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Electron-impact processes involving small molecular ions relevant for the astrochemistry

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Abstract. We investigated the electron-impact processes involving hydrogen, lithium and sodium molecular cations. Rate coefficients for the dissociative recombination in domains of principal quantum numbers $n \geq 4$ and temperatures from 500 K to 10 000K are reported. Considered collisional processes have an impact on the ionization level and atom excited-state populations as well on optical characteristics. The data are useful for the modeling of the kinetics of the Early Universe and for geocosmical plasma investigation.

Key words: atomic data – line profiles – Early Universe – astrophysical plasma–optical characteristics

1. Introduction

In modern science researchers are very interested in collision processes that involve hydrogen and alkali atoms and molecules (Iacob et al., 2019; Ignjatović et al., 2019, 2020; Coppola et al., 2013; Klyucharev et al., 2007). The reason is because of how they affect the spectral properties of astrophysical and laboratory plasmas (Srećković et al., 2014; Tielens, 2013; Beuc et al., 2018a). The ionization level, atom excited-state populations, and optical characteristics can all be affected by collisional events that involve electrons, atoms, ions, and small molecule ions (Schneider et al., 1991; Mihajlov et al., 2011; Srećković et al., 2017; Beuc et al., 2018b; Majlinger et al., 2020).

Atomic hydrogen, helium, lithium, and their cations are said to have been the first species generated by the nucleosynthetic activity that occurred after the Big Bang, according to theories of the early Universe (Epée Epée et al., 2022; Tielens, 2013). Later, simple molecules and their cations were created by the reactions of atoms. Dissociative recombination affects these molecules and molecules ions (Coppola et al., 2011; Djuissi et al., 2020).

For the examples involving lithium, sodium, and hydrogen, we obtained rate coefficients for dissociative recombination. For a wide range of parameters (500 K $\leq T \leq$ 5 000 K) and principal quantum numbers up to 20, the collisional data are acquired. Our goal is to produce high-quality data that can be correctly incorporated into current codes Hauschildt & Baron (2010); Hubeny & Lanz (2017) and databases for modeling planetary atmospheres, laboratory plasma, geocosmic plasma, and the ionosphere Albert et al. (2020); Marinković et al. (2017). The presented data may be of interest and for investigation and modelling of sodium clous on Iovian satellites Io Grava et al. (2014) and Europa Leblanc et al. (2005).

1.1. The method

We investigated the collisional processes i.e. electron driven processes involving molecular cations

$$e + A_2^+ \Longrightarrow A^*(n) + A, \tag{1}$$

Here A are hydrogen, lithium or sodium atoms in the ground states, $A^*(n)$ are highly excited atom i.e. Rydberg atoms, A_2^+ are the molecular ions in the ground electronic states.

The calculations were performed within the DRM i.e., the collisional reactions (1) have been treated by the so-called dipole resonant mechanism (DRM). In this characterization, the processes are caused by the dipole part of the electrostatic interaction between the outer highly excited i.e. Rydberg electron and the inner (ion-atom) system. This method is especially effective when used with the so-called decay approximation. A thorough and detailed description can be discovered in paper of Mihajlov and coworkers (Mihajlov et al., 2012; Mihajlov et al., 2003). Here, we present a brief description of the method with the basic theory.

We use the DRM to obtain the rate coefficients for the principal quantum number $4 \leq n \leq 20$ and for temperatures from 500 K to 10000 K. The data are presented and discussed in details in Section 2.

1.2. The obtained quantities

Rate coefficients for the dissociative recombination can be expressed as

$$K_r = C_n(T) \cdot \int_{R_{min}}^{R_n} \exp\left[\frac{U_{12}(R)}{kT} - \frac{U_1(R)}{kT}\right] \cdot X(R,T) \cdot \frac{R^4 dR}{a_0^5} \tag{2}$$

in accordance with the theory from (Mihajlov et al., 2003, 2011). Here $U_{12}(R) = U_2(R) - U_1(R)$, R is the internuclear distance, and $U_1(R)$ and $U_2(R)$ are the ground and first excited electronic states of the molecular ion. R_n is the largest root of the equation $U_{12}(R) = I_n$, and R_{min} is determined as in Mihajlov et al.

(2003). Quantity $C_n(T)$ is given by

$$C_n(T) = \frac{(2\pi)^{5/2}}{3^{3/2}} \frac{(\hbar e a_0)^2}{(mkT)^{3/2}} n^{-3} \exp\left(\frac{I_n}{kT}\right). \tag{3}$$

I_n denotes the ionization energy of the excited atom. Parameter $X(R,T)$ can be given by

$$X(R,T) = \begin{cases} \gamma\left(\frac{3}{2}; -\frac{U_1(R)}{kT}\right) / \Gamma\left(\frac{3}{2}\right) & U_1 < 0, \\ 0, & U_1 \geq 0 \end{cases} \tag{4}$$

where γ and Γ are incomplete gamma functions.

Various atmosphere models Hauschildt & Baron (2010) and spectrum synthesis codes Hubeny & Lanz (2017) depend on the rate coefficients and cross sections as input parameters. Our aim is to determine high quality data in order to be properly included in modern codes and databases for modelling planetary atmospheres, early Universe chemistry, geocosmic plasma, etc (Albert et al., 2020; Jevremović et al., 2020; Marinković et al., 2017).

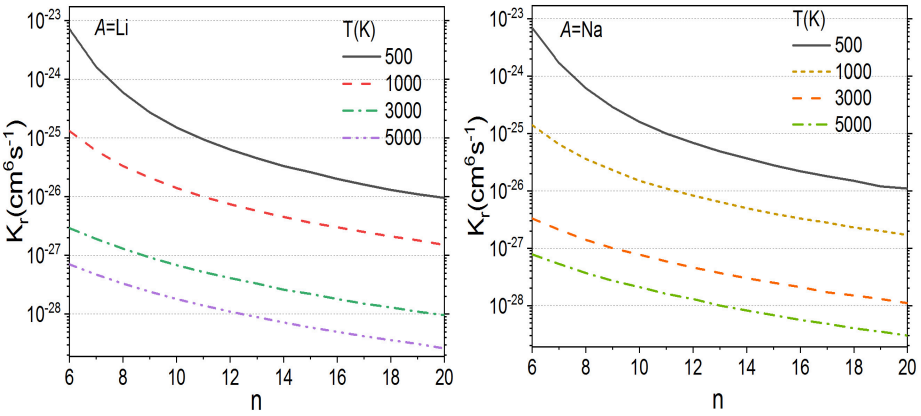

Figure 1. Left: Calculated values for rate coefficient Kr (cm^6 s^{-1}) as a function of n and T for lithium case (A=Li in Eq(1)); Right: Calculated values for rate coefficient Kr (cm^6 s^{-1}) as a function of n and T for sodium case (A=Na in Eq(1)).

2. Results and Discussion

The data i.e. the total recombination rate coefficients $Kr(n,T)$, obtained by Eq. (2), for lithium and sodium are presented in figure 1. The figs. 1a,b cover the

region $6 \leq n \leq 20$ and 500 K $\leq T \leq$ 5000 K. One can see that probability for dissociative recombination is higher for lower n and lower temperature. Thus apparently these collisions become one of the main reactions for the creation of Rydberg atoms for investigated environment under these conditions. Similar behavior is for the case of hydrogen i.e. A =H.

Table 1. The coefficients in the Eq.(5) for lithium case corresponding to the rate coefficient obtained by Eq.(2).

n	ζ_0	ζ_1	ζ_2
6	7.43209	- 16.86487	2.03664
10	-11.4306	- 6.51424	0.57043
15	-16.69436	- 3.79753	0.18394
18	-17.92629	- 3.24067	0.10772
20	-18.19294	- 3.16733	0.09762

To enable an easier use of data, we give for recombination rate coefficient a simple logarithmic second-degree polynomial formula, with n-dependent coefficients $\zeta_i(n)$. A straightforward analytical expression for the dissociative recombination rate coefficient $K_r(n,T)$

$$\log(K_r(n,T)) = \sum_{i=0}^{2} \zeta_i(n) \cdot (\log(T))^i \tag{5}$$

is valid in region of investigated plasma parameters in this study.

The selected fits (for $6 \leq n \leq 20$) for lithium and sodium collisions are listed in Tabs. 1 and 2. A=H fits (for $4 \leq n \leq 8$) are listed in Tab. 3.

Table 2. The coefficients in the Eq.(5) for sodium case corresponding to the rate coefficient obtained by Eq.(2).

n	ζ_0	ζ_1	ζ_2
6	6.30554	- 16.17964	1.93667
10	-11.24121	- 6.63408	0.59369
15	-16.41778	- 3.96127	0.21307
18	-17.73199	- 3.33623	0.12335
20	-17.96593	- 3.2857	0.11752

The fits are valid within the temperature range 500 $\leq T \leq$ 5000 K for lithium and sodium collisions and 3000 $\leq T \leq$ 10000 K for hydrogen case in reaction (1).

Table 3. The coefficients in the Eq.(5) for hydrogen case corresponding to the rate coefficient obtained by Eq.(2).

n	ζ_0	ζ_1	ζ_2
4	61.86661	- 42.61027	4.94202
5	-15.9987	- 4.15003	0.20879
6	-18.32435	- 3.07864	0.07813
7	-19.66572	- 2.49104	0.00637
8	-20.04561	- 2.38883	-0.00388

3. Summary

In this paper we have calculated the rate coefficients for the dissociative recombination in domains of principal quantum numbers $n \geq 4$ and temperatures from 500 K to 10 000 K for the electron-impact processes involving hydrogen H_2^+, lithium Li_2^+ and sodium Na_2^+ molecular cations. The numerical data show that the investigated processes have a considerable impact on the atom excited-state populations and ionization levels and consequently on the optical properties in the weakly ionized layers of atmospheres of various stars. Moreover the provided collisional data are ready to be used in the early Universe chemistry, modeling of interstellar medium and cold plasmas.

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