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The role of secondary processes in kinetics of triplet states of a hydrogen molecule in an ECR discharge

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Abstract. An electronic state sensitive semiempirical collision-radiative model of hydrogen plasma of ECR-discharge is used to analyze the applicability of emission of triplet states of molecular hydrogen for plasma diagnostics. It is shown that secondary processes make the greatest contribution to the kinetics of population-depopulation of triplet states $a^3\Sigma_g^+$, $c^3\Pi_u$, $d^3\Pi_u$, $e^3\Sigma_u^+$, $g^3\Sigma_g^+$, $h^3\Sigma_g^+$, $i^3\Pi_g$ and $r^3\Pi_g$. The secondary processes give the smallest contribution to the excitation and deactivation of triplet states $f^3\Sigma_u^+$ и $k^3\Pi_u$. Thus a simplified coronal model (electron impact excitation followed by radiative decay) can be used to process the intensities of the dipole allowed $f^3\Sigma_u^+ \rightarrow a^3\Sigma_g^+$, $g^3\Sigma_g^+$ and $k^3\Pi_u \rightarrow a^3\Sigma_g^+$ transitions. The complicated collision-radiative model should be used for other transitions.

1. Introduction

Interest in the hydrogen-containing low-temperature plasma of the ECR-discharge is associated with the problem of creating the gas-discharge sources of negative atomic hydrogen ions H^- [1]. Studies [2,3] show that the dominant role in the formation of H^- in the ECR-discharge is played by processes involving vibrationally excited hydrogen molecules in the ground electronic state $H_2(X^1\Sigma_g^+, v)$. An important stage in creating and optimizing the parameters of gas-discharge sources H^- is the development of non-perturbing and rapid methods for the diagnosis of $H_2(X^1\Sigma_g^+, v)$ (or vibrational temperature $T_v(X^1\Sigma_g^+)$ of the first level) in plasma.

Increasingly widespread in the diagnostics of the vibrational temperature of the ground state in hydrogen plasma are experimental-calculation techniques that are based on a combination of emission spectroscopy and collision-radiative plasma models [4-7]. A simplified coronal model is often used to process results of emission spectroscopy [8]. For example, in processing the emission spectra of the Fulcher system of the hydrogen molecule $H_2(d^3\Pi_u \rightarrow a^3\Sigma_g^+)$ it is assumed that the radiating state of the $d^3\Pi_u$ state is excited by the electron impact, and deactivated by radiative decay. The presence of additional (secondary) collision-radiative processes may violate this assumption. Neglecting of secondary processes in the simplified models can lead to overestimated values of $T_v(X^1\Sigma_g^+)$. The question on the role of secondary processes in the mechanisms of excitation of the triplet states of molecules is still not fully understood.

In the present paper this problem is investigated by modeling the processes of population and deexcitation of the triplet states of a hydrogen molecule in an ECR-discharge. It is a continuation of [8], in which studies of the distribution function for the rotational and vibrational levels of a hydrogen



molecule in triplet state $d^3\Pi_u$ in the ECR-discharge in hydrogen were performed by emission spectroscopy.

Results of study the problem for nonequilibrium DC and microwave discharges are presented in [7, 9]. From the point of view of the problem under consideration, the ECR-discharge is of particular interest, since the electron energy distribution function (EEDF) in this discharge differs significantly from the EEDF in other discharges in that it is enriched by electrons in the high-energy region compared to other discharges. This can lead to a change in the ratio of the channels in the triplet states kinetics.

2. Experimental conditions

The study of the processes of population and deexcitation of the triplet states of a hydrogen molecule is performed for the conditions described in [1]. ECR discharge was created in a chamber of cylindrical geometry (diameter $D = 100$ mm) made of stainless steel in a stream of hydrogen in the pressure range 0.001-0.01 Torr. The plasma was isolated from the chamber walls by a Pyrex cylinder. Microwave power in the range 200 - 1200 W at 2.45 GHz in continuous generation mode was supplied to four dipolar sources. The wall temperature of the T_w chamber was kept at room temperature. The value of the translational temperature T_g measured on the discharge axis in the region of dipolar sources measured by the emission spectroscopy method was 600 ± 650 K and decreased to 430 ± 50 K at a distance of 90 mm from them [8]. The EEDF measured by the probe method is bimaxwellian and enriched by electrons in the high-energy region [1]. It is determined by the temperatures (T_e^c , T_e^h) and the concentrations (N_e^c , N_e^h) of the "cold" (T_e^c , N_e^c) and "hot" (T_e^h , N_e^h) electrons corresponding to the low- and high-energy part of the EEDF. When the gas pressure p varied from 0.25×10^{-2} to 0.96×10^{-2} Torr, the concentration and temperature of the "cold" and "hot" electrons measured by the probe method lay in the ranges: $N_e^c = (0.13-2.3) \times 10^{10} \text{ cm}^{-3}$ and $N_e^h = (0.3-0.8) \times 10^{10} \text{ cm}^{-3}$; $T_e^c = 0.6-2.0$ eV and $T_e^h = 2.0-6.0$ eV. The ratio of the concentration of the negative ion of the hydrogen atom to the electron concentration measured by the laser-induced photo-detachment in the ECR-discharge is 0.01 – 0.1. The content of atomic hydrogen P_H in the plasma does not exceed 4%. Since the used collision-radiative model is semiempirical, the parameters T_e^c , T_e^h , N_e^c , N_e^h , T_g , p (or the total concentration of particles N), D , P_H and T_w are the initial data in the model. kinetics.

3. Semiempirical level-to-level collision-radiative model of hydrogen plasma in ECR-discharge

In the model developed in [7] and used in this paper, the number of electronically excited states of a hydrogen molecule is significantly increased, compared with those described in [4-6], and the kinetic scheme is extended in the part of the collisional-radiative processes of interest for emission spectroscopy of hydrogen plasma. It additionally takes into account processes involving hydrogen molecules in singlet ($N^1\Lambda_\sigma = 2B^1\Sigma_u^+$, $2C^1\Pi_u$, $3B'^1\Sigma_u^+$, $3D^1\Pi_u$, $4B''^1\Sigma_u^+$, $4D'^1\Pi_u$, $2EF^1\Sigma_g^+$, $3I^1\Pi_g$, $3H\bar{H}^1\Sigma_g^+$, $3GK^1\Sigma_g^+$, $3J^1\Delta_g$, $4P^1\Sigma_g^+$, $4O^1\Sigma_g^+$, $4R^1\Pi_g$, $4S^1\Delta_g$, $O^1\Sigma_g^+$) and triplet ($N^3\Lambda_\sigma = 2b^3\Sigma_u^+$, $2c^3\Pi_u$, $2a^3\Sigma_g^+$, $3e^3\Sigma_u^+$, $3d^3\Pi_u$, $3h^3\Sigma_g^+$, $3g^3\Sigma_g^+$, $3i^3\Pi_g$, $4f^3\Sigma_u^+$, $4k^3\Pi_u$, $4r^3\Pi_g$, $4s^3\Delta_g$) states. To determine the level-rate coefficients of the processes describing the collisions of electrons with heavy particles, we used the EEDF, obtained as a result of probe measurements for the experimental conditions from [1]. A list of collision-radiative processes with a corresponding database (or the total concentration of particles N), D , P_H and T_w are the initial data in the model. kinetics.

4. Results and discussion

As a result of calculations it was shown that the value of the electronic relaxation time of the populations of triplet states of the hydrogen molecule does not exceed a tenth of a second. The values of the stationary concentrations of the excited molecules $H_2(N^3\Lambda_\sigma)$ lie in the range 1.7×10^4 - $8.2 \times 10^7 \text{ cm}^{-3}$. The stationary distributions of the populations of the triplet states $N^3\Lambda_\sigma$ and the vibrational levels of the ground state of hydrogen molecule $X^1\Sigma_g^+$, differ from the Boltzmann distributions. The calculated values of the temperature of the first vibrational level $T_v(X^1\Sigma_g^+)$ lie in

the range from 1700 K to 3000 K. In the plasma under optimal conditions for the formation of vibrationally excited molecules $H_2(X^1\Sigma_g^+, v)$, processes involving $H_2(X^1\Sigma_g^+, v=1-4)$ can contribute to the excitation kinetics of triplet states $c^3\Pi_u$, $d^3\Pi_u$, $e^3\Sigma_u^+$, $h^3\Sigma_g^+$, $i^3\Pi_g$ and $r^3\Pi_g$.

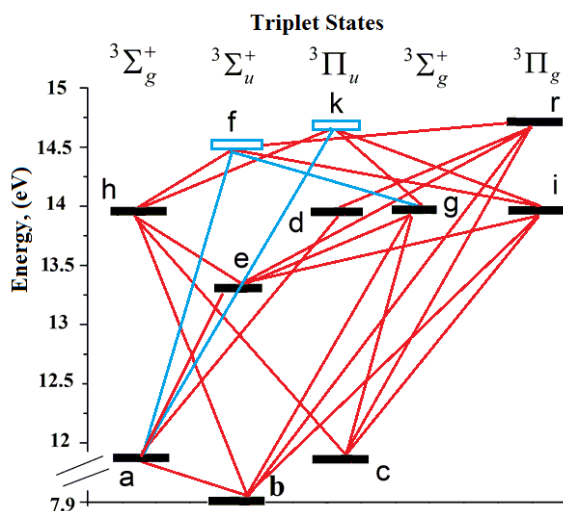
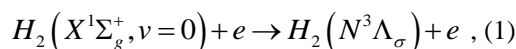


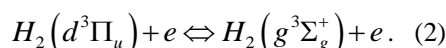
Figure 1. Diagram of radiative transitions between triplet states. Blue lines denote the transitions $f^3\Sigma_u^+ \rightarrow a^3\Sigma_g^+, g^3\Sigma_g^+$ and $k^3\Pi_u \rightarrow a^3\Sigma_g^+$, for processing the intensities of which a simplified coronal model can be applied. Red lines denote the transitions, for processing the intensities of which the semiempirical level-to-level collision-radiative model should be applied.

Calculations show that the mechanisms of excitation and deexcitation differ for different triplet states of the hydrogen molecule and they are determined by volumetric collisional-radiative processes. The composition and number of secondary processes and their hierarchy vary with the gas residence time in the discharge zone τ_D . Secondary processes make the greatest contribution to the kinetics of triplet states $a^3\Sigma_g^+$, $c^3\Pi_u$, $d^3\Pi_u$, $e^3\Sigma_u^+$, $g^3\Sigma_g^+$, $h^3\Sigma_g^+$, $i^3\Pi_g$ and $r^3\Pi_g$. The smallest contribution is made by secondary processes to the kinetics of triplet states $f^3\Sigma_u^+$ and $k^3\Pi_u$. Dipole allowed transitions $f^3\Sigma_u^+ \rightarrow a^3\Sigma_g^+, g^3\Sigma_g^+$ and $k^3\Pi_u \rightarrow a^3\Sigma_g^+$ can be used for spectral diagnostics of hydrogen plasma of ECR-discharge on the base of simplified coronal model. This is reflected in figure 1, which shows the radiative transitions, which can and cannot be used within the framework of the simplified coronal model.

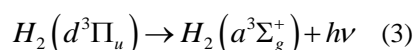
The results of analysis of population-depopulation mechanism of the $H_2(d^3\Pi_u)$ state are of particular interest, since this state is often used in the spectral diagnostics of gas discharges. At $\tau_D \geq 10^{-8}$ s, along with the process (1)



the processes (2) caused by collisions of the first and second kinds of electrons with excited hydrogen molecules $H_2(d^3\Pi_u)$ and $H_2(g^3\Sigma_g^+)$ begin to play an appreciable role in the excitation-deexcitation mechanism of the $d^3\Pi_u$ state of the hydrogen molecule



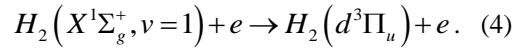
At $\tau_D \geq 10^{-7}$ s and $p = 0.25 \times 10^{-2}$ Torr, $N_e^c = 0.13 \times 10^{10} \text{ cm}^{-3}$, $N_e^h = 0.46 \times 10^{10} \text{ cm}^{-3}$ и $T_e^c = 0.7$ eV, $T_e^h = 2.7$ eV processes (1, 2) and



are responsible for the stationary concentration of hydrogen molecules in $d^3\Pi_u$ state ($1.9 \times 10^5 \text{ cm}^{-3}$).

The electronic relaxation time of the $d^3\Pi_u$ state population is equal to $\tau_R^e = 10^{-3}$ s. With increasing

the pressure up to $p = 0.96 \times 10^{-2}$ Torr at $N_e^c = 2.3 \times 10^{10} \text{ cm}^{-3}$, $N_e^h = 0.8 \times 10^{10} \text{ cm}^{-3}$, $T_e^c = 2.0 \text{ eV}$ и $T_e^h = 6.0 \text{ eV}$ an additional contribution to the kinetics of the production of the $d^3\Pi_u$ state can give a process involving hydrogen molecules $H_2(X^1\Sigma_g^+, v=1)$



Processes (1-4) determine the stationary concentration ($\sim 9 \times 10^6 \text{ cm}^{-3}$) of molecules in $d^3\Pi_u$ state. The electronic relaxation time τ_R^e of the $d^3\Pi_u$ state population is of $2 \times 10^{-2} \text{ s}$.

Prevailing of secondary processes (2) in the kinetics of the $d^3\Pi_u$ state of a hydrogen molecule in a wide range of plasma conditions limits the use of the Fulcher system $H_2(d^3\Pi_u^- \rightarrow a^3\Sigma_g^+)$ for spectral diagnostics of a stationary ECR-discharge in the approximation of simplified coronal model.

This conclusion differs from that obtained earlier for a microwave discharge [7] and a DC discharge [9]. This is due to the fact that the energy distribution of electrons in the ECR discharge is enriched by fast electrons in comparison with the distribution in these discharges. This difference leads to a higher rate of excitation of triplet states, an increase in their concentrations and, correspondingly, to an increase in the role of secondary processes in their population.

5. References

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