Modelling of the Excitation and Ionization Processes at the Atmospheric Pressure Glow Discharge in Helium

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Introduction

It is well known that atmospheric pressure glow discharge in (APGD) in helium is actively used in surface treatment of samples located in the discharge plasma. Experimental data accumulated so far describe mainly electric features of the discharge being responsible for its existence as short subsequent pulses and stability [1]. Meanwhile it is necessary to obtain information about optical properties of this discharge. It is important since various atomic and molecular states of the media are the source of chemically active vacuum ultra violet radiation. This problem in general is a consequence of discharge controlled via the dielectric barrier similarity to that used in obtaining of ultraviolet radiation in rare gases dimers, for example, excimer lasers. As it is known, ultra violet radiation there could be obtained in pulsed plasma at two different types of unequilibrium. These are unequilibrium of ionization and recombination. The present work is devoted to analysis of these types of unequilibrium and correspondent population of atomic and molecular states in APGD in helium.

Electron Distribution Function

Distribution function isotropic component have been obtained via numerical solution of the kinetic Boltzman equation with elastic and inelastic collisions. One can show, that for APGD conditions we can use local, quasistationary approximation. The one-dimensional kinetic Boltzman equation is formulated

$$\frac{d}{dw} D(w, E) \frac{df}{dw}(w, E) + V(w) f(w, E) = \sqrt{w} \nu^*(w) f(w, E) - \sqrt{w+w_i} \nu^*(w+w_i) f(w+w_i, E) ,$$

$$V(w) = 2 \frac{m}{M_g} w^{3/2} \nu^*_w(w) ,
D(w, E(t)) = \frac{2(eE)^2 w^{3/2}}{3m \nu^*_w(w)}$$

Here $w$ is electron kinetic energy, $t$ is time, $E = E(t)$ is longitudinal electric field, $m$ is electron mass, $M_g$ is mass of neutral atom, $\nu^*_w$ is transport frequency of atomic collisions, $\nu^*$ is total frequency of inelastic collisions, $w_i$ is first threshold of inelastic collisions. Inter-electron collisions are negligibly small under APGD condition (small ionization degree). The normalization condition for the EDF can be written as

$$\int_0^\infty f(w, E(t)) \sqrt{wdw} = 1$$

The kinetic equation has to be solved with zero boundary conditions at infinity and normalization conditions (2). The numerical method to solve this second order differential
equation with the shifted argument is based on its conversion into a set of linear algebraic equations. The examples of the calculated EDF are shown on the Fig.1

Using the solution of equation (1) with the normalization condition (2) one can obtained the time variations of the rate constants of the elementary processes in the following way

\[ k_x(t) = \sqrt{\frac{2}{m_{\varepsilon_x}}} \int_{-\infty}^{\infty} \sigma_x(w) f(w, E(t)) w \, dw \quad (3) \]

where \( k_x \) and \( \sigma_x \) are the rate constant and the cross section of the considered process \( \varepsilon_x \) is the threshold of this process. This time-dependent coefficients should be included into the set of the balance equations for charged and neutral particles.

**Balance equations for Helium APGD**

Simplified model of helium molecular and atomic states was discussed similar to the paper [2]. This model contents metastable and resonance atoms having strong trapping of resonance emission atomic and molecular helium ions, metastable helium molecules and helium molecules radiating Hopfield continuum in VUV spectrum range. The balance equation and list of processes resulting in creation or destruction of various helium particles are mentioned below. The following convention is used. M is metastable helium atoms density in \( 2s \, 3s_{1/2} \) state, A is helium atoms density in \( 2p \, 1P_{1/2} \) state (resonance level), I is the density of atomic helium ions \( 1s \, 2S_{1/2} \), Q is that of molecular \( He_2^+ \) ions \( (X^2\Sigma_u^+) \), P is \( P_1 \) is \( He_2 \) molecule density in \( A_1 \Sigma_u^+ \), \( D_1 \Sigma_u^+ \), \( P_2 \) is the same for metastable \( He_2 (a_3 \Sigma_u^+) \) molecules.

**Balance equation for metastable atoms is**

\[ \frac{dM}{dt} = m_N(t) N_e + m_{NQ}(t) N_e Q + m_{N_{\text{diff}}}(t) N_e^2 I - m_{\text{diff}} M - m_{\text{ion}} N_e M - k'' M \quad (4) \]

direct electron impact excitation + dissociative recombination of molecular \( He_2^+ \) ions + radiation-collision recombinatio of atomic He ions - pair collisions of metastable atoms accompanied by creation of charged particles - diffusion losses - stepwise metastable atoms ionization - conversion of metastable atoms (M) to molecules (P) at triple collisions.

**Balance equation for resonant atoms is**

\[ \frac{dA}{dt} = a_N(t) N_e + a_{NQ}(t) N_e Q + a_{\text{diff}}(t) N_e^2 I - a_{A}(A + A^2 - a_A A) \quad (5) \]

direct electron impact excitation + dissociative recombination Q + radiation-collision atomic ions recombinatio I – associative ionization reaction - spontaneou emission of excited atoms with radiation trapping effect.

**Balance equation for atomic ions**

\[ \frac{dI}{dt} = i_N(t) N_e + i_{\text{diff}}(t) M N_e + a_A A^2 + m_{\text{diff}} M^2 - i_{\text{diff}} I - i_{\text{diff}}(t) N_e^2 I \quad (6) \]

direct electron impact excitation + stepwise ionization from metastable states + associative ionization from excited states A,M – atomic ions I conversion to molecular ions Q - radiative-collision recombination I. Direct ionization processes under APGD conditions are negligibly small.

**Balance equation for molecular ions**

\[ \frac{dQ}{dt} = q_{pp} P^2 + q_{I} I + q_{M} (A + M) - q_{NQ}(t) N_e Q - \nu_{\text{diff}} Q \quad (7) \]
bimolecular collisions to form the molecular ions + atomic ions I conversion to molecular ones Q at triple collisions + associative ionization (Hornbeck-Molnar reaction) from excited states – dissociative recombination of molecular ions – molecular ions diffusion. Creation of complicated He$_2^+$ ions is also possible, but their concentration is less than 10% of whole entity of molecular ions He$_2^+$. It was estimated using dissociation equilibrium constant [3].

Balance equation for radiating helium molecules $P_1$

$$\frac{dP_1}{dt} = \frac{1}{2} p_{NQ}(t) N_e Q + \frac{1}{2} p_{M} M + p_{NP}(t) N_e P_1 -\frac{1}{2} p_{PP} P_1 P_2 - p_{p_{1}} P_1$$

(8)

dissociative recombination of molecular ions + metastable atoms conversion at triple collisions with helium atoms + electron excitation of metastable molecules – ionization at pair collisions of resonant and metastable helium molecules – Hopfield continuum spontaneous radiation of molecules.

Balance equation for metastable helium molecules $P_2$

$$\frac{dP_2}{dt} = \frac{1}{2} p_{NQ}(t) N_e Q + \frac{1}{2} p_{M} M - \frac{1}{2} p_{PP} P_2^2 - p_{NP}(t) N_e P_2 - p_{P} P_2$$

(9)

molecular ions dissociative recombination + metastable atoms conversion at triple collisions with helium atoms – ionization at pair collisions of metastable molecules – electron excitation of metastable molecules – diffusion of metastable molecules to plasma boundaries.

Solution of equations system (4-9) allows one to find out population of helium molecular and atomic excited states versus the reduced electric field E/p.

**Populations of helium atomic and molecular excited states under APGD conditions.**

Reduced balance equations system along with equation for the discharge current (in general, being time dependent) formed the quantitative base of selfconsistent solution of the problem of APGD in helium. The following results can illustrate the values obtained for some typical APGD conditions [1]. Figures corresponds to current maximum in discharge pulse. Average electron energy – 3.5 eV, molecular He$_2$ ions density - $10^{10}$ cm$^{-3}$, metastable atoms , resonant ones – $10^{10}$ cm$^{-3}$, the density of molecules radiating Hopfield continuum – $10^6$ cm$^{-3}$, metastable He molecular density - $10^{10}$ cm$^{-3}$, electric field in APGD was equal to1300 V/cm. The data of average electron energy and charged particles density obtained are enough close to those mentioned in [1].The charged particles formation process is stepwise ionization from metastable atoms and successive very effective conversion atomic ions ( and excited atoms) In molecular ions by triple collisions with normal He atoms. The loss processes of charged particles is ambipolar diffusion in the current direction to discharge electrodes.

The above mentioned values for different species is related to self consistent solution, steady state APGD conditions. Using these results as initial values in dynamical problem, we calculated excited atoms and molecules concentrations, charged particles density as time evolution function for periodically repeated current pulses [1]. Using the current data, we calculated the significance of E/p in the APGD positive column for different time moment. These meanings of the reduced E/p was used for the solution of the equations system (4 – 9). One can show, that electron density and metastable molecules density ( about $10^{10}$ cm$^{-3}$) is enough week changed in time interval between current pulses .

The results of the numerical calculations are shown on the Fig.2.

One can see, that absolute values of different particles density is more less than ones for steady state conditions. It is a consequence of the essential nonstationary situation under periodically repeated short APGD current pulses. It is interesting to note, that radiating
molecules of He are created as a result of metastable atoms excitation during of current pulse and as a result of the recombination of molecular helium ions after pulse as well.

Conclusion

The main optical processes in the plasma of the positive column APGD in He are: 1) the formation of the metastable atoms by electron impact from He ground state; 2) the conversion of these metastable atoms in helium radiating molecules at the triple collisions with normal He atoms, the creation radiating He molecules at the recombination processes; 3) He excimers emit VUV Hopfield continuum (in conditions of [1] the peak intensity of the VUV is equal about $10^{-3} \text{ W}$).

Such way, we would like to note that the simple model developed in our paper reveals existence of VUV periodic pulses following Fig.2 demonstrating time dependence of radiating He molecules (dimers) concentration. Since this APGD could be considered as a type of device producing excimer radiation under ionization and recombination nonequilibrium along with lasers and “filamentary” barrier discharge.
Figure 2. APGD parameters versus time: current (a), metastable atoms density (b), radiating molecules density (c).

References