J. Phys. B: At. Mol. Opt. Phys. 41 (2008) 025203 (7pp)

# The rate coefficients of the chemi-ionization processes in slow $Li^*(n)$ + Na collisions

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Received 12 September 2007, in final form 4 December 2007 Published 8 January 2008 Online at stacks.iop.org/JPhysB/41/025203

### Abstract

The semi-classical method for determining the rate coefficients of the chemi-ionization processes in slow non-symmetric atom–Rydberg atom collisions is applied to the Li\*(*n*) + Na case. Calculated rate coefficients are compared with the existing experimental data from the literature. Obtained results have confirmed that resonant mechanism of non-elastic processes in atom–Rydberg atom collisions are fully applicable to non-symmetric chemi-ionization processes. The rate coefficients of such processes in Li\*(*n*) + Na collisions are determined in the regions of principal quantum number and temperature  $4 \le n \le 20$  and  $700 \text{ K} \le T \le 1100 \text{ K}$  which can be of interest for possible further experiments. Also, the potential curves of several lowest  $\Sigma$  states of the molecular ion LiNa<sup>+</sup>, as well as the values of the square of dipole matrix element for the transition between  $X^2\Sigma^+$ - and  $A^2\Sigma^+$ -states, are

presented in this paper.

# 1. Introduction

Finding new experimental techniques, as well as new calculation possibilities, has been continually inciting interest in the chemi-ionization processes in atom–Rydberg atom collisions, which resulted in numerous experimental and theoretical papers dedicated to this problem (see for example [1-10]). Two groups of chemi-ionization processes were studied: the symmetric processes

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

and the non-symmetric processes

$$A^*(n) + B \Longrightarrow e + \begin{cases} AB^+, \\ A + B^+, \end{cases}$$
(2)

where A, B,  $A^+$  and  $B^+$  are atoms and their atomic ions in the ground states,  $A^*(n)$ —the atom in a highly excited (Rydberg) state with the principal quantum number  $n \gg 1$ ,  $A_2^+$  and  $AB^+$ —the molecular ions in the ground electronic states and e—a free electron. It is assumed that in (2) the ionization potential  $I_B$  of the *B* atom is less than the ionization potential  $I_A$  of the atom *A*.

All theoretical considerations and interpretation of the experimental data were made by means of semi-classical methods based on the same resonant mechanism which is shortly exposed below, but in the case of symmetrical processes (1) that resonant mechanism was applied within two different types of methods. Here we keep in mind the 'stochastic method' originated in [11] and then developed later in several papers (see for example [8] and [12]), which is applicable only to the symmetrical processes (1), and the 'quasi-static method' originated in [13], which is applicable to both types of processes (1) and (2). In [13], the basic version of the quasi-static method was developed, where the decay of the initial electronic state of the atom-Rydberg atom collision system was taken into account in a completely consistent way. Later was presented a simplified version of this method in [2]. where some effects of the decay mentioned were described in an approximative way. Just the simplified version of the quasi-static method was used and discussed in the papers of other authors which were dedicated to alkali-atom collisions in order to interpret experimental results, as well as for the comparison with other theoretical results [3, 6–8, 10, 12, 14]). A very good agreement was found in the cases of all symmetric

0953-4075/08/025203+07\$30.00

processes (1) which were directly studied in [2]. Some disagreement was noted only in the cases of the processes (1) with A = Li and Na, as well as the processes (2) with A = Li and B = Na, which were not considered in [2].

Because of that in [15], the detailed research of the processes (1) with A = Li and A = Na was undertaken. The main aim was to give the opportunity to the experimentalists to compare both stochastic and quasi-static methods. Here the basic method from [13], as well as the exact characteristics of the molecular ions  $\text{Li}_2^+$  and  $\text{Na}_2^+$ , was used. These characteristics were obtained by means of the calculating method described in detail in [15]. The comparison of the results obtained in [15] with the data from [3, 6–8, 10, 12, 14] has shown that there is a good agreement between both theoretical methods in the cases of the symmetric processes (1) with A = Li and A = Na.

Consequently, till now only one disagreement in the case of the non-symmetric processes (2) with A = Li and B = Na, noted in [5, 14], has remained. This disagreement was interpreted in [14] as a manifestation of non-applicability of the mentioned resonant mechanism in the case of non-symmetric processes (2). Although the data from [2], related to the processes (2) with A = K and B = Rb, dispute such a statement, the case noted in [5, 14] had to be examined in detail. It was important because of the expecting new experimental research of the processes (2) with atoms of different alkali metals [17].

We took into account that the experiments with low energy atomic beams have always been very complicated and knowing at least approximative values of the rate coefficients of investigated processes in advance makes the planning of the experiments easier. Since this relates the experimental investigation of chemi-ionization processes of type (2), the results obtained here in connection with the chemi-ionization processes in Li<sup>\*</sup> + Na collisions are addressed before of all to the experimentalists. However, we are aware that all interested are informed with disagreement between the theoretical and experimental results in connection with the chemi-ionization processes (2) with A = Li and B = Na noted in [5].

The mentioned disagreements required a clear solution for this problem, since only in that case the values of the rate coefficients for chemi-ionization processes in Li<sup>\*</sup> + Na collisions obtained in this paper should be recommended for usage. Such a solution could be found by means of the quasi-static method, because the mentioned stochastic method probably is not applicable to the chemi-ionization processes of type (2). We will start with the basic semi-classical method presented in [13] using the exact characteristics of the molecular ion LiNa<sup>+</sup> obtained by means of the method developed in [15].

Keeping in mind the above mentioned here we studied the chemi-ionization processes

$$\operatorname{Li}^{*}(n) + \operatorname{Na} \Longrightarrow e + \operatorname{LiNa}^{+},$$
 (3)

$$\operatorname{Li}^{*}(n) + \operatorname{Na} \Longrightarrow e + \operatorname{Li}^{+} + \operatorname{Na},$$
 (4)

where  $\text{LiNa}^+$  is the molecular ion in the electronic ground state  $(X^2\Sigma^+)$ . Since in all previous papers dedicated to the processes (1) and (2) with A = Li the atom  $\text{Li}^*(n)$  was in

(n, p)-state, throughout this paper one should assume that  $Li^*(n) \equiv Li^*(n, p)$ .

The resonant mechanism and the method used for the calculations of the rate coefficients of the processes (3) and (4) are shortly described in the next section. The calculations of these rate coefficients are performed for the principal quantum number  $4 \le n \le 20$  and temperatures 700 K  $\le T \le 1100$  K. Similar to [15] the processes (3) and (4) were treated under the conditions characteristic for crossing beams, single beam and cell. The results obtained, as well as the necessary discussion, are presented in section 4

### 2. Theoretical remarks

### 2.1. The resonant mechanism

As in the previous papers (see [15]) the processes (3) and (4) are treated here as the result of quasi-resonant energy exchange within the electronic component of the considered atom-Rydberg atom collision system. Such a mechanism, here named resonant, was introduced in [18] in connection with some of the inelastic processes in  $A^*(n) + A$  collisions, where A = H and He, and somewhat latter was applied to the chemi-ionization processes in the case when A is an alkali atom [11]. After that, the resonant mechanism was systematically applied to the chemi-ionization processes for both types of collision systems: symmetric  $A^*(n) + A$  and non-symmetric  $A^*(n) + B$ , where B is the atom with smaller ionization potential (see, e.g. [2, 12–14, 19, 20]). Here, this mechanism will be described concretely for the considered atom-Rydberg atom collision system Li<sup>\*</sup>(n) + Na.

Let *R* be the internuclear distance in the considered collision system, and  $r_n \sim n^2$  is the mean radius of atom  $\text{Li}^*(n)$ . The resonant mechanism works in that part of the region

$$R \ll r_n, \tag{5}$$

where the ion-atom sub-system  $\text{Li}^+ + \text{Na}$  of the system  $\text{Li}^*(n) + \text{Na}$  can be treated as a quasi-molecular complex (see figure 1(a)). It means that within such a part of the region (5) the initial electronic state of the ion-atom sub-system can be identified with the first excited electronic state  $A^2\Sigma^+ \equiv |2, R\rangle$  of the molecular ion LiNa<sup>+</sup>, and the final state—with the ground electronic state  $X^2\Sigma^+ \equiv |1, R\rangle$  of the same molecular ion. For the sake of brevity the mentioned part will be named as a reaction zone.

Resonant character of this mechanism in the case of processes (3) and (4) means that the transition of the outer electron of the atom Li<sup>\*</sup>(*n*) from the initial bound state  $|n\rangle$  with energy  $\epsilon_n < 0$  to the free state  $|k\rangle$  with energy  $\epsilon_k > 0$  is followed by a transition of the ion–atom sub-system from the initial electronic state  $|2, R\rangle$  to the final state  $|1, R\rangle$ , as it is illustrated in figure 1(b). This transition occurs in a narrow surroundings of the corresponding resonant point  $R_{nk}$ , which is the root of the equation

$$\epsilon_k - \epsilon_n = U_2(R) - U_1(R) \equiv U_{12}(R), \tag{6}$$

where  $U_1(R)$  and  $U_2(R)$  are the adiabatic potential curves of the molecular electronic states  $|1, R\rangle$  and  $|2, R\rangle$ . In connection



**Figure 1.** (a) Schematic illustration of  $Li^*(n) + Na$  collision (the reaction zone where the outer electron is collectivized is shaded). (b) Schematic illustration of the resonant transitions which cause processes (3) and (4).

with this, one should keep in mind that the zero of energy is chosen in such a way that  $U_2(R = \infty) = 0$ . It is assumed that the cause of these transitions is an interaction of the outer electron  $e_n$  with the dipole moment of the ion-atom subsystem. For a given R this interaction is characterized by the dipole matrix element

$$D_{12}(R) = \langle 1, R | \mathbf{D} | 2, R \rangle, \tag{7}$$

where **D** is the operator of the dipole moment mentioned.

### 2.2. The method of calculations

The approximative method applied here is proved to be successful in the case of chemi-ionization processes in  $H^*(n)$ + H and  $He^*(n)$ +He collisions (see for example [21–24]), where for  $n \gg 1$  the correction factors mentioned are close to unity. However, in the case of alkali atoms that correction factors are significantly less than unity and given by very complicated expressions which required additional simplification.

Because of that the basic theory from [13], with the exact potential curves  $U_1(R)$  and  $U_2(R)$  of the molecular ion LiNa<sup>+</sup> and the exact dipole matrix element  $D_{12}(R)$ , is used in this work. The values of  $U_1(R)$ ,  $U_2(R)$  and  $D_{12}(R)$  are obtained here by means of the calculation method described in detail in our previous paper (see [15]; appendix A, non-symmetric case). The potential curves  $U_1(R)$  and  $U_2(R)$  are presented in figure 2. In order to compare the results generated by this method with some other relevant results, the potential curves of two upper-lying  $\Sigma$ -states, as well as the corresponding data from [25], are also shown in the same figure. One can see a very good agreement of these data with the values of  $U_1(R)$ and  $U_2(R)$  used here. The behaviour of  $D_{12}^2(R)$  is shown in figure 3.

## 3. The chemi-ionization rate coefficients

In accordance with the basic paper [13] the processes (3) and (4) are treated here as a result of decay of the initial



**Figure 2.** The adiabatic potential curves of molecular ion  $LiNa^+$ . •, [25]



**Figure 3.** The square of dipole matrix element  $D_{12}^2$  (au).

electronic state of the net system  $\text{Li}^*(n)$  + Na along a part of the trajectory which describes the internuclear motion in the reaction zone in the potential  $U_2(R)$ . The decay mentioned, caused by the resonant mechanism, is described in the quasistatic approximation by means of the corresponding rate

$$W_n(R) = \frac{4}{3\sqrt{3}n_{\text{eff}}^5} D_{12}^2(R) G_{nk},$$
(8)

where  $n_{\text{eff}}$  and  $G_{nk}$  are the effective principal quantum number and the corresponding Gaunt factor, namely

$$n_{\text{eff}} \equiv n - \Delta(n, \mathbf{p}), \qquad G_{nk} = \frac{\sigma_{\text{ph}}(n, k)}{\sigma_{\text{ph}}^{\text{Kr}}(n, k)},$$
 (9)

where  $\Delta(n, p)$  is the quantum defect for p-states of the excited lithium atom (see e.g. [26]),  $\sigma_{ph}(n, k)$ —the photo-ionization cross section of the atom Li<sup>\*</sup>(n), and  $\sigma_{ph}^{Kr}(n, k)$ —the photoionization cross section for the same atom in Kramers's approximation ([27], see also [26]). In the case of the lithium atom  $\Delta(n, p) \cong 0.04$ . The Gaunt factor is set to value 1.2 as in [15]. Since the method for determining the rate coefficients of the processes (3) and (4) which was used here is essentially the same as the method presented in [15], all necessary expressions in further text are given in its final form, with minimal comments.

Let  $\rho$  be the impact parameter,  $M_{\text{red}}$ —the reduced mass of Li<sup>\*</sup>(n) + Na collision system, v and  $E = M_{\text{red}}v^2/2$ —the impact velocity and the energy, and  $v_{\text{rad}}(\rho, E; R)$ —the radial velocity of the nuclear motion in the potential  $U_2(R)$  given by

$$v_{\rm rad}(\rho, E; R) = \sqrt{\frac{2}{M_{\rm red}} \left[ E - U_2(R) - \frac{E\rho^2}{R^2} \right]}.$$
 (10)

Let afterwards,  $R_{\min}$  and  $R_{\max} \equiv R_{\max}(n)$  be the lower and upper boundary of the region of R where at least one of the processes (3) or (4) can occur for a given n, and  $R_{\max}^{(a)}$ —the upper boundary of the region of R, relevant for the process of associative ionization (3).

In accordance with [13] and [15] probability  $P_{ci}^{(a)}(n, \rho, E)$  of the associative ionization, caused by  $\text{Li}^*(n)$  + Na collision with given  $\rho$  and E, and total chemi-ionization probability  $P_{ci}^{(ab)}(n, \rho, E)$ , which describes the contribution of both processes (3) and (4), are given by relations

$$P_{\rm ci}^{(a)}(n,\rho,E) = p_{\rm in} \left( 1 - \exp\left(-2\int_{R_{\rm min}}^{R_{\rm max}^{(a)}} \frac{W_n(R)\mathrm{d}R}{v_{\rm rad}}\right) \right)$$
$$\times \exp\left(-\int_{R_{\rm max}^{(a)}}^{R_{\rm max}} \frac{W_n(R)\mathrm{d}R}{v_{\rm rad}}\right),\tag{11}$$

$$P_{\rm ci}^{(ab)}(n,\rho,E) = p_{\rm in} \left( 1 - \exp\left(-2\int_{R_{\rm min}}^{R_{\rm max}} \frac{W_n(R)dR}{v_{\rm rad}}\right) \right),\tag{12}$$

where  $W_n(R)$  and  $v_{rad} = v_{rad}(\rho, E; R)$  are defined by relations (8) and (10), and the factor  $p_{in} = 1$ . Consequently, the associative ionization cross section  $\sigma_{ci}^{(a)}(n, E)$  and the total chemi-ionization cross-section  $\sigma_{ci}^{(ab)}(n, E)$  can be presented in the form

$$\sigma_{\rm ci}^{(a,ab)}(n,E) = 2\pi \int_0^{\rho_{\rm max}^{(a,ab)}(E)} P_{\rm ci}^{(a,ab)}(n,\rho,E)\rho\,\mathrm{d}\rho, \quad (13)$$

where  $\rho_{\max}^{(ab)}(E)$  is the absolute upper limit of values  $\rho$  for a given *E*, and  $\rho_{\max}^{(a)}(E)$  is the upper limit of values  $\rho$  for the associative ionization channel only.

Finally, let  $K_{ci}^{(a)}(n, T)$ ,  $K_{ci}^{(b)}(n, T)$  and  $K_{ci}(n, T)$ , where

$$K_{\rm ci}(n,T) = K_{\rm ci}^{(a)}(n,T) + K_{\rm ci}^{(b)}(n,T),$$
(14)

be respectively the partial and the total rate coefficients which characterize the processes (3) and (4) separately and together. By definition,  $K_{ci}(n, T)$  and  $K_{ci}^{(a)}(n, T)$  are given by relations

$$K_{\rm ci}(n,T) = \int_0^\infty v \cdot \sigma_{\rm ci}^{(ab)}(n,E) f(v;T) \,\mathrm{d}v,$$

$$K_{\rm ci}^{(a)}(n,T) = \int_0^{E_{\rm max}^{(a)}(n)} v \cdot \sigma_{\rm ci}^{(a)}(n,E) f(v;T) \,\mathrm{d}v,$$
(15)

where the cross-sections  $\sigma_{ci}^{(a,ab)}(n, E)$  are determined by equations (8)–(13),  $E_{max}^{(a)}(n)$  is the upper limit of the region of *E* relevant for the associative ionization process (3), and f(v; T) is the impact velocity distribution function whose form depends on the temperature *T* and other experimental conditions. Then, the rate coefficient  $K_{ci}^{(b)}(n, T)$  for the process (4) is determined from the relation (14). In

accordance with that relation the relative contribution of the processes (3) and (4) can be characterized by the corresponding branch coefficients

$$X^{(a)}(n,T) = \frac{K_{ci}^{(a)}(n,T)}{K_{ci}(n,T)},$$

$$X^{(b)}(n,T) = \frac{K_{ci}^{(b)}(n,T)}{K_{ci}(n,T)} \equiv 1 - X^{(a)}.$$
(16)

We will characterize the processes (3) and (4) by means of the total chemi-ionization rate coefficient  $K_{ci}(n, T)$  and the associative ionization rate coefficient  $K_{ci}^{(a)}(n, T)$  or the corresponding branch coefficient  $X^{(a)}(n, T)$ .

The above introduced parameters  $R_{\min}$ ,  $\rho_{\max}^{(a,ab)}$  and  $E_{\max}^{(a)}$ are determined here in the same way as in [15], but keeping in mind that in the considered non-symmetric case  $U_{12}(R = \infty) \equiv I_{\text{Li}} - I_{\text{Na}}$ , where  $I_{\text{Li}}$  and  $I_{\text{Na}}$  are the ionization potential of the atoms Li and Na. The same goes for determination of  $R_{\max}$ for  $n \leq n_0$ , where  $n_0$  is the largest *n* for which  $U_2(R_{n0}) > 0$ , where  $R_{n0}$  is the root of equation (6) with  $\epsilon_k = 0$ . In the case of the system Li<sup>\*</sup>(*n*) + Na the curve  $U_2(R)$  changes its sign in the point  $R_{0:2} \cong 12.35$  au and we have that in this case  $n_0 = 5$ . The way of determination of  $R_{\max}$  for n > 5, where comparing with [15] the differences appear, is described in the next section where  $R_{\max}(n > 5) = 12.25$  au is obtained in the considered case.

Following our previous work [15] we will determine the rate coefficients of the considered chemi-ionization processes in three standard cases, namely: cell, crossed beams and single beams. The corresponding impact velocity distribution functions are taken from [14].

# 4. Results and discussion

In accordance with the aims of this work, first of all we will consider the processes of associative ionization (3), for  $n \ge 4$ and T = 920 K, in the case of crossed beams. Namely, just for this case in [5] were presented several values of the associative ionization rate coefficient, which were obtained in an indirect way by working out some of experimental data. They are shown by filled circles in figure 4. In the same figure the open circles show the values of the associative ionization rate coefficient for the same case which were obtained in [5] applying the approximative method from [2]. Let us recall that in this method decay of initial electronic state of the sub-system  $A^+ + B$  during the collision is taken into account by the approximative correction factor. For description of the characteristics of the molecular ion  $AB^+$ , simple analytical approximations are used. One can see a significant disagreement between these two groups of data that was noted in [14] as one possible cause of inapplicability of the resonant mechanism itself in the case of non-symmetric chemi-ionization processes (2).

Although this point is contradictory to the data obtained in [2], in an other case of non-symmetric chemi-ionization processes (in  $K^*(n)$  + Rb collisions), here we took into account the fact that these data relate only to such values of *n* which are lower than the corresponding  $n_0$ , as well as the above-mentioned property of the Li\*(*n*)+Na system. Because



**Figure 4.** The rate coefficient of associative ionization processes in  $Li^*(n) + Na$  collisions in the case of crossed beams at T = 920K: •, experimental data from [5];  $\circ$ , calculation from [5]; full curve, our calculations for  $R_{max}(n > 5) = 12.25$  au; dashed curve, dotted curve and dash-dotted curve, our calculations for  $R_{max}(n > 5) = 12.00$  au,  $R_{max}(n > 5) = 12.50$  au and  $R_{max}(n > 5) = 13.00$  au.

of that, here we have calculated the values of associative ionization rate coefficient  $K_{ci}^{(a)}(n, T)$ , for the same conditions as in [5]. These calculations are performed by means of expressions (8)–(13) and equation (15). Contrary to the method from [2] these expressions were obtained within the basic semi-classical theory from [13], by the procedure without any approximations (which were used in [2]) and with exact values of  $U_1(R), U_2(R)$  and  $D_{12}(R)$ . Consequently, they provide that decay of initial electronic state of the sub-system Li<sup>+</sup>+Na during the collision is taken into account in a consistent way.

The values of  $K_{ci}^{(a)}(n, T)$  for n = 4 and 5, for which the resonant distances  $R_{n0}$  fall into the region of  $R < R_{0,2}$  where  $U_2(R) > 0$ , were determined in the same way as in [15]. However, for n > 5 we have the case which was not studied in the previous papers, i.e. the case when the resonant distances  $R_{n0}$  fall into the region of  $R > R_{0,2}$  where  $U_2(R) < 0$ . In this case, there appears a special problem of determination of the corresponding values of  $R_{\max}(n)$ , which is closely connected with the problem of determining a region of R where the ionatom sub-system Li<sup>+</sup> + Na can be treated as a quasi-molecular complex. Namely, it is clear that  $R_{\max}(n > 5)$  should not exceed the quasi-molecularity region of this sub-system. Let us emphasize that the problem of determination of the region where an ion-atom collision sub-system can be treated as a quasi-molecular one was not solved even in the symmetric case, and generally, solving such a problem could be the subject of a special investigation.

Based on our best knowledge, the sub-system Li<sup>+</sup> + Na has to be treated as a quasi-molecular complex in the region  $R < R_{0;2}$  where  $U_2(R) > 0$ . Because of that we started solving the mentioned problem from the fact that the region of possible values of  $R_{\max}(n > 5)$  is strongly limited from below, since the lower boundary of this region has to be very close to the point  $R_{0;2} \cong 12.35$  au where the curve  $U_2(R)$  changes its sign.



**Figure 5.** Thick lines, the total rate coefficient for chemi-ionization processes in  $\text{Li}^*(n) + \text{Na}$  collisions in the case of crossed beams; and thin lines, the corresponding branch coefficients  $X^{(a)}(n, T)$ .

Owing to the mentioned fact, the problem of determining  $R_{\max}(n > 5)$  could be solved very precisely, since the existence of credible experimental data from [5] gives an exceptional opportunity to strongly limit the upper boundary of the region of  $R_{\max}(n > 5)$ . For this purpose we investigated the behaviour of the calculated values of the associative ionization rate coefficient when  $R_{\max}(n > 5)$  increases from 12 au to the distance 17.5 au which approximately corresponds to the minimum of the curve  $U_2(R)$ . We found that increasing of  $R_{\max}(n > 5)$ , out of the narrow interval from 12 au to 12.5 au, causes rapid local decreasing of the rate coefficient respecting the experimental values from [5]. In figure 4 this fact is illustrated by a curve which corresponds to  $R_{\text{max}}(n > 5) = 13$  au. Since it is difficult to explain such behaviour, we conclude that the upper boundary of the region of  $R_{\max}(n > 5)$  has also been very close to the point  $R_{0:2} \cong 12.35$  au. Just from this reason in all calculations in this paper  $R_{\text{max}}(n > 5) = 12.25$  au was accepted, which corresponds to the middle of the mentioned interval. In figure 4 the full curve corresponds just to this value. In the same figure the dashed and dotted curves, which correspond to the values 12 au and 12.5 au, illustrate that the error which we could make by our choice is very small. Consequently, our considerations show that the above-described resonant mechanism of non-elastic processes in atom-Rydberg atom collisions is applicable not only to symmetric chemi-ionization processes (1), but also to non-symmetric processes (2).

It is especially important that the obtained result factually represents the recipe which would be applicable for the determination of the upper boundary of the quasi-molecularity region in the case of other non-symmetric ion–atom collision systems. Naturally, this will have repercussion in the cases of symmetric ion–atom collision systems too. Of course, some further precise measurements of the associative ionization rate coefficient for processes (3), as well as for other non-symmetric processes, could significantly contribute to the determination of the upper boundary of the R region where the considered ion–atom sub-system can be treated as a quasi-molecular one.



Figure 6. Same as in figure 5, but in the case of cell.



Figure 7. Same as in figure 5, but in the case of single beams.

In this paper we calculate also the values of the total chemi-ionization rate coefficient  $K_{ci}(n, T)$  and the branch coefficients  $X^{(a)}(n, T)$ , which describe the relative contribution of the associative ionization process (3), in the regions  $4 \le n \le 20$  and 700 K  $\le T \le 1100$  K, for all the mentioned experimental conditions. The results of the calculations of  $K_{ci}(n, T)$  and  $X^{(a)}(n, T)$  are presented in figure 5 in the case of crossed beams; in figure 6, in the case of cell; and in figure 7, in the case of single beams.

Figures show that in the considered regions of *n* and *T* the process of associative ionization (3) dominates in comparison with the other chemi-ionization process (4). Also, one can see that the branch coefficient  $X^{(a)}(n, T)$  has the minimum at n = 6.

As one could expect in all the three cases (cell, crossed beams and single beams) the curves of total chemi-ionization rate coefficient  $K_{ci}(n, T)$  for the processes (3) and (4) have a similar form as the corresponding curves presented in [15] in the cases of a symmetric chemi-ionization process (1) with A = Li and Na. Also, we have that the behaviour of  $K_{ci}(n, T)$  in the case of cell is similar to the behaviour of the corresponding curves presented in [2] in connection with chemi-ionization processes in  $K^*(n)$  + Rb collisions.

### 5. Conclusions

The results of this work confirm the possibility of application of the resonant mechanism [18] for the description of chemiionization collision processes, not only in the symmetric case, when the particles of the same type collide, but in the nonsymmetric case too. This provides significant extension of the class of atom-Rydberg atom collision systems from the aspect of the research of chemi-ionization processes. Besides, the rate coefficients for the chemi-ionization processes in  $Li^*(n) + Na$ collisions were calculated. Calculations were performed for the three standard cases: cell, crossed beams and single beam. It was found that there is a very good agreement between the calculated rate coefficient for the process of associative ionization in  $Li^*(n)$  + Na collisions, and the corresponding experimental data which are known in the literature [5]. All calculations were done by means of new values of potential curves and the dipole matrix element.

# Acknowledgments

This work is part of the project 'Non-ideal laboratory and ionospheric plasma: properties and application' (Project number 141033) and supported by the Ministry of science of the Republic of Serbia, as well as by Russian Foundation for Basic Research Grant 05-03-33252.

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