COLLISIONAL-RADIATIVE MODEL
APPLIED TO A HF GENERATED ARGON PLASMA-JET

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Abstract

A nonlinear time-dependent collisional-radiative model for argon is presented to explain measurements of excited level population densities performed in a high frequency generated argon plasma-jet expanded in a 17 mBar vacuum chamber.

After verification of the electron induced processes, we show that the inelastic collisions between atoms are insufficient to obtain results close to the experimental ones. Considering reactions involving Ar$_2^+$, we show that this model calculates an excited states distribution relatively well correlated with the measurements.

1. Introduction

The electron density $n_e$ and the population densities of excited levels [Ar(i)] have been measured in a high frequency generated argon plasma-jet (van Ootegem [1]) having a weak ionization degree ($\alpha = 10^{-6}$). Figure (1) illustrates the experimental device.

The Boltzmann's graph of the population densities obtained reveals an excitation equilibrium at the temperature $T_{ex} = 5500$ K (see figure (6)).

![Figure (1): argon plasma-jet studied](image)

The measured population density [Ar(i)] is governed by the equation:

$$\text{div} \left( \frac{[\text{Ar(i)}]}{\nu} \right) = \frac{d[\text{Ar(i)}]}{dt}$$ (1)

$$\text{Coltrads}$$ (2)
The characteristic time of the term (1) is about $10^{-4}$ s whereas the characteristic time of the term (2) is up to $10^5$ s for the most excited levels. The latter are therefore in quasi steady-state condition: $[\text{Ar}(i)]$ is governed only by collisional and radiative processes.

In order to explain the excitation equilibrium observed, we have elaborated a collisional-radiative (C-R) model. It contains a large number of elementary processes to cover a wide range of conditions in terms of ionization degree, ground state density and temperatures.

2. Atomic model

We consider two types of particles in this C-R argon model: atoms (in fundamental and excited states), and ions (Ar$^+$ and Ar$^+_2$).

For excited Ar levels, we have adopted the energetic diagram of Vlcek [2]. This rare gas follows essentially the $(j,l)$ coupling. Since the core have the structure {Mg}3p$^6$, its angular momentum quantum number $j_c$ depends on the configuration of the last 3p electron, that is $j_c = 1 + s = 3/2$ and $j_c = 1 - s = 1/2$. This important particularity yields to two subsystems of levels: the first one ($j_c = 3/2$) has an ionization limit equal to $E_{3/2} = 15.755$ eV whereas the second one ($j_c = 1/2$) has this limit equal to $E_{1/2} = 15.932$ eV.

Due to this quantum effect, the 64 excited levels (see figure (2)) considered here are separated in two groups according to the value of $j_c$ without possibility of intercombination ($\Delta j_c \neq 0$) for the most excited ones. In the following, $i = 1$ corresponds to the ground state.

![Diagram](image)

**Figure (2):** energetic diagram for Ar, Ar$^+$ and Ar$^+_2$.

3. Collisional and radiative processes

3.1. Radiative processes

For the spontaneous emission, the transition probabilities involved here have been updated: in addition with NBS tables, we have used recent data of Wiese et al. [3] and Verner et al. [4]. For resonance lines, we have assumed complete self-absorption because of [Ar(1)]. For the other transitions, an escape factor is calculated in the same way as Vlcek.

We have treated the radiative recombination like him: this process is assumed to occur only for the low excited levels since the cross section depends on $n^*^{-3}$ where $n^*$ is their effective principal quantum number.
3.2. Electron induced processes

For the ionization processes, we have adopted the work of Drawin [2] except in the

case of the ground state for which Straub et al. [5] have measured the cross section.

For the excitation, we have used the expression of the cross sections proposed by

Drawin for the forbidden transitions. For the allowed transitions, several expressions of

cross sections have been tested: Drawin, Vriens et al. [6] and Seaton [7].

3.3. Atom induced processes

Few experimental data are available concerning these processes. Several authors have
determined the cross sections for the transitions between the 5 lowest levels (involving the

metastable 3p^4s ones) which are consequently relatively well known. Conversely, for the

more excited levels, there are no experimental data. Therefore we have tested the model of

Drawin [8] which is based on the adaptation of the cross section by electron impact for

allowed transitions. Concerning the forbidden transitions, these cross sections have been

treated in the same way as Vlcek.

Sobel’man [9] has proposed a quasiclassical model for inelastic collisions between

atoms assuming the trajectory of colliding particles to be rectilinear. Taking into account the

interaction potential energy, the calculation of the transition probability provides the cross

section. We have analyzed, as shown later, the influence of this model on the results of the C-

R model and compared with others.

For the very excited levels (Rydberg states) for which the peripheric electron is far

from the core, the excitation reaction can be understood as the interaction of the incoming

atom with a quasi-free electron. The previous cross sections do not take into account the

Ramsauer effect which leads to an important decrease of its value. We have adapted the

model of Kaulakys [10] devoted to the collisional angular momentum mixing considering the
differential elastic scattering amplitude of the Ar-e collision given by Weyhrer et al. [11].

Finally, for the ionization reactions:

\[ \text{Ar}(i) + \text{Ar}(1) \rightarrow \text{Ar}^+ (\text{j}_e) + e^- + \text{Ar}(1) \]

the cross sections used are due to Drawin, except for the ground state: in this case, the

experimental results of Haugjaa et al. [12] have been adopted.

3.4. Ar_2^+ involved processes

Bogaerts et al. [13] have recently pointed out the significant role of Ar_2^+ on the

kinetics of a direct current argon glow discharge mainly due to the dissociative recombination:

\[ \text{Ar}_2^+ + e^- \rightarrow \text{Ar}(1) + \text{Ar}(1) \]

In our case, the population densities of the excited levels depend also on the Hornbeck-

Molnar process, that is the associative ionization:

\[ \text{Ar}(i) + \text{Ar}(1) \rightarrow \text{Ar}_2^+ + e^- \]

with \( E(i) > E(\text{Ar}_2^+) = 14.71 \text{ eV} \). This process decreases \([\text{Ar}(i)]\). In order to determine its

accurate contribution at the heavy particle temperature \( T_A \) involved, we have elaborated a

quasiclassical model based on the calculation of the interaction potential energy curves

between \( \text{Ar}(1) \) and the core of the excited atom (Bultel et al. [14]). Due to the selection rules

and the different states of \( \text{Ar}_2^+ \) resulting from the core quantum configuration, only \( \text{Ar}(i, j_e = 3/2) \) contributes to the reaction and, for temperatures \( T_A \) equal to nearly 2000 K, the rate

constant is largely less than the value used by Bogaerts.

1295
Finally, other processes for which the influence of temperature is relatively well known are considered as atomic to molecular ion conversion, metastable-metastable associative ionization, direct electronic dissociation and mainly dissociative recombination to the metastable states (Ustinovskii et al. [15]):

\[ \text{Ar}_2^+ + e^- \rightarrow \text{Ar}(3p^5 4s) + \text{Ar} \]

4. Results and discussion

All processes previously described leads to the treatment of time-dependent non-linear equations. The calculations are done with the help of LSODE (Livermore Solver for Ordinary Differential Equation). Figure (5) shows an example of solution illustrating the determination of the quasi steady-state time denoted \( \tau_{\text{qss}} \).

4.1. Electron induced processes verification

Marie [16] have experimentally determined the population densities of excited levels in a recombination argon plasma at sufficiently high ionization degree (\( \alpha = 0.15 \)) for which the electrons ensure excitation (\( n_e = 1.5 \times 10^{20} \text{ m}^{-3} \), \( T_e = 5600 \text{ K} \) and \( T_A = 2000 \text{ K} \)). In these conditions, it is easy to verify all electron involved processes. The results are plotted in figure (3) using Drawin's model which allows to obtain the best fit. We have therefore adopted this model in the following.

![Figure (3): comparison of the experimental results of Marie with those of the C-R model using Drawin's model.](image)

4.2. Atom induced processes discussion

In quasi steady-state condition, figure (4) illustrates the comparison between our results (in the experimental conditions: \( n_e = 3 \times 10^{17} \text{ m}^{-3} \), \( T_e = 5500 \text{ K} \) and \( T_A = 1800 \text{ K} \)) and those resulting from the C-R model in the case the role of \( \text{Ar}_2^+ \) is assumed to be negligible. When the works of Sobel'man and Kaulakys are associated instead of those of Drawin, the agreement is slightly better but nevertheless obviously insufficient. Consequently, the cross
sections given by Sobel’man and Kaulakys have to be used and, moreover, other processes as those involving Ar$_2^+$ have to be arised for improving the agreement.

It is important to note that using Sobel’man and Kaulakys models introduces a large dispersion of the population densities which is questionable.

*Figure (4):* comparison between experimental and C-R model results without Ar$_2^+$

4.3. **Influence of Ar$_2^+$**

Considering our previous experimental conditions and taking into account the Ar$_2^+$ reactions, we obtain the solution plotted in figure (5) showing the quasi steady-state time for excited levels and 3p$^5$4s ones (including the metastable levels) to be $\tau_{QSS} = \text{some } 10^5 \text{ s.}$

*Figure (5):* calculated population densities time-evolution
Figure (6): Boltzmann’s graph for $\tau_{qss}$ and comparison with experimental results

The Boltzmann’s graph resulting from these calculations for $\tau_{qss}$ reproduces in part the experimental results (see figure (6)).

An accurate study, in term of sensibility, of the processes involving Ar$_2^+$ reveals the great influence of the dissociative recombination to the metastable states:

$$\text{Ar}_2^+ + e^- \rightarrow \text{Ar}(3p^5 4s) + \text{Ar}(1)$$

This reaction yields to a sufficient decrease of the electron density (which is a suitable situation, the ionization degree being weak) and to an over population of the metastable levels with respect to the case of low electron densities when Ar$_2^+$ is assumed to play a negligible role. Due to the electron induced collisions, the population densities of the excited levels are therefore more important and close to the experimental ones, leading to an excitation temperature nearly equal to the electron one.

5. Conclusion

A C-R model has been elaborated to explain the excitation equilibrium in a HF generated plasma-jet having a weak ionization degree. To take into account accurately the reactions involving the inelastic collisions between atoms and the Ar$_2^+$ processes is essential to reproduce experimental results. The molecular ions Ar$_2^+$ appear as an efficient species to ensure simultaneously a decrease of the electron density and an increase of the excited states concentrations.

We shall further study the atom induced processes to minimize the questionable large dispersion observed for the population densities. Due to the wide range of application of the C-R model presented in this paper, we plan to calculate the recombination rate constant and to compare its value with experimental works obtained in various conditions.

References

[1] B. van Ootegem, PhD thesis to be published, University of Rouen (2001)