1 + B_{yd} l y_e^2 & d < k \leq a \\
\left[ A_{yd} l \left( \frac{1 + A_{yd} l}{1 + y} \right) + AC \right] y_1 + \left[ B_{yd} l \left( -1 - B \right) \right] y_e^2 & k > a \\
\end{array} \right.$$ 

$$y_e^* = \left\{ \begin{array}{ll}
\left( \frac{1 - B}{1 + y} + B_{yd} l \right) y_e^2 + \left[ A_{yd} l \left( 1 - B \right) - \frac{A}{1 + y} \right] y_1 & 2 \leq k \leq d \\
\left( \frac{1 - B}{1 + y} - B_{yd} l \right) y_e^2 - \left( B + A_{yd} l \frac{A}{1 + y} \right) y_1 & d < k \leq a \\
A y_1 & k > a \\
\end{array} \right.$$ 

$$A = \frac{q_k}{q_a} \frac{1}{C} ; \quad B = \left( 1 + \frac{q_k}{1 + y} \frac{q_k}{q_a} \right) \frac{1}{C} ;$$ 

$$C = 1 + q_k \left( 1 - \frac{y}{1 + y} \frac{R_{1d}}{R_{1a}} + \frac{N_1}{N_e} \frac{\alpha d}{d} \right) + \frac{y}{1 + y} \frac{q_k}{q_a} ;$$ 

$$q_k = \frac{\alpha d N_e^2}{\beta} ; \quad \beta_k = \kappa_k N_1^2 ; \quad q_a = \alpha d N_e^2 R_{ae}$$

$\beta_k$ and $\alpha$ are the rate constants for the IC and TD processes respectively.

It is clear from the Eq (7) that the IMR lead to the formation of three groups of excited states: $2 \leq k \leq d$, $d < k \leq a$, $k > a$ (Fig.I).
Some possible distribution functions of atoms over the excited states. The dashed lines correspond to the distributions in the framework of the collisional radiative model. The solid lines correspond to the distributions with account of the ionic-molecular reactions (1), (2). a - recombining plasma, b - ionizing plasma.

The formulae (7), (8) describe the excited atom concentrations for the case when both the collisional radiative processes and the reactions (1), (2) are taken into account. One must note that the distribution function of atoms over their excited states is expressed here in terms of the basic plasma parameters $N_1, N_e, T_e$ and the rate constants of the processes responsible for the $A_2^+$ formation and destruction.

3. RECOMBINATION COEFFICIENTS

The expressions for the recombination coefficients obtained in early works taking into account ionic conversion are applicable only to the decay of a plasma with the low electron concentration and temperature. In this paper we have obtained the following expression for the rate of the electron concentration change:

$$\frac{dN_e}{dt} = \frac{N_1 N_e \beta^*}{n_f R_{le}} - \Delta^* N_e^3 = \frac{\gamma_1}{n_f R_{1e}} \left[ 1 + \frac{\gamma}{1+\gamma} \right] \frac{P_{ae}}{R_{1e}} (1 + \alpha_{A_2}) +$$

$$+ \frac{A N_1}{1+\gamma} \left[ 1 - A N_1 B_2 \right] - \frac{\gamma e^2}{R_{1e}} \left[ \frac{1 - B}{1+\gamma} + \gamma_{d} B - \gamma_{d} B \gamma e \right]$$
The recombination coefficient can be written as

\[ a^* = \frac{1}{N_0^2 N_e R_e} \cdot \frac{q_k \left( 1 - \frac{1}{1 + y} \frac{R_{d1}}{R_{1a}} \right) + q_d \left( 1 + \frac{1}{1 + y} \frac{R_{d1}}{R_{1a}} \right)(1 - 6c)}{1 + \frac{y}{1 + y} \frac{q_k}{q_d} + \frac{y}{1 + y} \frac{q_k}{q_d} + \frac{y}{1 + y} \frac{q_k}{q_d}} \]

\[ R_{km} = R_{me} - R_{ke} \]

Two particular cases follow from the Eq (10).
1. When \( \alpha_d = 0, \beta_k = 0 \) \( (q_k = 0, q_d = 0) \), we have the well-known expression for the collisional radiative recombination coefficient [2]:

\[ a^* = \frac{1}{N_e^2 N_e R_{ke}} \]

2. When \( \beta_k = \infty \) \( (N_e = N_{e+}) \), we have the expression for the DR coefficient given in [2]:

\[ a^* = \alpha_d \frac{1}{N_e} \frac{R_{de}}{R_{ke}} \]

4. APPROXIMATE EXPRESSIONS FOR THE PARAMETERS

The main parameters of the problem are \( \gamma, q_d, q_k, q_a, E_R, R_{km} \). The position of the R-level divides the level system into two parts. For the levels with the ionization energy \( E < E_R \), the transition kinetics is determined by the electron collisions. For \( E > E_R \), radiative processes dominate collisional processes. In the Ref [4,5] was obtained

\[ E_R = \left( \frac{N_e}{4.10^{12}} \right)^{0.17} \cdot T_e^{0.12} \]

\( N_e \) in \( \text{cm}^{-3} \), \( T_e \) in ev. In the works [4,5] was also obtained:

\[ R_{ke} \approx R_{ae} \approx R_{de} \approx R_{ke} \quad \text{for} \quad E_R < E_a \]
\[ R_{ke} \approx R_{de} \approx R_{ae} \quad \text{for} \quad E_a < E_R < E_d \]
\[ R_{de} > R_{ae} \quad \text{for} \quad E_R > E_d \]
The expressions for \( R_{\text{Ke}} \) are given in Ref [7]. Taking \( f \) in the form convenient for calculations we have

\[
f = 1.5 \times 10^8 \tau_0(a) \sum_i \frac{g_\alpha}{\Sigma_i} e^{-\frac{E_\alpha}{kT}} \left( \frac{kT}{R} \right)^{3/2} \chi_N(x_m) \beta^a N_i \frac{N_e}{N_e}
\]

Here

\[
\chi_m = \min \left\{ \frac{E_R}{\chi}, \frac{E_d}{\chi} \right\}
\]

\[
\chi_N(x) = \frac{1}{8.56} \int_0^\infty t^{3/2} e^{-t} dt
\]

If \( \tau_0(a) = 1 \) (the role of radiation is small) \( f \) is the function of ionization degree and \( T_e \). One can estimate the ionic conversion contribution to decay rate using the formula

\[
\frac{\beta_d}{\beta_k} = \frac{\rho_k}{N_e^2} = 1.03 \times 10^{-26} \frac{T_e}{N_e} 51 \chi_N \left( \frac{\min \left\{ E_R, E_d \right\}}{T} \right)
\]

\( T_e \) in eV, \( N_e \) in cm\(^{-3}\), \( \beta \) in cm\(^3\) sec\(^{-1}\).

Thus, relatively simple and reliable analytical expressions have been obtained for the excited-state population densities and the recombination coefficients taking into account the ionic-molecular reactions (1), (2). The expressions obtained allow to analyse various experimental situations.

REFERENCES