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Two Mechanisms of Recombination of Atomic Ions[1]

V. M. Azriel'[a], V. M. Akimov[a], E. V. Ermolova[a], D. B. Kabanov[a], L. I. Kolesnikova[a], L. Yu. Rusin[a, *], and M. B. Sevryuk[a]
[a] *Tal'roze Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences, Moscow, Russia*
**e-mail: rusin@chph.ras.ru*

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Abstract—We compare the dynamics of two elementary reactions of recombination of atomic ions, namely, of the termolecular process of two ions and the third body (1) and of the bimolecular interaction of an ion with the diatomic cluster (2) consisting of the second ion and the neutral atom. It is shown that, despite the fact that both processes yield the same products, the main dynamical characteristics of these processes differ. First of all this concerns the excitation function which confines recombination for (2) by a collision energy up to 2 eV. The opacity functions of both processes have different structures. The distributions of the product vibrational energy in both the processes exhibit a non-equilibrium character, while the rotational energy distributions are equilibrium.

Keywords: dynamics of recombination of ions, three-body recombination, recombination via a complex, trajectory simulation, cesium bromide, xenon

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The mechanisms of complicated chemical processes playing a big role in power engineering, technological plasma media, and in many other branches of science and technology can be described as a sequence of elementary reactions. In chemical kinetics, one distinguishes three main types of elementary reactions, namely, unimolecular, bimolecular, and termolecular reactions, depending on how many particles – one, two, or three, respectively – take part in the elementary process [1, 2].

1. RECOMBINATION CHANNELS IN TRIATOMIC SYSTEMS

Optimization of complicated chemical processes requires not only knowledge of the rates of the elementary acts constituting the brutto mechanism but also a profound understanding of the dynamics of the elementary reactions the brutto process is made up of. This is especially necessary if the process can be entirely or partially non-equilibrium.

The termolecular processes are the least explored ones from the dynamical viewpoint. The most widespread examples of such processes are the recombination reactions of free atoms or ions as well as of small radicals. If these particles are sufficiently active (like, for instance, atomic ions in plasma media), they may have a significant impact on the properties of the medium where they are located, and recombination reactions make their concentrations decline. Consequently, one pays considerable attention to taking all the recombination channels into account.

The simplest scheme of ionic recombination reactions is usually written down as

$$A^+ + B^- + M \to AB + M, \qquad (1)$$

where M is the third particle needed to remove a certain amount of energy from the nascent molecule to make it sufficiently stable.

However, in a system of three atomic particles, there exists one more recombination channel that can yield the same final product as the scheme (1) does. This channel includes the formation of intermediate ionic clusters like MA^+ or MB^- with their subsequent interaction with the corresponding partner of the recombining pair:

$$MA^+ + B^- \to AB + M \qquad (2)$$

or

$$MB^- + A^+ \to AB + M. \qquad (3)$$

It is worthwhile to note that here and henceforth, we do not consider the formation of excimer molecules the excimer lasers are based on, like M–M or M–B, where M is a noble gas atom and B is a halogen atom. In the sequel, M will denote a noble gas or mercury atom, A^+ will be an alkali ion, and B^- will stand for a halogen ion. The A^+ and B^- ions form in dissociation of the corresponding molecules.

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[1] The article was translated by the authors.

Thus, even in simple triatomic systems under appropriate conditions, an additional channel of the expenditure of active particles can occur. An investigation of this channel and a comparison of its dynamics with that of the classical termolecular reaction will allow one to determine more precisely the mechanism of the complicated brutto process in the medium under study.

The equilibrium recombination reactions of atomic ions (as well as of atoms or small radicals) under the scheme (1) are the most explored ones. For such reactions, a large number of the rate constants have been measured [3, 4], but one has not determined the rate constants of the processes of the types (2) and (3). On the other hand, to compare these reactions with that of the classical scheme (1), one can use the dynamical characteristics of these processes.

Unfortunately, the authors cannot provide explored examples of recombination reactions under the scheme (2) or (3). Nevertheless, in the works [5–9], one observed the formation of diatomic ions of the MCs^+ type in collision induced dissociation (CID) reactions. In these reactions, the formation of such ions is a parallel channel along with the formation of atomic ions. It is clear that the reaction reverse to this channel exemplifies recombination under the scheme (2) we are interested in.

In the papers [10–13], the dynamics of three-body interactions of the type (1) was examined as the dynamics of the processes reverse with respect to collision induced dissociation of molecules with an ionic bond. In particular, one has studied how the behavior of such systems depends on the masses of the particles involved, the collision energy of the recombining particles, and the third body energy with respect to the center of mass of the recombining particles, as well as on the orientation and other kinematic parameters.

The dynamics of the process

$$Cs^+ + Br^- + Xe \rightarrow CsBr + Xe \tag{4}$$

was investigated one of the first. Then one explored the dynamical peculiarities of recombination with $M = Kr$, Ar and the processes of recombination of the ions formed in CID of other cesium halides. One of the main conclusions of these dynamical studies was that such interactions are of a direct nature which is completely consistent with the direct nature of the dynamics of the CID process in the corresponding systems $CsB + M$. Using the example of the systems $Cs^+ + Br^- + M$ examined, one has shown that direct three-body recombination proceeds via at least two different mechanisms depending on the impact parameter of the third body with respect to the center of mass of the recombining pair of ions. In the region of small impact parameters, the principal channel of energy removal is the interaction of the M atom with both the ions at the ion approach stage. In the region of large impact parameters, the prevailing mechanism consists in energy removal via an encounter of the third atom with one of the ions at the stage of the ions' flying away from each other. The nascent products have a strongly non-equilibrium distribution of the vibrational energy and an almost equilibrium distribution of the rotational energy.

The concept and method of simulation of the dynamics of elementary processes described in the works [7–11] enable one to explore the dynamics of other reactions of similar type as well. Under some kinematic conditions [14], the potential energy surface (PES) governing the recombination and the CID process $CsBr + M$ opens the channel of formation of the diatomic complexes MCs^+ whose cross section is considerably smaller than that of the main channel of formation of the atomic ions. The process reverse to the MCs^+ complex formation,

$$MCs^+ + Br^- \rightarrow CsBr + M, \tag{5}$$

can be one of the important recombination channels that proceed in plasma media via intermediate complexes.

2. SIMULATION OF RECOMBINATION OF THE CESIUM AND BROMIDE IONS

In the present work, we consider the statistical dynamics (that is, the dynamics based upon integrating a large number of quasiclassical trajectories) of the formation of a stable AB molecule in recombination of atomic ions via a diatomic complex of the MA^+ type. This reaction is treated as an additional recombination channel not described before. The process dynamics is discussed using the example of interaction of the Br^- ion with the $XeCs^+$ ion, and the dynamical pattern of this reaction is compared with the dynamics of the classical picture of three-body recombination of free particles. Note that such reactions are also characteristic for other ionic complexes formed by a noble gas atom with the Cs^+ ion.

As was pointed out above, CID of cesium bromide with xenon as the third body can be represented by the scheme

$$CsBr + Xe \rightarrow \begin{cases} Cs^+ + Br^- + Xe, & (6) \\ XeCs^+ + Br^-. & (7) \end{cases}$$

These two channels are also characteristic for collisional dissociation of other cesium halides except for some processes involving Ar. It is worthwhile to note that an ion of the MB^- type was only observed for CID of the CsI molecule [5].

The dynamics of the processes of collisional dissociation (6) and (7) is almost quantitatively [7, 8] reproduced by trajectory simulation on a PES constructed of the pairwise potentials, where the potential of the CsBr molecule is represented by the truncated Rittner potential. The remaining interactions were described by the Mayer–Born repulsion and long-range interactions: the ion–induced dipole and the dispersion attraction $-C/R^6$. The interaction potential Xe–Cs^+ can be with good accuracy represented by the expression

$$U(R) = A\exp(-R/\rho) - \alpha_M/(2R^4) - C/R^6, \qquad (8)$$

where R is the distance between the particles, A and ρ are the parameters of the Mayer–Born wall, α_M is the polarizability of the projectile atom, and C is the dispersion constant.

In the work [15], the interaction potentials of the cesium ion with the noble gas atoms M are determined including the particle attraction region. The potential parameters for M = Xe are:

the potential well depth $\varepsilon = 0.1194$ eV,

the location of the potential well minimum R_m = 4.016 Å,

the location of the potential zero R_0 = 3.44 Å.

Thus, the $XeCs^+$ ion is relatively weakly bound and its size is comparatively large. Note that a detailed annotated bibliography of the works on the interaction potentials in all the systems A^+–B^-, M–A^+, and M–B^- is presented in the report [16].

According to the microscopic reversibility principle, recombination of the ions formed in the CID processes in the system CsBr + Xe proceeds through the two channels,

$$\left.\begin{array}{l} Cs^+ + Br^- + Xe \quad (9) \\ XeCs^+ + Br^- \quad (10) \end{array}\right\} \rightarrow CsBr + Xe$$

on the same potential energy surface as the processes (6) and (7) do. In both the channels (9) and (10), the original CsBr molecule forms as a result of recombination of the two ions Cs^+ and Br^-, but the process in the channel (9) operates like a classical termolecular reaction while in the channel (10) it proceeds as a bimolecular interaction that yields the same products. That is why, as was already noted above, it seems interesting to compare the dynamics of both reactions governed by the same PES which describes the direct two-channel CID process almost quantitatively.

The technique of trajectory calculations in the present work is similar to the one used previously (see, e.g., [11]) for the reaction (9) and can be described in brief as follows.

At the beginning of the trajectory, the distance between the center of mass of the ionic complex $XeCs^+$ and the negatively charged ion Br^- was set equal to 250 a.u. so as to be able to neglect the influence of the potential $XeCs^+$–Br^- on the relative motion of the particles at the beginning of the trajectory. From the viewpoint of the computational procedure, this requirement means the constancy of the momenta of the relative motion of the colliding particles at first integration steps.

The orientation angles of the axis of the ionic complex with respect to the line of its approach to the negative ion were chosen by the Monte Carlo method so that all the spatial configurations of the collision would be equiprobable.

The maximal value of the impact parameter of the negatively charged ion with respect to the center of mass of the ionic complex was fixed to be sufficiently large and equal to 100 a.u., since at collision energies of tenths of electron volt recombination occurs at values close to this quantity.

The equations of motion were integrated by the sixth order Adams method, while the first five steps for this method were calculated by the fourth order Runge–Kutta procedure. The time length of the integration step of the equations of motion was chosen to be equal to 50 a.u. This was enough to ensure the conservation of the total energy and momentum to be no worse than unit in the sixth significant digit throughout the whole trajectory.

The termination criterion for a trajectory yielding the formation of a stable CsBr molecule is the following conditions: the distance between the Cs^+ and Br^- ions does not exceed 30 a.u., the total energy of this pair is negative, while the distances from both the ions to the third atom are larger than 250 a.u. and the corresponding pairwise energies are positive. If a molecule forms, its vibrational and rotational energies are determined at the end of the trajectory.

The recombination probability is defined as the ratio of the number of "successful" (in the recombination sense) trajectories to the total number of trajectories integrated.

3. THE DYNAMICAL CHARACTERISTICS OF RECOMBINATION

Figure 1 shows the excitation functions of the recombination processes of the Cs^+ and Br^- ions through the channel (9) via the atomic ions and the neutral atom (line *1*) and through the channel (10) via the diatomic complex $XeCs^+$ (line *2*). The excitation function is one of the most important dynamical characteristics of the reaction and determines its energy range, i.e., the energy domain of the existence of the process. Line *1* is calculated for the initial energy $E_{\rm ini}$ of the central encounter of the atomic ions equal to 0.2 eV and for the collision energy $E_{\rm rel}$ with the Xe atom up to 10 eV. Note that the shape of the excitation functions for processes of this type persists in the whole interval of the collision energies of the recombining pair with the atom (i.e., also for energies larger than 10 eV) and at various energies $E_{\rm ini}$ of the ion approach. In contrast to this excitation function, line *2* goes down very fast from unity to almost zero in the range of interaction energies of Br^- with the ionic complex from 0 to about 2 eV and remains zero for larger collision energies. The comparison between the

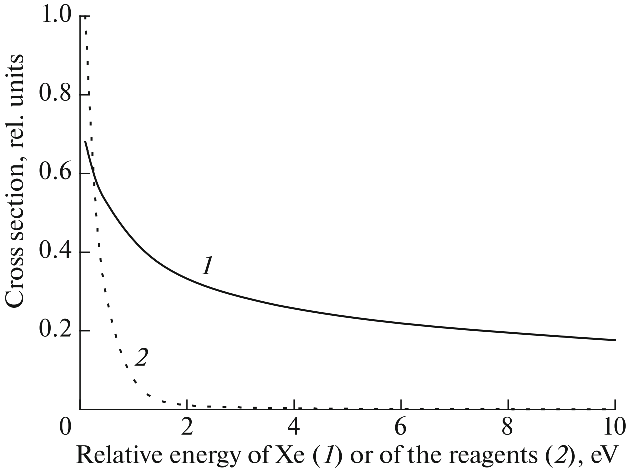

Fig. 1. The excitation functions of the two recombination processes of the Cs^+ and Br^- ions, via three-body interaction at $E_{ini} = 0.2$ eV (line *1*) and via the diatomic ion $XeCs^+$ (line *2*).

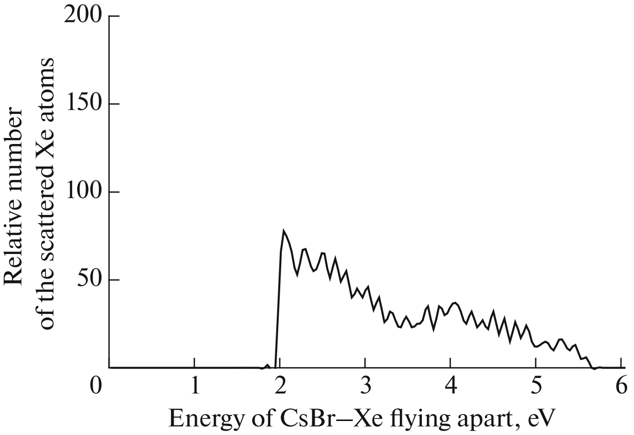

Fig. 2. The distribution of the energies of the Xe atoms that stabilize the CsBr molecule in three-body recombination at $E_{ini} = E_{rel} = 1$ eV.

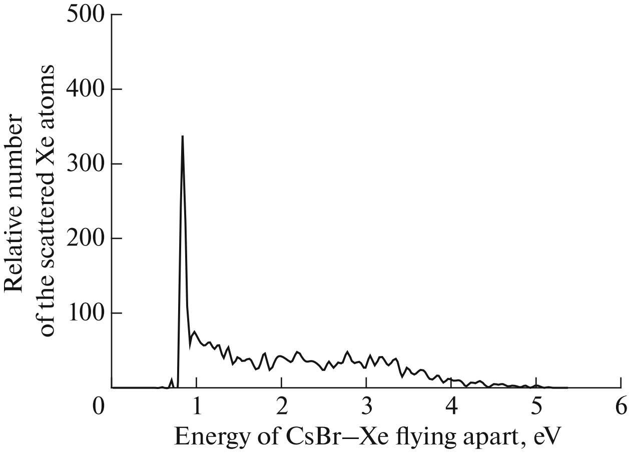

Fig. 3. The distribution of the energies of the Xe atoms that stabilize the CsBr molecule in the reaction of the Br^- ion with the ionic complex $XeCs^+$ at $E = 1$ eV.

two functions shows that recombination through the channel (9) occurs in a much wider interval of collision energies.

Both the channels are characterized by sufficiently complicated dynamics which includes taking away considerable energy from the nascent CsBr molecule, and the amount of the energy being removed grows as the ion approach energy increases (if the other energy characteristics of the system are kept constant). The corresponding mechanisms of stabilization of the product molecule are significantly different. Indeed, in the first case the Xe atom is scattered at one of the recombining ions and rarely at both the ions, while in the second case the Xe atom is not scattered in a collision with an atom or ion but gains energy directly from the nascent molecule. Since the bond strength in the molecular ion $XeCs^+$ is no larger than 0.12 eV, the two mechanisms of ion recombination can well proceed via the diatomic ion, namely, just by knocking out the Xe atom or through an interaction of the Br^- ion with the Cs^+ ion and a subsequent stabilization of the product molecule by the Xe atom which takes away an excess of energy.

Figures 2 and 3 show the energy distributions of the Xe atoms after stabilization of the product molecule. Figure 2 presents the distribution of the energy of the Xe atom that has stabilized the CsBr molecule formed in interaction of the ions with the approach energy $E_{ini} = 1$ eV and the Xe atom with the energy $E_{rel} = 1$ eV. The sum of these energies gives the threshold of the distribution which occupies the energy range from 2 eV to about 6 eV taking into account the dissociation energy of the formed molecule (4.3919 eV). The interpretation of the analogous energy distribution of the Xe atoms appearing in the process (10) with the collision energy $E = 1$ eV is somewhat more complicated (Fig. 3). The narrow peak of scattering of Xe atoms near 1 eV is probably connected with directly knocking out the atom from the weakly bound ion $XeCs^+$ by the Br^- ion. The distribution adjacent to this peak reflects the stabilization process of the nascent CsBr molecule by the Xe atom (which takes away energy) after the product forms. A more precise picture can be obtained from studying the detailed dynamics of this reaction, that is, dynamics within the framework of individual trajectories.

In dynamics of the elementary process, the so called opacity function plays a substantial role. This is the dependence of the process probability on the impact parameter of the collision of the projectile atom with respect to the center of mass of the diatomic target. Figure 4 shows the opacity function of the process (9) at $E_{ini} = E_{rel} = 1$ eV. As one sees in the figure, the range of impact parameters where the reaction is possible extends from 0 to about 20 a.u. The distribution of impact parameters exhibits a clearly pronounced maximum and some structure. The work [13] discusses the relationship between the shape of the opacity function of classical three-body recombina-

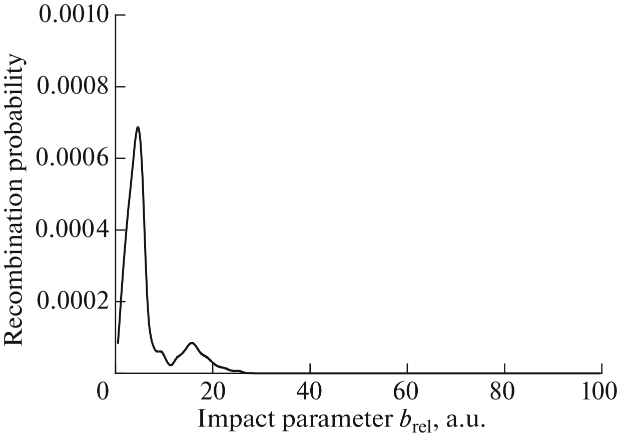

Fig. 4. The opacity function of the process (9) at the collision energy of the ions and the third body energy equal to 1 eV.

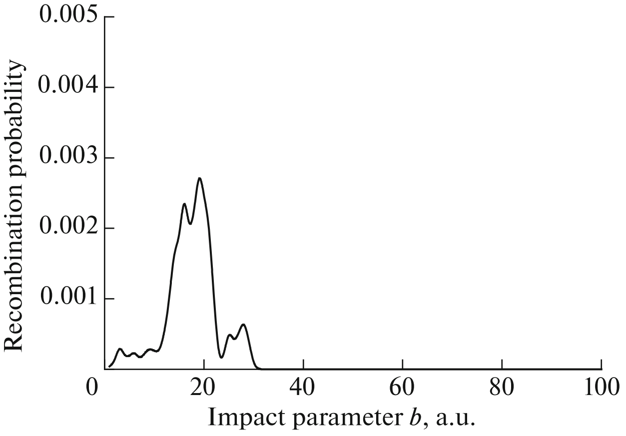

Fig. 5. The opacity function of the process (10) at the reagent collision energy equal to 1 eV.

tion and the dynamical mechanism of the process and its changes depending on the configuration of the particle collision and other kinematic parameters of the collision.

Figure 5 presents the opacity function of the process (10) at the reagent collision energy $E = 1$ eV. In its structure, this function is somewhat similar to that shown in Fig. 4. However, a more detailed examination implies that it has a much more complex structure both in the region of small impact parameters and in the region of large ones. This indicates a significant difference in the dynamical patterns of both processes, which coincide in the composition of the particles and in the nature of the three-body interaction (where the third body is necessary to stabilize the nascent molecule).

One more evidence for dynamical differences of the processes (9) and (10) is the distributions of the internal energies of the corresponding products. Figures 6 and 7 show the distributions of the vibrational energy of the CsBr molecules formed in these reactions. As follows from a comparison between these figures, the two distributions of the vibrational energy are very different from the equilibrium ones and also differ markedly between themselves. On the other hand, the rotational distributions shown in Figs. 8 and 9 are also different (this is especially true for the distribution in Fig. 9a).

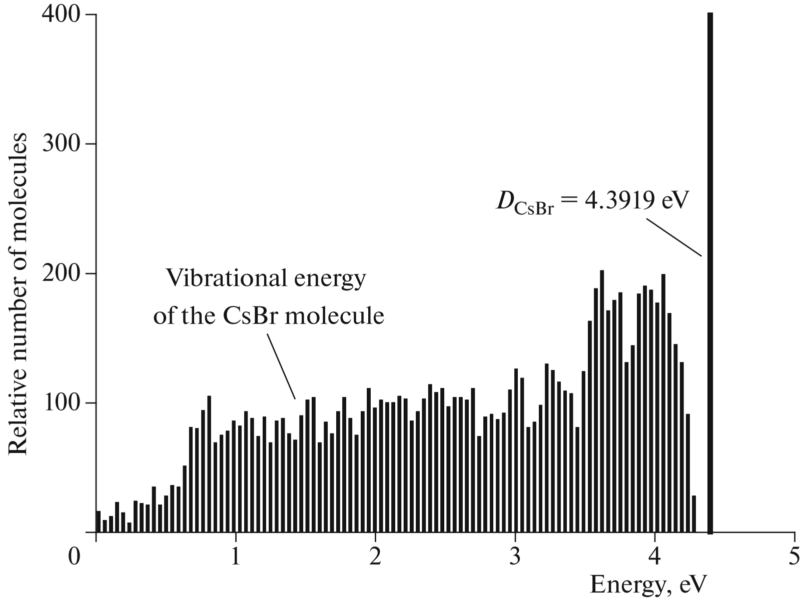

Fig. 6. The distribution of the vibrational energy of the recombination products in the system $Cs^+ + Br^- + Xe$ at $E_{\text{ini}} = E_{\text{rel}} = 1$ eV.

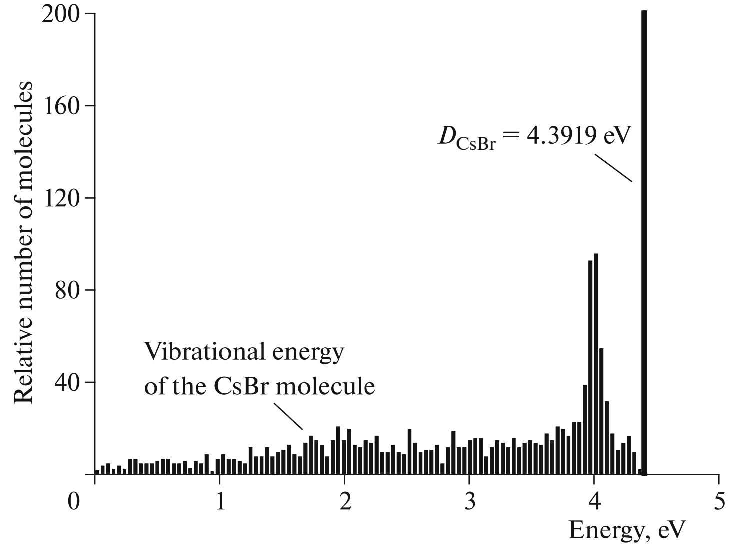

Fig. 7. The distribution of the vibrational energy of the recombination products in the system $\mathrm{XeCs}^+ + \mathrm{Br}^-$ at $E = 1$ eV.

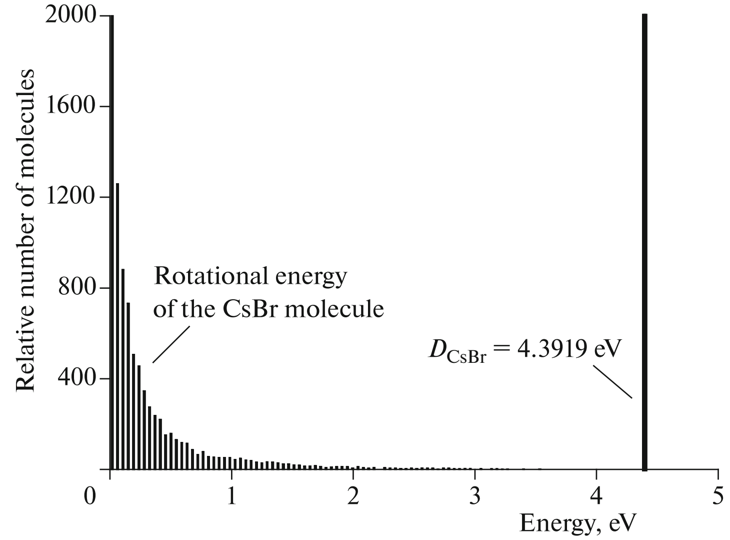

Fig. 8. The distribution of the rotational energy of the recombination products in the system $\mathrm{Cs}^+ + \mathrm{Br}^- + \mathrm{Xe}$ at $E_{\mathrm{ini}} = E_{\mathrm{rel}} = 1$ eV.

The essential dynamical differences between the processes (9) and (10) caused by fact that in the recombination process there participate free ions and the third body, on the one hand, and the bound pair consisting of the ion and the atom accepting excess energy, on the other hand, manifest themselves at very low energies of approach of the reacting ions. Figure 10 presents the opacity function of the process (10) at the reagent collision energy equal to 0.2 eV. As is seen from the figure, the range of impact parameters for which the recombination process is possible extends from 0 to more than 80 a.u. in this case. Moreover, the recombination probability grows almost linearly as the impact parameter increases to 75 a.u. and linearly goes down the same way as the impact parameter grows further. The most probable reason for this behavior of the opacity function is the preferential interaction of the ions in the long-range Coulomb field. A kinetic energy of 0.2 eV in this field cannot have a significant effect on the mechanism of the ion approach. At the collision energy equal to 0.1 eV the upper bound of the range of impact parameters for which the process (10) is possible increases to more than 100 a.u. As the collision energy grows, the interval of suitable impact parameters shrinks and the shape of the dependence of the recombination probability on this parameter changes drastically, to the shape presented in Fig. 5 at the collision energy equal to 1 eV.

The above comparison between the dynamics of the two mechanisms of recombination of the atomic

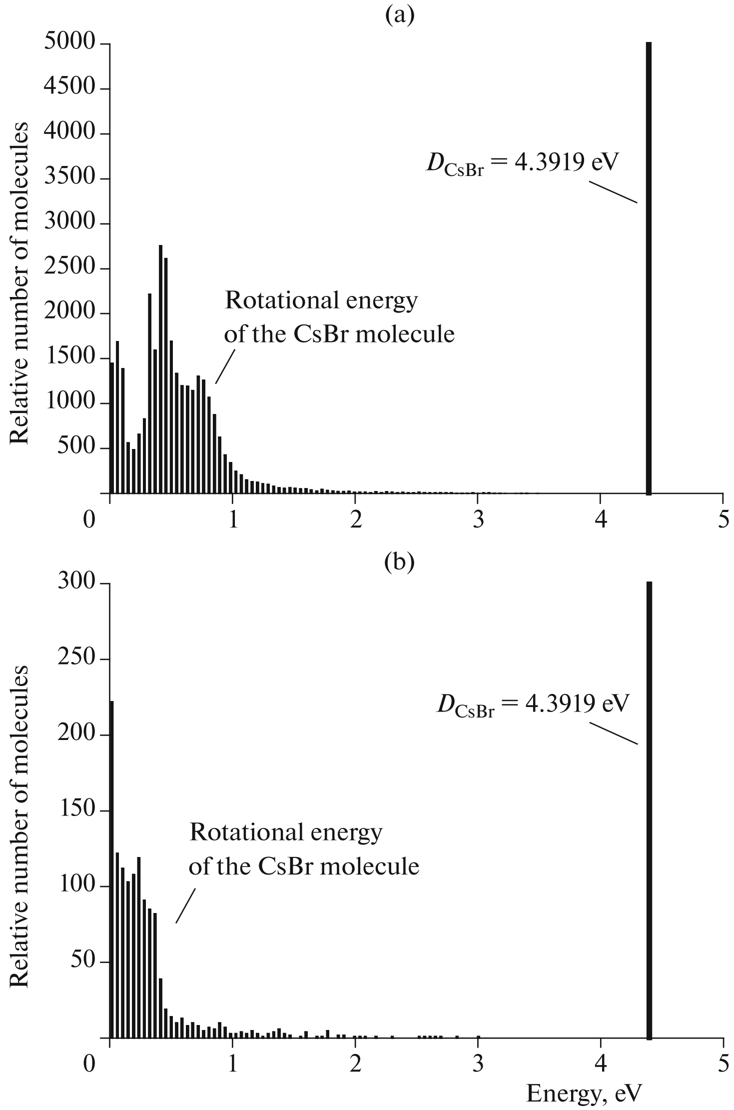

Fig. 9. The distribution of the rotational energy of the recombination products in the system $XeCs^+ + Br^-$ at: (a) $E = 0.2$ eV, (b) $E = 1$ eV.

ions, through the direct interaction of the three particles and through the interaction of the diatomic charged complex with the ion, showed a significant difference in the dynamics of these processes. In spite of the complete identity of the particles involved in the recombination reactions under consideration and the same structure of the potential energy surface that governs both reactions, the key dynamical characteristics of these reactions have little in common. Apparently, this is due to the peculiarities of the interaction among the particles in the course of each process. In the reaction (9), the interaction of the Cs^+ and Br^- ions depends largely on the encounters of each of the ions with the Xe atom or on the encounter of Xe with both the ions when a part of the energy of the ionic pair is being taken away. This ensures the formation of a stable product in one or another excited state. In the

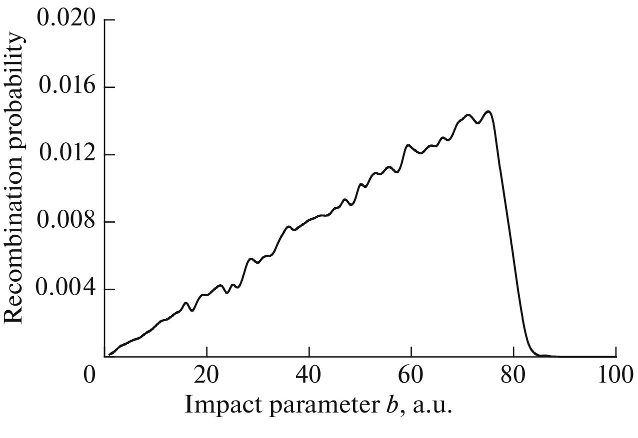

Fig. 10. The opacity function of the process (10) at the reagent collision energy equal to 0.2 eV.

reaction (10), interference of the interactions Br^-–Xe and Cs^+–Xe in the basic Coulomb interaction between the ions is minimal, and the removal of energy from the nascent product molecule is only due to the transfer of energy to the Xe atom weakly bound with the Cs^+ ion.

Apparently, the dynamics of the process (10) is much more complicated than one can imagine from the statistical studies. To examine the dynamics of recombination via the ionic cluster in a more comprehensive way, one has to explore the detailed dynamics of the possible channels of this process. One has to understand, however, that recombination through a weakly bound complex has so far been poorly studied, and it may turn out that under certain conditions in plasma media, it will be comparable or strongly prevail in its rate over the classical process, which can cause an unforeseen death of ions.

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