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Rate coefficient for the chemi-ionization in slow Li$^*(n)$+Li and Na$^*(n)$+Na collisions

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The chemi-ionization processes in slow-atom–Rydberg-atom collisions are considered in this paper. A version of the semiclassical method of rate coefficient calculation that is free of the presumptions which significantly limited its applicability previously is presented. The method is applied to the cases of Li$^*(n)$+Li and Na$^*(n)$+Na collisions for the principal quantum numbers $5 \leqslant n \leqslant 25$ and temperatures $600 \leqslant T \leqslant 1200$ K. The results of calculation of the rate coefficients of the corresponding chemi-ionization processes are compared to the existing experimental data from the literature.

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I. INTRODUCTION

Researchers have been directing their attention for a long time to some of the chemi-ionization processes in slow-atom–Rydberg-atom collisions, namely,

$$A^*(n) + A \Rightarrow e + A_2^+, \tag{1.1a}$$

$$A^*(n) + A \Rightarrow e + \begin{cases} A + A^+, \\ A^+ + A, \end{cases} \tag{1.1b}$$

where A and A^+ are atoms and their positive ions in their ground states, A^* is an atom in a highly excited (Rydberg) state with the principal quantum number $n \gg 1$, A_2^+ are the corresponding molecular ions in ground electronic states, and e is a free electron. The main interest is in chemi-ionization processes in which A are atoms of alkali metals (see, e.g., [1–5]).

Due to the interest in chemi-ionization processes, several methods of rate coefficient calculations were presented within a short time. The methods developed in [3,4,6,7] treated the considered atom–Rydberg-atom systems within the semiclassical approach, while in [8] an attempt at quantum-mechanical description of the internuclear motion was made. All these methods were based on the same mechanism of quasiresonant energy exchange within the electronic component of the atom–Rydberg-atom system. This mechanism was introduced in [9] in connection with some inelastic processes in slow $A^*(n)+A$ collisions. Here it is named the *resonant mechanism*.

The resonant mechanism of the considered inelastic processes is effective in the region of internuclear distances

$$R \ll r_n, \tag{1.2}$$

where $r_n \sim n^2$ is the mean radius of atom $A^*(n)$, as illustrated in Fig. 1(a). In this region the system $A^*(n)+A$ is taken in the form $(A^+ + A) + e_n$, where A^+ and e_n are the core and the outer electron of Rydberg atom $A^*(n)$. The inelastic processes are treated as a result of the interaction of the outer electron e_n with the dipole momentum of the subsystem $A^+ + A$.

The electronic state of the $A^+ + A$ subsystem during the collision is described as a group of adiabatic electronic states of the molecular ion A_2^+, adiabatically correlated with the electronic states of this subsystem at $R = \infty$. In the case when A is an atom with one or two s electrons outside closed shells (A=H, He, Li, Na, etc.), only two Σ^+ states of A_2^+, the ground and the first excited states, compose such a group. These states are denoted here as $|1\rangle$ and $|2\rangle$. When A is an alkali-metal atom $|1\rangle$ and $|2\rangle$ are the Σ_g^+ and Σ_u^+ states, respectively.

It is assumed that in the region of R where the considered inelastic process takes place the optical electron of the atom A is collectivized within the $A^+ + A$ subsystem [see Fig. 1(a)]. The main contribution to the considered inelastic process is within the range of R where the energy exchange between the outer electron e_n and the electron component of the subsystem $A^+ + A$ has an almost resonant character.

In [9] the resonant mechanism was applied to the transitions between the states $|n\rangle$ and $|n'\rangle$ of the outer electron of Rydberg atom with the energies ϵ_n and $\epsilon_{n'}$, where $n \neq n'$. The internuclear motion was described within the straight trajectory approximation, neglecting the influence of the outer electron on the electronic state of the $A^+ + A$ subsystem. In such an approximation the dipole momentum of this sub-

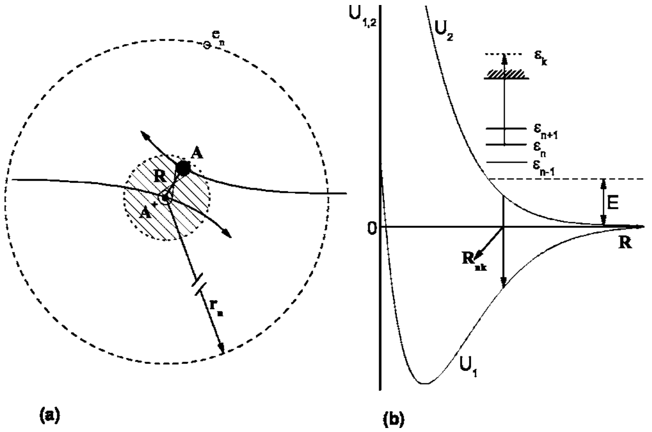

FIG. 1. (a) Schematic illustration of $A^*(n)+A$ collision (the region of R where the outer electron is collectivized is shaded). (b) Schematic illustration of the resonant transitions $|2;n\rangle \rightarrow |1;k\rangle$ which cause the processes (1.1a) and (1.1b).

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system can be expressed as a function of time $\mathbf{D}_{12}(R(t))$, known in advance, oscillating with the frequency $\omega(R(t)) = U_{12}(R(t))/\hbar$, where

$$U_{12}(R) = U_2(R) - U_1(R). \tag{1.3}$$

The potentials $U_i(R)$ are defined as

$$U_i(R) = E_i(R) - E_i(R=\infty), \quad i = 1,2, \tag{1.4}$$

where $E_1(R)$ and $E_2(R)$ are the adiabatic energies of the ground and the first excited electronic states of ion A_2^+ for a given R. The intervals of R containing the resonant points, i.e., the points where the frequencies of the transitions $|\epsilon_n - \epsilon_{n'}|/\hbar$ are equal to $\omega(R)$, provided the main contributions to the considered processes. However, the way of description of the dipole momentum made possible simultaneous transitions of types $n \to n \pm p$ and $n \pm p \to n \pm p \mp p'$, where $p,p' \geqslant 1$. Because of that the transition probabilities could be determined by the special procedure of "smearing" the initial probability ($\delta_{nn'}$) over the states of the discrete spectrum.

The resonant mechanism was examined in detail for the same inelastic processes in $A^*(n)+A$ collisions in [10]. In this paper the system $A^*(n)+A$ was also treated in the straight trajectory approximation, but the influence of the outer electron on the $A^+ + A$ subsystem was taken into account. It was possible to follow the behavior of different two-electron states $|i;n\rangle = |i\rangle|n\rangle$, where $i=1,2$, of the system $A^*(n)+A$. In this case it was not possible to treat the dipole momentum of the $A^+ + A$ subsystem as a previously known function of time. It was shown that only the transitions $|2;n\rangle \to |1;n'\rangle$ with $n' > n$ and $|1;n\rangle \to |2;n'\rangle$ with $n' < n$ contribute to the considered inelastic processes; namely, the contribution of the transitions $|1;n\rangle \to |2;n'\rangle$ with $n' > n$ and $|2;n\rangle \to |1;n'\rangle$ with $n' < n$ can be neglected, and the transitions $|i;n\rangle \to |i;n'\rangle$ with $i=1,2$ and $n' \neq n$ have to be interpreted as virtual ones. This means that such transitions are manifested only through the adiabatic crossing of the outer electron from one to another center. It follows that the resonant mechanism makes possible only the transitions $n \to n \pm p_1 \to n \mp p_2 \to n \pm p_3 \cdots$, where $1 \leqslant p_1 \leqslant p_2 \leqslant p_3 \cdots$, which excludes application of the smearing procedure similar to the procedure from [9]. In addition, it was noticed in [10] that the one-trajectory approximation was not applicable; namely, this approximation provided correct determination of the probability of the inelastic transitions only in the region of large impact parameters, where the impact energy (0.3–0.5 eV) was much greater than the transition energy (~0.03 eV).

A modified version of the method from [9] was applied to chemi-ionization processes in [3]. The modification consisted in changing the smearing procedure, because the final states of the outer electron in this case were continuum states $|k\rangle$ with energies $\epsilon_k > 0$. All other main elements (the straight trajectory, neglecting the outer electron's influence, and the dipole momentum description) were the same. More details were given in [4] where the "diffusion" model for describing the behavior of the outer electron in the field of an oscillating dipole was introduced.

Different semiclassical methods were presented in [6,7], where the results obtained in [10] were taken into account. First of all, the internuclear motion was described within the approximation of two trajectories determined by impact parameter ρ and impact energy E: one in the potential $U_1(R)$ and the other in the potential $U_2(R)$. From the symmetry of the system each of these trajectories is realized with the probability $p_{in} = 1/2$, equal to the statistical factor of the states $|1\rangle$ and $|2\rangle$. The dipole momentum of the $A^+ + A$ subsystem was defined by the relations

$$D_{12}(R) = |\mathbf{D}_{12}(R)|, \quad \mathbf{D}_{12}(R) = \langle 1|\mathbf{D}|2\rangle, \tag{1.5}$$

where $\mathbf{D}$ is the operator of the electronic dipole momentum of the molecular ion A_2^+. The chemi-ionization processes (1.1a) and (1.1b) were treated as results of strictly resonant transitions $|2;n\rangle \to |1;k\rangle$, where $|1;k\rangle = |1\rangle|k\rangle$, in the neighborhood $(R_{nk} - \delta R_{nk}, R_{nk} + \delta R_{nk})$ of the resonant points $R = R_{nk}$ where

$$\epsilon_k - \epsilon_n = U_{12}(R_{nk}), \tag{1.6}$$

as illustrated in Fig. 1(b). Consequently, only the collisions during which the internuclear motion occurred in the potential $U_2(R)$ were taken into account. It means that in the approximation described only one-half of all $A^*(n)+A$ collisions contributed to the processes (1.1a) and (1.1b). The difference between [6,7] consists in the way of taking into account the decay of the initial electronic state $|2;n\rangle$ during the $A^*(n)+A$ collision. In [6] the decay was directly taken into account in the frame of the procedure used, while in [7] the influence of decay was taken into account with the help of a special parameter. Due to a need to interpret experimental results, in [7] the focus was on chemi-ionization processes involving atoms of heavy alkali metals (K, Rb, Cs).

Apart from [6,7], in [8] the processes (1.1a) and (1.1b) were treated as results of strictly resonant transitions $|2;n\rangle \to |1;k\rangle$. It represents a unique attempt to describe processes (1.1a) and (1.1b) along with the quantum-mechanical treatment of the internuclear motion. For this purpose the quasiclassical approach was used, with an additional assumption about the possibility of smearing rovibrational spectrum of molecular ion A_2^+. Here we will not discuss this method because it was applied only to the processes (1.1a) and (1.1b) with $A = \mathrm{Cs}$, which will not be considered in this paper.

The method from [3,4] was developed later on the basis of the diffusion model in [11], and this development was continued in [12–14]. In all these papers the internuclear motion has also been treated in the approximation of a unique trajectory, which made it possible to treat the dipole momentum of the $A^+ + A$ subsystem as a previously known function of time. However, contrary to the previous papers, this trajectory was not a straight line. Let us point out that this trajectory in [12–14] was not determined in the average potential $\bar{U}(R) \approx (U_1 + U_2)/2$ as one would expect, but in the potential $U_2(R)$, similarly as in [6,7]. The diffusion model was adopted to describe the behavior of the outer electron in the field of dipole momentum, which oscillates with frequency $\omega(R(t))$. The results presented in [12,13] regarding

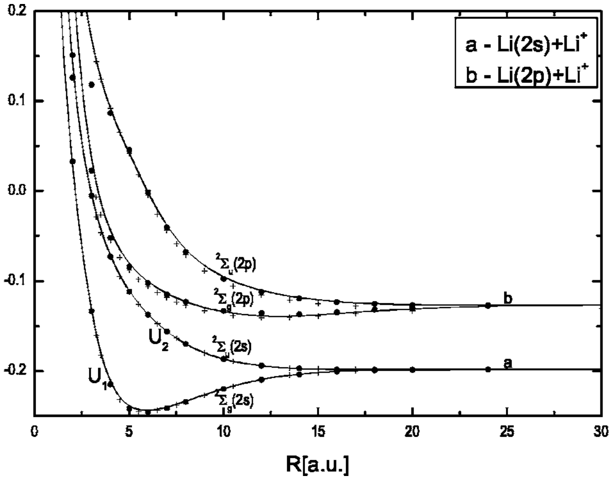

FIG. 2. The adiabatic potential curves of molecular ion Li_2^+. ● [35]; + [36].

the processes (1.1a) and (1.1b) with A=Na are relevant to this work and are discussed in the further text.

Further development and improvement of the method from [7] was connected to the cases A=H and He and their application in astrophysics (see, e.g., [15–20]). However, there was a permanent interest in the processes (1.1a) and (1.1b) involving atoms of alkali metals [11,21–23]. The results obtained in [7] concerning such processes have been discussed in the literature repeatedly ever since [11–14,21–27]. Therefore, we considered it necessary to study again the processes (1.1a) and (1.1b) in the cases when A is an alkali atom.

The basic method from [7], which is very good for the processes (1.1a) and (1.1b) in the hydrogen and helium cases, must be significantly modified so that it can be successfully applied to the case of atoms of alkali metals. That is, within this method the effect of decay of the initial electronic state $|2;n\rangle$ during $A^*(n)+A$ collision was not taken into account directly. For this reason we used here an improved version of the method from [6], where this effect was taken into account from the beginning.

The disadvantage of the methods from [6,7] was the use of approximate analytical expressions for the adiabatic potential curves $E_1(R)$ and $E_2(R)$ of the states $|1\rangle$ and $|2\rangle$, and for the quantity $D_{12}(R)$ defined by relations (1.5). Therefore, we will limit ourselves here to the processes (1.1a) and (1.1b) with A=Li and Na, as we have the well-determined values of $E_1(R)$, $E_2(R)$, and $D_{12}(R)$ for molecular ions Li_2^+ and Na_2^+, presented in Figs. 2–4. The method of the calculations of these quantities is given in the Appendix.

Within this paper the rate coefficients of the processes (1.1a) and (1.1b), with A=Li and Na, are determined for $5 \leqslant n \leqslant 25$ and temperatures $600 \leqslant T \leqslant 1200$ K. These ranges of n and T have not been treated in literature so far. The rate coefficients calculated have been compared to the existing experimental as well as the relevant theoretical data found in the literature.

Note that throughout the paper, if not stated otherwise, all quantities are expressed in atomic units.

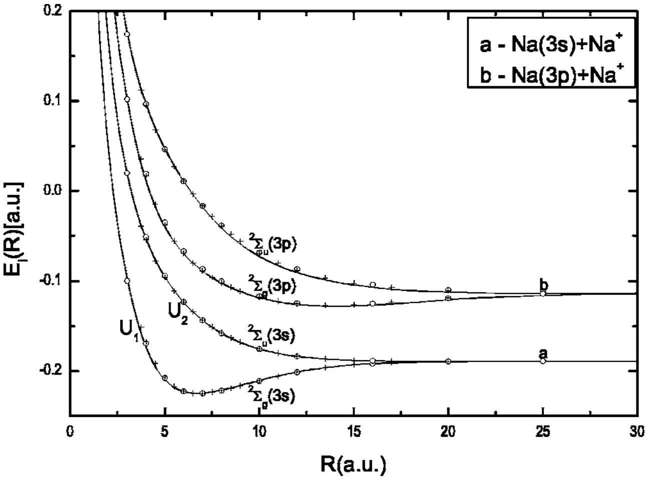

FIG. 3. The adiabatic potential curves of molecular ion Na_2^+. ○ [37]; + [38].

II. THEORY

The processes (1.1a) and (1.1b) are treated here as a result of decay of the initial electronic state of the net system $A^*(n)+A$, caused by the resonant mechanism along a part of the relevant trajectory within the region (1.2). From the behavior of the potential curves $U_1(R)$ and $U_2(R)$ for molecular ions Li_2^+ and Na_2^+, within the range of temperature discussed, it can be proved that only the part of the region (1.2) where Eq. (1.6) for ϵ_k has only one root matters to processes (1.1a) and (1.1b). Accordingly, the processes (1.1a) and (1.1b) happen inside the region

$$R \leqslant R_n, \tag{2.1}$$

where $R_n = R_{n0} + \delta R_{n0}$, and R_{n0} is a root of Eq. (1.6) at $\epsilon_k = 0$. For the sake of simplicity, in [6] it has been accepted that $\delta R_{n0} = 0$, although it was clear that even in the hydrogen case one should take $\delta R_{n0} \cong 1$ a.u. (see [10]). Having this in mind, here we took $\delta R_{n0} = (R_{n;1/2} - R_{n0})/2$, where $R_{n;1/2}$ is the root of the equation obtained from Eq. (1.6) by replacing ϵ_k with

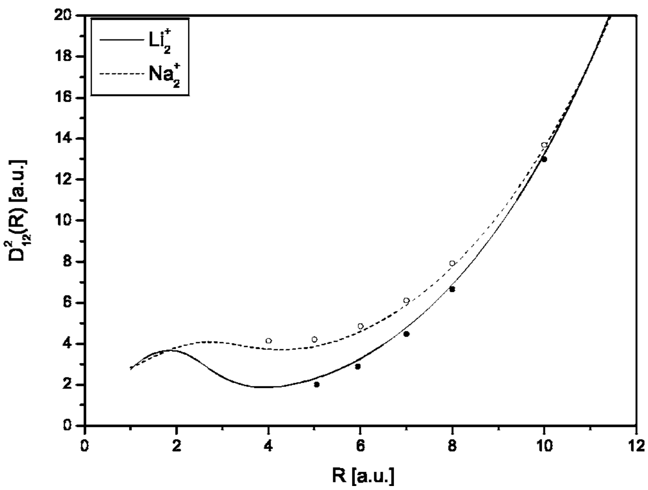

FIG. 4. The square of dipole matrix element D_{12}^2 (a.u.). ● [35]; ○ [37].

$\epsilon_n/2$. On the base of our estimation, R_n is determined with accuracy ±0.25 a.u.

Let now $R_0 = R_0(\rho, E)$ be the minimum value of R reached by the collision system for given ρ and E in the case when the internuclear motion is realized in the potential $U_2(R)$. For our further consideration we shall keep in mind that processes (1.1a) and (1.1b) take place only if

$$R_0(\rho, E) < R_n. \tag{2.2}$$

Consider that each one of the processes (1.1a) and (1.1b) is realized in the corresponding part of the region $R_0 \leqslant R \leqslant R_n$. The lower and upper limits of these parts will be denoted here by $R_{min}^{(\alpha)} = R_{min}^{(\alpha)}(\rho, E)$ and $R_{max}^{(\alpha)} = R_{max}^{(\alpha)}(\rho, E)$. In the case that only one of the processes (1.1a) and (1.1b) is realized, the following relations hold for these limits:

$$R_{min}^{(\alpha)} = R_0, \quad R_{max}^{(\alpha)} = R_n, \tag{2.3}$$

and in the case that both processes are realized, the relations will be

$$R_{min}^{(a)} = R_0, \quad R_{min}^{(b)} = R_{max}^{(a)} = R_E, \quad R_{max}^{(b)} = R_n, \tag{2.4}$$

where R_E denotes a root of the equation

$$U_{12}(R) = E \tag{2.5}$$

under the condition that $E \geqslant U_{12}(R_n)$.

According to these considerations, the chemi-ionization processes (1.1a) and (1.1b) at given ρ and E can be characterized by the ionization probability $P_{ci}^{(\alpha)}(n, \rho, E)$, given by the relation

$$P_{ci}^{(\alpha)}(n, \rho, E) = p_{in}[P_d^{(\alpha;1)}(n, \rho, E) + P_d^{(\alpha;2)}(n, \rho, E)]. \tag{2.6}$$

Here $\alpha = a$ and b, and $P_d^{(\alpha;1)}(n, \rho, E)$ and $P_d^{(\alpha;2)}(n, \rho, E)$ denote the decay probabilities of the collision system's initial electronic state within the region $R_{min}^{(\alpha)}(\rho, E) \leqslant R \leqslant R_{max}^{(\alpha)}(\rho, E)$ in the phase of approaching and the phase of parting, respectively. In order to define the probabilities $P_d^{(\alpha;\beta)}(n, \rho, E)$ we shall introduce the quantity $P_d(t) = P_d(t, \rho, E)$, where $t_{st}^{(n)} \leqslant t \leqslant t_{fin}^{(n)}$, which has the meaning of the decay probability of that initial electronic state within the time interval from $t_{st}^{(n)}$ to t. Here $t_{st}^{(n)}$ and $t_{fin}^{(n)}$ denote the moments of the system's entrance into the region of ionization and of leaving it, respectively. According to [6], the probability $P_d(t)$ is defined as the solution of the equation

$$\frac{dP_d(t)}{dt} = [1 - P_d(t)]W_n(R(t)), \tag{2.7}$$

where $W_n(R)$ denotes the rate of the decay at a given R. As this solution must satisfy the condition $P_d(t_{st}^{(n)}) = 0$, it is given by the expression

$$P_d(t) = 1 - \exp\left(-\int_{t_{st}^{(n)}}^{t} W_n(R(t'))dt'\right). \tag{2.8}$$

According to the meaning of the quantities $P_d^{(\alpha;\beta)}$ and $P_d(t)$ we have that

$$P_d^{(\alpha;\beta)} = P_d(t_{fin}^{(\alpha;\beta)}) - P_d(t_{st}^{(\alpha;\beta)}), \tag{2.9}$$

where $t_{st}^{(\alpha;1)}$ and $t_{fin}^{(\alpha;1)}$ are the respective moments of the system's entrance into the region $R_{min}^{(\alpha)}(\rho, E) \leqslant R \leqslant R_{max}^{(\alpha)}(\rho, E)$ and of departure from it in the phase of approaching, and $t_{st}^{(\alpha;2)}$ and $t_{fin}^{(\alpha;2)}$ are the respective moments of the entrance and the departure in the phase of parting.

In [7] it was taken that the factor $[1 - P_d(t)]$ in Eq. (2.7) may be replaced by 1, which neglected the decay of the initial electronic state of the atom–Rydberg-atom system observed during the collision. This approximation was justified in the case of chemi-ionization processes (1.1a) and (1.1b) with $A = \mathrm{H}$ and He. However, in the case of atoms of alkali metals the mentioned decay had to be taken into account. Because of that in [7] it was necessary to make an *a posteriori* calculation. It required an additional parameter which could not be properly determined within the method used in [7]. For that reason we shall follow the basic work in [6], and use Eq. (2.7) here without the above simplification.

Now we shall replace the variable t with R in Eqs. (2.7)–(2.9), taking into account that $dt = dR/v_{rad}(\rho, E; R)$, where $v_{rad}(\rho, E; R)$ is the radial collision velocity defined by the relation

$$v_{rad}(\rho, E; R) = \sqrt{\frac{2}{M_{red}}\left(E - U_2(R) - \frac{E\rho^2}{R^2}\right)}. \tag{2.10}$$

Here M_{red} is the reduced mass of the $A^+ + A$ subsystem. According to Eqs. (2.6), (2.8), and (2.9), together with the relations (2.3) and (2.4), it can be proved that in the case when just one of the processes (1.1a) and (1.1b) is realized, the ionization probability $P_{ci}^{(a,b)}(n, \rho, E)$ is given by the expression

$$P_{ci}^{(\alpha)}(n, \rho, E) = p_{in}\left[1 - \exp\left(2\int_{R_0}^{R_n} \frac{W_n(R)dR}{v_{rad}}\right)\right], \tag{2.11}$$

and in the case when both processes are realized by the expressions

$$P_{ci}^{(a)}(n, \rho, E) = p_{in}\left[1 - \exp - \left(2\int_{R_0}^{R_E} \frac{W_n(R)dR}{v_{rad}}\right)\right] \times \exp - \left(\int_{R_E}^{R_n} \frac{W_n(R)dR}{v_{rad}}\right), \tag{2.12}$$

$$P_{ci}^{(b)}(n, \rho, E) = p_{in}\left[1 - \exp - \left(\int_{R_E}^{R_n} \frac{W_n(R)dR}{v_{rad}}\right)\right] \times \left[1 + \exp - \left(2\int_{R_0}^{R_n} \frac{W_n(R)dR}{v_{rad}}\right)\right], \tag{2.13}$$

where $p_{in} = 1/2$ and $v_{rad} = v_{rad}(\rho, E; R)$ is given by Eq. (2.10). Regarding Eqs. (2.11)–(2.13) it is useful to note that p_{in} in the expression for ionization probability in [6] appears as a factor multiplying the decay rate, instead of a factor multiplying the whole expression for that probability. This mistake did not affect either the results presented in [6] or the results obtained later in [7], but might cause confusion if the expression was applied in the form given in [6].

Using the probability $P_{ci}^{(a,b)}(n,\rho,E)$, one determines the cross sections for the chemi-ionization processes (1.1a) and (1.1b)

$$\sigma_{ci}^{(a,b)}(n,E) = 2\pi \int_0^{\rho_{max}^{(a,b)}(E)} P_{ci}^{(a,b)}(n,\rho,E)\rho\, d\rho, \qquad (2.14)$$

where $\rho_{max}^{(a,b)}(E)$ is the upper limit of values ρ at which the corresponding region R is reached for a given E. In the case when just one of the processes (1.1a) and (1.1b) is realized, it is the region (2.1), and in the case when they are both realized it is the region

$$R \leqslant R_E \qquad (2.15)$$

for the process (1.1a) and the region (2.1) for the process (1.1b). The rate coefficients of the processes (1.1a) and (1.1b) are determined thereafter by the expressions

$$K_{ci}^{(a,b)}(n,T) = \int_{E_{min}^{(a,b)}(n)}^{\infty} v\sigma_{ci}^{(a,b)}(n,E) f(v;T) dv, \qquad (2.16)$$

where $E_{min}^{(a,b)}(n)=0$ if $U_2(R_n)\leqslant 0$, and $E_{min}^{(a,b)}=U_2(R_n)$ if $U_2(R_n)>0$, and $f(v;T)$ is the velocity distribution function at a given temperature T which is different in cells and the single-beam and crossed-beam cases (see, e.g., [24]). Finally, using $K_{ci}^{(\alpha)}(n,T)$, one determines the quantities

$$K_{ci}(n,T) = K_{ci}^{(a)}(n,T) + K_{ci}^{(b)}(n,T) \qquad (2.17)$$

and

$$X^{(a,b)}(n,T) = \frac{K_{ci}^{(a,b)}(n,T)}{K_{ci}(n,T)}, \qquad (2.18)$$

which are treated here as the total rate coefficients for the processes (1.1a) and (1.1b) and the corresponding branch coefficients.

In [6] it was assumed that the decay rate $W_n(R)\sim n^{-5}$, which corresponded to the case when the atoms $A^*(n)$ in Rydberg states with small orbital quantum numbers ($l=0,1$), contributed negligibly to the processes (1.1a) and (1.1b). In such a case it is possible to assume that the outer electron in the atom $A^*(n)$, irrespective of the value of l, is in a hydrogenlike state with energy $\epsilon_n=-0.5/n^2$. On the contrary, here we want to take into account the case when Rydberg atoms in states with small l take part in the processes (1.1a) and (1.1b); the binding energy of the outer electron may be taken in the form

$$\epsilon_n = -Ry/n_{eff}^2, \quad n_{eff} = n - \Delta(n,l), \qquad (2.19)$$

where $\Delta(n,l)$ is the corresponding quantum defect (see, e.g., [28]). We shall follow [7] where this difference was taken into account. Consequently, we shall take $W_n(R)$ in the form

$$W_n(R) = \frac{4}{3\sqrt{3}n_{eff}^5} D_{12}^2(R) G_{nk}, \qquad (2.20)$$

where $D_{12}(R)$ is defined by Eq. (1.5). G_{nk} denotes the generalized Gaunt factor, defined by the expression

$$G_{nk} = \frac{\sigma_{ph}(n,k)}{\sigma_{ph}^{Kr}(n,k)}, \qquad (2.21)$$

where $\sigma_{ph}(n,k)$ is the photoionization cross section of the atom $A^*(n)$ with transition of the outer electron to the state with the energy ϵ_k, and $\sigma_{ph}^{Kr}(n,k)$ denotes the same photoionization cross section in Kramers's approximation ([29]; see also [28]).

III. RESULTS AND DISCUSSION

The processes (1.1a) and (1.1b) in fact act as the channels of broader symmetrical chemi-ionization processes. Therefore we shall characterize them by total rate coefficients $K_{ci}(n,T)$ and branch coefficients $X^{(a)}(n,T)$, which describe the relative influence of the associative ionization channel (1.1a). The calculations of those values are carried out for the cases of (1) cells for the atom $\mathrm{Li}^*(n)$, as well as for the atom $\mathrm{Na}^*(n)$, which is in one of the (nl) states, $0\leqslant l\leqslant n-1$, with probabilities proportional to the statistical weights of those states; (2) single beams for the atom $\mathrm{Na}^*(n)$, which is in one of the (ns), (np), or (nd,f) states; (3) crossing beams for the atom $\mathrm{Li}^*(n)$, as well as for the atom $\mathrm{Na}^*(n)$, which are in (np) states.

These cases mainly differ in the shapes of the distribution function $f(v;T)$ which appears in Eq. (2.16) for the partial rate coefficients $K_{ci}^{(\alpha)}(n,T)$. In the case of a cell $f(v;T)=f_{cell}(v;T)$, where $f_{cell}(v;T)$ is the Maxwell distribution function

$$f_{cell}(v;T) = \frac{4}{\sqrt{\pi}}\frac{1}{v_T}x^2 e^{-x^2}, \qquad (3.1)$$

while in the cases of crossing beams and single beams $f(v;T)=f_{cb}(v;T)$ and $f(v;T)=f_{sb}(v;T)$, respectively, where $f_{cb}(v;T)$ and $f_{sb}(v;T)$ are given by the expressions taken from [24]:

$$f_{cb}(v;T) = \frac{1}{v_T}x^5 e^{-x^2}, \qquad (3.2)$$

$$f_{sb}(v;T) = \frac{C}{v_T}e^{-x^2/2}\left[e^{-x^2/2}x(2-x^2) + \sqrt{\frac{\pi}{2}}(3-2x^2+x^4)\operatorname{erfc}\left(\frac{x}{\sqrt{2}}\right)\right]. \qquad (3.3)$$

In all these expressions $x=v/v_T$, $v_T=\sqrt{2kT/M_{red}}$, and C in Eq. (3.3) is the normalization factor.

Within the procedure used here the potential curves $E_1(R)$ and $E_2(R)$, and the dipole matrix element $D_{12}(R)$, are determined numerically by the method described in the Appendix. The behavior of these quantities as functions of R for mo-

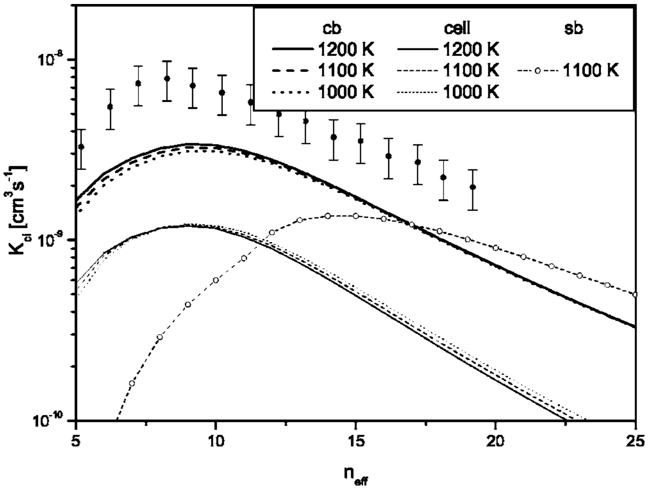

FIG. 5. The rate coefficient for chemi-ionization in $Li^*(n)+Li$ collisions. ● [30].

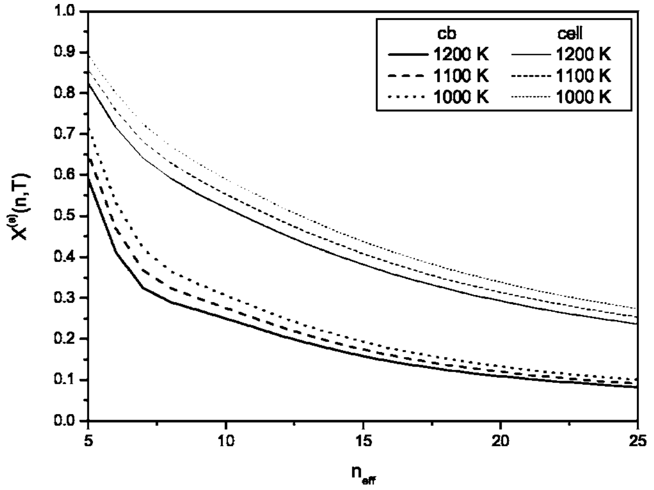

FIG. 6. The branch coefficient $X^{(a)}(n,T)$ for chemi-ionization in $Li^*(n)+Li$ collisions.

lecular ions Li_2^+ and Na_2^+ is illustrated in Figs. 2–4. The other parameters introduced above, $\rho_{max}^{(a,b)}(E)$, $R_0(\rho,E)$, R_E, and R_n are also determined numerically. Then, the determination of the decay rate $W_n(R)$ is performed here with the factor $G_{nk} \equiv 1$ in all cases of a cell, as was done in [6,7]. In other cases, however, on the basis of our estimations, it was taken that $G_{nk}=1.5$, 1.3, and 1.0 for (ns), (np), and (nd,f) states of $A=\mathrm{Na}$, respectively and 1.2 for (np) states of $A=\mathrm{Li}$.

The processes (1.1a) and (1.1b) are considered here in the region of the principal quantum numbers $5 \leqslant n \leqslant 25$ for (np) states of the lithium atom, (np,d,f) states of the sodium atom, and in the region $6 \leqslant n \leqslant 25$ for (ns) states of the sodium atom. Here we took into account that, in accordance with [10], the basic theory is strongly valid if there is no crossing between the potential curves of the systems $A^*(n)+A$ and $A^+ + A^-$, where A^- denotes a stable negative ion. The choice of lower boundaries of considered regions of n provide that this condition is satisfied.

The values of the total rate coefficients $K_{ci}(n,T)$ and branch coefficients $X^{(a)}(n,T)$ were determined in the region $1000 \leqslant T \leqslant 1200$ K for $A=\mathrm{Li}$ and in the region $600 \leqslant T \leqslant 900$ K for $A=\mathrm{Na}$. Figures 5–10 illustrate the results of our calculation of these quantities. Each of Figs. 5–8 contains two groups of curves: the first is related to the cell cases, and the second to the crossed-beam cases. The curves within both of them correspond to temperatures $T=1000$, 1100, and 1200 K in Figs. 5 and 6 for $A=\mathrm{Li}$, and to temperatures $T=700$, 800, and 900 K in Figs. 7 and 8 for $A=\mathrm{Na}$.

Figure 5 also shows the values of the rate coefficient for $A=\mathrm{Li}$, experimentally determined at $T=1100$ K in [30], the only ones that can be found in the literature for this case. Taking into account that these experimental values are obtained in the case of a single beam, the same figure that shows the results of our calculation for $K_{ci}(n,T)$.

Some of our results for $A=\mathrm{Na}$ are presented in Figs. 9 and 10. These are the results related to the cases of crossed and single beams for which one can find the experimental data in the literature. Figure 9 shows the experimental values of the rate coefficient from [5], obtained in the case of crossed beams at $T=600$ K, and from [30] obtained in the case of single beam at $T=720$ K, for sodium atoms in (np) states. In order to compare our results with the experimental data related to crossed beams, the same figure shows the curve $K_{ci}(n,T)$ obtained for the same atom states at $T=600$ K with the velocity distribution function (3.2). As one can see there is a very good agreement between the calculated and experimental data from [5], particularly if one takes into account that the calculation error, caused by the error in determining R_n, is estimated to be about 10%.

Our results and the experimental data from [30] related to the single-beam case are shown in Fig. 9. The curve $K_{ci}(n,T)$ is obtained at $T=720$ K with the velocity distribution function (3.3). In this case there is a significant disagreement between our results and the experimental data. Because of that the curve $K_{ci}(n,T)$, obtained at $T=720$ K with Maxwell distribution function (3.1), is shown on the same figure. It can be concluded that the existing disagreement between our and the experimental results is caused by the deviation of the velocity distribution function in the single beam used in [30]

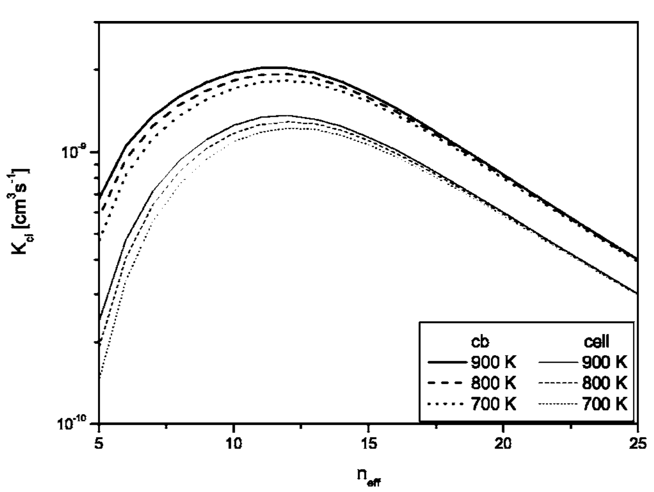

FIG. 7. The rate coefficient for chemi-ionization in $Na^*(n)+Na$ collisions.

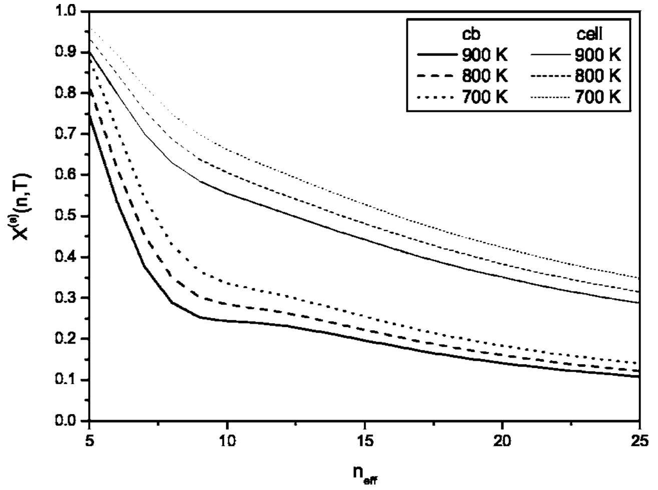

FIG. 8. The branch coefficient $X^{(a)}(n,T)$ for chemi-ionization in $Na^*(n)+Na$ collisions.

from the distribution function Eq. (3.3). In connection with this we would like to emphasize that a similar situation exists in the case of the experimental data from [30] related to the single beam with $A=Li$, reflected in Fig. 5.

Figure 10 shows the experimental [23] and calculated curves $K_{ci}(n;T)$ related to the single beams with $A=Na$, namely, for (ns) and (nd,f) states at $T=1000$ K, and for (np) states at $T=600$ K. There is a good agreement for (ns) states at $T=1000$ K. However, for (np) states at $T=600$ K and for (nd,f) states at $T=1000$ K there is a significant disagreement between our and the experimental results, similarly as in the case of a single beam, shown in Fig. 9. Because of that, in Fig. 10 we also show the curve $K_{ci}(n;T)$, obtained at $T=1000$ K with the Maxwell distribution function Eq. (3.1). As in Fig. 9 one can see a better agreement with the corresponding experimental values. These comparisons suggest that the physical conditions in single beams were probably not determined well.

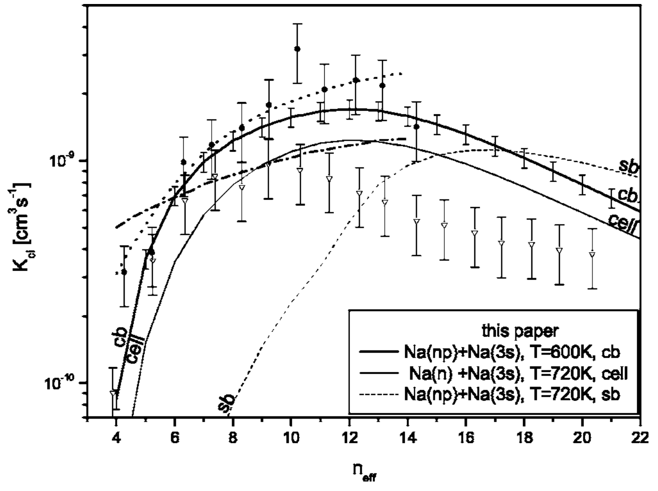

FIG. 9. The rate coefficient for chemi-ionization in $Na^*(n)+Na$ collisions. ●, $Na^*(np)+Na(3s)$, $T=600$ K, crossed beams (cb) [5]; ▽, $Na^*(np)+Na(3s)$, $T=720$ K, single beam (sb) [30,39]. The calculation for $T=600$ K, cb, -·- [12]; … [13].

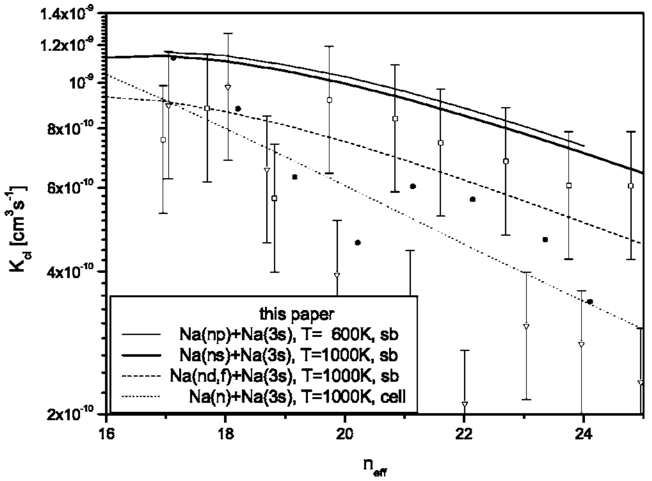

FIG. 10. The rate coefficient for chemi-ionization in $Na^*(n)+Na$ collisions. ●, $Na^*(np)+Na(3s)$, $T=600$ K, sb; □, $Na^*(ns)+Na(3s)$, $T=1000$ K, sb; ▽, $Na^*(nd,f)+Na(3s)$, $T=1000$ K, sb [23].

The experimental data in [12,13] and the results of calculations of the total rate coefficients for the case of crossed beams with $A=Na$ at $T=600$ K are presented in Fig. 9. The reason why only two curves are presented here is that there are no other published results related to the cases of $A=Li$ and Na, obtained by the method from [12,13]. All other results presented in the previous papers [3,4,11,31] are related to the cases of heavy alkali metals which are not considered here.

Regarding the method from [12] one should keep in mind several facts. It is based on the theory presented in [3,4,11], where the internuclear motion was treated in the approximation of the unique trajectory, and the transitions of the outer electron of an atom $A^*(n)$ were considered as a result of its interaction with the oscillating dipole moment of the $A^+ + A$ subsystem. This approximation is correct if the impact energy E during $A^*(n)+A$ collision is at least several times greater than $U_{12}(R)$. However, in the cases considered here, the values of $U_{12}(R)$ in the region (2.1) can be several times greater than 0.1 eV, while the values of kT change from about 0.05 to about 0.1 eV. It means that the mentioned condition cannot be satisfied in the environment with such a temperature. It is clear that the approximation of the unique trajectory would be helpful if determined in the average potential $\bar{U}(R) \approx [U_1(R)+U_2(R)]/2$. However, in this case the threshold for the processes (1.1a) would not exist, and the corresponding rate coefficients would change slowly with n decreasing. From Fig. 9 one can see that the curve taken from [12] behaves just in such a way.

The single-trajectory approximation cannot be applied to the associative ionization process (1.1a). In spite of that, a method based on the approximation of the unique trajectory has still been developed and used in some modified form in [13,14]. The effect of this modification is presented by the curve taken from [13]. This curve is closer to the experimental data from [5] in the region $n \leqslant 12$, and has quite different behavior compared with the curve from [12] in the region of relatively small n. Such a difference is the result of using the unique trajectory determined in the potential $\bar{U}(R)=U_2(R)$. However, one should keep in mind that this approximation completely excludes the possibility of internuclear motion in the attractive potential $U_1(R)$ in $A^*(n)+A$ collisions.

On the basis of what has just been said, one could expect a significant difference between our calculations and the calculations based on the method from [12]. Figure 9 illustrates the existence of such differences, which have both qualitative and quantitative character. Thus it can be seen that for effective quantum numbers $n_{eff}>6$ our values of $K_{ci}(n;T)$ are much higher than the values of the total rate coefficient from [12]. This deserves attention considering the fact that generally, within the framework of the method [12], all $A^*(n)+A$ collisions are being taken into account, while the method presented here deals with just one-half of such collisions, namely, with those in which the relative motion of the nuclei within the region (2.1) is described by a trajectory determined in the potential $U_2(R)$.

Comparing the curves from [12,13] with the curve obtained in this work, which are related to the same case of crossed beams ($A=\mathrm{Na}$, $T=600$ K), one can conclude that in the region $n\leqslant 12$ the curve obtained here is much closer to the experimental data from [5] than the curve from [12] and very close to the curve from [13]. However, Figs. 9 and 10 show that in the region $n>12$ the values of chemi-ionization rate coefficients obtained here decrease with increasing n and agree with the experimental data, while the behavior of the curves from [12,13] shows a tendency to further increase.

The results presented in this paper highly recommend the method of calculating the rate coefficients of the processes (1.1a) and (1.1b) both for theoretical research in the field of weakly ionized plasmas, and for interpretation of corresponding experimental data. Thus, in the cases of the processes involving atoms of alkali metals, it would completely replace the method from [7], fully applicable only in hydrogen and helium cases. Accordingly, it appears as the immediate task to apply this method to the same processes involving atoms of heavier alkali metals (K, Rb, and Cs), as well as to very important nonsymmetrical chemi-ionization processes, involving atoms of two different alkali metals.

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APPENDIX: THE WAVE FUNCTIONS OF ADIABATIC ELECTRONIC STATES OF MOLECULAR IONS

In order to calculate adiabatic potential curves and dipole matrix elements of the molecular ions we shall use here a modified version of the method developed previously, concerning the radiative processes in slow-ion–atom collisions [32]. The method is applicable to determine characteristics of the Σ state of each of the molecular ions AB^+,

$$AB^+ = A^+ + B^+ + e, \tag{A1}$$

where A^+ and B^+ are atomic ions in their ground states with completely occupied shells. Within this method the observed molecular ion is treated in the single-electron approximation, under the condition

$$R \gg r_{A^+,B^+}, \tag{A2}$$

where R is the distance between the centers of the ions A^+ and B^+, and r_{A^+} and r_{B^+} are the effective radii of these ions. Considering the conditions for application of the adiabatic approximation satisfied, we shall determine the electronic states of the ions AB^+ at a given R and fixed positions of the centers of the ions A^+ and B^+. The wave functions of the considered Σ states are denoted by $\Psi_i(r_1,r_2;R)$, where r_1 and r_2 are the distances of the electron e from the centers of the ions A^+ and B^+, respectively. Within the method used these wave functions must satisfy the Schrödinger equation

$$\hat{H}(r_1,r_2;R)\Psi_i(r_1,r_2;R) = E_i(R)\Psi_i(r_1,r_2;R), \tag{A3}$$

under the usual normalization conditions and additional orthogonality conditions stated below. In Eq. (A3), $E_i(R)$ denotes the corresponding eigenenergy, and the Hamiltonian $\hat{H}(r_1,r_2;R)$ is given by the expression

$$\hat{H}(r_1,r_2;R) = -\frac{1}{2}\Delta + V_A(r_1) + V_B(r_2), \tag{A4}$$

where the terms V_A and V_B describe the interaction of the electron e with ions A^+ and B^+, respectively. These terms are

$$V_{A,B}(r) = -\frac{1}{r} + v_{A,B}(r), \tag{A5}$$

where v_A and v_B are the corresponding non-Coulomb parts.

In Eq. (A5) the terms $v_{A,B}$ are

$$v_{A,B}(r) = -\frac{Z_{A,B}-1}{r} + \frac{1}{r}\int_0^r \rho^{(A^+,B^+)}(r')4\pi r'^2 dr' + \int_r^\infty \frac{\rho^{(A^+,B^+)}(r')}{r'}4\pi r'^2 dr', \tag{A6}$$

where $Z_{A,B}$ are the charges of the nuclei of atoms A and B, and $\rho^{(A^+,B^+)}(r)$ the spherical-symmetric electron densities of closed shells of the ions A^+ and B^+ at the distance r from the corresponding nuclei.

Let now $\psi_{j,l,m}^{(A^+)}$ and $\psi_{j,l,m}^{(B^+)}$ be the wave functions of A^+ and B^+ ion single-electron states with the principal, orbital, and azimuthal quantum numbers j, l, and m, respectively. It is assumed that the axis of quantization coincides with the axis of symmetry of the ion AB^+. The mentioned electron densities can be taken in the form

$$\rho^{(A^+,B^+)}(r) = 2\sum_j \sum_l (2l+1)|R_{j,l,m}^{(A^+,B^+)}(r)|^2 \qquad \text{(A7)}$$

where $R_{j,l,m}^{(A^+,B^+)}(r)$ are the radial parts of the wave functions $\psi_{j,l,m}^{(A^+,B^+)}$. In this expression the summation is performed over all single-electron states of ions A^+ or B^+, and the factor 2 takes into account the spin of an electron.

The additional conditions mentioned are analogous to the conditions of orthogonality in the well-known method of pseudopotentials [33]. In this case these conditions are

$$\langle \Psi_i | \psi_{j,l,0}^{(A^+)} \rangle = 0 \qquad \text{(A8)}$$

for $0 \leqslant l \leqslant j-1$ and $1 \leqslant j \leqslant j_{A^+}$, and the conditions

$$\langle \Psi_i | \psi_{j,l,0}^{(B^+)} \rangle = 0 \qquad \text{(A9)}$$

for $0 \leqslant l \leqslant j-1$ and $1 \leqslant j \leqslant j_{B^+}$, where j_{A^+} and j_{B^+} are the principal quantum numbers of the outer electron shells of the ions A^+ and B^+.

Since we are interested in Σ states of considered molecular ions only, we will solve Eq. (A3) in elliptical coordinates μ and ν,

$$\mu = \frac{r_1 + r_2}{R}, \quad \nu = \frac{r_1 - r_2}{R}, \qquad \text{(A10)}$$

changing within the ranges $1 \leqslant \mu < \infty$ and $1 \leqslant \nu \leqslant 1$. In these coordinates Eq. (A3) takes the form

$$\left[-\frac{1}{2}\Delta_{\mu,\nu} + V_A\left(R\frac{\mu+\nu}{2}\right) + V_B\left(R\frac{\mu-\nu}{2}\right)\right]\Psi_i(\mu,\nu) = E_i(R)\Psi_i(\mu,\nu), \qquad \text{(A11)}$$

where $\Delta_{\mu,\nu}$ is the Laplacian in elliptical coordinates, given by

$$\Delta_{\mu,\nu} = -\frac{2}{R^2(\mu^2-\nu^2)}\left(\frac{\partial}{\partial\mu}(\mu^2-1)\frac{\partial}{\partial\mu} + \frac{\partial}{\partial\nu}(1-\nu^2)\frac{\partial}{\partial\nu}\right). \qquad \text{(A12)}$$

We shall seek the solution of this equation in the form

$$\Psi_i = N_i\left(\sum_{p=1}^{P_A} a_p^{(A)}\psi_p^{(A)} + \sum_{q=1}^{Q_B} a_q^{(B)}\psi_q^{(B)} + \sum_{j=1}^{J_{A^+}}\sum_{l=0}^{j-1} b_{j;l}^{(A)}\psi_{j;l}^{(A^+)} + \sum_{j=1}^{J_{B^+}}\sum_{l=0}^{j-1} b_{j;l}^{(B)}\psi_{j;l}^{(B^+)}\right), \qquad \text{(A13)}$$

where N_i is the normalization constant, and P_A and Q_B the numbers of basis functions $\psi_p^{(A)}$ and $\psi_q^{(B)}$ centered on the ions A^+ and B^+; the coefficients $b_{j;l}^{(A)}$ and $b_{j;l}^{(B)}$ are determined by the conditions (A8) and (A9), and accordingly they are expressed through the coefficients $a_p^{(A)}$ and $a_q^{(B)}$. The latter are determined from the variational principle, i.e., ultimately from the system of equations

$$\sum_{s=1}^{P_A+Q_B} (H_{st} - ES_{st})a_t = 0, \quad t = 1,2,\ldots,P_A+Q_B, \qquad \text{(A14)}$$

where the matrix elements $H_{st} = \int \psi_s^* \hat{H}\psi_t dV$, the overlap integrals $S_{st} = \int \psi_s^* \psi_t dV$; ψ_s and ψ_t represent, depending on s and t, either function $\psi_p^{(A)}$ or $\psi_q^{(B)}$, and the volume element $dV = 2\pi(R/2)^3(\mu^2-\nu^2)d\mu\, d\nu$. In this way the problem of finding coefficients $a_p^{(A)}$ and $a_q^{(B)}$ is reduced to solving the generalized eigenproblem (A14), where the matrix $\|H_{st}\|$ is symmetrical and $\|S_{st}\|$ is symmetrical and positively definite. In our calculations instead of functions $\psi_p^{(A)}$ and $\psi_q^{(B)}$, the functions

$$\psi_{\beta\delta\gamma}^{(A^+)}(\mu,\nu) = \mu^\beta\nu^\delta \exp\left(-\gamma\frac{R}{2}(\mu+\nu)\right),$$

$$\psi_{\beta\delta\gamma}^{(B^+)}(\mu,\nu) = \mu^\beta\nu^\delta \exp\left(-\gamma\frac{R}{2}(\mu-\nu)\right) \qquad \text{(A15)}$$

have been used, where β and δ are integer numbers, and γ is a positive real number. Within the method used the possibility of varying the parameter γ is understood.

As a result of the procedure explained one gets the wave functions Ψ_i for a number of adiabatic electronic Σ states of molecular ions, together with the corresponding adiabatic potential curves $E_i(R)$.

The ion H_2^+ was used to test the convergence of the procedure as the number of basis functions increases. The expansion of the basis stopped when the values of the adiabatic potential curves for the ground, the first excited, and several other energetic states, within the range $1 \leqslant R \leqslant 100$ a.u., differed from the corresponding values from [34] by less than 10^{-9} a.u.. In this example it was also found that within the procedure described it is reasonable to consider all the parameters γ in the expressions for the basis functions to have the same values, which had as a consequence that only one parameter varies within this procedure.

In the case of an asymmetric molecular ion AB^+ the above procedure was repeated twice. The first time it was used in order to determine the wave function Ψ_1 and the adiabatic potential curve $E_1(R)$ of the ground electronic state of this molecular ion, and the second time to determine the wave functions Ψ_i and the adiabatic potential curve $E_i(R)$ of the first excited and several higher electronic states of the same ion ($i \geqslant 2$). In the latter case the conditions (A8) and (A9) were accompanied by the condition of orthogonality with respect to the already found ground state, namely,

$$\langle \Psi_i | \Psi_1 \rangle = 0, \qquad \text{(A16)}$$

which involved an additional term in the expression within parentheses in Eq. (A13). The main intention for this procedure is to provide values of the potential curve $E_2(R)$ of the first excited electronic state of the ion AB^+ as low as possible, together with its orthogonality with respect to the ground state of the ion.

In the case of symmetrical molecular ions A_2^+ the procedure was applied only once, taking into account that the ground and the first excited states of such an ion are always orthogonal, as one of them is Σ_g, and the other Σ_u. Additional simplification comes from the fact that in the case of the ions A_2^+ we have

$$v_A(r) = v_B(r), \quad P_A = P_B, \tag{A17}$$

where $v_{A,B}$ are non-Coulomb term in Eq. (A5), and $P_{A,B}$ the numbers of basis functions in Eq. (A13). Consequently, the corresponding basis functions centered on each one of the ions must have the same values of all the relevant parameters, and the same applies to the wave functions of single-electron states of these atomic ions.

The procedure of determining the molecular wave functions requires a knowledge of the wave functions $\psi_{j,l,m}^{(A^+,B^+)}$ of the single-electronic states of ions A^+ and B^+, and the wave functions $\psi^{(A,B)}(r)$ describing the states of the valence s electron in the atoms A and B. Because of that, we had to consider the initial problem of the isolated atoms A and B. It is assumed that all these functions are proportional to the exponents $\exp - \gamma_{jl}^{A^+,B^+}$ and $\exp - \gamma^{A,B}$. The wave functions $\psi^{(A,B)}(r)$ are approximated by the wave functions that describe the lowest s state of an electron in the potentials $V_{A,B}(r)$ given by Eqs. (A5)–(A7). These conditions are

$$\langle \psi^{(A)} | \psi_{j,l,0}^{(A^+)} \rangle = 0, \quad \langle \psi^{(B)} | \psi_{j,l,0}^{(B^+)} \rangle = 0, \tag{A18}$$

which are similar to the conditions Eq. (A8) and (A9). Under these conditions the functions $\psi^{(A,B)}(r)$ are determined by the variational principle as a linear combination of chosen basis functions. One can see that these functions depend on the parameters $\gamma_{jl}^{A^+,B^+}$ through Eqs. (A5)–(A7) and through the conditions (A18) at the same time. The procedure of determining the wave functions $\psi^{(A,B)}(r)$ consists of varying the parameters $\gamma_{jl}^{A^+,B^+}$, as well as the parameters $\gamma^{A,B}$. The final values of all parameters are determined from the following additional conditions: (1) the variational wave functions $\psi^{(A)}(r)$ and $\psi^{(B)}(r)$ provide the correct values of the ionization potentials of the atoms A and B; (2) the simultaneously determined wave functions of the resonant states of these atoms provide the excitation energies of these states; and (3) the oscillator strength for the transition to the ground state coincides with the exact values within the accuracy requested.

The final values of parameters $\gamma_{jl}^{A^+,B^+}$ do not change during the procedure of determining the molecular ion wave functions. However, the final values of parameters $\gamma^{A,B}$ are taken as initial values of the corresponding parameters of the molecular wave functions. In the symmetric case $(A=B)$ considered here the final value of parameter γ^{A} is taken as the starting value of parameter γ in Eq. (A15).

The method described has been applied to determine the adiabatic potential curves of the molecular ions Li_2^+ and Na_2^+. The results of the calculation are presented in Figs. 2 and 3, where the potential curves $E_1(R)$ and $E_2(R)$ of the ground and the first excited states of these ions are shown, as well as the ones of the next two higher states. The results of these calculated potential curves have been compared to the results of calculations from [35,36] for the case of lithium and with the results from [37,38] for the case of sodium. The values of the molecular potential curves calculated for particular points in these papers are also conveniently presented in Figs. 2 and 3. From these results a very good agreement can be seen between the values of the adiabatic potential curves used here, obtained by the method explained, and the corresponding values from the papers cited.

Apart from the molecular potential curves of several electronic states of the ions Li_2^+ and Na_2^+, the dipole matrix elements for the transitions between these states have been calculated too. The results of these calculations are illustrated in Fig. 4, where the quantities $D_{12}^2(R)$, defined by Eq. (1.5) have been presented, characterizing the transitions between the ground and the first excited states of the molecular ions.

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