Collisional and thermal ionization of sodium Rydberg atoms I.
Experiment for $nS$ and $nD$ atoms with $n=8-20$

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Abstract. Collisional and thermal ionization of sodium $nS$ and $nD$ Rydberg atoms 
with $n=8-20$ has been studied. The experiments were performed using a two-
step pulsed laser excitation in an effusive atomic beam at atom density of about 
$2 \times 10^{10}$ cm$^{-3}$. Molecular and atomic ions from associative, Penning, and thermal 
ionization processes were detected. It has been found that the atomic ions were 
created mainly due to photoionization of Rydberg atoms by photons of blackbody 
radiation at the ambient temperature of 300K. Blackbody ionization rates and effective 
lifetimes of Rydberg states of interest were determined. The molecular ions were 
found to be from associative ionization in Na($nL$)+Na(3S) collisions. Rate constants 
of associative ionization have been measured using an original method based on relative 
measurements of Na$^+_2$ and Na$^+$ ion signals.

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1. Introduction

Collisional ionization of atoms may often be associated with highly excited quasimolecular systems, which are formed temporarily in course of the collision. Such quasimolecules may, at certain internuclear distances, couple to the ionization continuum and emit an electron. Depending on the total excitation energy of the system and relative positioning of the covalent and ionic molecular potential curves, the quasi-molecule may end up as a stable molecular ion (associative ionization), or ionize and dissociate into an atomic ion and a neutral atom (Penning process). Conventional theory \[1, 2, 3\] treats such processes deterministically in terms of interaction of a few covalent bound states with the ionization continuum. In the reality, however, the incoming covalent state interacts with a large number of other molecular Rydberg states. Moreover, since the density of Rydberg states is very high, it may be impossible to single out separate interactions between two Rydberg states at a time. Obviously, under such conditions it is not practicable to apply the exact quantum mechanical description. This drawback of the deterministic description of ionization dynamics can be overcome by involving a new alternative approach, the so-called stochastic ionization model \[4\].

The stochastic model describes the collisions with Rydberg atoms as a chaotic migration of highly excited electron accompanying the motion of both colliding nuclei. The electron “diffuses” through the dense energy spectrum of the highly excited quasi-molecule, eventually ending up in the ionization continuum. The stochastic theory has already yielded encouraging results by properly describing some of the earlier experimental results on associative ionization involving Rydberg atoms \[5, 6, 7\].

The aim of the present work was to test experimentally the ranges of validity of the stochastic theory developed in \[4, 5, 6, 7, 8\]. For this purpose, we studied the ionizing collisions of sodium Rydberg atoms Na\((nL)\) with atoms in the 3S ground state Na\((3S)\). In what follows we describe the measurements of ionization signals occurring after excitation of sodium atoms to \(nS\) and \(nD\) Rydberg states with \(n=8-20\) in a single atomic beam at a source temperature of 635 K. To the best of our knowledge, there are no data in the literature on ionization of sodium atoms in \(nS\) and \(nD\) states for this range of principal quantum numbers. In particular, the processes of interest are:

\[
\text{Na}(nL) + \text{Na}(3S) \rightarrow \text{Na}_2^+ + e \quad \text{Associative Ionization (AI)};
\]

\[
\text{Na}(nL) + \text{Na}(3S) \rightarrow \text{Na}^+ + \text{Na}(3S) + e \quad \text{Penning Ionization (PI)};
\]

where \(\text{Na}^+\) is an atomic ion, and \(\text{Na}_2^+\) is a molecular ion.

The earlier experiments on collisional ionization of Na Rydberg atoms are reported in \[9, 10, 11, 12, 13, 14, 15\]. The measurements of absolute rate constants have been done in \[9\] for \(nP\) states \((n = 5 - 15)\) in a crossed beam experiment at source temperatures of 600 K and pulsed laser excitation. The rate constants for \(nP\) states \((n = 5 - 21)\)
in a single atomic beam at 700 K source temperature and continuous excitation were reported in [10, 11]. The measurements for \( nS, nP, \) and \( nL(L > 1) \) states \((n = 17 - 27)\) in a single Na beam at 1000 K and pulsed laser excitation have been made in [12]. The use of pulsed excitation in [9, 12] allowed the authors to distinguish between AI and PI channels and to determine the AI rate constants alone, while only the total (AI+PI) rates could be measured in [10, 11]. The compilation of the AI rates from [9, 12] is shown in figure 1. It exhibits a maximum in the AI rate constant for Na\((nP)\) states near \( n=12\). Similar dependences on the principal quantum number were observed in experiments with other alkali Rydberg atoms [15]. Comparison of these data with the theory of [1, 2, 3] has shown a remarkable disagreement of the absolute values and shapes of experimental and theoretical \( n \) dependences. Therefore new experiments and further development of the theory are necessary.

One can see from figure 1 that no experimental data for sodium \( nS \) and \( nD \) states with \( n < 17 \) are available. Meanwhile, the range of \( n = (8 - 20) \) is of particular interest, since this is where the maximum in the ionization rate is expected. In addition, S and D states have different quantum defects and orbits of electron motion from those of P states, and the \( n \) dependences for S and D states may be considerably different.

One of the main difficulties in measurements of AI rates for \( nS \) and \( nD \) states at low \( n \) is related with their short lifetimes. According to the calculations of Theodosiou [16], radiative lifetimes of the 10S and 10D states are about 0.9 \( \mu s \), while the lifetime of the 10P state is about 8 \( \mu s \), which is by an order of magnitude larger. Since one must usually provide a sufficiently long time (1-2 \( \mu s \)) for the collisional interaction of...
Rydberg and ground-state atoms in experiments, care must be taken to renormalize the ionization signals and thus to account for the short lifetimes.

Experimental data on effective lifetimes of most of the Rydberg states are lacking, therefore they must be accurately calculated. Such calculations should take into account the fact that lifetimes are affected by blackbody radiation (BBR), which is always present in the experiments. It induces transitions between neighboring Rydberg states and shortens the effective lifetimes \[17\]. Moreover, BBR may photoionize Rydberg atoms and contribute \( \text{Na}^+ \) ions to the measured collisional signals. Our numerical calculations have shown (see summary Table 1 in Section 4 below) that the rate of direct photoionization by BBR is as high as \( 1147 \, \text{s}^{-1} \) for the 17D state at the ambient temperature \( T=300 \, \text{K} \), so that the measured \( \text{Na}^+ \) signals in room-temperature experiments are rather due to the BBR photoionization than due to the PI. This effect was studied experimentally earlier in \[13, 14, 18\], while numerical calculations of direct BBR photoionization rates were performed in \[18, 19\]. Experimental measurements of BBR photoionization rates for various \( n \) were reported only for barium Rydberg atoms \[20\].

In order to decrease the BBR in the experiments with Rydberg atoms, special thermal shields cooled by vacuum cryostats are often used. However, this method does not allow a precise determination of the effective temperature and density of blackbody photons. Even with liquid nitrogen or helium cooled shielding, the blackbody photons can penetrate into the reaction zone from the hot atomic beam source (oven) or through openings in the detection system. Although our setup was equipped with a nitrogen cryostat, we decided to work without cooling for the sake of exact knowledge of temperature and frequency distribution of BBR photons. Under such conditions, reliable measurements of PI rates were impossible because the expected \( \text{Na}^+ \) signals due to PI were much smaller than those from BBR photoionization.

At the same time, the BBR photoionization signals may be calculated or measured and serve as a reference for measurements of the AI rates. In this case, however, the mixing of neighboring Rydberg states by BBR must also be taken into account, because it may significantly redistribute the populations of excited states during the interaction time \[21, 22\]. Note that the AI rates can still be extracted directly from the measured \( \text{Na}_2^+ \) signals, since the BBR photoionization leads only to the formation of \( \text{Na}^+ \) ions and does not affect the \( \text{Na}_2^+ \) signals.

2. Experiment

Experimental setup was similar to that used for microwave spectroscopy of Na Rydberg atoms \[23\]. Experiments were performed with a single effusive Na atomic beam in a vacuum chamber at background pressure of \( 5 \times 10^{-7} \) Torr (figure 2). The temperature of the Na oven was stabilized at 635 K. The atomic beam was formed by expansion of sodium vapor through a 2 mm dia opening in the oven at a distance of 9 cm from the reaction zone. Collimation of the beam was achieved by a metallic shield with 1.5 mm dia aperture located 4 cm upstream from the excitation volume. The effective diameter
of the atomic beam in this volume was about 4 mm.

The metallic shield screened the most of thermal radiation of the oven. This shield and other parts of the vacuum chamber surrounding the reaction zone were kept at room temperature, ensuring an isotropic 300 K environment. The estimated flux of "hot" BBR photons originating from the beam source and penetrating through the collimating aperture contributed to less than 1% of the total BBR ionization rate in the reaction zone, and it was therefore disregarded in the data analyses.

Sodium $nS$ and $nD$ Rydberg states were excited using the two-step scheme $3S_{1/2} \rightarrow 3P_{3/2} \rightarrow nS$, $nD$ by radiation of two tunable lasers pulsed at 5 kHz repetition rate. In the first step, 50 ns pulses from a Rhodamine 6G dye-laser with linewidth of 50 GHz were used. They saturated the $3S_{1/2} \rightarrow 3P_{3/2}$ transition at 589 nm. The resonance fluorescence on this transition was detected by a photomultiplier to monitor the relative changes in density of the atomic beam. In the second step, the second harmonic of a Ti:sapphire laser was used. It yielded 50 ns pulses with 10 GHz linewidth, tunable in the 400-455 nm range. When not focused, this radiation did not saturate the $3P_{3/2} \rightarrow nS,nD$ transitions. The two laser beams were crossed at a right angle in the reaction zone, both of them crossing the atomic beam at an angle of 45°. Laser beam profiles were spatially limited by 2 mm dia apertures at the entrance windows of the vacuum chamber. Such configuration ensured a sufficiently small excitation volume of 2 mm size in the central part of the atomic beam, where the spatial variation of atom density was insignificant (<20%).

The ion detection system shown in figure 2 used a channeltron multiplier VEU – 6.
The atomic beam passed between two stainless-steel plates with diameter of 70 mm each, spaced by 10 mm. The plates formed a homogeneous electric field to guide the ions from the reaction zone through the entrance window of the channeltron. The extraction electric field pulses of 100 V/cm amplitude and 250 ns duration were applied to the upper plate. The lower plate was grounded and had a 6 mm dia opening covered by a mesh with the transmittance of 70%. The ions that passed through the mesh were accelerated by the electric field of the channeltron to energies of about 3.5 keV. This energy was sufficient to detect the ions with probability close to unity.

A special microwave-spectroscopy experiment, similar to that described in [23], has proven that the electric field from the channeltron very weakly penetrated into the interaction region through the fine mesh of the lower ionization plate, as well as other stray electric fields. The measured Stark shift of the microwave transition $^{37}\text{S} \rightarrow ^{37}\text{P}$ was about 4 MHz, corresponding to the $<0.3$ V/cm stray electric field. This field had no effect on our measurements or on Rydberg states under study.

Single ion output pulses of the channeltron were amplified, discriminated, and registered by two gated counters. The measurements were performed in the pulse counting regime, keeping the frequencies of the detected ion signals much lower (0.2-1 kHz) than the 5 kHz repetition rate of laser pulses. On average, less than one ion per laser shot was detected. The measured frequencies of ion signals were determined as the total number of ions detected during the measurement time of 10 s, i.e., signals were counted for 50000 laser pulses. In order to ensure the single-ion counting regime, the intensity of the laser driving the second excitation step was attenuated with calibrated neutral density filters by a factor of 10 to 100.

The present study concentrated on measurements of relative dependence of ionization rate constants on the principal quantum number $n$ of Rydberg states, and it did not require precise knowledge of absolute values of the number density $n_{3S}$ of the ground-state Na(3S) atoms in the beam. It was therefore calculated from the geometry of the effusive beam and the Nesmeyanov’s formula relating temperature and pressure of saturated Na vapor in the beam source. This formula coincides to within better than 50% with other available data, for example, [25]. Monitoring of the fluorescence on the saturated resonance transition showed that the atomic number density was almost constant during the experiments. The temperature of the oven was measured by a calibrated thermocouple with an accuracy of $\pm 2$ K. Taking into account all the uncertainties, we estimate the absolute number density of atoms in the reaction zone as $n_{3S}=(2\pm 0.7)\times 10^{10} \text{ cm}^{-3}$ at the oven temperature of $T=(635\pm 2)$ K.

The time sequence of excitation and detection pulses is illustrated in figure 3. Two identical electric field pulses with the 100 V/cm amplitude and 250 ns duration (figure 3(b)) were applied to the repelling plate after each laser excitation pulse (figure 3(a)).

The first electric pulse was applied immediately after the laser pulse to remove the atomic and molecular ions produced during the laser pulse. These ions were always observed in our experiments, even at non-resonant excitation by the first-step (yellow)
laser only. Their origin was investigated in many earlier studies, which identified them to be due to multiphoton ionization of Na\textsubscript{2} dimers by yellow laser [26, 27] (dimers are always present in an effusive beam at an amount of \(~(0.1-1)\%)\), due to photoassociative ionization of Na(3P) atoms by yellow laser [28, 29, 30], and due to photoionization of Rydberg Na(nL) atoms by the resonant radiation of yellow and blue lasers. These ions represent an undesirable background to the collisional-ionization signals from Rydberg atoms, and therefore the first electric pulse was required to clean up the reaction zone from any ions created during the laser excitation.

The second electric pulse extracted to the channeltron those ions, which were produced in the time interval between \(t_1=0.3\ \mu s\) and \(t_2=2.1\ \mu s\) after the laser excitation pulse. These ions corresponded to the collisional and BBR photoionization of Rydberg atoms. In the mass spectrum detected by the channeltron, the signals of the atomic Na\textsuperscript{+} and the molecular Na\textsubscript{2}\textsuperscript{+} ions were separated by 0.6 \(\mu s\) and thus well resolved (figure 3(c)). Gated pulse counters registered the signals of the atomic and molecular ions independently (figure 3(d)).

Figure 3. Timing diagram of signals: (a) laser excitation pulse; (b) 100 V/cm electric field pulses for ion extraction; (c) ion signals; (d) counter gates for measurement of Na\textsuperscript{+} and Na\textsubscript{2}\textsuperscript{+} signals.
3. Determination of collisional rate constants

3.1. Rate equations

The registered $\text{Na}^+$ and $\text{Na}_2^+$ ion signals result from ionization occurring in the reaction zone during the time interval $(t_2-t_1)=1.8 \, \mu s$ between the two extraction electric field pulses. This time is comparable with the lifetimes of Rydberg states; therefore, time evolution of ionization processes must be analyzed. The main processes leading to the formation of $\text{Na}^+$ ions are Penning ionization and photoionization by BBR. The $\text{Na}_2^+$ ions can be created only in the associative ionization. Contribution of the collisions with background gases can be safely disregarded. We have verified experimentally that the variation of background pressure within the range of $5 \cdot 10^{-7} \leq P \leq 1 \cdot 10^{-6}$ Torr did not affect the measured $\text{Na}^+$ and $\text{Na}_2^+$ signals by more than 5%. Under such conditions, the rate equations describing the evolution of the numbers of $\text{Na}^+$ and $\text{Na}_2^+$ ions following the laser excitation at time $t=0$ are

\[
\begin{align*}
\frac{dN_{\text{Na}}^+(t)}{dt} &= k_{\text{PI}} N_{nL}(t) \, n_{3S} + W_{\text{BBR}} N_{nL}(t); \\
\frac{dN_{\text{Na}}^{+2}(t)}{dt} &= k_{\text{AI}} N_{nL}(t) \, n_{3S}.
\end{align*}
\]  

(1)

Here, $N_{nL}(t)$ is the time-dependent number of $\text{Na}(nL)$ Rydberg atoms in the reaction zone, $n_{3S} \approx 2 \cdot 10^{10} \, \text{cm}^{-3}$ is the number density of ground state atoms, $k_{\text{AI}}$ and $k_{\text{PI}}$ are the rate constants of associative and Penning ionization in $\text{Na}(nL)+\text{Na}(3S)$ collisions respectively.

The function $N_{nL}(t)$ evolves in time as

\[N_{nL}(t) \approx N_{nL}(0) \exp\left\{-t/\tau_{\text{eff}}\right\}.
\]  

(2)

The initial number of Rydberg atoms, $N_{nL}(0)$, created during the laser excitation, can be written as

\[N_{nL}(0) = N_{3P} W (3P_{3/2} \rightarrow nL),
\]  

(3)

where $N_{3P}$ is the average number of atoms in the $3P_{3/2}$ state during the yellow-laser pulse, and $W (3P_{3/2} \rightarrow nL)$ is the probability of excitation of the $\text{Na}(3P_{3/2})$ atoms to the $nL$ state by a single blue-laser shot.

The effective lifetime $\tau_{\text{eff}}$ describing the decay of Rydberg states in equation (2) is determined by the spontaneous lifetime and the rate of other processes depleting the laser excited Rydberg state. These include BBR induced transitions between Rydberg states, BBR induced photoionization, and collisional quenching. The results of our numeric calculations of the rates of these processes will be given in Section 4 and summarized in Table 1.

The depletion of Rydberg states with $n=8-20$ by collisional ionization is negligible at atom densities used in the present experiment. We find from figure 1 that the rate of associative ionization, $k_{\text{AI}} n_{3S}$, does not exceed $50 \, \text{s}^{-1}$ and is therefore much smaller than
the spontaneous decay rates, which range from $10^5$ to $10^6$ s$^{-1}$ for the studied Rydberg states. The rate of PI, $k_{PI}n_{3S}$, is expected to be below $10$ s$^{-1}$ for $n\sim20$, and close to zero for lower $n$. Comparing the PI rate with the direct BBR photoionization rate $W_{BBR}$ (Table 1), one can see that Na$^+$ ions are produced mainly in the BBR photoionization. As will be shown below, this seemingly undesirable background ionization process can be favorably exploited for the determination of absolute AI rate constants.

With the above considerations in mind, the solution of equations (1) can be written as

$$\begin{align*}
\text{Na}^+ &= N_{nL}(0) \ W_{BBR} \ t_{eff} \\
\text{Na}_2^+ &= N_{nL}(0) \ k_{AI}n_{3S} \ t_{eff}
\end{align*}$$

(4)

where $t_{eff}$ is the effective time of interaction that takes into account the short radiative lifetimes of Rydberg states:

$$t_{eff} = \tau_{eff} \left[ \exp \left( -t_1/\tau_{eff} \right) - \exp \left( -t_2/\tau_{eff} \right) \right].$$

(5)

Here, $t_1$ and $t_2$ are the time moments marking the end of the first and the beginning of the second extraction electric field pulses, respectively (see figure 3(b)).

3.2. Method of measurements

Equations (4) can be used for the direct measurement of $k_{AI}$ and $W_{BBR}$ values, provided that $N_{nL}(0)$ is known. The only reliable method to measure $N_{nL}(0)$ is the Selective Field Ionization (SFI) technique [31]. Rydberg atoms ionize in an electric field with probability close to unity if the field strength has reached the critical value $E_c$. The latter depends strongly on the effective quantum number $n_{eff}=n-\delta_L$, where $\delta_L$ is the quantum defect (1.348 for $nS$ states and 0.015 for $nD$ states):

$$E_c \approx 3.2 \cdot 10^8 n_{eff}^{-4} \ (V/cm)$$

(6)

Unfortunately, it is difficult to apply the SFI method for Rydberg states with low $n$, since they require too strong electric field ($\sim30$ kV/cm for $n\sim10$). In the present study we were interested mainly in relative measurements of $k_{AI}$ for various $n$. Therefore we could use a normalization procedure for $N_{nL}(0)$ based on numerically calculated excitation probabilities $W(3P_{3/2} \rightarrow nL)$. Since the $3S_{1/2} \rightarrow 3P_{3/2}$ transition was saturated, $N_{nL}(0)$ was dependent only on the respective transition moments and power of the blue laser. In the absence of saturation at the second excitation step (this was the case in our experiments), the probability of excitation of Rydberg states from the $3P_{3/2}$ state can be written as

$$W(3P_{3/2} \rightarrow nL) = C_L \cdot P_b \cdot R^2 \ (3P_{3/2} \rightarrow nL),$$

(7)

where $P_b$ is the power of the blue laser, $R(3P_{3/2} \rightarrow nL)$ is the radial part of the transition dipole moment, and $C_L$ is a normalization constant, which depends on $L$ and is proportional to the square of angular part of the matrix element. The value of
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$W (3P_{3/2} \rightarrow nL)$ falls as $n_{\text{eff}}^{-3}$ for high Rydberg states, but for the states with $n \sim 10$ this scaling law does not work quite well. This was established in our numeric calculations of $R (3P_{3/2} \rightarrow nL)$ for the $3P_{3/2} \rightarrow nS$, $nD$ transitions, therefore we used the calculated values instead of the above scaling law for the evaluation of the experimental data.

In order to compare the absolute signals due to BBR and collisional ionization of $S$ states with those of $D$ states, it is necessary to know also the ratio $C_D/C_S$. The analysis of angular parts of the transition matrix elements, taking into account the hyperfine structure, showed that for excitation with linearly polarized light in the first and the second excitation steps, the ratio $C_D/C_S$ may vary from approximately 1.6 (if there is no collisional, radiative, or magnetic field mixing of the magnetic sublevels) to 2 (if the level mixing is complete). For excitation by non-polarized light, the ratio always equals to 2 regardless the degree of level mixing. Finally, we find that the ratio $W (3P_{3/2} \rightarrow nD)/W (3P_{3/2} \rightarrow nS)$ may vary between the values of 3.5 and 5.

In principle, one could normalize the ion signals measured for different $nL$ states using the calculated probabilities $W (3P_{3/2} \rightarrow nL)$ and measuring only the power $P_b$ of the blue laser radiation in equation (7). However, the applicability of such normalization may be complicated by technical imperfections of the blue laser. Since the linewidth of this laser (10 GHz) was much larger than the widths of the absorption profiles at the second excitation step ($\sim$500 MHz Doppler broadening), variations of the spectral density of laser radiation could affect the probability of excitation even if $P_b$ would be kept constant. Therefore we had to verify experimentally the applicability of normalization by equation (7). As discussed above, the only reliable way to measure the number of Rydberg atoms was to apply the SFI technique. For this purpose, we built a high-voltage generator yielding pulses with rise time of 1 $\mu$s and amplitude of up to 8 kV. This allowed us to field-ionize Rydberg states with $n \geq 17$. The SFI signals were detected at a 1 $\mu$s delay with respect to the laser pulse, i.e., the measured SFI signal was:

$$S_{\text{SFI}} \sim N_{nL}(0) \exp(-1 \mu s/\tau_{\text{eff}}).$$  \hspace{1cm} (8)

Equation (8) was used to derive $N_{nL}(0)$ from the measured SFI signals and the calculated values $\tau_{\text{eff}}$ of Table 1. Figure 4 shows the measured $N_{nL}(0)$ dependences on the principal quantum number $n$ for $nS$ and $nD$ states. These data are normalized on $P_b$, because it varied as blue laser frequency was tuned to resonance with different $nL$ states. The solid curves are approximations made using equation (7). It is seen that experimental points have noticeable deviations from theory although the general trend is correct. These deviations may be explained by the variations of spectral density of blue laser light. We concluded that equation (7) can be used for the normalization of $N_{nL}(0)$, but at price of limited accuracy. We also find from figure 4 that on average the ratio $W (3P_{3/2} \rightarrow nD)/W (3P_{3/2} \rightarrow nS)$ was close to 3.5. Hence, no considerable mixing of the magnetic sublevels took place during the laser excitation, and the ratio $C_D/C_S$ was close to 1.6.
Since SFI technique was not applicable for the direct determination of $N_{nL}(0)$ for $n=8-17$, the use of equation (7) was somewhat inadequate in our experiment. Therefore ways had to be found to eliminate this value from the determination of rate constants. This can be done by measuring the ratio $R$ of atomic and molecular signals derived from equations (4):

$$R = \frac{N_{2+}}{N_{+}} = \frac{k_{AI}n_{3S}}{W_{BBR}}.$$  \hspace{1cm} (9)

This ratio does not depend on the values of $N_{nL}(0)$, $\tau_{eff}$ and $t_{eff}$. Thus, the rate constant of the AI process can be directly obtained from the measured ratio of the $Na^+$ and $Na^{+}$ signals:

$$k_{AI} = \frac{Na^+}{Na^{+}} \cdot \frac{W_{BBR}}{n_{3S}}.$$  \hspace{1cm} (10)

The BBR ionization rates $W_{BBR}$ have thus become one of the key values necessary for the determination of the AI rate constants. The accuracy with which the $W_{BBR}$ values are known directly affect the accuracy of the experimental $k_{AI}$ values obtained using equation (10). Therefore, the process of BBR ionization must be examined in all details.

4. BBR ionization rates

4.1. Direct BBR photoionization and effective lifetimes

First, we have numerically calculated the effective lifetimes $\tau_{eff}$ and the rates $W_{BBR}$ of direct BBR photoionization of $nS$ and $nD$ Rydberg states of Na with $n=8-20$ at the
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room temperature of 300 K. The BBR photoionization rates were calculated using the formula (here and below the atomic units are used) [18]:

\[ W_{BBR} = c \int_{\omega_{nL}}^{\infty} \sigma_\omega \rho_\omega d\omega, \]  

(11)

where \( c \) is the speed of light, \( \omega_{nL} = 1/(2n_{eff}^2) \) is the threshold frequency of the \( nL \) Rydberg state, and \( \sigma_\omega \) is the photoionization cross-section at frequency \( \omega \). The volume density \( \rho_\omega \) of BBR photons at temperature \( T \) is given by the Planck distribution:

\[ \rho_\omega = \frac{\omega^2}{\pi^2 c^3 [e^{\omega/(kT)} - 1]^2}, \]  

(12)

where \( k \) is the Boltzmann constant. For isotropic and non-polarized thermal radiation field, \( \sigma_\omega \) is determined by the radial matrix elements \( R(nL \rightarrow E, L \pm 1) \) of dipole transitions from discrete \( nL \) Rydberg states to continuum states with \( L' = (L \pm 1) \) and photoelectron energy \( E \):

\[ \sigma_\omega = \frac{4\pi^2 \omega}{3c(2L + 1)} \sum_{L'=L \pm 1} L_{max}^2 R^2 (nL \rightarrow EL \pm 1), \]  

(13)

where \( L_{max} \) is the largest of \( L \) and \( L' \). The values of \( R(nL \rightarrow E, L \pm 1) \) were calculated numerically using the semi-classical formulae of Dyachkov and Pankratov [32]. Their method gives orthogonal and normalized continuum wavefunctions, and the calculated photoionization cross-sections were found to be in good agreement with the more sophisticated quantum-mechanical calculations for \( nS \) states by Aymar [33]. Other theoretical methods developed in [34, 35] give close results. High-precision values of quantum defects of Dyubko et al [36] were used in our calculations.

In order to determine the effective lifetimes of \( nL \) states, the radial matrix elements \( R(nL \rightarrow n'L') \) of all dipole transitions to other \( n'L' \) states with \( L' = L \pm 1 \) were also calculated using the quasi-classical formulae of [32]. The rate of a specific BBR-induced transition between the states \( nL \) and \( n'L' \) are given by:

\[ W(nL \rightarrow n'L') = \frac{4}{3c^3 2L + 1} \frac{L_{max}^2 R^2 (nL \rightarrow EL \pm 1)}{\omega_{nn'}^3} \]  

(14)

where \( \omega_{nn'} = 1/(2n^2) - 1/(2n'^2) \) is the frequency of the transition. The total decay rates were obtained by summing the probabilities of all spontaneous and BBR-induced transitions. The results of numerical calculations of \( W_{BBR} \) and effective lifetimes at \( T=300\text{K} \) are presented in Table 1.

4.2 BBR-induced mixing of Rydberg states

Earlier studies of BBR-induced processes have revealed that BBR causes not only direct photoionization to the continuum [18], but also induces transitions in the discrete spectrum [21, 22]. In our case, several discrete \( nP \) and \( nF \) levels are populated from the initially excited \( nS \) and \( nD \) states during the interaction time. For example, after laser excitation of the \( 16S \) state, the BBR-induced transitions populate the neighboring
Table 1. Effective lifetimes $\tau_{eff}(\mu s)$ and BBR induced transition rates of $nS$ and $nD$ states of sodium for the surrounding environment at $T=300$ K. $W_{BBR}$ - direct photoionization rates of laser excited Rydberg states; $W_R$ - ionization rates by the second extraction field pulse of states with $n' > 40$, which are populated in BBR induced transitions from the initial laser excited levels; $W_{mix}$ - rate of BBR induced ionization of $n'L'$ levels populated by spontaneous decay and BBR-induced $nL$ mixing; $W_{tot}^{BBR}$ - total theoretical BBR ionization rate; $W_{exp}^{BBR}$ - experimental BBR induced ionization rate.

| State | $\tau_{eff}(\mu s)$ | $W_{BBR}(s^{-1})$ | $W_R(s^{-1})$ | $W_{mix}(s^{-1})$ | $W_{tot}^{BBR}(s^{-1})$ | $W_{exp}^{BBR}(s^{-1})$ |
|-------|---------------------|--------------------|---------------|-------------------|--------------------------|--------------------------|
| 8S    | 0.395               | 0.059              | 0.022         | 0.404             | 0.485                    | 6±2                      |
| 9S    | 0.581               | 0.823              | 0.316         | 3.62              | 4.76                     | 25±2                     |
| 10S   | 0.812               | 4.555              | 1.78          | 13.7              | 20.0                     | 47±3                     |
| 11S   | 1.095               | 14.48              | 5.76          | 30.9              | 51.2                     | 93±10                    |
| 12S   | 1.431               | 32.36              | 13.2          | 52.5              | 98.0                     | 141±16                   |
| 13S   | 1.824               | 57.42              | 23.9          | 73.9              | 155                      | 204±23                   |
| 14S   | 2.278               | 87.07              | 37.4          | 91.8              | 216                      | 268±24                   |
| 15S   | 2.795               | 118.3              | 52.6          | 104               | 275                      | 367±33                   |
| 16S   | 3.376               | 148.8              | 68.6          | 111               | 329                      | 499±55                   |
| 17S   | 4.024               | 176.3              | 85.0          | 114               | 375                      | 614±59                   |
| 18S   | 4.731               | 200.9              | 101           | 113               | 415                      | 741±66                   |
| 19S   | 5.518               | 221.5              | 117           | 109               | 448                      | 1007±110                 |
| 20S   | 6.378               | 238.1              | 133           | 104               | 475                      | 16±7                     |
| 8D    | 0.474               | 12.70              | 4.19          | 5.7               | 22.6                     | 83±14                    |
| 9D    | 0.665               | 52.76              | 17.4          | 15.1              | 85.3                     | 188±25                   |
| 10D   | 0.909               | 138.0              | 45.6          | 28.4              | 212.0                    | 369±38                   |
| 11D   | 1.189               | 268.8              | 89.4          | 43.8              | 401.9                    | 633±67                   |
| 12D   | 1.524               | 424.3              | 145           | 58.0              | 627.2                    | 830±69                   |
| 13D   | 1.905               | 603.4              | 207           | 69.8              | 879.9                    | 1025±128                 |
| 14D   | 2.341               | 770.4              | 270           | 78.3              | 1119                     | 1281±70                  |
| 15D   | 2.835               | 920.0              | 331           | 83.4              | 1335                     | 1420±82                  |
| 16D   | 3.387               | 1046               | 389           | 85.4              | 1521                     | 1463±67                  |
| 17D   | 4.001               | 1147               | 443           | 85.1              | 1675                     | 1804±88                  |
| 18D   | 4.680               | 1225               | 492           | 82.9              | 1800                     | 1978±96                  |
| 19D   | 5.423               | 1280               | 538           | 79.3              | 1897                     | 2036±60                  |
| 20D   | 6.235               | 1317               | 580           | 74.9              | 1972                     | 2036±60                  |

$nP$ states (figure 5(a)). These states have significantly larger $W_{BBR}$ values than that of the 16S state, so that population transfer to the $nP$ states may affect the resultant BBR photoionization signal. As an example, the calculated rates of spontaneous and BBR-induced transitions from the 16S and the 16D states to the $nP$ states are shown in figures 5(b) and 5(c).

Another feature is that BBR also induces transitions to high Rydberg states (figure 5(a)), which are field ionized by the second electric field pulse extracting the ions to channeltron for detection. This 100 V/cm pulse ionizes Rydberg states with $n \geq$
40, according to equation (14). Numerical calculations showed that high lying Rydberg states are populated at rates comparable with the direct photoionization rate $W_{BBR}$ given in Table 1. Since all the states above $n_c = 40$ are field ionized, all BBR populated states with $n' \geq 40$ will contribute to the detected Na$^+$ ion signal. The total rate $W_R$ of BBR transitions to all Rydberg states with $n' \geq 40$ was calculated by summing the individual $nL \rightarrow n'L'$ contributions given by equation (14):

$$W_R = \sum_{n' \geq 40} \sum_{L'=L \pm 1} W(nL \rightarrow n'L').$$  (15)
The calculated values are given in Table 1. Note, that these ionization rates amount to between 30 to 50 % of the direct photoionization rate values, \( W_{BBR} \), and they obviously cannot be ignored.

Another kind of processes that may also lead to the redistribution of populations between Rydberg states is \( nL \) mixing in collisions with the abundant ground state atoms. However, the estimated rates of this process for a beam of density \( n_{3S} \approx 2 \times 10^{10} \text{ cm}^{-3} \) produced by a source at 635 K were found to be much lower than the rates of spontaneous and BBR-induced transitions. Therefore the contribution of collisional \( nL \) mixing can be safely disregarded.

### 4.3. Total BBR ionization rates

When the rates of redistribution of population over \( n' L' \) Rydberg states following laser excitation of a single \( nL \) Rydberg level are known, the total ionization rate leading to the production of \( \text{Na}^+ \) ions can be calculated. Assume that some \( nS \) state is initially laser excited. If the rate of Penning ionization is negligible, the production of \( \text{Na}^+ \) ions is described by the rate equation

\[
\frac{dN_{\text{Na}^+} (t)}{dt} = W_{nS}^{\text{BBR}} N_{nS} (t) + \sum_{n'} W_{n'n'}^{\text{BBR}} N_{n'n'} (t).
\]

Here, \( W_{nS}^{\text{BBR}} = W_{BBR} + W_R \) is the total BBR ionization rate of the laser excited \( nS \) state, and it consists of two contributions: the direct BBR photoionization rate \( W_{BBR} \) of the \( nS \) state given by equation (11), and the rate \( W_R \) of equation (15) for BBR induced excitation of states with \( n \geq 40 \), which are subsequently field ionized by the second extraction field pulse. The main contributions to the sum in equation (16) are those of \( n'P \) states with \( n' = n, (n-1) \), which are the nearest neighbors to the initial \( nS \) state (see figures 5(b) and 5(c)). The time evolution of the number of \( n'P \) atoms is described as follows:

\[
\frac{dN_{n'n'} (t)}{dt} = W (nS \rightarrow n'P) N_{nS} (t).
\]

Solving equations (16) and (17), we obtained the total effective ionization rate of the \( \text{Na}(nS) \) atoms:

\[
W_{BBR}^{\text{tot}} = W_{BBR} + W_R + W_{\text{mix}},
\]

where \( W_{\text{mix}} \) is a contribution from the spontaneous and BBR-induced mixing of neighboring states:

\[
W_{\text{mix}} = \sum_{n'} W (nS \rightarrow n'P) W_{n'n'}^{\text{BBR}} \left( \frac{t_2 - t_1}{t_{\text{eff}}} - 1 \right) \tau_{\text{eff}}.
\]

Here \( t_{\text{eff}} \) is the effective interaction time given by equation (5), and \( \tau_{\text{eff}} \) is the effective lifetime of the laser excited \( nS \) state. Similar equations were derived for \( nD \) states, except that \( W_{\text{mix}} \) accounted for the transitions to both \( n'P \) and \( n'F \) states. Results of numerical calculations using the semi-classical formulae for matrix elements from [32] are summarized in Table 1.
4.4. Comparison of theory and experiment for BBR ionization rates

Experimental and theoretical data on the total BBR photoionization rates are compared in figure 6. The solid curves are the theoretical values of $W_{BBR}^{\text{tot}}$ from Table 1. The squares and circles are the corresponding experimental values $W_{BBR}^{\text{exp}}$ obtained using equations (4) and (7) (in equation (4) the value of $W_{BBR}$ was replaced with $W_{BBR}^{\text{tot}}$). Experimental data were averaged over 5 measurements. The normalization coefficient $C_D$ in equation (7) was the only parameter whose absolute value was adjusted to fit the experiment to the theory. A good agreement between the experimental and theoretical data was found for $nD$ states (figure 6(b)). However, the data for $nS$ states, obtained with the ratio $C_D/C_S=1.6$ measured earlier, exhibit considerable discrepancies for states with higher $n$ (figure 6(a)), while a better agreement for states with lower $n$ is seen. The values of $W_{BBR}^{\text{exp}}$ exceed the values of $W_{BBR}^{\text{tot}}$ by 2.1 times for $n=20$, and the shape of the experimental $n$ dependence is significantly different from the theoretical one.

One possible explanation of such anomaly for $nS$ states is related to their specific orbit that penetrates into the atomic core. The penetration causes a strong interaction between the Rydberg electron and the core, e.g., due to core polarization [33]. This results in a large quantum defect and in a Cooper minimum in the photoionization cross-sections. Each $nS$ state has its individual photoionization cross-section and position of the Cooper minimum. The accuracy of theoretical frequency-dependent cross-section values affects the total BBR ionization rate when integration over the Planck distribution in equation (11) is performed. It is likely that the accuracy of theoretical models for $nS$ states is affected by difficulties to account for the core penetration. This assumption is supported by good agreement of theory and experiment for the hydrogen-like $nD$ states, which have a small quantum defect and an almost non-penetrating orbit.

We conclude that our theoretical calculations of $W_{BBR}^{\text{tot}}$ are correct to better than
Figure 7. Experimental ratio $R$ of Na$_2^+$ and Na$^+$ ion signals as a function of the effective quantum number $n_{\text{eff}}$ for (a) nS states and (b) nD states.

10% for nD states and lower nS states, and probably incorrect for higher nS states. New more accurate calculations of S state ionization rates are required if equation (10) is to be used for the determination of absolute AI rate constants $k_{AI}$ for nS states. However, such calculations require development of new approaches that are not yet available for Rydberg states. Until new theoretical data become available, we rely on our experimental data for nS states instead of theoretical BBR ionization rates. The experimental values of $W_{BBR}^{exp}$ are summarized in the last column of Table 1. These are our recommended values of the BBR ionization rates at 300 K, which should be used in equation (10).

5. Experimental results for associative ionization rate constants

5.1. Ratio of molecular and atomic ion signals

Figure 7 shows the ratio $R$ of equation (9) averaged over eight independent measurements at the density of atoms in the atomic beam $n_{3S}=2\times10^{10}$ cm$^{-3}$. For the lowest states, the values of $R$ reach 2.5 and 1.4 for nS and nD states, respectively. In both cases, $R$ drops off rapidly and asymptotically approaches the value of 0.06 for highest $n$.

Such nearly constant $n$ dependence of $R$ at higher $n$ was unexpected. In order to verify whether the origin of the measured signal is collisional, the dependence of $R$ on the atomic beam density was measured for low (9D and 10S) and high (19S and 18D) Rydberg states (figure 8). For the 9D and 10S states, $R$ has a linear dependence on $n_{3S}$, and hence the Na$_2^+$ signal has a quadratic one. For 18D and 19S states, $R$ is almost independent of $n_{3S}$, hence the dependence of Na$_2^+$ is linear. This means that for high $n$ the apparent Na$_2^+$ signal was not due to the associative ionization. Instead, it was
Figure 8. Experimental dependences of the ratio $R$ of $\text{Na}_2^+$ and $\text{Na}^+$ ion signals on the density $n_{3S}$ of ground state atoms in the beam for the (a) 10S state, (b) 9D state, (c) 19S state, and (d) 18D state.

The magnitude of this noise signal can be expressed by the formula

$$N_{\text{noise}} = N_{nL}(0)\ W_{\text{BBR}}^{\text{tot}}\ e^{-t_2/\tau_{\text{eff}}}\Delta t,$$

where $\Delta t$ is the time interval of the second electric extraction pulse, during which those $\text{Na}^+$ ions are created, which can fall into the gate for molecular ions, and the time $t_2$ corresponds to the beginning of the extraction pulse. The noise is proportional to $W_{\text{BBR}}^{\text{tot}}$, which grows rapidly with increasing $n$ (figure 6). The time interval $\Delta t$ was calculated...
from the geometry of the detection system and the duration of the gate counting the molecular ions, and it was found to be about 150 ns. To find the contribution \( \alpha \) of the noise to the value of \( R \), equation (20) must be divided by equation (4) for Na\(^+\) ions:

\[
\alpha = \frac{\Delta t}{\tau_{\text{eff}} e^{\Delta t/\tau_{\text{eff}}}}.
\]

When this contribution is known, the absolute rate constant for AI in Na\((nL)+\text{Na}(3S)\) collisions can be extracted from the experimental ratios \( R \) of the molecular and atomic ion signals using equation (10) modified by the correction \( \alpha \) of equation (21):

\[
 k_{AI} = (R - \alpha) \cdot \frac{W_{\text{BBR}}^{\text{tot}}}{n_{3S}}.
\]

The values of \( \alpha \) for \( n_{S} \) and \( n_{D} \) states were calculated using equation (21). For highest \( n \) of the experiment they practically coincide with the measured ratios (figure 8(c) and 8(d)).

5.2. AI rate constants

The experimental dependences of \( k_{AI} \) on \( n_{\text{eff}} \) were obtained from equation (22) using the measured ratios of Na\(_2^+\) and Na\(^+\) signals and the data of Table 1. These dependences are shown in figure 9. For the sake of completeness, we present two sets of results. Figure 9(a) shows the rate constants determined with the experimental values \( W_{\text{BBR}}^{\text{tot}} \) of the BBR ionization rate, while figure 9(b) shows the same but using the theoretical \( W_{\text{BBR}}^{\text{exp}} \) values. The plots in both figures are nearly identical, except for some minor differences in the absolute values of \( k_{AI} \). Noteworthy, all dependences show the maximum in the AI rate near \( n_{\text{eff}} \approx (11 - 12) \), and fall off rapidly with increasing \( n_{\text{eff}} \).

Comparing our results with those of earlier AI studies, shown in figure 1, we see a noticeable difference with the earlier data of [12] on \( k_{AI} \) for \( n_{S} \) and \( n_{D} \) states which were also obtained in a single beam experiment: (i) in our study the rate constants of AI for \( n_{D} \) states are nearly twice larger than those for \( n_{S} \) states, while opposite ratio was reported in [12], and (ii) our values of \( k_{AI} \) fall off more rapidly with increasing \( n \) than those of [12]. We believe that our measurements are more reliable, since, in contrast to [12], using equation (22) we did not need to measure the number of Rydberg atoms and the effective lifetimes, and thus we could avoid the related experimental uncertainties.

The only important parameter, which was not exactly known in the present experiment, was the density \( n_{3S} \) of ground state atoms in the beam, which was calculated using the vapor pressure formula of Nesmeyanov [24]. At the same time, care was taken to ensure that the source temperature and the density of atoms in the beam were constant during the experiment. Therefore, the relative values of \( k_{AI} \) for different \( n_{S} \) and \( n_{D} \) states are not affected by this uncertainty.

Another interesting observation can be made by comparing our data of figure 9(b) with the \( n \) dependence for \( n_{P} \) states of figure 1. Such comparison is given in figure 10.
One can see that both data sets have similar absolute values and similar dependences on the effective quantum number $n_{\text{eff}}$. Note, however, that the data reported for $nP$ states in \cite{12} consist actually of the AI rate constants for the states with $5 \leq n \leq 15$, which were measured in \cite{9} under quite different conditions of a crossed beam experiment, and the rate constants for $n > 15$, which were actually measured in a single beam experiment \cite{12}. Joining of the two data sets was used in \cite{12} for scaling their relative cross section values for $n > 15$.

6. Discussion

Our measurements of associative ionization rate constants were based on use of equation (22). The accuracy of the measured $k_{\text{AI}}$ values depends on the accuracy with which the values of parameters $R$, $\alpha$, $W_{\text{BBR}}^{\text{tot}}$, and $n_{3S}$ are known. The ratio $R$ of $Na^+_2$ and $Na^+$ ions was measured directly and was found to be independent of laser intensities, detunings, and effective lifetimes. The measured $n$ dependences of figure 7 were reproduced in several experiments, which allow us to be confident that the values of $R$ are determined correctly. However, with increasing $n$ the fluctuations of $R$ became important, because equation (22) uses a product of $(R-\alpha)$, which decreases for high $n$ to values close to 0, and $W_{\text{BBR}}^{\text{tot}}$, which rapidly grows with increasing $n$. Therefore the reported values of $k_{\text{AI}}$ can be considered as reliable for lower $n \leq 16$, whereas for higher $n$ the error of determination of $k_{\text{AI}}$ is relatively large. More reliable data for higher $n$ could be obtained by increasing the density of atoms in the beam by an order of magnitude or more. Unfortunately such increase inevitably leads to complications in the analysis due to additional phenomena, like radiation trapping, which was found to strongly affect the velocity distributions of excited atoms in a beam experiment at
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Effective quantum number

Figure 10. Comparison of the experimental associative ionization rate constants for \( n_S \) (open circles) and \( n_D \) (open squares) states obtained in the present study (figure 9(b)) with the experimental rate constants for \( n_P \) states (solid circles) obtained in [9] and [12] (figure 1).

Figure 10. Comparison of the experimental associative ionization rate constants for \( n_S \) (open circles) and \( n_D \) (open squares) states obtained in the present study (figure 9(b)) with the experimental rate constants for \( n_P \) states (solid circles) obtained in [9] and [12] (figure 1).

Another possible source of errors in the determination of \( k_{AI} \) is the choice of values of the total BBR induced ionization rate \( W_{BBR}^{tot} \). Figure 6 shows a good agreement of experimental and theoretical values for all \( n_D \) states, while for higher \( n_S \) states the agreement is rather poor. Therefore, one must choose whether the theoretical or the experimental values of BBR ionization rates, given by the last two columns of Table 1, will be used in equation (22). Since the experimental results of figure 6 were reproduced in many experiments, we believe that the experimental values \( W_{BBR}^{exp} \) are more reliable. Therefore, figure 9(a) should be considered as the final result of the \( k_{AI} \) measurements.

The absolute values of \( k_{AI} \) depend also on the absolute value of \( n_{3S} \) calculated using the Nesmeyanov’s formula [24]. Numerous studies involving alkali atoms have confirmed its accuracy in predicting the vapor pressures of alkali gases (see, e.g., the argumentation in [38]) within a few tens of per cent. Note, that the relative values of \( k_{AI} \) were not affected by the absolute value of \( n_{3S} \), since it was kept constant during the experiment. We conclude that on average our absolute values of \( k_{AI} \) are accurate to within better than 50%, while the relative values of \( k_{AI} \) are accurate to within (10-20)%.

However, due to the specific \( n \) dependence of the term \((R - \alpha)\) in equation (22), the reliability of \( k_{AI} \) values is better for lower \( n \).

In conclusion, we have measured, for the first time, AI rate constants for sodium \( n_S \) and \( n_D \) states in the range of \( 8 \leq n \leq 20 \). In this study, we have implemented a novel method, in which the absolute values of rate constants were determined from the measurements of relative ratios of the molecular and atomic ion signals, with atomic
ions being from the BBR ionization of Rydberg atoms. The main advantage of this approach is that the measurements of absolute populations and effective lifetimes, which are associated with large experimental uncertainties, can be avoided.

To implement this method, we have measured BBR ionization rates for \( nS \) and \( nD \) states of sodium with \( n = 8-20 \). Comparison of these data with the theory showed a good agreement for \( nD \) states, and disagreement for \( nS \) states with \( n > 15 \). This discrepancy cannot be attributed to any of the experimental uncertainties, and the theory must substantially revise the calculations for \( nS \) states.

The comparison of our experimental data on AI rates with other experiments for \( nS \) and \( nD \) states is hampered by lacking overlap of the studied ranges of \( n \). However, for the high \( n \) range, where some overlap with the data of [12] exists, notable differences were observed. This may be explained by the way we accounted for the background Na\(^+\) ions. These ions were created due to ionization during the extraction electric field pulse, and they arrived to the detector simultaneously with Na\(^+\). Such possibility was not considered in earlier studies [9, 10, 11, 12], and it is not possible to reconstruct whether such background was present in these experiments.

Curiously, our results for \( nS \) and \( nD \) states are in a good agreement with the data of [9] for \( nP \) states, though that experiment was performed with two crossed atomic beams. In the present single-beam study, ionization is due to head-tail overtaking collisions between ground-state and Rydberg atoms. Accordingly, the collision energies are about three times lower than those in the crossed-beam experiment, which used beam sources of the same temperature. In the second part of our article [39] we provide a detailed comparison of the existing experimental data on associative ionization rate constants with the theoretical calculations for various relative velocity distributions. The calculations are based on the stochastic ionization model [4, 8, 5, 6, 7], and they take into account all possible collisional, spontaneous, and BBR-induced mixing processes.

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8. References

[1] Janev R K and Mihajlov A A 1980 Phys. Rev. A 21 819
[2] Mihajlov A A and Janev R K 1981 J. Phys. B 14 1639
[3] Duman E L and Shmatov I P 1980 Sov. Phys. JETP 51 1061
[4] Bezuglov N N, Borodin V M, Klyucharev A N, Fusio F, Allegrini M, Orlovsky K V and Janson M L 1999 Opt. Spektros. 86 824
[5] Bezuglov N N, Borodin V M, Ekers A and Klyucharev A N 2002 Opt. Spektros. 93 661
[6] Bezuglov N N, Borodin V M, Grushevskyi V, Klyucharev A N, Michulis K, Fusio F and Allegrini M 2003 Opt. Spektros. 95 515
[7] Bezuglov N N, Borodin V M, Kazanskii A K, Klyucharev A N, Matveev A A and Orlovskii K V 2002 Opt. Spektros. 91 19
Collisional and thermal ionization of sodium Rydberg atoms I

[8] Bezuglov N N, Borodin V M, Klyucharev A N, Orlovsky K V and Allegrini M 1997 Opt. Spectrosc. 82 334
[9] Boulmer J, Bonanno R and Weiner J 1983, J. Phys. B 16 3015
[10] Zagrebin S B and Samson A V 1984 Pisma Zh. Tekhn. Fiz. 10 114 (in Russian)
[11] Zagrebin S B and Samson A V 1985 J. Phys. B 18 L217
[12] Weiner J and Boulmer J 1986 J. Phys. B 19 599
[13] Burkhardt C E, Garver W P, Kushawaha V S and Leventhal J J 1984 Phys. Rev. A 30 652
[14] Burkhardt C E, Corey R L, Garver W P, Leventhal J J, Allegrini M and Moi L 1986 Phys. Rev. A 34 80
[15] Klucharev A N and Janson M L Elementary processes in the plasma of alkali metals (Energoatomizdat, Moscow, 1988) (in Russian).
[16] Theodosiou C E 1984 Phys. Rev. A 30 2881
[17] Gallagher T F Rydberg atoms (Cambridge University Press, Cambridge, 1994)
[18] Spencer W P, Vaidyanathan A G, Kleppner D and Ducas T W, 1982 Phys. Rev. A 26, 1490
[19] Lehman G W 1983 Phys. Rev. A 16 2145
[20] Allegrini M, Arimondo E, Menchi E, Burkhardt C E, Ciocca M, Garver W P, Gozzini S, Leventhal J J and Kelley J D 1988 Phys. Rev. A 38 3271
[21] Cooke W E and Gallagher T F 1980 Phys. Rev. A 21 588
[22] Galvez E J, Lewis J R, Chaudhuri B, Rasweiler J J, Latvakoski H, De Zela F, Massoni E and Castillo H 1995 Phys. Rev. A 51 4010
[23] Ryabtsev I I, Tretyakov D B, Beterov I I 2003 J. Phys. B 36 297
[24] Nesmeyanov A N Vapur pressure of the chemical elements (Elsevier, Amsterdam / London / New York, 1963)
[25] Handbook Physical values /Edited by Grigoryev I (Energoatomizdat, Moscow, 1991)(in Russian).
[26] Boulmer J and Weiner J, 1983 Phys. Rev. A 27 2817
[27] Burkhardt C E, Garver W P and Leventhal J J, 1985 Phys. Rev. A 31 505
[28] Meijer H A J, Pelgrim T J C, Heideman H G M, Morgensten R and Andersen N 1989 J. Chem. Phys. 90 738; Meijer H A J 1990 Z. Phys. D 17 257; Meijer H A J, van der Meulen H P and Morgenster R 1987 ibid 5 299; Meijer H A, Schoh S, Muller M W, Dengel H, Ruf M -W and Hotop H 1991 J. Phys. B 24 3621
[29] Huynh B, Dulieu O, and Masmou-Seeuws F 1998 Phys. Rev. A 57 958
[30] Blange J J, Urbain X, Rudolph H, Dijkerman H A, Beijerinck H C W, and Heideman H G M 1997 J. Phys. B 30 565
[31] Stebbings R F, Latimer C J, West W P, Dunning F B and Cook T B 1975 Phys. Rev. A 12 1453; Ducas T, Littman M G, Freeman R R and Kleppner D 1975 Phys. Rev. Lett. 35 366; Gallagher T F, Humphrey L M, Hill R M and Edelstein S A 1976 Phys. Rev. Lett. 37 1465
[32] Dyachkov L G and Pankratov P M 1994 J. Phys. B 27 461
[33] Aymar M 1978 J. Phys. B 11 1413
[34] Zimmerman M L, Littman M G, Kash M M and Kleppner D 1979 Phys. Rev. A 20 2251
[35] Bezuglov N N and Borodin V M 1999 Opt. Spectrosc. 86 467
[36] Dyubko S F, Efimenko M N, Efremov V A, Podnos S A 1995 Quantum Electronics 25 914
[37] Kaufmann O, Ekers A, Bergmann K, Bezuglov N, Miculis K, Auzinsh M and Meyer W 2003 J. Chem. Phys. 119 3174.
[38] Ekers A, Glodz M, Szonert J, Bieniak B, Fronc K and Radelitski T 2000 Eur. Phys. J. D 8 49
[39] Miculis K, Beterov I I, Bezuglov N N, Ryabtsev I I, Tretyakov D B, Ekers A, Klyucharev A N 2005 J. Phys. B (submitted).