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Rate coefficients for the chemi-ionization processes in sodium- and other alkali-metal geocosmical plasmas

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Abstract

The chemi-ionization processes in thermal and sub-thermal collisions of excited alkali atoms with atoms in ground and excited states were considered, with a particular accent to the applications for geocosmical plasma research. An improved version of semi-classical method for the rate coefficients calculation is presented. The method is applied to the cases of excited alkali atoms with the principal quantum numbers $5 \leq n \leq 25$. The results of calculation of the considered chemi-ionization processes rate coefficients are compared to the existing experimental data. Their good agreement recommends to use the rate coefficients obtained for analysis of geocosmical plasma processes.

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Contents

1. Introduction	548
2. Chemi-ionization in binary collisions of atoms in low-lying excited states	549
2.1. Rate coefficients for binary collisions of alkali-metal atoms in the first excited resonant states	549
2.2. Ionization in binary collisions of low-lying excited atoms in states higher than the resonant one	550
3. Collision ionization with RA participation: symmetrical case.	550
3.1. Ionization in Rydberg-atom-atom collisions	550
3.1.1. The resonant mechanism.	550
3.1.2. The stochastic dynamics approach: the unique trajectory model	552
3.1.3. The decay approximation: the two-trajectories model.	553
3.1.4. The comparison of the experimental and theoretical results	554
3.2. Ionization in binary Rydberg-atom collisions.	555
4. Collision ionization with Rydberg atom participation (non-symmetrical collision)	558
4.1. Rydberg atom collisions with molecules	558

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4.2. Non-symmetrical atom–atom chemi-ionization processes	559
5. Photoplasma	559
6. Conclusion	560
Acknowledgements	561
References	561

1. Introduction

Elementary processes involving ions, atoms and molecules in geocosmical plasmas, traditionally attract researchers attention for a longer time (see e.g. Herbst and Klemperer, 1973). Among these processes, those involving highly excited Rydberg atoms are also of interest for stellar atmospheres of late spectral classes, interstellar H II clouds where Rydberg atoms form as a result of electron–proton recombination processes, as well as in other astrophysical plasmas. Recently was reported in Harth et al. (2004) that Rydberg molecules of atmospheric gases influence even on terrestrial biosphere. At first, our attention will be paid here on a group of ionization processes in Rydberg atom collisions with ground state parent atoms, known in literature as chemi-ionization processes, namely



where A , A^+ are atoms and their positive ions in their ground states, $RA(n)$ an atom in a highly excited (Rydberg) state with the principal quantum number $n \gg 1$, A_2^+ corresponding molecular ions in ground electronic states, and e a free electron, AI – associative ionization, PI – Penning-like ionization. Besides, we will consider shortly on the ionization processes in collisions of atoms in the weakly excited states.

The processes (1) with participation of alkaline atoms are studied for a long time experimentally (Devdariani et al., 1978; Boulmer et al., 1983; Zagrebin and Samson, 1985; Weiner and Boulmer, 1986), as well as theoretically (Janev and Mihajlov, 1980; Mihajlov and Janev, 1981; Duman and Shmatov, 1980). In all just mentioned papers, the processes (1) were treated exclusively in the laboratory conditions. In the hydrogen and helium cases however, the (1) processes later were considered in the conditions of stellar photospheres by Mihajlov et al. (1997), Mihajlov et al. (2003a). However, the processes (1) involving alkali atoms continued to be studied exclusively from the laboratory aspect. But for a longer time were collected data on the possible significant presence of alkali atoms, especially of sodium atoms, in some moons and planet atmospheres, as well as in comet tails and brown dwarfs and cooler star atmospheres (Mekler et al., 1976; Coroniti et al., 1976; Combi et al., 1997; Jonson, 2000; Takahashi et al., 2000; Burrows and Volobuyev, 2003; Schaefer and Fegley, 2005; Dalgarno and Block, 1976; Bezuglov et al., 1997b).

Chemi-ionization processes, leading to formation of molecular ions, can play an essential role in the sequence of ion-molecular reactions on surfaces of solid particles or in associative processes of the binary collisions leading to surprising variety of molecular formations in interstellar gas (Dalgarno and Block, 1976).

From above mentioned it follows that it became interesting to consider the processes (1) where A is an alkali metal atom, because such results begin now to enter as a subject of the astronomical data's publications (Bezuglov et al., 1997b). In this paper, we will consider the most significant case when $A \equiv \text{Na}$.

The considered processes are interesting from two points of view: first, they could be quite effective sources of the charged particles generation in the optically excited gaseous media; second, they could be studied as a prototype of the elementary process of the radiation energy transformation into electrical one, which is of interest for the physics of geocosmos.

We will continue on the example of the hydrogen-like alkali metal atoms, so that the obtained results should directly correlate with analogous conclusions for hydrogen – the most spread and the most abundant component of the Universe.

It is well known from solar photospheric and planet absorption spectrum, chemical analysis of asteroid fragments, meteorites and cosmic dust that alkali metals, especially such as Na and K, are present in large number of studied cosmic objects including solar system (Burrows and Volobuyev, 2003; Schaefer and Fegley, 2005). In spite of the fact that alkali metals are not so wide spread compared to hydrogen, the logarithm of sodium abundance, for example, is 6.31 in meteorites and 6.30 in Solar photosphere (hydrogen – 12.00 in both cases).

It is known also that for particular astrophysical objects abundances of elements from the Mendeleyev periodic table could be 4–6 orders of magnitude larger than its averaged cosmic abundance (Aslanov et al., 1973). In such a way, alkali metal cosmic plasma can be the subject of direct astrophysical investigations. For example sodium plasma clouds are found in the atmosphere of the Jovian satellite Io. Apart of that, alkali plasma became and the object of astrophysically inspired laboratory experiments for the modeling of processes in geocosmos (D'Angelo et al., 1966).

At the end, on the approach of astrophysics and new sophisticated technologies, projects of the alkali metal photoplasma application in devices for direct conversion of Solar energy into the electrical one are known (Palmer, 1977).

A certain interest for the processes of aerosol forming in conditions of geocosmos can represent and the effect of solid particles of micron size forming in collisions of optically excited alkali atoms with hydrogen (Tam et al., 1977).

The rate of the collisional ionization processes in an absorbing gaseous medium depends on the characteristics of the medium itself which are determined by its possibility to absorb and, then, to reemit radiation. As a result of joint investigations carried out in the Pisa and St. Petersburg Universities, analytical methods for solving a wide class of integro-differential equations, describing both the processes of radiation transfer in optically dense media (Bezuglov et al., 1995a, 1999b) and the processes of the valence electron transition in the set of quasi-continuous energy levels, were developed (Bezuglov et al., 1997b). Here, we will consider only the second-collisional-aspect of the general problem of energy transfer in an optically excited medium, which leads to its ionization.

Investigations of elementary ionization processes in the thermal and subthermal energy ranges have a direct relation to investigations of low-temperature photoplasma creation via optical excitation (Klyucharev and Vujnović, 1990). Any sophisticated set of equations describing a plasma medium has the right to exist only under the condition of knowledge of accurate values of the cross sections of elementary collisional processes occurring in it.

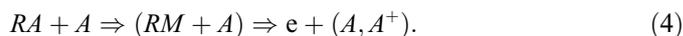
In the literature, the following gradation of temperature ranges of atomic collisions is commonly used: thermal ($T = 10^2$ – 10^3 K), subthermal or cold ($10^{-3} < T < 10^2$ K), and ultracold ($T \ll 10^{-3}$ K) collisions. Experimental investigation of ultracold collisions requires the use of special equipment for laser cooling and trapping of the particles. At the same time, the conditions for subthermal collisions can be rather easily realized in effusive atomic beams owing to the specific features of the relative velocity distribution of atoms. The existence of directed fluxes of matter in the gaseous phase, as e.g. due to effects of particle explosive vaporization provoked by radiation, is quite typical in the conditions of geocosmos.

Under the situation when the sum of the excitation energies of atoms-partners is smaller than the ionization potential of the individual atom and of thermal or subthermal energies of collisions, two main processes are known that lead to a considerable energy transfer, namely, AI and energy pooling (EP):



In process (2), practically the whole internal energy of two colliding particles is transferred to one of them. The EP-process itself is not ionization process, but it leads to the appearance of new ionization channels due to the formation of highly excited atoms. Two above-mentioned cases, (1b) and (2), imply the interaction between discrete strongly coupled atomic states (2) or between discrete states and the electron continuum (1b). Other situation can appear in the case of the AI-process

occurring via an intermediate stage – a Rydberg quasi-molecule (RM):



The RM-system with one Rydberg electron and the other strongly bound inner electron may be represented as a real model of a nonlinear system.

2. Chemi-ionization in binary collisions of atoms in low-lying excited states

2.1. Rate coefficients for binary collisions of alkali-metal atoms in the first excited resonant states

In low-temperature plasma physics, chemi-ionization processes are traditionally regarded as providing an effective channel for the production of molecular ions. This refers in the first instance to studies involving inert-gas and alkali-metal atoms in the lowest of all the possible (resonance) excited states because of their extensive applications in science and technology. Two possibilities are then found to arise.

$$\sum E^* > U_i \quad (5)$$

$$\sum E^* < U_i \quad (6)$$

where $\sum E^*$ is the total excitation energy, U_i is the ionization potential of an individual atom.

Case (5) includes the ionization of the hydrogen atoms, inert gases, the halogens, nitrogen, and oxygen, whereas case (6) includes the ionization of alkali-metals, rare-earth elements, uranium, etc.

Table 1 lists experimental results included for the first time in Saint-Petersburg University for the gas-cell conditions in 1975–1977s (Dobrolege et al., 1975; Klyucharev and Ryazanov, 1971). When the activation energy $\Delta U > 0$ the expression for the reaction rate contains the factor $\exp(-\Delta U/kT)$, which largely determines the temperature $k(T)$ function. The strong dependence on temperature of the reaction rate for the chemi-ionization (associative ionization) must be taken into account in any real condition. From the data's analysis it can be seen, that the efficacy of threshold (AI) processes depends significantly on the shape of the particle velocity distribution (Bezuglov et al., 1984). When the conditions are different, the data must be re-examined and this can only be done if we know the corresponding terms of the quasi-molecules and molecular ion. One needs the temperature dependence of the AI cross-section too.

For example, on the one hand, sodium is the most abundant of alkalis; whilst, on the other hand, newly published data are not entirely free from internal contradiction. This is so-called the “sodium paradox”.

The data in the tables are obtained without identification of the total moment values for fine structure components of $^2P_{1/2,3/2}$ term. According to Carre et al. (1981), depending on values of quantum numbers $J = 1/2, 3/2$, colliding atoms AI rate constant can change 2.5 times. We

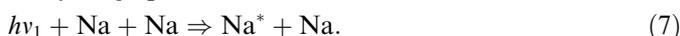
Table 1
AI rate coefficients for the process $\text{Na}(3^2\text{P}) + \text{Na}(3^2\text{P}) \Rightarrow \text{e} + \text{Na}_2^+$

Experimental conditions	Beam source temperature	Original value K ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)	Corrected value (Bezuglov et al., 1984)	Reference
Gas cell, resonant lamp	550 K	3.8 ($\pm 20\%$)	3.8	Klyucharev et al. (1977)
Single beam, laser	580 K	0.015 (factor 2)	0.03	De Iong and van der Valk (1979)
Gas cell, laser	650 K	0.56 ($\pm 40\%$)	1.1	Huennekens and Gallager (1983)
Beams crossing at 90° , laser	520 K	0.34 ($\pm 50\%$)		Carre et al. (1984)
Uncollimated single beam, laser	570 K	1.8 ($\pm 40\%$)	3.4	Bonanno et al. (1983)
Single beam, laser	“Effective temperature” $60 \times 10^{-3} \text{ K}$	6.3 + 1.8		Thorsheim et al. (1989)
Optical trap	$0.75 \times 10^{-3} \text{ K}$	11 + 1.3		Gould et al. (1988)

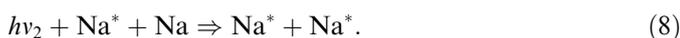
shall not discuss here the influence of polarizing effects on reaction rate coefficients since this is not so essential for the corresponding estimations in space plasma.

Note that the unexpectedly large value of K in cold collisions ($T \sim 10^{-3} \text{ K}$) may be explained in terms of the increased de Broglie wavelength at such conditions (Weiner et al., 1989).

The interesting aspect of very cold collisions between two resonantly-excited sodium atoms was discussed in Gallager (1991). It is suggested that the production of Na_2^+ ions at low light intensities can be considered as the following many stage process:



The particle pair moves in the attractive potential of quasi-molecule with the simultaneous absorption of the photon $h\nu_2$ and the associated production of a pair of resonantly excited atoms

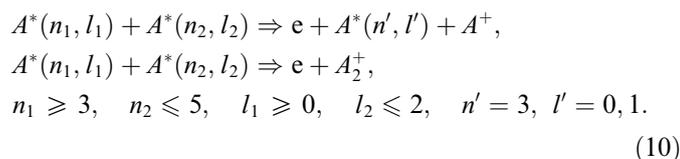


The two excited atoms interact and produce the molecular ion, namely



2.2. Ionization in binary collisions of low-lying excited atoms in states higher than the resonant one

The collisional ionization (10) in effusive beams with the participation of alkali atoms in low-lying excited states was successfully studied by the methods of high-resolution electron spectrometry (Dengel et al., 1993).



The effect of inter-configuration interaction on the efficiency of processes (10) can be neglected for the 4d4p, 4p4s, 5s5p, 5s4p, 4s4s, and 3p3d initial configurations. In Table 2 are presented the calculation data of the total ion-

Table 2
Calculated data on ionization in binary collisions of low excited sodium atoms, $E = 0.28 \times 10^{-3} \text{ eV}$ (Bezuglov et al., 1999a)

Configuration	σ_i (a.u.)	σ_i (a.u.), in the channel S-state creation	σ_i (a.u.), in the channel P-state creation
3p3d	1687	1687	
4p4s	13	13	
5s5p	135		135
5s4p	875	24	851

ization cross-section σ_i for reaction (10) for four of the above-mentioned configurations; the calculation was performed within the framework of the first-order approximation of the dipole–dipole interatomic interaction. The effect of the Cooper minimum in the photo-ionization cross sections of excited atoms on the probability of allowed dipole transitions leads to a decrease in the values for 4p4s and 5s5p configurations. The similar effect, relative to the corresponding values of the spectral line strength, results in a decrease of the magnitude of σ_i for the 5s4p states. As the limiting case, Table 2 also gives the value of σ_i calculated with the allowance made for the phenomenon of twisting. The comparison with experimental data proved to be possible only for the case of 3p3d initial configuration (Dengel et al., 1993; $\sigma_i = 0.5 \times 10^{-13} \text{ cm}^2$ – theory, and $\sigma_i = 10^{-13} \text{ cm}^2$ – experiment) because the results of measuring the cross section by electron spectroscopy methods do not give, as a rule, their absolute values. In the general case, the line strength S increasing leads to an increase in the efficiency of channel, accompanied by the appearance of slow electrons and by the population of the excited states close to the initial one.

3. Collision ionization with RA participation: symmetrical case

3.1. Ionization in Rydberg-atom–atom collisions

3.1.1. The resonant mechanism

Recently, in connection with development of basic researches in the field of interaction of radiation with the

single atoms and molecules the circle of problems in which RA play the main role was significantly enlarged. Here it is necessary to name first of all such fundamental and applied researches as laser cooling of atoms and Bose–Einstein condensation, management of the single atom states, new prospects in creation of logic devices of quantum computers, quantum teleportation, etc. All this increases interest to experimental and theoretical researches with RA participation, including the processes leading to their ionization in atom collisions. Let us note that the first results in this area have been received in 1978 (experiment Devdariani et al., 1978) and 1980 (the theory Janev and Mihajlov, 1980; Mihajlov and Janev, 1981; Duman and Shmatov, 1980) years.

Present experimental facilities on laser excitation allow to achieve the highly excited RA population compared with the normal one. Under primary selective excitation resonant atomic states the energy pooling processes may provide the RA effective population. So the high selectivity of the optical excitation in the experimental investigation with excited atoms in many cases may be treated as a “nice blue idea”. The ionization over new opened Rydberg channels takes the part on such channels.

Two ionization channels are possible in binary collisions such as (1). The first series of quantitative measurements of the rate coefficients K for (1) started in 1978 for group one elements (Devdariani et al., 1978).

Due to the interest in chemi-ionization processes, several methods of rate coefficients calculations were presented within short time. The methods developed in Janev and Mihajlov (1980), Mihajlov and Janev (1981) treated the considered RA-atom systems within the semi-classical approach, while in Duman and Shmatov (1980) an attempt at quantum-mechanical description of the internuclear motion was made. All these methods were based on the same resonant mechanism of quasi-resonant energy exchange within the electronic component of the RA-atom system. This mechanism was introduced in Smirnov and Mihajlov (1971) in connection with some inelastic processes in slow RA + A collisions.

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

$$R \ll r_n, \quad (11)$$

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

The electronic state of $A^+ + A$ 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 sub-system at $R = \infty$. In the case when A is an atom with one or two s-electrons outside closed shells ($A = \text{H, He, Li, Na, etc.}$), only two Σ^+ -states

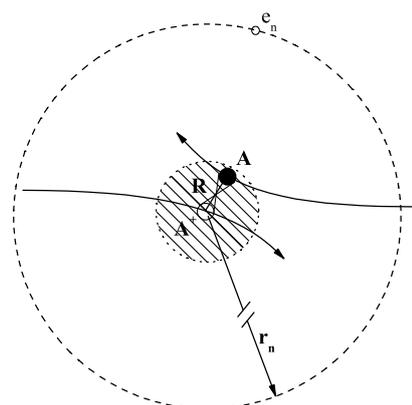


Fig. 1. Schematic illustration of RA + A collision (the region of R where the outer electron is collectivized is shaded; Ignjatović and Mihajlov, 2005).

of A_2^+ , the ground and the first excited states, compose such a group. When A is an alkali atom they are 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). The ranges of R where the energy exchange between the outer electron e_n and the electron component of the $A^+ + A$ sub-system has an almost resonant character give the main contribution to the considered inelastic process. Such ranges represent the neighborhoods of crossing-points of the potential curves for different Λ_u and Λ_g states of RA + A quasi-molecular system, which is illustrated by Fig. 2.

Until now, this resonant mechanism was used in three different approximations: two semi-classical and one quantum mechanical. The first semi-classical one, used already in Smirnov and Mihajlov (1971), understands that the relative nuclear motion occurs in some average effective

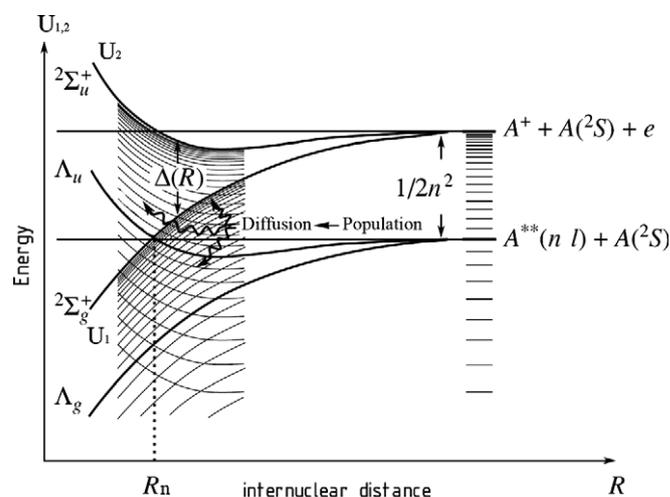


Fig. 2. Illustration of the mechanism of the RA + A collision process. $2^2\Sigma_u^+$, $2^2\Sigma_g^+$ – the ionic states, Λ_u , Λ_g – the initial quasi-molecular states. The Λ_u state crosses the ionic state at $R = R_n$.

potential along the unique trajectory. In Smirnov and Mihajlov (1971) it was shown that in such a case the dipole moment $D(R)$ of $A^+ + A$ sub-system can be represented as a known function of the time, namely

$$D(R(t)) = \frac{R(t)}{2} \cos \left[\int_{-\infty}^t \Delta E(R(\tau)) d\tau \right], \quad (12)$$

where $R(t)$ is the internuclear distance in the moment of time t , $\Delta E(R)$ is the splitting term

$$\Delta E(R) = U_2(R) - U_1(R), \quad (13)$$

and $U_1(R)$ and $U_2(R)$ are the adiabatic potentials of the ground and the first excited electronic states of the molecular ion A_2^+ . In this case the behavior of outer electron e_n is described by means of time dependent Schrödinger equation, where the perturbation is known function of the time. This approach was applied in the case of ionization processes in symmetric atom-Rydberg atom collisions in Devdariani et al. (1978).

The other semi-classical approach, developed in Janev and Mihajlov (1980), Mihajlov and Janev (1981), understands that the relative nuclear motion occurs with the probability 1/2 along the trajectory which corresponds to the potential $U_1(R)$, and with the same probability 1/2 – along the trajectory which corresponds to the potential $U_2(R)$. Consequently, such semi-classical approach should be treated as the approximation of two classical trajectories. In the case of ionization processes the initial electronic state of the sub-system $A^+ + A$ is the first excited $^2\Sigma_u^+$ -state. Accordingly, the trajectory which corresponds to the potential $U_2(R)$ is relevant in this case, and the ionization process is treated as the result of the transition of the sub-system $A^+ + A$ from $^2\Sigma_u^+$ to $^2\Sigma_g^+$ -state together with the transition of outer electron e_n from the considered Rydberg state to continuum.

The third approach, applied in Duman and Shmatov (1980), understands that the relative nuclear motion is treated in quantum mechanical way, by means of superposition of two adiabatic nuclear wave functions which describe the motion in the potentials $U_1(R)$ and $U_2(R)$, separately. The ionization process is treated similarly as in the second semi-classical approximation.

Authors (Duman and Shmatov, 1980) represent unique attempt to describe processes (1) along with the quantum-mechanical treatment of the internuclear motion with an additional assumption about the possibility of smearing ro-vibrational spectrum of molecular ion A_2^+ . Here we will not discuss this method because it was applied only to the processes (1) with $A = Cs$. The first theoretical results obtained within the framework of semi-classical method (Janev and Mihajlov, 1980; Mihajlov and Janev, 1981) and quantum mechanical one (Duman and Shmatov, 1980) was in a good agreement with the experiment.

The theoretical results based on two last approaches (Janev and Mihajlov, 1980; Mihajlov and Janev, 1981; Duman and Shmatov, 1980) are called in the literature as the DSMJ model (the abbreviation consists of the first let-

ters of the author names). The further development and improvement of the theory was connected to the hydrogen and helium atom cases and their application in astrophysics (see e.g. Mihajlov et al., 1992, 1996, 1997, 1999, 2003a,b). However there was a permanent interest in the processes (1) involving atoms of alkali metals (Boulmer et al., 1983; Zagrebin and Samson, 1985; Weiner and Boulmer, 1986; Bezuglov et al., 1997b).

The experimental and theoretical results obtained in the world laboratories till today concerning AI and PI processes including RA have been discussed in the literature repeatedly ever since. For example effect of decay of the initial electronic state during $A^{**}(n) + A$ collision, using of approximate analytical expressions for the adiabatic potential curves $U_1(R)$ and $U_2(R)$, see Fig. 3; decoupling the RE motion from the internuclear one, and correctness of the unique straight line approximation to the particles motion, were discussed. For that reasons it was necessary to return again to the chemi-ionization in the alkali atoms case.

Now will be considered the results obtained with authors participation in last time (Ignjatović and Mihajlov, 2005; Miculis et al., 2005; Beterov et al., 2005) namely the chemi-ionization rate coefficients obtained taking into account results for the RA for principal quantum numbers $5 \leq n \leq 25$, where there is no crossing of the systems $A^{**}(n) + A$ and $A^+ + A^-$, where A^- denotes a stable negative ion.

3.1.2. The stochastic dynamics approach: the unique trajectory model

The first results on the investigation of chemi-ionization in RA -atom collisions are summarized in Klucharev and Lazarenko (1980). The more substantial disadvantage of such work was the neglecting of the large number of crossings of the initial ion term U_2 . In the case of multiple crossing of terms, the attempt to take into account each particular crossing in theoretical approaches traditional

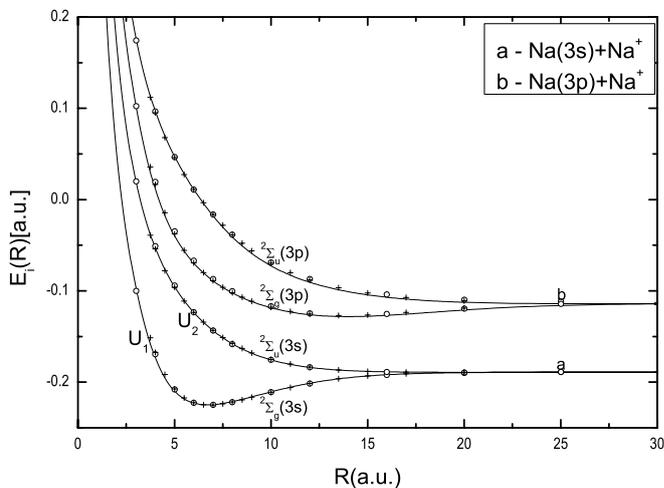


Fig. 3. The adiabatic potential curves of molecular ion Na_2^+ (Ignjatović and Mihajlov, 2005): (a) $Na(3s) + Na^+$, (b) $Na(3p) + Na^+$.

for atom collision physics does not lead to any kind of general results. Namely, the Rydberg electron (*RE*) energy change occurring for each of the multiple crossing of the terms is $\delta E \leq 1/n^3$, so that $\delta E/E_n \sim 1/n \ll 1$, where $E_n = 0.5/n_2$ is the binding energy of *RA*. This lead to the idea of the possibility of a diffusion approach to solution of the atomic collisions problem with *RA* participation, having in mind diffusion over the energy states of the quasi-molecule in one collision event (Devdariani et al., 1988). Unfortunately, the proposed model was largely qualitative: no actual physic process causing the *RE* to diffuse was suggested.

Note that the idea that the *RE* diffuses over the discrete energy spectrum of *RA* was successfully used earlier in Delone et al. (1983) to interpret anomalously high photo-ionization cross sections in experiments on laser irradiation of gases (see also Koch and Leeuwen, 1995). This logically suggests that for the ionization of the considered *RA*, the quasi-monochromatic electric field formed by charge transfer can also cause *RE* to diffuse over the discrete electronic spectrum, a process that can result in the “smearing” of the position of point R_i .

The latest stochastic version of chemi-ionization on *RA*-atom collisions extends the treatments of the DSMJ model by taking into account redistribution of population over a range of Rydberg states prior to ionization. That redistribution is modelled as diffusion of the *RE* in the Rydberg energy spectrum using a Fokker–Plank–Kolmogorov type equation (FPK).

The first obtained results give the reasons to believe that, during a single slow collision, the motion of the *RE* experiences the action of internal nonlinear dynamic resonances that arise due to the coincidence of the overtones of the *RE* motion over the Keplerian orbit with the frequency of the inner electron transfer. As a result, the motion of the *RE* becomes unstable. In this case, the transitions of the *RE* acquire the character of random walks over the network of crossing potential energy curves, thereby admitting a kinetic description of the time evolution of the distribution $f(n, t)$ of the *RE*.

The process of *l*-mixing of Rydberg states at large inter-nuclear distances and twisting of the collision trajectories on attractive potential $U_2(R)$ have been taken into account too (Ignjatović and Mihajlov, 2005; Miculis et al., 2005; Beterov et al., 2005).

3.1.2.1. Model of stochastic diffusion. Stochastic dynamics describe the random walk of *RE* within the hydrogen like discrete energy spectrum caused by the coupling of *RE* with internal electrical field ($E(t)$). The initial covalent Λ_u state crosses the ionic ${}^2\Sigma_g^+$ state at $R = R_n$, becoming auto-ionizing for $R = R_n$.

3.1.2.1.1. Characteristic times

- (1) Inter-nuclear distance $R(t)$ depends on time according to collision dynamics of the system.
- (2) Factorization of FPK (with respect to R and n) means introduction of an “effective time” t_{eff} .

- (3) Total effective time t_{tot} for the collision event with fixed ρ means time spent while $R(t)$ goes from $R = \infty$ to turning point R_{turn} .
- (4) Average effective diffusion time (t_{eff}): the average time $t_{\text{diff}}(n_0, \rho)$ for the *RE* to diffuse from n_0^* level to the ionization limit determined from steady-state solution of FPK.

3.1.2.1.2. Diffusion equation. *RE* perturbation by internal electrical field $E(t)$ causes appearance of auto-ionization width $W(n_{\text{eff}}, R)$ of terms and can lead to dynamics chaos regime of classic trajectories. Stochastic motion of *RE* in energy space is described by (FPK) diffusion equation for the distribution function $f(n_{\text{eff}}, t)$:

3.1.2.1.3. Area of dynamics chaos regime. Stochastic diffusion of *RE* in energy space is based on Chirikov criteria (Chirikov, 1979) with Kepler mapping.

- (1) Restrictions on the random motion (“lower limit”): The diffusion is forbidden in the energy region $n_{\text{eff}} < N_{\text{min}}(R)$, because energy difference between the neighboring levels becomes too large.
- (2) Restriction on random motion (“upper limit”): Chirikov criteria for global chaos onset breaks down.

The ionization occurs whenever *RE* enters levels $n_{\text{eff}} > N_{\text{max}}(R)$ where the direct quantum photo-ionization channel becomes open and the corresponding auto-ionization width $W(n_{\text{eff}}, R)$ is expressed via the photo-ionization cross-section σ_{ph} . Important key-point for the stochastic diffusion processes: long collision times. It makes the model suitable for future application to treat collisions between cold atoms.

3.1.3. The decay approximation: the two-trajectories model

The processes (1) are treated here as a result of decay of the initial electronic state of the system $A^{**} + A$, caused by the resonant mechanism along a part of the relevant trajectory determined in the potential $U_2(R)$ by the impact-parameter ρ and the impact-energy E . In Janev and Mihajlov (1980) it was shown that the corresponding decay rate is given by expression

$$W_n(R) = \frac{4}{3\sqrt{3}n_{\text{eff}}^5} D_{12}^2(R) G_{nk}, \tag{14}$$

where $D_{12}(R)$ is module of the dipole matrix element for the electronic transition from the ground to the first excited state of the molecular ion Na_2^+ , and G_{nk} denotes the generalized Gaunt factor, defined by the expression

$$G_{nk} = \frac{\sigma_{\text{ph}}(n, k)}{\sigma_{\text{ph}}^{\text{Kr}}(n, k)}, \tag{15}$$

where $\sigma_{\text{ph}}(n, k)$ is the photo-ionization cross section of the atom $A^{**}(n)$ with transition of the outer electron to the state with the energy ϵ_k , and $\sigma_{\text{ph}}^{\text{Kr}}(n, k)$ denotes the same photo-ionization cross section in Kramers’s approximation.

According to (Janev and Mihajlov, 1980), the chemi-ionization processes at given ρ and E can be characterized by the ionization probability $P_{ci}(t, n, \rho, E) = (1/2)P_d(t, n, \rho, E)$, where the probability $P_d(t)$ is defined as the solution of the equation

$$\frac{dP_d(t)}{dt} = [1 - P_d(t)] \cdot W_n(R(t)), \quad P_d(t = t_{in}) = 0 \quad (16)$$

namely

$$P_d(t) = 1 - \exp \left[- \int_{t_{in}}^t W_n(R(t')) dt' \right], \quad (17)$$

where t_{in} is the moment, when the distance R between Na^+ and Na becomes smaller than R_n .

In Mihajlov and Janev (1981) it was taken that the factor $[1 - P_d(t)]$ in (16) may be replaced by 1, so that the decay of the initial electronic state of the atom-Rydberg atom system observed during the collision was neglected. This approximation was justified in the case of chemi-ionization processes (1) with $A = \text{H}$ and He . However, in the case of alkali metal atoms the mentioned decay had to be taken into account. Because of that, in Mihajlov and Janev (1981) was necessary to make a posteriori calculation. It required an additional parameter which could not be properly determined within the method used in Mihajlov and Janev (1981). For that reason we shall follow the basic work in Janev and Mihajlov (1980), and use (16) here without the above simplification.

Using the probability $P_{ci}(t = t_{fin}, n, \rho, E)$, where t_{fin} is the moment, when the distance R between Na^+ and Na becomes larger than R_n , one determines the cross sections for the chemi-ionization processes (1)

$$\sigma_{ci}(n, E) = 2\pi \int_0^{\rho_{\max}(E)} P_{ci}(t_{fin}, n, \rho, E) \rho d\rho, \quad (18)$$

where $\rho_{\max}(E)$ is the upper limit of values ρ at which the corresponding region R is reached for a given E . Rate coefficients for processes (1) are determined thereafter by the expressions

$$K_{ci}(n, T) = \int_{E_{\min}(n)}^{\infty} \sigma_{ci}(n, E) F(v_c; T) dv_c, \quad (19)$$

where v_c is the impact velocity, corresponding to the given E , $E_{\min}(n) = 0$ if $U_2(R_n) \leq 0$, and $E_{\min}(n) = U_2(R_n)$ if $U_2(R_n) > 0$, $F(v_c, T)$ is the velocity distribution function at a given temperature T which is different in cells, single beams and crossed beams cases (see e.g. Bezuglov et al., 1987; Wang and Weiner, 1987; Bezuglov et al., 1989 and Fig. 4). Finally, taking $K_{ci}(n, T)$, in the form

$$K_{ci}(n, T) = K_{ci}^{(a)}(n, T) + K_{ci}^{(b)}(n, T), \quad (20)$$

where $K^{(a)}$ and $K^{(b)}$ are partial rate coefficients for the processes (1), we will also characterize these processes by the branch coefficients

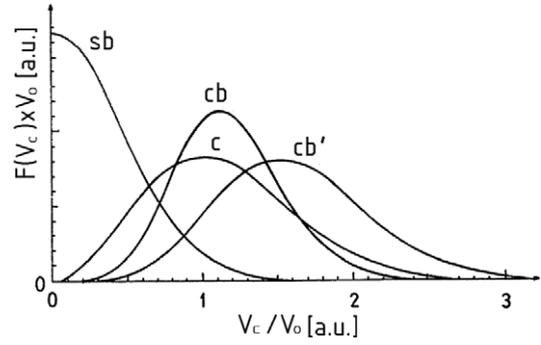


Fig. 4. Distribution function $F(v_c, T)$ of relative velocity v_c of short-living excited and normal atoms of the same mass M in a crossed beam (cb), counter beam (cb') and gas cell (c); $T_{sb} = T_{cb} = T_{cb'} = T_c$, T – represent the gas temperature in the beam sources and cell. The characteristic thermal velocity is $v_0 = \sqrt{kT/M}$ (Klyucharev and Vujnović, 1990).

$$X^{(a,b)}(n, T) = \frac{K_{ci}^{(a,b)}(n, T)}{K_{ci}(n, T)}, \quad X^{(a)}(n, T) + X^{(b)}(n, T) \equiv 1. \quad (21)$$

The determination of the partial rate coefficients $K_{ci}^{(a,b)}(n, T)$ is made in a similar way as $K_{ci}(n, T)$, i.e. by Eqs. (16)–(19), with the corresponding initial conditions (see Ignjatović and Mihajlov, 2005).

3.1.4. The comparison of the experimental and theoretical results

In the recent works (Ignjatović and Mihajlov, 2005; Miculis et al., 2005; Beterov et al., 2005), the results of the systematic experimental and theoretical studies of chemi-ionization of sodium RA in n^2S , n^2P , n^2D states with $n_{\text{eff}} = 5-25$ in symmetrical collisions with ground-state atoms have been presented.

The shapes of experimental dependencies of AI rate coefficients on the effective quantum number exhibit a broad maximum near $n_{\text{eff}} \approx 10$. Note that such peculiar $K(n_{\text{eff}})$ dependence was observed in the first work of such kind for RA (n^2P)– A collisions (Klyucharev and Vujnović, 1990) (See Figs. 5–12).

The experimental absolute values of the rate coefficients are close to the theoretical calculation results for 2P and 2D states, but not for 2S states (see Fig. 9).

From (Miculis et al., 2005; Beterov et al., 2005) comparison with experimental results it follows that stochastic diffusion model requires a further development in order to account for possible correlation effects between electronic and nuclear degrees of freedom in slow atomic collisions.

Strictly speaking in the experimental crossed beams conditions the resulting Na_2^+ signal is described by a sum of the respective AI rate constants

$$K_{AI}^{(\Sigma)} = K_{AI}^{(\text{sb})} + K_{AI}^{(\text{cb})} \quad (22)$$

with considerably different relative collision velocity distribution. In this relation K_{AI}^{cb} is the pure crossed beam AI rate constant which describes only the collisions between atoms

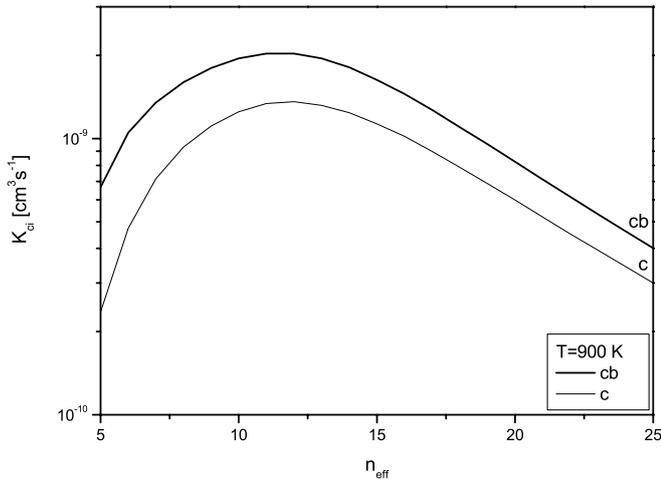


Fig. 5. The total rate coefficients K_{ci} for chemi-ionization in $\text{Na}^*(n_{\text{eff}}^2\text{P}) + \text{Na}$ collision theory, within the semi-classical approach (Ignjatović and Mihajlov, 2005). The curves K_{ci} correspond to the crossing beams (cb) and the cell conditions (c), T – the beam sources or the gas cell temperature respectively, $T = 900$ K.

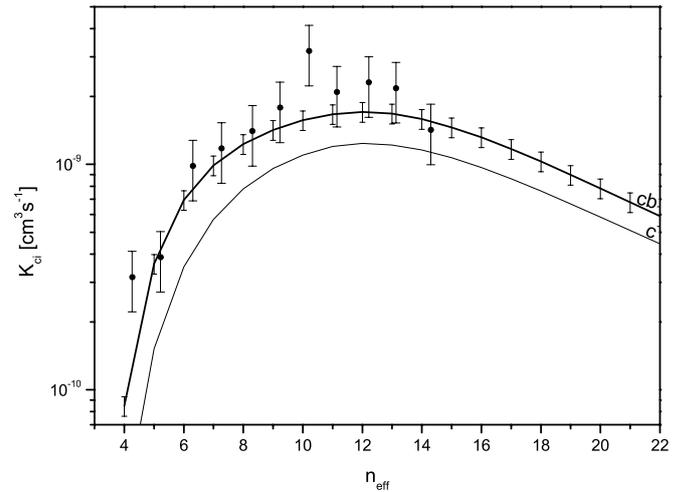


Fig. 7. The associative ionization rate coefficients for chemi-ionization in $\text{Na}^*(n_{\text{eff}}^2\text{P}) + \text{Na}$ collisions; dots: cb-conditions, $T = 600$ K, associative ionization experiment (Boulmer et al., 1983) the full curve: cb ($T = 600$ K), $c = \text{cell}$ ($T = 720$ K), theory (Ignjatović and Mihajlov, 2005).

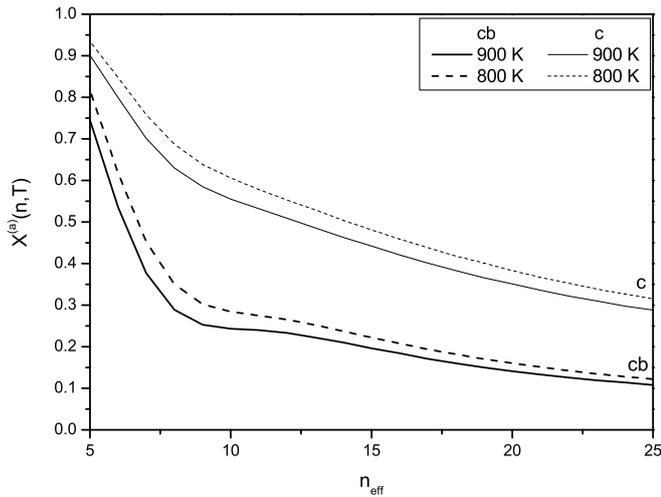


Fig. 6. The branch coefficients $X^{(a)}(n_{\text{eff}}, T)$ for chemi-ionization in $\text{Na}^*(n_{\text{eff}}^2\text{P}) + \text{Na}$ collisions. The main designations are the same as on the previous figure, $T = 900$ K, the dotted line, $T = 800$ K (Ignjatović and Mihajlov, 2005).

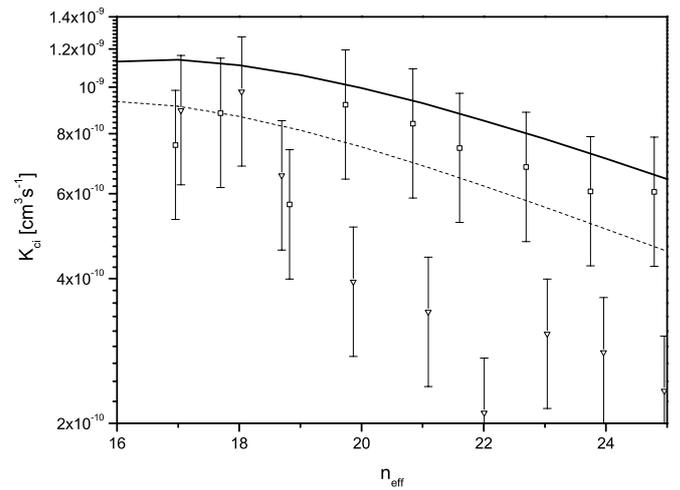


Fig. 8. The K_{ci} rate coefficients for chemi-ionization in $\text{Na}^*(n_{\text{eff}}, l) + \text{Na}$ single beam's collisions at $T = 1000$ K. The full and broken curves are the semi-classical theory results for $l = 0$ and $l = 2, 3$, respectively (Ignjatović and Mihajlov, 2005); open square – experiment, associative ionization, for $l = 0$; open triangle – experiment, associative ionization, for $l = 2$ (Weiner and Boulmer, 1986).

belonging to different beams and K_{AI}^{sb} applies to collisions with atoms from the same beam. The extraction of pure crossed beam rate constant K_{AI}^{cb} was performed in Beterov et al. (2005) for $n^2\text{S}$ and $n^2\text{D}$ states.

The experimental dependencies of K_{AI}^{Σ} and K_{AI}^{cb} on n_{eff} from (Beterov et al., 2005) are presented in Fig. 11 ($8 < n_{\text{eff}} < 18$). They have similar shapes but the absolute values of K_{AI}^{Σ} are about two time larger than K_{AI}^{cb} . These dependencies have a wide maximum at $n_{\text{eff}} = 8-16$ and a more narrow one at $n_{\text{eff}} = 11-14$ for $n^2\text{S}$ states. The figure presents the results of theoretical ionization model. Note that in the widely known publication (Boulmer et al., 1983) cited above, the total K_{AI}^{Σ} was only presented.

Fig. 12 shows the comparison of the experimental values $K_{AI}^{\Sigma}(l, n_{\text{eff}})$ in crossed beams for $n^2\text{S}$, $n^2\text{P}$ and $n^2\text{D}$ states.

Note that experimental K_{AI} dependencies on n_{eff} in two ranges of n_{eff} : $8 < n_{\text{eff}} < 18$ (crossed beam Boulmer et al., 1983) and $n_{\text{eff}} > 18$ (single beam Weiner and Boulmer, 1986) for $n^2\text{S}$ and $n^2\text{D}$ states are turned out on their absolute values. That unexpected results require a further elaboration.

3.2. Ionization in binary Rydberg-atom collisions

Let us briefly look at the ionization processes in two RA collisions.

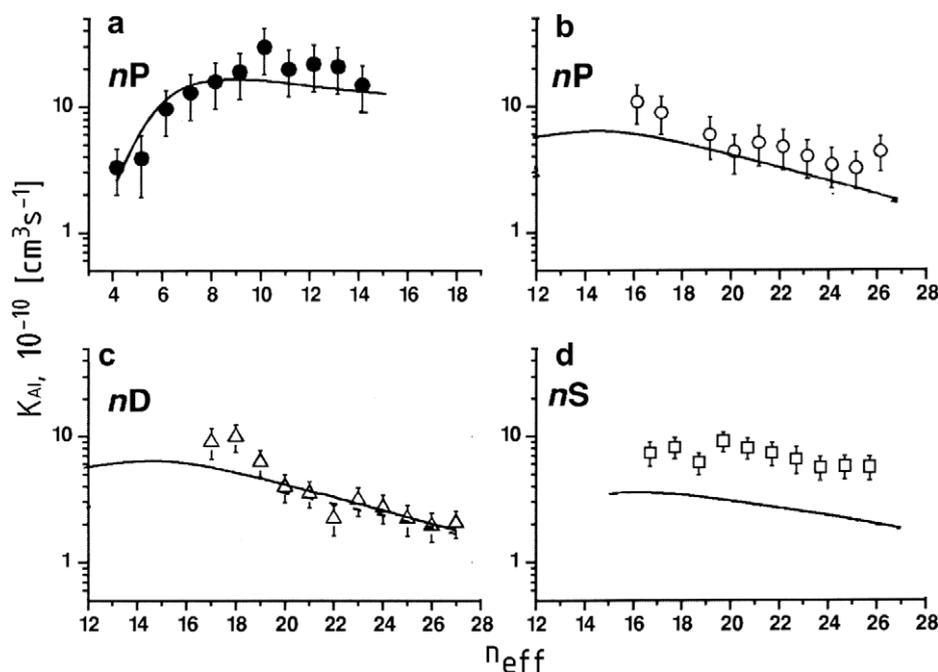


Fig. 9. Experimental and theoretical $\text{Na}^*(n_{\text{eff}}, l) + \text{Na}$ AI rate coefficients. (a) dots – cb conditions, $l = 1$, $T = 600$ K (Boulmer et al., 1983); (b) open circle, sb-conditions, $l = 1$, $T = 1000$ K (Weiner and Boulmer, 1986); (c) open triangle, sb-conditions, $l = 2$, $T = 1000$ K (Weiner and Boulmer, 1986); (d) open square, sb-conditions, $l = 0$, $T = 1000$ K (Weiner and Boulmer, 1986) full curves – theory, stochastic theory results (Miculis et al., 2005).

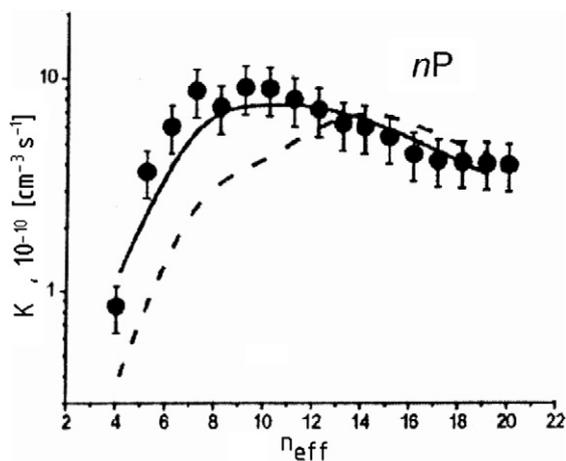


Fig. 10. Experimental and theoretical chemi-ionization rate coefficients in sb-conditions: dots – the experimental results (Zagrebin and Samson, 1985) obtained under non-accurate quantitative spectrometric identification of the ions mass and possibly poor atom collimation (Miculis et al., 2005), broken curve – AI stochastic model results, obtained with non-corrected (Zagrebin and Samson, 1985) collision velocity distribution; full curve – AI stochastic model results with velocity distribution correction (Miculis et al., 2005).



In such processes, the total energy of two RA exceeds the ionization potential U_i of the individual atom. Therefore, as a result of binary RA collisions, the ionization-stable

covalent atomic configurations (RA, RA) are converted into the Σ, Π, Δ , etc. auto-ionization states of the quasi-molecule which may decay into the positive ion A^+ and the excited atom A^* with a transition to low-lying states whose excitation energy is smaller than the energy of the initial RA state. Unfortunately, ionization in collisions of two Rydberg atoms is still the insufficiently studied field of atomic collision physics.

As a result of the non-adiabatic interaction of the initial $RA-RA$ configuration with the neighboring ones, including unstable configurations, additional ionization channels are opened, such as the ionization through intermediate states and the formation of a pair consisting of the excited negative ion (A^*) in the auto-ionization state and the positive ion A^+ ; in addition, the initial states can also change without ionization. Despite the fact that stable negative ions A^- were experimentally detected in the output channel of the reactions, the process (23) is the main ionization channel (Olson, 1979).

In calculating the total auto-ionization width, of a Rydberg quasi-molecule with respect to PI channels in Bezuglov et al. (1995b), was used the first-order perturbation theory of the interatomic dipole-dipole interaction and the straight-line trajectory approximation. The role of this long-range interaction noticeably increases in the range of cold velocities. The above-mentioned conditions imply that the collisions with the impact parameters, larger than the sum of the Bohr radii of the colliding particles (equal to $4n^2$), make the main contribution to the ionization. In the case of alkali atoms, the presence of the quantum defect significantly influences the value of σ_i because it leads to a

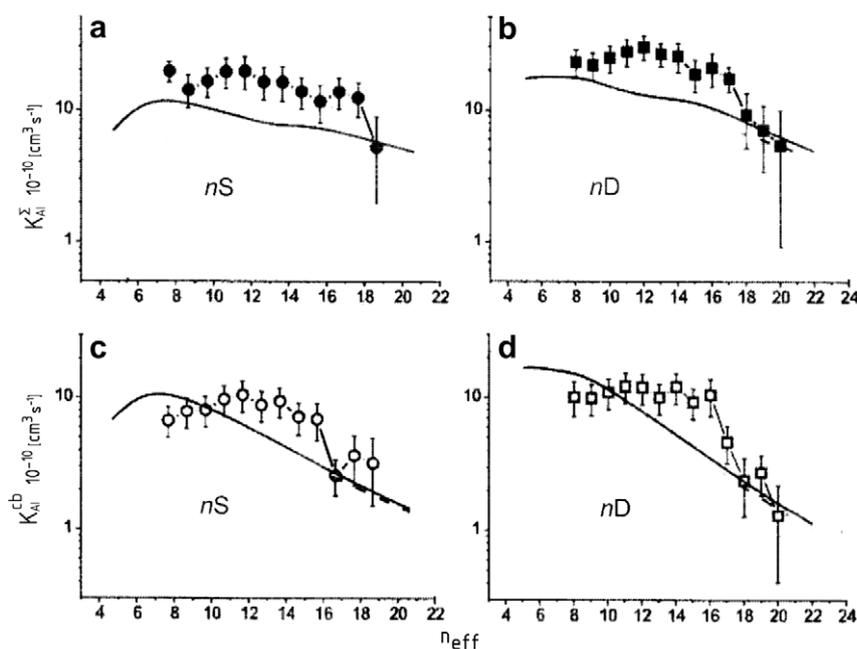


Fig. 11. Experimental and theoretical $\text{Na}^*(n_{\text{eff}}, l) + \text{Na}$ AI rate coefficients $8 \leq n_{\text{eff}} \leq 18$ for cb conditions, $T = 600$ K. Dots, open circle, open and full square experiment, full curves – stochastic theory results (Beterov et al., 2005). (a) $K_{AI}^{\Sigma}, l = 0$; (b) $K_{AI}^{\Sigma}, l = 2$; (c) $K_{AI}^{\text{cb}}, l = 0$; (d) $K_{AI}^{\text{cb}}, l = 2$.

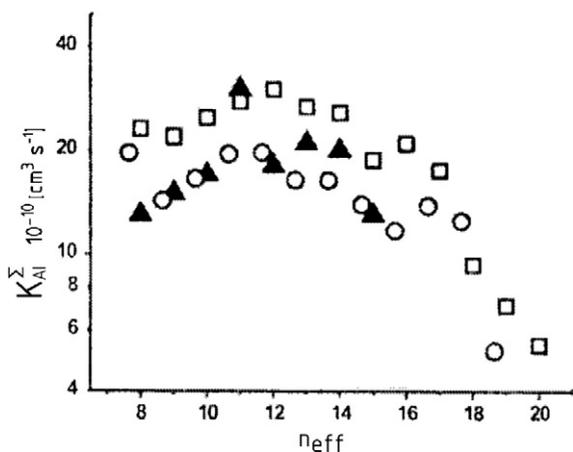


Fig. 12. Comparison of AI rate coefficients K_{AI}^{Σ} for $n^2\text{S}$ (open circles) $n^2\text{D}$ (open squares) states measured in cb-conditions $8 \leq n_{\text{eff}} \leq 18$, $T = 600$ K (Beterov et al., 2005) with the experimental results for $n^2\text{P}$ states (solid triangles) obtained in Boulmer et al. (1983).

difference of the electrostatic field close to the ion core from the pure Coulomb field. Within the framework of the model in Bezuglov et al. (1995b) have been calculated the cross sections of process for symmetric collisions of the first-group atoms H, Li, Rb (Figs. 13–15). The expression for σ_i averaged over the values of the orbital angular momentum $L < n$ and integrated over all the low states $n''A^*$ with $n'' < n/\sqrt{2}$ has the form:

$$\sigma_i = 23.6v^{-2}n^{-8}. \quad (24)$$

Because of the mixing of the nearest atomic configuration in the PI process, the population of the states can occur with violation of the selection rules for optically allowed

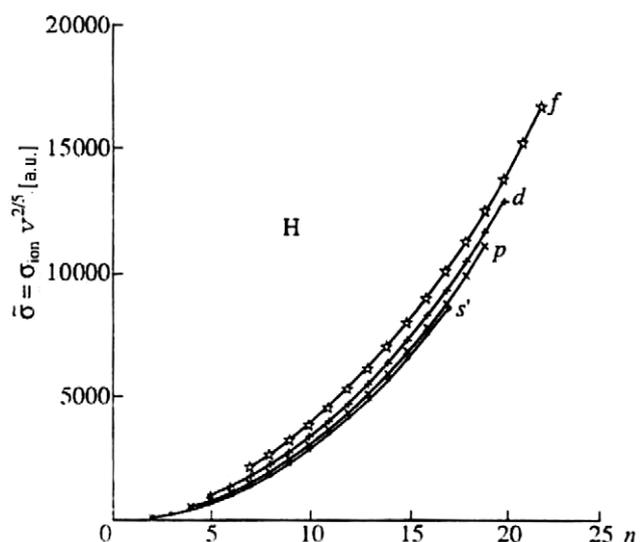


Fig. 13. PI ionization cross-section in the pair collisions of Rydberg hydrogen atom in the s, p, d and f states vs. principal quantum number (calculation) (Bezuglov et al., 1995b).

transitions. So, even in the case of the initial selective population of two highly excited $n^2\text{P}$ states, the population of the lower-lying $n'^2\text{P}$ states ($n' < n$) via the intermediate ($S + S$) configuration is also possible (Bezuglov et al., 1997a).

In McGeoch et al. (1988) RA Penning-type ionization in $Li^{**} + Li^*$ collisions was considered in another way using a classical trajectory Monte-Carlo method (CTMC). It has been noted that at low collision velocities CTMC method greatly overestimated the cross sections (Olson, 1979).

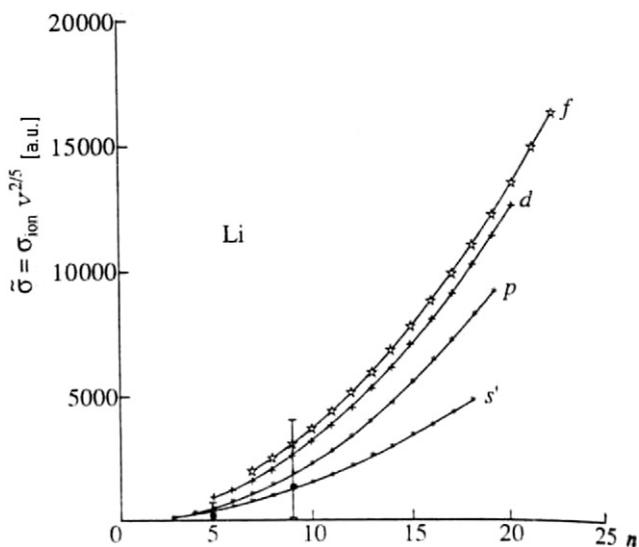


Fig. 14. The same as in Fig. 13, but for the lithium atoms (Borodin et al., 1995). The experimental point corresponds to the cb conditions with the n^2P states, $T = 1090$ K and molecular channel of the ionization (McGeoch et al., 1988).

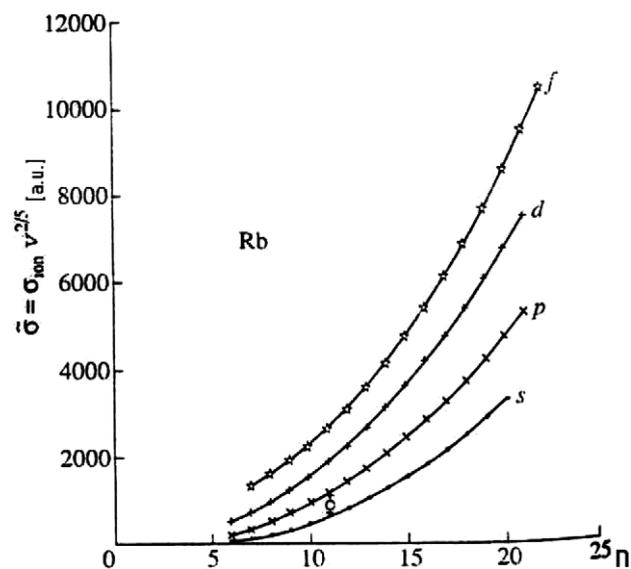


Fig. 15. The same as in Fig. 12, but for the rubidium atoms. The experimental point corresponds to the single beam experiment with the n^2P states $T = 380$ K and Rb_2^+ creation (Borodin et al., 1995).

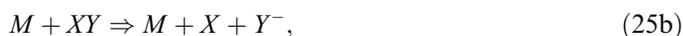
4. Collision ionization with Rydberg atom participation (non-symmetrical collision)

4.1. Rydberg atom collisions with molecules

Note that it would expect high enrichment of alkali and halogen elements in volcanic gases on Io, so that the abundances of Na and Cl in Io's atmosphere may be compared (Schaefer and Fegley, 2005). Appreciable cross section (10^{-14} – 10^{-15} cm²) for thermal collisions between a metal atom (M) and a homo-nuclear (X_2) or

hetero-nuclear (XY) halogen molecule was first noted in 1930s.

Chemi-ionization processes in atom-molecule collisions are usually multi-channel phenomena:



The cross section for the production of an ion pair depends on the degree of excitation of halogen-containing molecules and alkali metal atoms. For halogen-containing molecules, characterized by high rate coefficients ($K \approx 10^{-7}$ cm³ s⁻¹, SF₆), the negative-ion yield in thermal collisions with RA is determined by the RE attachment probability. This follows from the theory and is confirmed by measurements of the ionization rate constants for RA with $n = 20$ – 100 in collisions with halogenides.

Table 3 lists the ionization rate coefficients and cross sections for collisions between $4^2D_{5/2}$ ($E_1^* = 0.86$ eV) or $5^2S_{1/2}$ ($E_1^* = 1.02$ eV) sodium atoms, and halogen containing molecules for sodium beam-source temperature $T = 600$ K.

The cross section for the production of an ion pair was found in Moutinho et al. (1971) to be a function of the degree of vibrational excitation of halogen-containing molecules colliding with alkali-metal atoms. For the $RA + SF_6 \Rightarrow A^+ + SF_6^-$ reaction, the cross section is inversely proportional to the orbital velocity of the electron in its highly excited state: $\sigma(v) = (4.2 \pm 1.0) \times 10^{-7}/v$. Since the Rydberg states of all atoms are similar, an analogous result is also obtained for xenon RA . As the principal quantum number is varied in the range $n = 23$ – 106 , the RA chemi-ionization rate constant for collisions with SF₆ is found to lie in the range 4×10^{-7} – 4.5×10^{-7} cm³ s⁻¹ and is practically independent of n .

In Beterov et al. (1987) it was found that the ionization data of n^2P Rydberg atoms of sodium ($n = 24$ – 32) in collisions with SF₆ molecules have a reasonable agreement with previously published data for Xe(nF) ($n = 25$ – 40), Rb(nS) ($n = 49$ – 62), and Rb(nD) ($n = 38$ – 106). An interesting new result is that there is a systematic discrepancy between the rate constants measured in experiments on the attachment of slow electrons to molecules, on the one hand, and the chemi-ionization measurements on RA , on the other. For other complex molecules, K either increases with increasing n (CCl₄, CCl₃F, CH₃I) or decreases (C₇F₁₄). The detailed dependence of σ on n is determined by the properties of the scattering of ultra-slow RE by molecules. Associative and Penning ionization in collisions between potassium atoms in metastable autoionizing states and D₂, NO, N₂, CO, CO₂, N₂O, H₂O, and H₂S molecules was investigated semi-quantitatively in Moutinho et al. (1971). According to these data, the Penning ionization cross sections are of the order of 10^{-15} cm².

The published data clearly illustrate the basic difficulties encountered when attempts are made to construct universal models of chemi-ionization in a wide range of values of n

Table 3

Rate coefficients for chemi-ionization at thermal energies in collision of sodium atoms in $4^2D_{5/2}$ or $5^2S_{1/2}$ states and halogen-containing molecules, $T = 600$ K (Beterov et al., 1982, 1983)

	Atom, molecule	K (10^{-10} cm ³ s ⁻¹)	σ (10^{-13} cm ²)	Resulting negative ions
1	Na(4^2D), SF ₆	2.8 ± 0.8	1.6 ^(*) , 4.6	SF ₆ ⁻
2	Na(4^2D), CH ₃ Br	0.35 ± 0.1	8.4, 2.5	Br ⁻
3	Na(4^2D), CCl ₂ F ₂	0.54 ± 0.2	2.84	23%Cl ₂ ⁻ + 77% Cl ⁻ or F ₂ ⁻
4	Na(4^2D), C ₆ F ₆	0.08 ± 0.03	1.2×10^{-4}	C ₆ F ₆ ⁻
5	Na(4^2D), C ₆ F ₅ H	0.18 ± 0.06	2.7×10^{-4}	
6	Na(4^2D), CH ₃ I	2.1 ± 0.6		I ⁻
7	Na(5^2S), O ₂	0.13 ± 0.04		O ₂ ⁻
8	Na(5^2S), SF ₆	0.16 ± 0.05		SF ₆ ⁻

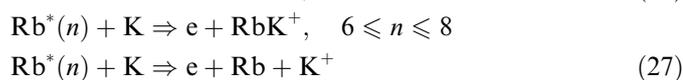
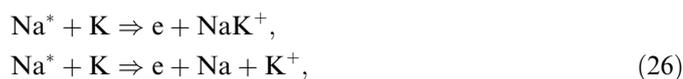
(*) Reactions 1–4 and 7 are endothermic so that the value is based on E_a used in the analysis of measured reaction rates.

even for a given atom. The high rate constants for the production of the SF₆⁻ ions are due to the fact that this ion appears in a long-lived excited state with lifetime $\tau > 0.001$ s. A different situation arises for the intermediate states in collisions between the alkali metals and O₂ molecules: the lifetime of the resulting (O₂)^{*} ion is very short ($t_{\text{eff}} \sim 10^{-9}$ s) and, in the absence of a stabilizing mechanism, we have electron autodetachment (Walter et al., 1986). The interaction with the ion core of the Rydberg atom can serve as a stabilizing factor. If stabilization is less effective for smaller n , then, in contrast to, the above case of collisions with SF₆, the rate constant K for O₂ should decrease with n . This may be the explanation of the low value of K (10^{-12} cm³ s⁻¹) and the reduction in K with increasing n ($8 \leq n \leq 12$) reported in Dunning and Stebbings (1983).

Ionization cross section for RA colliding with dipolar molecules such as H₂O, NH₃, SO₂, C₂H₅OH, and CH₃NO₂ are given in Dunning and Stebbings (1983) and Smirnov (1982). For $n > 30$, the corresponding rate constants tend to their asymptotic limit (10^{-6} cm³ s⁻¹, H₂O, NH₃).

4.2. Non-symmetrical atom–atom chemi-ionization processes

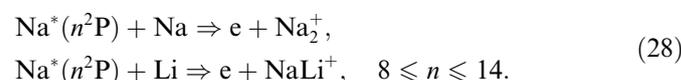
In Klyucharev and Lazarenko (1980), under the optical excitation of the excited potassium vapors, ionization with n^2P excited sodium atoms $4 \leq n \leq 7$ has been registered. Sodium was presented in potassium vapor as a slight admixture less than one per cent. Excited n^2P sodium states with $n = 5$ are situated beyond the potassium ionization threshold. That makes it possible to assume the non-symmetrical ionization process:



exceeds 10^{-10} cm³ s⁻¹.

In Harth et al. (1986), AI cross-sections during $\text{Ne}^*(nS, nD) + \text{He}$ collisions yielding HeNe^+ ions have been measured. In the cross-sections maximum closes to $n_{\text{eff}} \sim 10$ the AI cross-section in the case $\text{Ne}^* + \text{He}$ collisions about twenty times smaller than in the symmetrical $\text{Ne}^* + \text{Ne}$ one.

At last in Jonsson et al. (1988) non-direct experimental estimations have been performed to evaluate the production rate of homo- and heteronuclear molecular ions Na_2^+ – K_1 and $\text{NaLi} - K_2$ in AI reactions:



The obtained result shows that the ratio K_1/K_2 is less than unity.

It appears as the immediate task to work up on the theoretical models for very important in the weakly ionized gas media's conditions, non-symmetrical chemi-ionization processes involving two different atoms.

5. Photoplasma

The investigation of elementary processes at slow particle energies is closely related to the investigation of low temperature plasmas (LTP). A sophisticated system of equations describing such plasma states is useful only with the accurate knowledge of the rate coefficients of the elementary processes. Many scientific and technological today problems have promising solution in LTP with alkali atoms.

For instance, the optically stimulated alkali plasma is one of the promising tools for the development of ecologically clean devices for direct transformation of light energy to electric one in upper atmosphere (Palmer, 1977).

Chemi-ionization processes are responsible for the formation of LPT when an absorbing medium is optically excited by the light of an intensity which is neither sufficient for the multi-photon transitions neither for stimulated radiation, nor has photons capable to ionize the medium in a direct photo-ionization process. In the first experiment to report a new physical phenomenon so called “photoplasma” or “photoresonant plasma” a quasistationary plasma was observed with $N_e = 10^{12}$ cm⁻³ after cesium vapor was illuminated with light from alkali gas discharged lamp (Morgulis et al., 1967).

Calculations show that for alkali-metal vapor with $10^{15} \leq N_0 \leq 10^{17}$ cm⁻³ and light illumination of $10^5 \leq I \leq 10^6$ W cm⁻² (line width about 0.05 nm), AI is the dominant source of primary electrons in Na.

Scheme (see Fig. 16) illustrates possible mechanisms for the evolution of photoplasma during absorption of resonant radiation. Here are included 1 – optical excitation of the resonant atomic states, 2 – energy pooling processes, 3 – *AI* in binary resonant excited atom collisions, 4 – collisional production of negative and positive ion pair, 5, 6 – *AI* and *PI* processes with *RA*, correspondingly, 7 – the collisions leading to the fast electron formation, 8 – excitation and 9 – subsequent ionization with the fast electrons participation.

It is useful to note that optical (laser) experiments concerned with ionization phenomena for $I \geq 10^5 \text{ W cm}^{-2}$ have not revealed any saturation effects in the charged-particle current. However, optical-signal saturation, i.e., resonant fluorescence, is seen for much lower illumination power densities (see, for example, Weiner and Polak-Dingels, 1981). This means that the dynamics of the colliding atoms system may change significantly in the laser radiation field, and laser-induced associative and Penning ionization processes may come into play. The measured cross

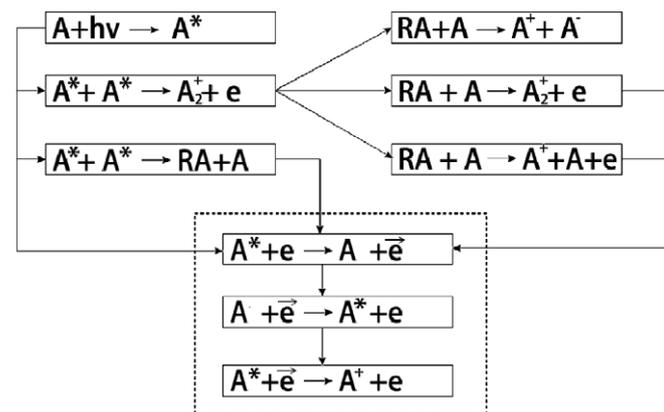


Fig. 16. Photoplasma steps creation.

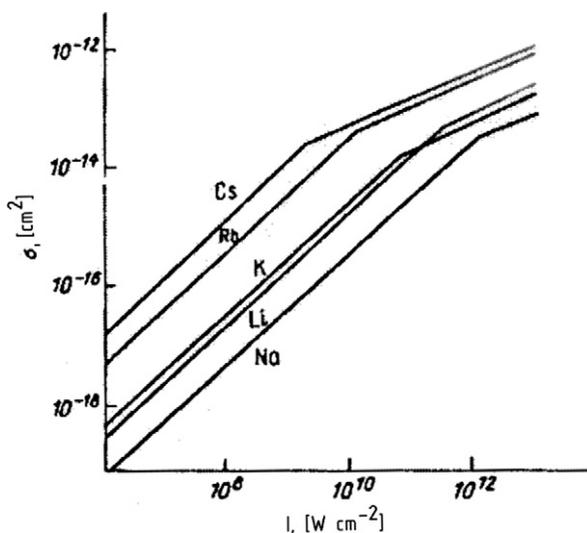


Fig. 17. Cross sections for Penning ionization stimulated by radiation (Geltman, 1988).

section for such processes with $I \approx 10^6 \text{ W cm}^{-2}$ are $3 \times 10^{-19} \text{ cm}^2$ for Na and is in reasonable agreement with calculations (Geltman, 1988) (Fig. 17). When the exciting laser pulse length is comparable with the lifetime of the excited states, one begins to see the effects of the photo-dissociation of molecular ions produced in *AI* channels. Thus, in crossed-beam experiments using sodium beams ($N_0 = 10^9 \text{ cm}^{-3}$), the Na_2^+ ions for 10^5 W cm^{-2} undergo partial photo-dissociation during the laser pulse. Since molecular ions produced in dimmer *AI* and photo-ionization channels have different vibrational excitation, the photo-dissociation cross sections are correspondingly different (Roussel et al., 1983).

6. Conclusion

The efficiency of collision-induced ionization of chemi-ionization type at thermal ($E > 10^2 \text{ K}$) and subthermal ($E < 10^2 \text{ K}$) collisions involving excited atoms was examined. In contrast to the rate constants for ultracold ($E < 10^{-3} \text{ K}$) collisions, which need special theoretical approaches because the motion of the nuclei cannot be treated here as classical, the rate constants for subthermal and thermal collisions are modeled essentially in the same way.

The results obtained show that the theoretical models proposed for collision-induced ionization are adequate in a wide range of principal quantum numbers of the excited hydrogen-like atoms. It was established that for slow collisions, in systems with few degrees of freedom, the stochastic dynamics processes occurring during the single collision may be observed.

Above considered models of the chemi-ionization processes with alkaline atoms are equally applicable to ionized gas and gas dynamics media as well as to atomic beams (thermal and subthermal conditions). This opens up prospects for consideration of the alkali metals, first of all sodium, present significantly in a number of cosmic objects, which is of interest from the astrophysical aspect.

Recently, in connection with development of basic researches in the field of interaction of radiation with single atoms and molecules the circle of problems in which highly excited atoms play the leading part was essentially extended. Laser cooled atoms, Bose–Einstein condensation, and management of the single atom conditions, new prospects in creation of logic devices of quantum computers, quantum teleportation etc. concern to them. All this increases interest to experimental and theoretical researches with participation of excited and, first of all, highly excited atoms, including the processes of their atomic collision ionization.

The classical model describing the ionization process in collisions of Rydberg atom with ground-state one (Ignjatović and Mihajlov, 2005) was supplemented in Miculis et al. (2005) and Beterov et al. (2005). The most substantial modification was the modeling of the quasi-molecular manifold of Rydberg states using the stochastic dynamics

of the Rydberg electrons. The results presented above may be recommended for the interpretation of the hydrogen-like excited atom species in the weakly ionized astrophysical formations of alkalis, specifically in volcanic gases on Io.

We note that this work is not envisaged as a particular one, but as a basis for planned modelling of sodium formations in Io atmosphere, representing the most impressive object where the sodium problem is actual. Namely, results of this work provide part of kinetics for the modelling of sodium formations in Io atmosphere, not investigated before. The other needed processes are well known and could be easily included in the model. One should take into account that the atmosphere of Io is not calm, and that processes there are in the presence of numerous powerful electric discharges. Consequently, one could assume that sodium vapor is there under strong influence of UV radiation and discharge products, so that the processes investigated here are present and presented results could be useful.

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