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### Atom-Rydberg atom chemi-ionization/recombination processes in the hydrogen clouds in broad-line region of AGNs

V. A. Srećković,<sup>1,2</sup>\* M. S. Dimitrijević<sup>2,3,4</sup>\* and Lj. M. Ignjatović<sup>1,2</sup>\*

<sup>1</sup>University of Belgrade, Institute of Physics, PO Box 57, 11001 Belgrade, Serbia

<sup>2</sup>Isaac Newton Institute of Chile, Yugoslavia Branch, Volgina 7, 11060 Belgrade, Serbia

<sup>3</sup>Astronomical Observatory, Volgina 7, 11060 Belgrade, Serbia

<sup>4</sup>LERMA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universites, UPMC (Univ. Pierre & Marie Curie) Paris 06,

5 Place Jules Janssen, F-92190 Meudon, France

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#### ABSTRACT

The possibility that the chemi-ionization processes in atom–Rydberg atom collisions, as well as the corresponding chemi-recombination processes, may be useful for the diagnostics, modelling, and confirmation of existence or non-existence of very dense weakly ionized domains in clouds in broad-line region of active galactic nuclei, has been considered. The obtained results demonstrate the fact that the considered chemi-ionization/recombination processes, which influence on the ionization level and atom excited-state populations, must have a very significant influence on the optical properties of the weakly ionized regions where the neutral hydrogen densities are larger than  $10^{12}$  cm<sup>-3</sup> since in such conditions they dominate over the relevant concurrent electron–atom collision processes. This can be used as a diagnostic method to find out if the domains with such densities exist or not. Additionally, our previous results obtained for principal quantum number  $2 \le n \le 8$  and 4000 K  $\le T \le 10\,000$  K are extended for principal quantum number  $9 \le n \le 20$  and  $10\,000$  K  $< T \le 20\,000$  K and also for low-temperature region (T < 4000 K) for  $2 \le n \le 20$ .

Key words: atomic processes - galaxies: active - galaxies: nuclei.

#### **1 INTRODUCTION**

In order to develop and improve diagnostic methods needed for the estimation of the physical conditions in the particular parts of active galactic nuclei (AGNs), the investigation of the influence of various relevant atomic and molecular collisional processes is needed (Netzer 1990; Jogee 2006; Osterbrock & Ferland 2006). For example in Crosas & Weisheit (1993), 18 different atomic and molecular collisional processes, including the associative chemiionization, were included in the investigation of hydrogen molecule formation in quasar's broad-line region (BLR) clouds. Using the more or less approximate estimates and hydrogen densities  $10^4$ –  $10^{10}$  cm<sup>-3</sup>, they concluded that the influence of the associative chemi-ionization processes

$$\mathbf{H}^*(n=2) + \mathbf{H}(n=1) \Rightarrow \mathbf{H}_2^+ + e, \tag{1}$$

and

$$\mathbf{H}^*(n=3) + \mathbf{H}(n=1) \Rightarrow \mathbf{H}_2^+ + e, \tag{2}$$

is negligible in BLR clouds. However, for example in Marziani et al. (2011), Negrete et al. (2012) and Marziani et al. (2015), hydrogen atom density 7.00  $\leq \log n_{\rm H} \leq 14.00$  has been used for various simulations in BLR with the code CLOUDY (Ferland et al. 2013). On the other hand, the illuminated surface of the BLR clouds is highly ionized, but if they are sufficiently large the temperature may decrease to the much lower values, e.g. up to around 2000 K, as was taken in Crosas & Weisheit (1993), where gas is weakly ionized with large amount of hydrogen molecules (Crosas & Weisheit 1993). If very dense weakly ionized regions exist, these and other chemi-ionization/recombination processes could be important and could change the optical characteristics. This fact can be used for the investigation if such regions exist in BLR clouds. The aim of this work is to find out at what plasma conditions (neutral hydrogen and electron densities) such processes become important and could be used for numerical simulations and modelling and the confirmation of existence of regions with such characteristics. This topic is very current because of existence of uncertainties on the rate coefficients due to hydrogen collisions (Barklem 2007), and the need for accurate ones in order to be properly included in modern codes like Ferland et al. (1998, 2013, 2017).

<sup>\*</sup> E-mail: vlada@ipb.ac.rs (VAS); mdimitrijevic@aob.rs (MSD); ljuba@ipb.ac.rs (LMI)



**Figure 1.** (a) The surface plot of the partial cross-section  $\sigma_{ci}^{(a)}(n, E)$  equation (10) of the chemi-ionization processes (3), i.e. associative ionization channel. (b) The surface plot of the partial cross-sections  $\sigma_{ci}^{(b)}(n, E)$  equation (10) of the chemi-ionization processes (4), i.e. non-associative ionization channel.



**Figure 2.** Plot of collisional ionization H(n) + H(1s) rate coefficients for selected excited states (n = 4, 7, 10). The black lines are the data analysed in Barklem (2007) for non-associative channel (4), where A = H. The data from Mihajlov and coworkers based on the same mechanism as here are plotted as thick full lines. The calculated data of Soon (1992) are presented with full lines and the dot–dashed line (see Barklem 2007 for detailed explanation). The data of Drawin (1968, 1969) are presented with dotted lines, and the results of the analytic formula from Soon with dashed lines. The red lines are summary rate coefficients for associative (3) and non-associative (4) channels (this work).

#### 2 THE CHEMI-IONIZATION/ RECOMBINATION PROCESSES

An atom  $A^*(n)$  excited into a Rydberg state, with large principal quantum number *n*, is very sensitive even to inelastic thermal collisions that are often enough energetic to produce ionization reactions. They represent chemi-ionization reactions that can be divided in accordance with the products of the reaction. Such symmetric reactions are for example the processes of associative ionization:

$$A^*(n) + A \Rightarrow A_2^+ + e, \tag{3}$$

and the non-associative ionization channel

$$A^*(n) + A \Rightarrow A + A^+ + e, \tag{4}$$

where *e* is a free electron. The reactions such as  $A^*(n) + B \rightarrow B^+ + A + e$ , where *B* is an atom or molecule with the ionization potential less than the internal energy of  $A^*(n)$ , are called Penning ionization. However,  $A^*(n)$  Rydberg atom in the equation (4) does not have the energy needed to ionize the atom *A*, so that a part of the energy necessary for ionization should come from the collision process. Because of this fact, we will denote the process given by equation (4) as collisional ionization. Both the process of associative ionization and the inverse one, called dissociative recombination, are less studied than the Penning ionization but an extensive literature exists for them as well.

For the investigation of chemi-ionization processes, the dipole resonant mechanism is used here, described in detail in Mihajlov et al. (2012).

The chemi-ionization processes (3) and (4) as well as the inverse chemi-recombination processes

$$A_2^+ + e \Rightarrow A^*(n) + A, \tag{5}$$

and

$$A + A^+ + e \Rightarrow A^*(n) + A. \tag{6}$$

The cases A = H(1s) and  $He(1s^2)$  have been analysed in Mihajlov, Dimitrijević & Djurić (1996) and Mihajlov et al. (1997b) with the emphasis on their influence on the populations of excited atoms in the weakly ionized H and He plasmas. In order to investigate the efficiency of these processes, they should be compared with the processes

$$A^*(n) + e \Rightarrow A^+ + 2e, \tag{7}$$

$$A^{+} + 2e \Rightarrow A^{*}(n) + e, \tag{8}$$

$$A^+ + e \Rightarrow A^*(n) + \varepsilon_{\lambda}, \tag{9}$$

where A = H(1s) or  $He(1s^2)$  and  $\varepsilon_{\lambda}$  is the energy of a photon with wavelength  $\lambda$ . The rate coefficients for chemi-ionization and chemi-recombination processes have been determined theoretically in Mihajlov et al. (1996, 1997b). On the basis of obtained results, it

Table 1. Calculated Values of Coefficient  $K_{ci}$  [cm<sup>3</sup> s<sup>-1</sup>] as a function of *n* and *T*. A portion is shown here for guidance regarding its form and content.

T/n	10	11	12	13	14	15	16	17	18	19	20
3000	1.92E-10	1.51E-10	1.19E-10	9.44E-11	7.56E-11	6.11E-11	4.98E-11	4.09E-11	3.39E-11	2.82E-11	2.37E-11
4000	2.17E-10	1.68E-10	1.31E-10	1.03E-10	8.19E-11	6.57E-11	5.32E-11	4.35E-11	3.58E-11	2.97E-11	2.49E-11
5000	2.36E-10	1.81E-10	1.40E-10	1.09E-10	8.62E-11	6.88E-11	5.55E-11	4.52E-11	3.72E-11	3.08E-11	2.57E-11
6000	2.51E-10	1.90E-10	1.46E-10	1.14E-10	8.94E-11	7.12E-11	5.73E-11	4.65E-11	3.82E-11	3.16E-11	2.63E-11
7000	2.62E-10	1.98E-10	1.51E-10	1.17E-10	9.20E-11	7.30E-11	5.86E-11	4.76E-11	3.89E-11	3.22E-11	2.68E-11
8000	2.71E-10	2.04E-10	1.55E-10	1.20E-10	9.40E-11	7.45E-11	5.97E-11	4.84E-11	3.96E-11	3.26E-11	2.72E-11
9000	2.79E-10	2.09E-10	1.59E-10	1.22E-10	9.57E-11	7.57E-11	6.06E-11	4.90E-11	4.01E-11	3.30E-11	2.75E-11
10000	2.85E-10	2.13E-10	1.62E-10	1.24E-10	9.71E-11	7.67E-11	6.14E-11	4.96E-11	4.05E-11	3.34E-11	2.77E-11
11000	2.91E-10	2.17E-10	1.64E-10	1.26E-10	9.83E-11	7.76E-11	6.20E-11	5.01E-11	4.09E-11	3.36E-11	2.79E-11
12000	2.96E-10	2.20E-10	1.66E-10	1.28E-10	9.93E-11	7.83E-11	6.25E-11	5.05E-11	4.12E-11	3.39E-11	2.81E-11
13000	3.00E-10	2.23E-10	1.68E-10	1.29E-10	1.00E-10	7.90E-11	6.30E-11	5.09E-11	4.14E-11	3.41E-11	2.83E-11
14000	3.04E-10	2.25E-10	1.70E-10	1.30E-10	1.01E-10	7.96E-11	6.35E-11	5.12E-11	4.17E-11	3.43E-11	2.84E-11
15000	3.08E-10	2.28E-10	1.71E-10	1.31E-10	1.02E-10	8.01E-11	6.38E-11	5.15E-11	4.19E-11	3.44E-11	2.86E-11
16000	3.11E-10	2.30E-10	1.73E-10	1.32E-10	1.02E-10	8.06E-11	6.42E-11	5.17E-11	4.21E-11	3.46E-11	2.87E-11
17000	3.14E-10	2.31E-10	1.74E-10	1.33E-10	1.03E-10	8.10E-11	6.45E-11	5.19E-11	4.23E-11	3.47E-11	2.88E-11
18000	3.16E-10	2.33E-10	1.75E-10	1.34E-10	1.04E-10	8.14E-11	6.48E-11	5.21E-11	4.24E-11	3.48E-11	2.89E-11
19000	3.19E-10	2.35E-10	1.76E-10	1.34E-10	1.04E-10	8.17E-11	6.50E-11	5.23E-11	4.26E-11	3.50E-11	2.90E-11
20000	3.21E-10	2.36E-10	1.77E-10	1.35E-10	1.04E-10	8.20E-11	6.52E-11	5.25E-11	4.27E-11	3.51E-11	2.90E-11

Table 2. The fits of the equation (13) to the rate coefficients.

n	$k_1$	$k_2$	<i>k</i> <sub>3</sub>
4	19.91758	- 15.14785	1.98009
5	-20.60455	5.21174	-0.57122
6	-17.85054	3.94548	-0.43315
7	- 16.16158	3.1383	-0.34519
8	- 15.03989	2.57737	-0.28382
9	-14.20649	2.14118	-0.23553
10	- 13.64156	1.82851	-0.20101
11	- 13.26126	1.60326	-0.17639
12	-12.96479	1.41629	-0.1557
13	- 12.75919	1.27432	-0.14016
14	- 12.62833	1.1705	-0.12912
15	-12.4765	1.05481	-0.11608
16	-12.37305	0.96497	-0.10616
17	-12.31258	0.89712	-0.09875
18	- 12.24943	0.82884	- 0.09113
19	-12.19548	0.76602	-0.08407
20	- 12.16014	0.71392	-0.07827

has been concluded that the influence on excited-atom populations of these processes is dominant or comparable to the influence of electron–atom and electron–ion processes for  $n \le 8$  and the ionization degree of the considered plasma  $\le 10^{-3}$ .

These results, as well as the papers Mihajlov & Dimitrijević (1986, 1992) etc., with the analysis of radiation ion-atom processes, suggested that the chemi-ionization processes (3) and (4) and the chemi-recombination processes (5) and (6) may have a significant influence on excited-atom populations in the weakly ionized plasma of stellar atmospheres. The importance of the hydrogen case for the corresponding layers in solar photosphere is examined and demonstrated in Mihajlov et al. (1997a, 2011, 2016), and for the helium case in the atmospheres of DB white dwarfs with  $T_{\rm eff} = 12000 - 18000$  in Mihajlov et al. (2003a, 2015, 2016). We note as well that in Mihajlov et al. (2003b, 2007), the chemiionization processes with A = H(1s) have been included *ab initio* in the PHOENIX code (see Baron & Hauschildt 1998), in order to investigate their influence on the excited H atom populations, the electron density, and the profiles of H lines in the atmosphere of an M red dwarf with the effective temperature  $T_{\rm eff} = 3800$  K. It has been shown that these processes with  $n \le 8$  have a strong influence on the population of excited states in H atom as well as to the electron density. Due to the change of electron density, the significant change of the profiles of H  $\alpha$ , H  $\delta$ , H  $\varepsilon$ , and Pa  $\varepsilon$  has been found.

#### **3 THE CALCULATED QUANTITIES**

## **3.1** The partial cross-sections, the rate coefficients, and branch coefficients of the chemi-ionization/ recombination processes

The partial cross-sections  $\sigma_{ci}^{(a,b)}(n; E)$  of the chemi-ionization processes (3) and (4), i.e. associative and non-associative ionization channel are determined as in Mihajlov et al. (2011):

$$\tau_{\rm ci}^{(a,b)}(n,E) = 2\pi \int_{0}^{\rho_{\rm max}^{(a,b)}(E)} P_{\rm ci}^{(a,b)}(n,\rho,E)\rho d\rho,$$
(10)

where  $\rho_{(la,b)}^{\max}(E)$  is the upper limit of the values of impact parameter  $\rho$ , and  $P_{ci}^{(a,b)}(n, \rho, E)$  is the ionization probabilities explained in details in Mihajlov et al. (2011).

With the help of cross-sections  $\sigma_{ci}^{(a,b)}(n; E)$ , one can obtain the corresponding partial rate coefficients of the chemi-ionization processes (3) and (4), denoted here with  $K_{ci}^{(a,b)}(n; T)$ , where *T* is the temperature of the considered plasma. The partial rate coefficients of the inverse chemi-recombination processes (5) and (6) are denoted as  $K_{cr}^{(a,b)}(n; T)$ .

Using the partial, one can determine the total rate coefficients as

$$K_{\rm ci,cr}(n,T) = K_{\rm ci,cr}^{(a)}(n,T) + K_{\rm ci,cr}^{(b)}(n,T),$$
(11)

characterizing the efficiency of both considered processes together.

In Mihajlov et al. (2011), the processes (3), (4), (5), and (6) with A = H have been considered for  $2 \le n \le 8$ . However, Netzer (1990) in section 4.3.2 underlined that in the broad-line clouds in AGN, many atoms are in excited states due to the high density and large optical depth. Also, it has been mentioned that in BLR clouds exist hydrogen atoms with  $n \ge 10$ , collisionally coupled to the continuum. Wills, Netzer & Wills (1985) and Dietrich et al. (2003) assumed for example, that higher order Balmer lines, are merging to a pseudocontinuum in QSO. Modelling the pseudocontinuum spectra in type 1 AGNs, Kovačević, Popović & Kollatschny (2014)



Figure 3. The plot of the quantity  $F_{i;ea}^{(ab)}(n)$  equation (16), as a function of *T* and *n*, for the neutral hydrogen atom in the ground state densities  $N_1 = 10^{12}$  and  $10^{13}$  cm<sup>-3</sup> and the electron density of 0.01  $N_1$ .

have taken into account Balmer lines with the principal quantum number of the upper level up to 400. Consequently, in order to provide all relevant data for the investigation and modelling of BLR clouds, the above-mentioned processes will be considered here for n up to 20. The H atoms with  $5 \le n \le 20$  and  $2 \le n \le 4$  will be considered separately as in Mihajlov et al. (2011), due to the behaviour of the adiabatic potential curves of atom-atom systems  $H^*(n) + H(1s)$ . In fact, within the first region the atom-atom curves are for any *R* above the adiabatic curve of the ion-ion system  $H^+ + H^-(1s^2)$  so that the dipole resonant mechanism is without any exceptions applicable for  $n \ge 5$ , so that for  $n \ge 5$  the rate coefficients of these processes will be determined as in the previous papers (Mihajlov et al. 1997a, 2011).

In the region  $n \le 4$  as in Mihajlov et al. (2011) we used the data from Janev, Langer & Evans (1987) to obtain the semi-empirical rate coefficients  $K_{cr,ci}^{(a)}(n = 3, T)$  and  $K_{cr,ci}^{(a)}(n = 4, T)$ . For chemiionization/recombination processes with n = 2 the rate coefficients used by us are 10–30 per cent larger from the coefficients obtained with the help of data from Janev et al. (1987).

Relative contribution of associative and non-associative channels i.e. partial chemi-ionization and recombination processes for given *n* and *T* can be characterized by corresponding branch coefficients  $X_{ci}^{(a,b)}(n, T)$ , namely

$$X_{\rm ci}^{(\rm a,b)}(n,T) = \frac{K_{\rm ci}^{(\rm a,b)}(n,T)}{K_{\rm ci}(n,T)}, \quad X_{\rm cr}^{(a,b)}(n,T) = \frac{K_{\rm cr}^{(\rm a,b)}(n,T)}{K_{\rm cr}(n,T)}.$$
 (12)

Since  $X_{ci,cr}^{(b)}(n, T) = 1 - X_{ci,cr}^{(a)}(n, T)$  and  $X_{ci}^{(a,b)}(n, T) = X_{cr}^{(a,b)}(n, T) \equiv X^{(a,b)}(n, T)$ , it is enough to present only the values of one of the coefficients  $X^{(a,b)}(n, T)$ .

#### **4 RESULTS AND DISCUSSION**

The values of the partial cross-sections  $\sigma_{ci}^{(a,b)}(n; E)$  of the chemiionization processes (3) and (4) are determined for the principal quantum number  $2 \le n \le 20$  and energies *E* up to 20 eV. This is illustrated by Figs 1(a) and 1(b) by surface plot. These data are very useful since according to Janev, Reiter & Samm (2003) crosssection data are not available at present for the non-associative ionization channel (4).

In Fig. 2, the comparison of collisional ionization rate coefficients for selected excited states is presented. The black lines are the data from the existing literature analysed in Barklem (2007) but only for non-associative channel (4), in the narrow parameter region ( $T < 10\,000$  K and n < 10). The red lines are total rate coefficients obtained in this work for associative and non-associative channels (3) and (4). It is noticeable the present uncertainties on the rate coefficients due to hydrogen collisions in almost all cases as concluded in Barklem (2007). One can see the observable importance of associative channel in the region of lower temperatures (the red line is much higher than the full black line in the oval marked region). This provides important information about presence and abundance of molecular ion  $H_2^+$ . It is visible that the importance of associative channel decreases with the increase of temperature and, after some value, the second channel prevails (right-hand side of figure).

In Mihajlov et al. (2011), the values of the total chemi-ionization and recombination rate coefficients  $K_{ci}(n,T)$  and  $K_{cr}(n,T)$  and of the branching coefficient  $X^{(a)}(n,T)$  have been calculated for principal quantum number  $2 \le n \le 8$  and 4000 K  $\le T \le 10000$  K. As can be seen from Table 1, in this work we extended the region of *n* and  $T (T \ge 10000$  K for n > 8 and low-temperature region T < 4000 K for all analysed *n*, i.e.  $2 \le n \le 20$ ) for both collisional ionization processes.

The values of the total chemi-ionization and recombination rate coefficients,  $K_{ci}(n,T)$  and  $K_{cr}(n,T)$ , are shown in the corresponding tables (Tables 3–8) in the online version of this article. Here, in Table 1, only a sample of the results is provided in order to demonstrate the content of additional data and their form. These tables cover the regions  $2 \le n \le 20$  and  $3000 \text{ K} \le T \le 20000 \text{ K}$  that are relevant for moderately ionized layers of very dense parts of clouds in the BLR region as well as for such layers in solar photosphere and photospheres of solar-like stars. Rate coefficients data for quantum

numbers  $n \le 8$  are presented here in the extended range of temperatures  $T \ge 10\,000$  K and, for the first time, for quantum numbers n > 8 for 3000 K  $\le T \le 20\,000$  K. This enables the inclusion of these processes in the modelling not only of particular moderately ionized layers of the photospheres of the Sun and solar-like stars, but also of very dense parts of the clouds in AGN BLR region that could be used to confirm or exclude their existence.

Here, the values of the coefficient  $X^{(a)}(n,T)$ , which directly describe relative contributions of the associative ionization and dissociative recombination processes, are presented in Tables and in the online version of this article. One can see that associative channel is dominant for lower *n* and *T*. This provides important information about presence of molecular ion  $H_2^+$ . The importance of associative channel decreases with temperature increase when non-associative channel takes dominant place. It is also interesting to examine in detail the influence of charge exchange reactions of the type A + H<sup>+</sup> = A<sup>+</sup> + H between metals (A) and proton since they can have large rate coefficients (Netzer 1990, section 4.3.5), in particular if metal is oxygen or nitrogen (Netzer 1990; Osterbrock & Ferland 2006). This can modify the influence of the non-associative channel since a part of created protons in the process (4) will become again H atoms due to charge exchange with metals.

In order to enable the better and more adequate use of data, we give for the rate coefficients a simple and accurate fitting formula based on a least-squares method, which is logarithmic and represented by a second-degree polynomial (Sahal-Bréchot et al. 2014):

$$\log(K_{\rm ci}(T)) = k_1 + k_2 \log(T) + k_3 (\log(T))^2.$$
(13)

The fits are valid over the temperature range of  $2000 \text{ K} \le T \le 20000 \text{ K}$ . Also, it is possible that the fit is applicable outside this area but with caution. In the Table 2, the selected fits are presented (for  $4 \le n \le 20$ ).

 $I_{ci}(n, T)$ ,  $I_{cr}(n, T)$  are the total chemi-ionization and chemirecombination fluxes due to processes (3, 4) and (5, 6), i.e.

$$I_{\rm ci}(n,T) = K_{\rm ci}(n,T) \cdot N_n N_1,$$
  

$$I_{\rm cr}(n,T) = K_{\rm cr}(n,T) \cdot N_1 N_i N_e,$$
(14)

and  $I_{i;ea}(n,T)$ ,  $I_{r;eei}(n,T)$ , and  $I_{r;ph}(n,T)$  are the fluxes for ionization and recombination processes (7), (8), and (9), i.e.

$$I_{i;ea}(n, T) = K_{ea}(n, T) \cdot N_n N_e,$$
  

$$I_{r;eei}(n, T) = K_{eei}(n, T) \cdot N_i N_e N_e,$$
  

$$I_{r;ph}(n, T) = K_{ph}(n, T) \cdot N_i N_e.$$
(15)

Here,  $N_1$ ,  $N_n$ ,  $N_i$ , and  $N_e$  are the densities of the ground and excited states of a hydrogen atom, of ion, and of free electron, for given *T*.

With the help of these relations, we calculated  $F_{i,ea}(n,T)$  that is given by the expression

$$F_{i,ea}(n,T) = \frac{I_{ci}(n,T)}{I_{i;ea}(n,T)} = \frac{K_{ci}(n,T)}{K_{ea}(n,T)} \cdot N_1 N_e.$$
 (16)

This quantity characterizes the relative efficiency of partial chemiionization processes (3) and (4) together and the impact of electronatom ionization (7). The impact ionization rate coefficients  $K_{ea}(n,T)$ are taken as in Mihajlov et al. (2011). In Fig. 3, the behaviour of the quantities  $F_{i,ea}(n,T)$  (for  $2 \le n \le 8$ , the neutral hydrogen atom in the ground-state densities  $N_1 = 10^{12}$  and  $10^{13}$  cm<sup>-3</sup> and the electron density of 0.01  $N_1$ ), as functions of temperature, is shown. One can see that the efficiency of the considered chemi-ionization processes compared to the electron-atom impact ionization increases with increasing temperature and  $N_1$  density from  $10^{12}$  to  $10^{13}$  cm<sup>-3</sup> when it become dominant for  $2 \le n \le 5$  and comparable for n = 6, 7, and 8.

We can see as well that even around the value of  $N_1 = 10^{12} \text{ cm}^{-3}$  the inclusion of the considered chemi-ionization/recombination processes could improve the modelling and analysis of such regions not only in photospheres of the Sun and solar-like stars but also in clouds in AGN BLR. Additionally, Fig. 3 demonstrates as well the high sensitivity of the influence of these processes to the relatively small changes of  $N_1$  that can be of interest for the determination of limiting  $N_1$  densities in clouds in AGN BLR. The same conclusion goes for influence of the chemi-recombination processes (5) and (6) together on the same block of excited hydrogen atom states. Namely, the influence of analysed processes increases linearly with N, and, for example for  $N = 10^{13}$  cm<sup>-3</sup> some optical characteristics may be different than for  $N = 10^{12}$  cm<sup>-3</sup>, for example due to changes in energy level populations, electron density, influence on the formation of hydrogen molecule, opacity, line profiles etc. It will be very useful to perform an analysis for example with the code CLOUDY in order to see which changes in optical characteristics may be used in order to establish the presence of such dense layers.

The results show that the considered chemiionization/recombination processes could be used for determination of limiting high densities in clouds in AGN BLR region and for the improvement of modelling of dense moderately ionized layers in them. Of course, the presented values of the rate coefficients and branch coefficient are also very useful for the modelling and analysis of similar layers in the photospheres of the Sun and solar-like stars (Przybilla & Butler 2004a,b; Barklem 2007; Mashonkina 2009).

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#### SUPPORTING INFORMATION

Supplementary data are available at MNRAS online.

Additional Supporting Information (Tables 3–8) may be found in the online version of this article. The tables are available in its entirety for  $2 \le n \le 20$ , and  $3000 \text{ K} \le T \le 20000 \text{ K}$  in machine-readable form in the online journal as additional data.

**Table 3.** Calculated Values of Coefficient  $K_{ci}$  [cm<sup>3</sup> s<sup>-1</sup>] as a function of *n* and *T* ( $2 \le n \le 10$  and 3000 K  $\le T \le 20000$  K).

**Table 4.** Calculated Values of Coefficient  $K_{ci}$ [cm<sup>3</sup> s<sup>-1</sup>] as a function of *n* and *T* (11  $\le$  *n*  $\le$  20 and 3000 K  $\le$  *T*  $\le$  20 000 K).

**Table 5.** Calculated Values of Coefficient  $K_{cr}[\text{cm}^3 \text{ s}^{-1}]$  as a function of *n* and  $T (2 \le n \le 10 \text{ and } 3000 \text{ K} \le T \le 20000 \text{ K})$ .

**Table 6.** Calculated Values of Coefficient  $K_{cr}$ [cm<sup>3</sup> s<sup>-1</sup>] as a function of *n* and *T* (11  $\le$  *n*  $\le$  20 and 3000 K  $\le$  *T*  $\le$  20 000 K).

**Table 7.** Calculated Values of Branch Coefficient  $X^{(a)}$  equation (12) as a Function of *n* and  $T (2 \le n \le 10 \text{ and } 3000 \text{ K} \le T \le 20000 \text{ K})$ .

**Table 8.** Calculated Values of Branch Coefficient  $X^{(a)}$  equation (12) as a function of *n* and  $T(11 \le n \le 20 \text{ and } 3000 \text{ K} \le T \le 20 000 \text{ K})$ .

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