Review

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Non-Elastic Processes in Atom Rydberg-Atom Collisions: Review of State of Art and Problems

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Abstract. In our previous research, it has been demonstrated that inelastic processes in atom Rydberg-atom collisions, such as chemi-ionization and $(n-n')$ mixing, should be considered together. Here we will review the present state-of-the-art and the actual problems. In this context, we will consider the influence of the $(n-n')$-mixing during a symmetric atom Rydberg-atom collision processes on the intensity of chemi-ionization process. It will be taken into account $H(1s) + H^*(n)$ collisional systems, where the principal quantum number is $n \gg 1$. It will be demonstrated that the inclusion of $(n-n')$ mixing in the calculation, influences significantly on the values of chemi-ionization rate coefficients, particularly in the lower part of the block of the Rydberg states. Different possible channels of the $(n-n')$-mixing influence on chemi-ionization rate coefficients will be demonstrated. The possibility of interpretation of the $(n-n')$-mixing influence will be considered on the basis of two existing methods for describing the inelastic processes in symmetrical atom Rydberg-atom collisions.

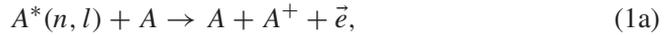*Key words.* Atomic and molecular processes—plasmas—spectral line profiles.

1. Introduction

Exploring and improving the new calculation possibilities and simulation techniques, attracted extensive attention in the chemi-ionization and $(n-n')$-mixing processes
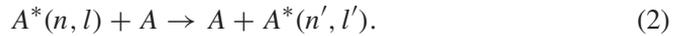
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in atom Rydberg-atom collisions, which resulted in numerous papers dedicated to this problem in various research fields like astrophysics, plasma physics, chemistry (see for example, Bohr *et al.* 2012; Barklem 2007; Mihajlov *et al.* 2007a; Ryabtsev *et al.* 2005).

Two groups of inelastic processes in slow atom Rydberg-atom collisions will be considered in this paper:

The chemi-ionization processes,

$$A^*(n, l) + A \rightarrow A + A^+ + \vec{e}, \tag{1a}$$

$$A^*(n, l) + A \rightarrow A_2^+ + \vec{e}. \tag{1b}$$

The processes of $(n-n')$-*mixing*,

$$A^*(n, l) + A \rightarrow A + A^*(n', l'). \tag{2}$$

Here A and $A^*(n, l)$ denote atom in the ground and in the highly excited (Rydberg) state with the given principal and orbital quantum numbers n and l, A^+ and $\vec{e}$ are atomic ion in the ground state and free electron, while A_2^+ denotes the molecular ion in the ground state.

The processes (1) and (2), illustrated in Figures 1(a) and 1(b), were examined and discussed in the literature for a long time (see Mihajlov & Janev 1981; Janev *et al.* 1987). These processes are conditioned by the dipole resonant mechanism which was described in detail in Mihajlov *et al.* (2012). Significant contribution of processes (1) and (2) in modeling of solar atmosphere is shown in Mihajlov *et al.* (2011a, 2011b) Barklem (2007), Mashonkina (2009, 2010), while the papers of Mihajlov *et al.* (2003) and Srećković *et al.* (2013) are devoted to the influence of these processes on the kinetic of helium-rich star atmospheres. Another important contribution is that the presented results suggest that these processes, due to their influence on free electron density and excited state populations in the atmospheres of M red dwarfs, should also influence the atomic spectral line shapes (see e.g. Mihajlov *et al.* 2007b).

In spite of the fact that processes (1) and (2) are caused by the same mechanism, they are considered separately up to now. The main aim of this work is to determine the influence of processes (2) on the processes of chemi-ionization (1a) and (1b). Namely, already from Fig. 1(b) one can notice the following: in the case when the considered atomic collision proceed in accordance with the excited molecular term $U_2(R)$, before it enters in the zone where the chemi-ionization processes (1a) and (1b) occur, the system $A^*(n, l) + A$ passes through the zone where the processes (2) with $n' > n$ take place.

First, the way the inclusion of process (2) in the procedure of calculation of rate coefficients of the chemi-ionization processes (1a) and (1b) will be described. For this purpose their values will be determined under the conditions characteristic for the solar photosphere in the case $A = \text{H}(1s)$ and compared with the rate coefficients of the same chemi-ionization processes, determined in Mihajlov *et al.* (2011a), but without inclusion of $(n-n')$-mixing processes. We draw attention to the fact that, as a difference from this previous article, chemi-ionization rate coefficients are here without the simplification of the expression for Gaunt factor, connected with the photo-ionization cross sections for the transitions of Rydberg electron $\varepsilon(n, l) \rightarrow \varepsilon(k)$. Besides, here, as a difference from Mihajlov *et al.* (2011a), the average chemi-ionization rate coefficient for a given n is obtained as a result of
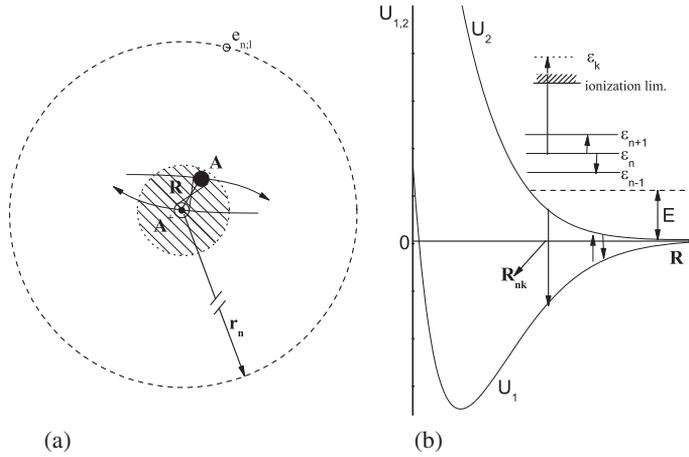
Figure 1. (**a**) Schematic illustration of $A^*(n, l) + A$ collision within the domain of internuclear distances $R \ll r_{n;l}$, where $r_{n;l} \sim n^2$ is the characteristic radius of Rydberg atom $A^*(n, l)$. (**b**) Schematic illustration of the simultaneous resonant transitions of the outer electron from the initial bound to the final state and the sub-system $A^+ + A$ from initial excited to the final ground electronic state. If the outer electron becomes free ($\varepsilon_k > 0$) the processes (1) occur, while if the outer electron remains in the bound state ($\varepsilon_{n'} < 0$) the processes (2) occur.

the corresponding averaging of partial chemi-ionization rate coefficients for every l where $0 \leq l \leq n - 1$.

Atomic units will be used throughout the paper.

2. Theory

2.1 *General formulas*

Let $K_{1a}(n, l; T)$ and $K_{1b}(n, l; T)$ are rate coefficients of processes (1a) and (1b), separately determined for a given n, l and T, where T is the temperature of the considered plasma, and $K_1(n, l; T)$ is the total rate coefficient of processes (1a) and (1b) together, namely $K_1(n, l; T) = K_{1a}(n, l; T) + K_{1b}(n, l; T)$.

Because of further applications, we will then determine the average total rate coefficient

$$K_{1;n}(T) = \frac{1}{n^2} \cdot \sum_{l=0}^{n-1} (2l + 1) \cdot K_1(n, l; T), \tag{3}$$

and average rate coefficient of associative ionization $K_{1b;n}(T)$,

$$K_{1b;n}(T) = \frac{1}{n^2} \cdot \sum_{l=0}^{n-1} (2l + 1) \cdot K_{1b}(n, l; T). \tag{4}$$

Partial rate coefficients $K_1(n, l; T)$ and $K_{1b}(n, l; T)$ are determined on the basis of standard expressions

$$K_1(n, l; T) = \int_{E_{n;i}}^{\infty} \sigma_1(n, l; E) \left(\frac{2E}{\mu_{\text{red}}} \right)^{1/2} f_T(E) \mathrm{d}E, \tag{5}$$

$$K_{1b}(n, l; T) = \int_{E_{n;i}}^{\infty} \sigma_{1b}(n, l; E) \left(\frac{2E}{\mu_{\text{red}}} \right)^{1/2} f_T(E) \mathrm{d}E, \qquad (6)$$

where E is the impact energy, $\sigma_1(n, l; E)$ and $\sigma_{1b}(n, l; E)$ are the corresponding cross sections, μ_{red} is the reduced mass of the subsystem H(1s)+H$^+$, and $f_T(E)$ is the Maxwell distribution function: $f_T(E) = \exp(-E/kT)\sqrt{E}$. Parameter $E_{n;i}$ is given here with the relation $E_{n;i} = U_2(R_{n;i})$, where $R_{n;i}$ is the upper limit of the chemi-ionization zone which is the root of the equation $U_{12} = 1/2n^2$.

The mentioned cross sections are determined here within the semi-classical approximation, with the help of the standard expressions

$$\sigma_1(n, l; E) = 2\pi \int_0^{\rho_{1;\text{max}}} P_1(n, l; \rho; E)\rho \mathrm{d}\rho,$$

$$\sigma_{1b}(n, l; E) = 2\pi \int_0^{\rho_{1b;\text{max}}} P_{1b}(n, l; \rho; E)\rho \mathrm{d}\rho, \qquad (7)$$

where ρ is the impact parameter, $\rho_{1;\text{max}}$ and $\rho_{1b;\text{max}}$ are the corresponding maximal values of this parameter, and $P_1(n, l; \rho; E)$ and $P_{1b}(n, l; \rho; E)$ are the total probability of chemi-ionization and the probability of associative ionization, respectively determined for the given values of n, l, ρ and E. We will determine these probabilities in the form

$$P_1(n, l; \rho; E) = \frac{1}{2} \cdot p_{\text{keep}}(n, l; \rho; E) \cdot p_{i;1}(n, l; \rho; E), \qquad (8)$$

$$P_{1b}(n, l; \rho; E) = \frac{1}{2} \cdot p_{\text{keep}}(n, l; \rho; E) \cdot p_{i;1b}(n, l; \rho; E), \qquad (9)$$

where $1/2$ is the probability that the subsystem H(1s)+H$^+$ develops in accordance with the term $U_2(R)$, $p_{\text{keep}}(n, l; \rho; E)$ the probability that in the domain of values of R where the processes (2) with $n' > n$ are possible, the state of this subsystem is held on, i.e. the excited electronic state with the energy $U_2(R)$, while $p_{i;1}(n, l; \rho; E)$ and $p_{i;1b}(n, l; \rho; E)$ are the corresponding ionization probabilities determined under the condition that subsystem H(1s) + H$^+$ enters into the ionization zone with probability equal to 1.

2.2 *Probability of ionization decay*

As in the previous papers, probabilities $p_{i;1}(n, l; \rho; E)$ and $p_{i;1b}(n, l; \rho; E)$ are determined here within the quasi-static decay approximation. Since these probabilities are determined in a similar way as in the previous works of Mihajlov *et al.* (2007a) and Mihajlov *et al.* (2011a), here they are taken in the form

$$p_{i;1}(n, l; \rho; E) = 1.0 - \exp(-2q_{i;1}),$$

$$p_{i;1b}(n, l; \rho; E) = \exp(-q_{i;2}) \cdot [1.0 - \exp(-2q_{i;as})], \qquad (10)$$

where the quantities $q_{i;1}$, $q_{i;2}$ and $q_{i;as}$ are given as

$$q_{i;as} = q_{i;1} - q_{i;2}, \quad q_{i;1} = \int_{R_0}^{R_{n;i}} \frac{W_i(n, l; R)}{\upsilon_{\text{rad}}(E, \rho; R)} \mathrm{d}R,$$

$$q_{i;2} = \int_{R_{1b;\max}}^{R_{n;i}} \frac{W_i(n, l; R)}{\upsilon_{\text{rad}}(E, \rho; R)} \mathrm{d}R. \tag{11}$$

The rate coefficient of ionization decay $W_i(n, l; R)$ and radial ion-atom velocity $\upsilon_{\text{rad}}(E, \rho; R)$ are given by the expressions

$$W_i(n, l; R) = \frac{1}{2\pi} \cdot c \cdot U_{12}^3(R) \cdot D_{12}^2(R) \cdot \sigma_{ph.i}(n, l, \varepsilon_{ph}),$$

$$\upsilon_{\text{rad}}(E, \rho; R) = \left(\frac{2}{\mu_{\text{red}}} \left[E - U_2(R) - \frac{E\rho^2}{R^2} \right] \right)^{1/2}, \tag{12}$$

where c is the speed of light, $D_{12} = |\langle 1|\hat{d}_{m.i}|2\rangle|$ is the molecular-ion dipole matrix element, $\sigma_{\text{ph}.i}(n, l, \varepsilon_{\text{ph}})$ is the cross section for photoionization of excited hydrogen atom $H^*(n, l)$ by a photon with energy $\varepsilon_{\text{ph}} = U_{12}(R)$, and $U_{12}(R) = U_2(R) - U_1(R)$.

In the expression for dipole matrix element $\hat{d}$ denotes the operator of ion dipole momentum H_2^+ and $|1\rangle$ and $|2\rangle$ are the ground and first excited state of this ion.

In equation (11), R_0 is denoted by the lower limit of the domain R which is reached during the collision with a given ρ and E, and with $R_{1b;\min}$, the upper limit of the domain R where only the process of associative ionization (1b) is possible. Consequently, parameters R_0 represents the roots of the equation: $U_2(R) = E \cdot (1 - \rho^2/R^2)$ and $R_{1b;\max}$ is the root of the equation $U_{12}(R) = E$. Let us draw our attention to where it is assumed in expressions (10) and (11) that $R_{1b;\max} < R_{n;i}$ In the case of $R_{1b;\max} > R_{n;i}$ we have that the quantity $q_{i;2} = 0$ and $q_{i;as} = q_{i;1}$.

We draw our attention that already at this point there exist a difference compared to previous works concerning the chemi-ionization processes in stellar atmospheres (Mihajlov *et al.* 2007a, 2011a). Namely, in the mentioned works, the chemi-ionization rate coefficients were determined with the averaged ionization decay rate, obtained by averaging partial rates over the whole shell with a given n. This gives possibility to use the average over shell Kramers photo-ionization cross-section adjusted with the help of approximate Gaunt factor. As a difference, the rate coefficients $K_1(n, l; T)$ and $K_{1b}(n, l; T)$ were determined here on the basis of equations (5) and (6) with the help of partial cross sections for photo-ionization, determined here on the basis of exact expressions from Sobelman (1979).

2.3 *Probability of pre-ionization decay*

From equations (8) and (9) one can notice that the basic difference, in comparison with previous papers, represents taking into account of the effect of decay of the initial electronic state of the considered atom Rydberg-atom system, due to the possibility of execution of excitation processes (2) with $n' > n$. This one is taken into account by the introduction of probability of maintenance of this state $p_{\text{keep}}(n, l; \rho; E)$. One determines this probability on the basis of the modified

version of approximate method described in Mihajlov *et al.* (2004) dedicated to the $(n - n')$-mixing processes. Let us remind that the essence of this method is that, at a given n, each block of Rydberg states from $n' = n + p_1$ to $n' = n + p_2$ is 'spreading' in a part of 'quasicontinuum' limited by values $n + p_1 - \delta_n$ and $n + p_2 + 1 - \delta_n$, where the parameters δ_n are determined from the condition of maintainance of total number of states and total oscillator strengths for transitions from initial state of Rydberg electron to all states of the separated block. The mentioned modification has been conditioned with the fact that in the just mentioned work, an average rate of decay of the initial state of system connected with the transition of Rydberg electron from the state with the given n in states with $n' = n + p$, where $p \geq 1$, was determined while we must consider transitions of Rydberg electron from the state $|n, l\rangle$ to the states $|n + p, l - 1\rangle$ and $|n + p, l + 1\rangle$. In accordance, it is considered here that the preionization zone form the domain of internuclear distances such that $R_{n;i} < R < R_{n;n+1-\delta_n}$, where $\delta_n = 0.5 \cdot [1 - (1/3) \cdot O(1/n)]$, and domains R corresponding to the mentioned transitions with $p = 1, 2, 3...$ make intervals $(R_{n;n+2-\delta_n}, R_{n;n+1-\delta_n})$, $(R_{n;n+3-\delta_n}, R_{n;n+2-\delta_n})$ and $(R_{n;n+4-\delta_n}, R_{n;n+3-\delta_n})$. The limits of these domains $R_{n;n+p-\delta_n}$ are roots of the equations: $U_{12}(R) = 0.5 \cdot [1/n^2 - 1/(n + p - \delta_n)^2]$.

In this work, the transitions with $1 \leq p \leq 5$ are taken into account. Consequently, the probability $p_{\text{keep}}(n, l; \rho; E)$ could be represented as

$$p_{\text{keep}}(n, l; \rho; E) = \prod_{p=1}^{5} p_{p;\text{keep}}(n, l; \rho; E), \tag{13}$$

where $p_{p;\text{keep}}(n, l; \rho; E)$ is the probability of the maintenance of the initial state of the system within the interval $(R_{n;n+p+1-\delta_n}, R_{n;n+p-\delta_n})$.

Since the mechanism of the pre-ionization decay is the same as in the case of the ionization one, we take immediately that probabilities $p_{p;\text{keep}}(n, l; \rho; E)$ are given by the relations

$$p_{p;\text{keep}}(n, l; \rho; E) = \exp(-x_p),$$
$$x_p = \int_{R_{n;n+p+1-\delta_n}}^{R_p} \frac{w_{n;n+p}(n, l : R)}{v_{\text{rad}}(E, \rho, R)}, \tag{14}$$

where the decay rate $w_{n;n+p}(n, l; R)$ is conditioned by the dipole mechanism within the interval $(R_{n;n+p+1-\delta_n}, R_{n;n+p-\delta_n})$.

The upper limit R_p is given by

$$R_p = \begin{cases} R_{n;n+p-\delta_n}, & R_{n;n+p-\delta_n} \leq R_{up;\text{mix}}(E, \rho) \\ R_{up;\text{mix}}(E, \rho), & R_{n;n+p-\delta_n} > R_{up;\text{mix}}(E, \rho) \geq R_{n;n+p} \end{cases} \tag{15}$$

where $R_{n;n+p}$ is the resonant distance of the process (2) for a given $n - n' = n + p$, determined as the root of the equation

$$U_{12}(R) = \frac{1}{2} \cdot \left[\frac{1}{n^2} - \frac{1}{(n + p)^2} \right]. \tag{16}$$

The parameter $R_{up;\text{mix}}(E, \rho)$ is separately discussed in Appendix 4. Let us draw attention that in the case when $R_{up;\text{mix}}(E, \rho) < R_{n;n+p}$, it is considered that

$p_{p;\text{keep}}(n, l; \rho; E) = 0$. Thus the decay rate $w_{n;n+p}(n, l; R)$ is given by the relation

$$w_{n;n+p}(n, l; R) = \frac{2\pi}{3} \cdot U_{12}^4(R_{n;n+p}) \cdot \tilde{n}^3 \cdot D_{12}^2 \cdot r_{n,l;n+p}^2,$$
$$\tilde{n} = n \cdot [1 - 2n^2 \cdot U_{12}(R)]^{-1/2}, \tag{17}$$

where $r_{n,l;n+p}^2 = |\langle n, l|\hat{d}_{at}|n, l-1\rangle|^2 + |\langle n, l|\hat{d}_{at}|n, l+1\rangle|^2$, $\hat{d}_{at}$ is the operator of the dipole moment of hydrogen atom, and $|n, l\rangle$, $|n, l-1\rangle$ and $|n, l+1\rangle$ denote the corresponding states of Rydberg electrons.

3. Results and discussion

It follows from the above presented material that the total rate coefficients of the processes (1a) and (1b) together, and rate coefficients for the associative ionization (1b), i.e. $K_{1;n}(T)$ and $K_{1b;n}(T)$ are determined on the basis of equations (3)–(17). Let us draw attention that, strictly speaking, chemi-ionization processes (1a) and (1b) can be described on the basis of dipole resonant mechanism only in the case of the state with $n \geq 5$, for which the potential curves of the system $H^*(n, l) + H(1s)$ lie above the potential curve of the system $H^+ + H^-(1s^2)$, where $H^-(1s^2)$ is a stable negative hydrogen ion. However, it can be shown that the points of the intersection of potential curves of the system $H^*(n, l)+H(1s)$ with $n = 2, 3$ and 4 with the potential curve of the system $H^+ + H^-(1s^2)$ are located on the internuclear distances, which are several times larger than the average atomic radius $H^*(n, l)$ so that the existence of these intersections can not significantly affect the values of the corresponding rate coefficients of the processes (1a) and (1b). Consequently the applicability of the dipole resonance mechanism for the states with $n < 5$ depends to what degree it may be regarded as fulfilled condition $R_{n;n+1} \ll r_{n;l}$, where $r_{n;l}$ is the mean radius of the corresponding orbit of the outer electron. One notices that from this aspect, the dipole resonant mechanism can not be applied in the case of $n = 2$, while in the case of the states $n = 3$ and 4 the application of this mechanism can be completely justified.

Total values of the rate coefficients of chemi-ionization processes $K_{1;n}(T)$ within the range $3 \leq n \leq 15$ are presented in Table 1. Bearing in mind the main application (of the results obtained here), on the photosphere and lower chromosphere of the Sun, calculations of these rate coefficients were performed for temperatures 4000 K $\leq T \leq 10000$ K. The processes (1b) are characterized in this paper via the corresponding branch coefficient $X_{1b;n}(T)$ given as

$$X_{1b;n}(T) = \frac{K_{1b;n}}{K_{1;n}}. \tag{18}$$

Values of coefficients $X_{1b;n}(T)$ for the same n and T are presented in Table 2. In accordance with the above, rate coefficients are determined by summing the probability of the decay of the initial state of the collisional system in preionization zone with Rydberg electron transitions from state $|n\rangle$ to state $|n + p\rangle$, where $1 \leq p \leq 5$.

In order to demonstrate significance of the presented calculation, we will compare the chemi-ionization rate coefficients $K_{i;n}(T)$ with the corresponding rate coefficients $K_{i;n}^*(T)$ from Mihajlov *et al.* (2011a). Let us note that the coefficients
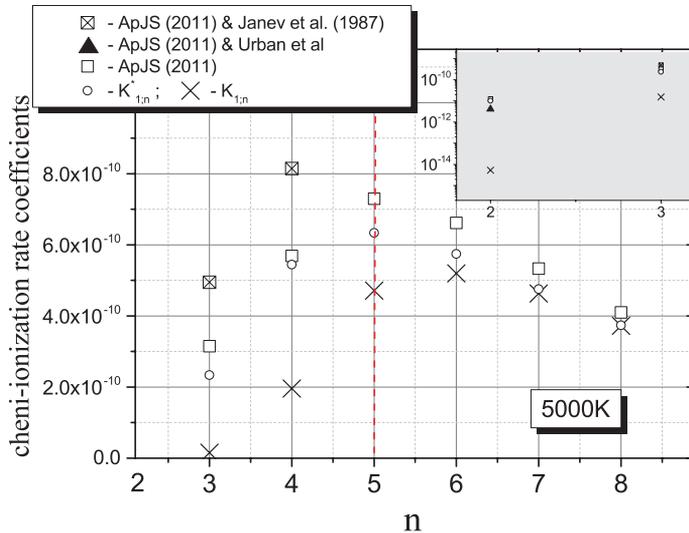
Table 1. Calculated values of the coefficient $K_{1;n}(T)$ (cm^3 s^{-1}) as a function of n and T.

T							n						
	3	4	5	6	7	8	9	10	11	12	13	14	15
4000	7.17E-12	1.54E-10	3.58E-10	4.28E-10	3.98E-10	3.30E-10	2.61E-10	2.06E-10	1.63E-10	1.28E-10	1.02E-10	8.14E-11	6.62E-11
4250	9.01E-12	1.63E-10	3.88E-10	4.52E-10	4.15E-10	3.42E-10	2.69E-10	2.11E-10	1.66E-10	1.31E-10	1.04E-10	8.28E-11	6.72E-11
4500	1.11E-11	1.72E-10	4.16E-10	4.76E-10	4.32E-10	3.53E-10	2.76E-10	2.16E-10	1.70E-10	1.33E-10	1.06E-10	8.40E-11	6.81E-11
4750	1.33E-11	1.83E-10	4.43E-10	4.98E-10	4.48E-10	3.63E-10	2.83E-10	2.20E-10	1.73E-10	1.35E-10	1.07E-10	8.51E-11	6.89E-11
5000	1.53E-11	1.96E-10	4.71E-10	5.20E-10	4.63E-10	3.72E-10	2.89E-10	2.24E-10	1.76E-10	1.38E-10	1.09E-10	8.62E-11	6.97E-11
5250	1.73E-11	2.12E-10	4.98E-10	5.42E-10	4.77E-10	3.81E-10	2.95E-10	2.28E-10	1.78E-10	1.40E-10	1.10E-10	8.73E-11	7.05E-11
5500	1.96E-11	2.31E-10	5.26E-10	5.63E-10	4.90E-10	3.89E-10	3.01E-10	2.31E-10	1.80E-10	1.41E-10	1.11E-10	8.84E-11	7.12E-11
5750	2.30E-11	2.51E-10	5.53E-10	5.83E-10	5.03E-10	3.96E-10	3.06E-10	2.35E-10	1.82E-10	1.43E-10	1.13E-10	8.94E-11	7.19E-11
6000	2.81E-11	2.71E-10	5.79E-10	6.03E-10	5.15E-10	4.04E-10	3.11E-10	2.38E-10	1.84E-10	1.44E-10	1.14E-10	9.03E-11	7.25E-11
6250	3.53E-11	2.91E-10	6.03E-10	6.21E-10	5.26E-10	4.11E-10	3.16E-10	2.41E-10	1.86E-10	1.46E-10	1.15E-10	9.12E-11	7.30E-11
6500	4.37E-11	3.11E-10	6.26E-10	6.39E-10	5.37E-10	4.17E-10	3.20E-10	2.44E-10	1.88E-10	1.47E-10	1.16E-10	9.19E-11	7.36E-11
7000	6.01E-11	3.50E-10	6.70E-10	6.72E-10	5.59E-10	4.30E-10	3.28E-10	2.50E-10	1.92E-10	1.49E-10	1.18E-10	9.33E-11	7.46E-11
7500	7.08E-11	3.90E-10	7.13E-10	7.03E-10	5.80E-10	4.43E-10	3.36E-10	2.55E-10	1.95E-10	1.51E-10	1.20E-10	9.46E-11	7.57E-11
8000	7.91E-11	4.31E-10	7.54E-10	7.31E-10	5.99E-10	4.55E-10	3.44E-10	2.60E-10	1.98E-10	1.54E-10	1.21E-10	9.57E-11	7.68E-11
8500	8.91E-11	4.71E-10	7.93E-10	7.57E-10	6.14E-10	4.65E-10	3.51E-10	2.64E-10	2.01E-10	1.56E-10	1.22E-10	9.66E-11	7.75E-11
9000	9.91E-11	5.13E-10	8.27E-10	7.82E-10	6.27E-10	4.74E-10	3.56E-10	2.68E-10	2.04E-10	1.58E-10	1.23E-10	9.74E-11	7.81E-11
9500	1.06E-10	5.56E-10	8.57E-10	8.06E-10	6.40E-10	4.82E-10	3.61E-10	2.72E-10	2.06E-10	1.59E-10	1.25E-10	9.82E-11	7.86E-11
10000	1.07E-10	6.03E-10	8.82E-10	8.30E-10	6.55E-10	4.90E-10	3.66E-10	2.75E-10	2.08E-10	1.61E-10	1.26E-10	9.91E-11	7.93E-11

$K_{i;n}^*(T)$ are obtained in the same way as the coefficients $K_{i;n}(T)$ by taking $p_{\text{keep}}(n, l;$ $\rho; E) = 0$, where $p_{\text{keep}}(n, l; \rho; E)$ is the total probability of the preionization decay given by equations (13)–(17). All the mentioned quantities are presented in Fig. 2 for the case of $T = 5000$ K. Note that in relation to the previous work of Mihajlov *et al.* (2011a), in this figure are presented not only the total rate coefficients, determined on the basis of dipole resonance mechanism for $3 \leq n \leq 8$ but also rate coefficients are determined on the basis of data from Janev *et al.* (1987) for $n = 3$ and 4, and from

Table 2. Calculated values of the branch coefficient $X_{1b;n}$ as a function of n and T.

							n						
T	3	4	5	6	7	8	9	10	11	12	13	14	15
4000	0.684	0.608	0.458	0.365	0.306	0.243	0.218	0.208	0.201	0.186	0.169	0.154	0.137
4250	0.607	0.563	0.437	0.346	0.284	0.232	0.211	0.202	0.195	0.178	0.160	0.143	0.129
4500	0.543	0.519	0.421	0.329	0.265	0.222	0.206	0.198	0.189	0.170	0.152	0.132	0.122
4750	0.497	0.475	0.407	0.314	0.248	0.213	0.201	0.194	0.184	0.162	0.144	0.122	0.114
5000	0.467	0.431	0.395	0.301	0.232	0.205	0.197	0.190	0.180	0.155	0.137	0.112	0.108
5250	0.473	0.427	0.370	0.284	0.223	0.201	0.193	0.185	0.172	0.146	0.130	0.109	0.104
5500	0.467	0.419	0.347	0.269	0.215	0.197	0.189	0.181	0.164	0.137	0.123	0.107	0.101
5750	0.442	0.411	0.328	0.254	0.208	0.193	0.186	0.177	0.157	0.128	0.116	0.104	0.098
6000	0.397	0.403	0.310	0.242	0.201	0.190	0.183	0.173	0.150	0.119	0.110	0.101	0.095
6250	0.349	0.380	0.294	0.229	0.197	0.187	0.179	0.166	0.142	0.116	0.107	0.099	0.092
6500	0.308	0.360	0.279	0.218	0.194	0.184	0.175	0.159	0.134	0.113	0.104	0.096	0.089
7000	0.263	0.327	0.254	0.198	0.187	0.178	0.169	0.146	0.118	0.106	0.098	0.092	0.083
7500	0.223	0.292	0.234	0.190	0.180	0.172	0.157	0.133	0.112	0.101	0.093	0.086	0.078
8000	0.199	0.263	0.216	0.183	0.173	0.167	0.146	0.120	0.105	0.096	0.087	0.081	0.073
8500	0.198	0.243	0.194	0.178	0.169	0.161	0.134	0.112	0.100	0.092	0.083	0.075	0.070
9000	0.198	0.225	0.175	0.173	0.165	0.156	0.123	0.105	0.095	0.087	0.080	0.069	0.067
9500	0.201	0.210	0.164	0.167	0.161	0.142	0.116	0.099	0.091	0.084	0.075	0.067	0.065
10000	0.218	0.196	0.155	0.161	0.156	0.129	0.109	0.095	0.087	0.081	0.071	0.066	0.063

Figure 2. Comparison of the calculated values of rate coefficients of the chemi-ionization processes (1a) and (1b) with the data from Mihajlov *et al.* (2011a).

Urbain *et al.* (1991) for $n = 2$. One can notice from this figure that there are notice-able differences between the values of the rate coefficients determined in Mihajlov *et al.* (2011a) and values $K_{i;n}^*(T)$, while the differences in relation to the rate coeffi-cients $K_{i;n}(T)$ are very large for $n \leq 6$ and decreases quickly with the increase of n in $n > 6$.

In previous works (Mihajlov *et al.* 2003, 2007b) related to the photosphere of a *M* red dwarf with temperature near to 4000 K, it has been shown that on populations of hydrogenic Rydberg states in this photosphere as well as on its other characteristics, the chemi-ionization processes (1a) and (1b) influence strongly with $4 \leq n \leq 8$. It is clear that because of this, it is indispensable to take into account the changes of rate coefficients of these processes, which, in accordance with our results, are particularly large for $n \leq 6$. From the material presented here, further investigation of the properties of decay of the initial state of the collisional system $H^*(n, l) + H(1s)$ in the pre-ionization zone is of great importance.

Additionally, results obtained here suggest that the rate coefficients of the chemi-ionization processes (1a) and (1b) could be affected by other channels of influence of the processes (2). Here we have in view the processes of $(n-n')$ mixing taking place in two or more steps.

4. Conclusions

In this work, it is shown that the processes of $(n-n')$-mixing (equation (2)) influence considerably the rates of chemi-ionization processes (1a) and (1b). Cal-culations, which characterize this influence on the quantitative level have been performed. As one can see from figure 2, inclusion of the $(n-n')$ mixing pro-cesses reduce the chemi-ionization rate coefficients. The obtained results are finalized in tabular form, where the values of total constants for rates of the processes (1a) and (1b) together, and rates for the process of associative ion-ization (1b) are presented. The tables cover the range of values, of the princi-pal quantum number of Rydberg states of the hydrogen atom, from $n = 3$ to $n = 15$ and the temperature range from $T = 4000$ K to $T = 10000$ K, so that they can be directly applied in connection with the modeling of photosphere and lower chromosphere of the Sun. Moreover, investigation of the influence of $(n-n')$-mixing processes on the chemi-ionization processes taking into account $(n-n')$ mixing processes which occur in two or more steps have been discussed.

Acknowledgements

Appendix

The characteristic length $R_{up;\text{mix}}$ is defined here as the upper limit of the domain R where at a given E and ρ, we can consider that the inner electron is in the subsystem $H^+ + H(1s)$ and that is sufficiently delocalized, so that this subsystem could be

treated as a quasi-molecular complex. As a qualitative characteristics of the mentioned delocalization, one takes here the probability of resonant charge exchange $P_{c.\text{exc}}(R; E; \rho)$ in the subsystem $H^+ + H(1s)$ as a function of R at a given ρ and E. As a basis for this, is taken the theory of the process: $H^+ + H(1s) \rightarrow H(1s) + H^+$ developed in Firsov (1951) and Bates & Boyd (1962). From this theory it follows that

$$P_{c.\text{exc}}(R; E; \rho) = \sin^2(\varphi(R; E; \rho)), \tag{A1}$$

where the phase $\varphi(R; E; \rho)$ is given by the relation

$$\varphi(R; E; \rho) = \frac{1}{2} \int_R^\infty \frac{U_{12}(R')}{\upsilon_{\text{rad}}(R', \rho, E)} \, dR', \tag{A2}$$

which can be used in the considered case since $P_{c.\text{exc}}(R; E; \rho)$ becomes noticeably different from zero only deeply inside the orbit of the Rydberg electron at a given n. On the basis of the data from Firsov (1951) and Bates & Boyd (1962), it can be considered that in the case when $P_{c.\text{exc}}(R; E; \rho)$ reaches the value of $1/2\pi$, the corresponding R may be considered as the upper limit of the charge exchange zone at a given ρ and E, and consequently, as the upper limit of domain with a sufficient degree of delocalization of electron in the subsystem $H^+ + H(1s)$. Thus, the parameter $R_{up;\text{mix}}$ is determined here as the root of the equation

$$\sin^2(\varphi(R; E; \rho)) = \frac{1}{2\pi}, \tag{A3}$$

where $\varphi(R; E; \rho)$ is given by equation (A2) under condition that this root is in the domain of monotonical increase of the left side of equation (A3).

The behavior of phase $\varphi(R; E; \rho)$ is illustrated in Table 3, where its values for $E = E_{n;i}$, $\rho = 0$ and $R = R_{n;n+1}$ within the range $3 \leq n \leq 15$ are shown. Of course, these data should be treated as qualitative ones since equations (A1) and (A2) have strict sense in the case $E \gg U_{12}(R)$ while in our case, this condition is fulfilled only for $n > 7$.

Table 3. Calculated values of the parameters which characterize pre-ionization zone. Phase $\varphi(R_{n,n+1}, E_{n;i}; \rho = 0)$ is given by equation (A2).

n	R_{ni}	$E_{n;i} = U2(Rn; i)$	$R_{n,n+1}$	$\varphi(R_{n,n+1}, E_{n;i}; \rho = 0)$	$P_{c.\text{exc}}(\varphi(R_{n,n+1}, E_{n;i}; \rho = 0))$
3	4.79	0.02738	5.839	1.840	0.92929
4	5.52	0.01431	6.777	1.143	0.82824
5	6.08	0.00871	7.497	0.782	0.49618
6	6.52	0.00581	8.087	0.567	0.28891
7	6.89	0.00413	8.580	0.433	0.17619
8	7.21	0.00306	9.010	0.341	0.11201
9	7.49	0.00234	9.380	0.278	0.07544
10	7.73	0.00183	9.725	0.229	0.05167
11	7.95	0.00146	10.035	0.193	0.03667
12	8.16	0.00119	10.317	0.165	0.02691
13	8.34	0.00098	10.551	0.146	0.02108
14	8.51	0.00081	10.839	0.122	0.01489
15	8.66	0.00068	11.002	0.114	0.01297

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