

Statistical Dynamics of Direct Three-Body Recombination of Heavy Ions in the Presence of Argon and Xenon Atoms

V. M. Azriel, L. I. Kolesnikova, and L. Yu. Rusin*

Tal'roze Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

*e-mail: rusin@chph.ras.ru

Received July 29, 2015

Abstract—Recombination of singly charged heavy Cs^+ and Br^- ions with stabilization with neutral Ar or Xe atoms was studied by the classic trajectory method in the range of ion collision energy and third body energy from 1 to 10 eV. The elementary reaction of recombination was studied on the potential energy surface (PES), which quantitatively reproduces the experimental results of collision-induced dissociation of CsBr molecules (the reverse of recombination). An analysis of the statistically reliable number of trajectories revealed a complex multifactor dynamics of recombination, which involves various mechanisms whose realization depends both on the mass and energy ratio of colliding particles and on the PES structure and spatial configurations of collision determined by impact parameters, orientation angles, etc. The molecules that formed as a result of recombination have nonequilibrium vibrational energy distributions and rotational energy distributions comparable to equilibrium.

Keywords: dynamics of elementary processes, recombination of ions, direct three-body recombination, statistical dynamics, detailed dynamics, potential energy surface

DOI: 10.1134/S1990793116040205

Recombination of atoms and ions [1–3] is one of the main channels of the destruction of active centers and/or formation of excited products in many complex chemical processes and active media. One of such active media is, e.g., low-temperature plasma in ionic or plasma engines excited in noble gases or mercury vapors [4, 5] and in other devices with additions of various substances depending on the required properties of the medium. The three-body recombination of ions underlies the functioning of excimer lasers on inert gas monohalides [6, 7], where the interaction of positive noble gas ions and negative halide ions gives rise to light-emitting states:

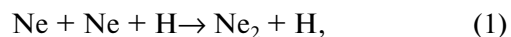


These and other such processes form the basis of a new class of plasma light sources, which use spontaneous ultraviolet emission of exciplex molecules [8].

Association of two particles is accompanied by liberation of certain amount of energy sufficient for decomposition of the associate. Therefore, recombinations can occur as bimolecular associations with energy dissipation in inner degrees of freedom or as trimolecular interactions. In the latter case, the excess energy is withdrawn by the third body, providing the transfer of products from the region with a continuous energy spectrum to the region with a discrete spectrum corresponding to the bonded molecule. These three-body interactions can occur by two mecha-

nisms, one of which involves the formation of some intermediate complex and the other is direct interaction of three particles, forming the product. In this case, the efficiency of recombination and hence the concentration of recombining particles depend on the efficiency of the third body, which, in turn, is determined by its physical properties and conditions of collision with the recombining pair. This circumstance can in principle provide an opportunity to control, to a certain extent, the concentration of ions, for example, by varying the composition of the third component.

The dynamics of trimolecular processes is considerably more complex than that of bimolecular ones because the trimolecular reactions involve three particles whose interactions can occur by the routes involving all possible pair collisions with a transfer of some part of the energy of the recombining pair to the third body. The formation of products in these processes can be described in terms of the relatively simple hard sphere model. The most interesting examples of such three-body interactions are dimerizations of noble gas atoms such as Ne (see [9] and references therein) and He [10]:



The validity of the hard sphere approximation was discussed in [11], where the pulse model of the three-body recombination of ions bonded by the long-range Coulomb potential was described on the example of the model reaction



where R = Hg, Xe, Kr, and Ar.

For recombinations of particles with more or less extended interaction potentials, the pulse interpretation is evidently rather simplified. The dynamics of reaction (3) for R = Hg, Xe, and Kr was studied by the quasiclassic trajectories method on diabatic potential energy surfaces (PESs), governing the reverse process of dissociation of CsBr molecules induced by collisions with the corresponding R atoms [12–15]:



In these studies, the dynamics of recombination was investigated based on the statistically significant number of trajectories calculated in the given ranges of kinematic parameters (initial trajectory conditions). This statistical approach (called below the statistical dynamics) allows us to consider the dynamic behavior of the systems in a wide range of initial conditions. Thus, the statistic dynamics data for the direct or reverse reaction make it possible to determine the parameters of the suggested PES model by comparing these data with the experimental dynamic characteristics of the process.

One of the main problems in studies of the elementary processes of recombination is the mechanism of stabilization of the recombination product and the efficiency of the third body as an acceptor of the excess energy of the associate of the recombining particles. Based on the general analysis, it was suggested [12–15] that the dynamic peculiarities of stabilization of the products of direct recombinations are determined by at least two main factors: the mass of the third body and the structure of PES governing the collisions of particles.

The goal of this study was to compare the statistical dynamics of recombination in two reactions (3) involving the Ar and Xe atoms, which differ in mass more than threefold. Moreover, these two systems are characterized by PES structures that differ to a certain extent because of the quantitative discrepancies of the potential curves of interaction of both atoms with Cs⁺ and Br⁻ ions. In [11] recombinations (3) for R = Ar and R = Xe were already compared, but only within the framework of the pulse model.

The trajectory calculation technique is based on the ideal concept about the simultaneous collision of three particles at the center of mass of the ion pair. Using the known interaction potentials makes this model quite realistic. The calculation procedure was as follows. At the beginning of the trajectory, the Cs⁺ and Br⁻ ions lie at a distance R_i from one another (in

our calculations, $R_i = 250$ a.u.), and the third R particle lies at a distance R_R from the center of mass of the Cs⁺–Br⁻ pair (this distance is determined in terms of the atomic energy and the time of approach for the ion pair). Then all the three particles start to move toward the center of mass of the ion pair. The Cs⁺ and Br⁻ ions can start to move without an initial velocity (under the action of the long-range Coulomb part of the potential) or with a given initial velocity determined by the energy of approach of ions E_i . We can consider to a good approximation that the Coulomb force is the only force that affects the ions on the major part of the trajectory because of the long distance between them. The problem of the motion of a pair of ions in the Coulomb field is solved analytically to give the time in which they meet at the center of mass of the ion pair. The third R body has to reach this point simultaneously, which, together with the energy E_R of this particle, unambiguously determines its initial distance to the center of mass of the ion pair. It is believed that the velocity of R changes insignificantly on the main part of the route because of the weak interaction of the neutral atom with the ions at long distances. To preserve the generality, some part of calculations admitted a possible delay of the arrival of the third body to the meeting point of two ions. This was achieved by artificially increasing the initial distance from this particle to the center of mass of the ion pair: for example, the delay $T_{\text{del}} = 0.1$ corresponded to an increase in R_R by 10% relative to the value found for this parameter in an assumption of a simultaneous collision of three particles.

The given calculation procedure supposes that the impact parameter b_i of the ion pair and the impact parameter b_R of the third body relative to the center of mass of the ion pair are zero. If one of these parameters or both are nonzero, the procedure for choosing the initial conditions is slightly modified as described in [13, 15]. The maximum value of the b_i impact parameter was chosen to be 40 a.u. in all calculations, since at higher values of this parameter, there was no recombination. At the same time, the maximum impact parameter b_R of the R atom relative to the center of mass of the ion pair depended on the delay of the arrival of the neutral atom. For $T_{\text{del}} = 0, 0.1, \text{ and } 0.2$, this value was chosen equal to 20, 40, and 100 a.u., respectively. The step of integration of the equations of motion over time was chosen to be 50 a.u. This provided that the total energy and momentum were conserved not worse than unity in the sixth significant digit throughout the whole length of the trajectory. The criterion of the end of the trajectory that led to the recombination of Cs⁺ and Br⁻ ions is the condition that the distance between them does not exceed 30 a.u., the total energy of this pair is negative, the distances from both ions of the molecule to the third atom are longer than 250 a.u., and the corresponding pair energies are positive. If a CsBr molecule forms, its vibra-

tional and rotational energies are calculated at the end of the trajectory. The probability of recombination was determined as the ratio of the number of effective (from the viewpoint of recombination) trajectories to the total number of calculated trajectories.

The potential energy surface that governs reactions (3) and (4) can be represented with a good approximation as additive, i.e., equal to the sum of three pair potentials of interaction of the ions with one another and of each ion with the third body:

$$U(r_1, r_2, r_3) = U_1(r_1) + U_2(r_2) + U_3(r_3).$$

Here U_1 , U_2 , U_3 and r_1 , r_2 , r_3 are the potential energies and distances in the Cs^+-R , Cs^+-Br^- , and Br^--R pairs, respectively. The interaction of ions in the alkali metal halide M^+X^- molecule is well described by the truncated Rittner potential, which has the following form in the atomic unit system:

$$U_{\text{M}^+\text{X}^-}(r) = A \exp(-r/\rho) - 1/r - (\alpha_{\text{M}^+} + \alpha_{\text{X}^-})/2r^4 - C/r^6.$$

The pair interactions of the noble gas atom with each ion are described by the same equations:

$$U_{\text{RM}^+, \text{RX}^-}(r) = A \exp(-r/\rho) - \alpha_{\text{R}}/2r^4 - C/r^6.$$

The semiempirical PES used in our study, which quantitatively correctly describes the experimental data in molecular beams for dissociation (4) of CsBr molecules induced by collisions with the R atoms, actually contains a cross term and has the following form in the atomic unit system:

$$U(r_1, r_2, r_3) = A_2 \exp\left(-\frac{r_2}{\rho_2}\right) - \frac{1}{r_2} - \frac{\alpha_2 + \alpha_3}{2r_2^4} - \frac{C_2}{r_2^6} + A_1 \exp\left(-\frac{r_1}{\rho_1}\right) + A_3 \exp\left(-\frac{r_3}{\rho_3}\right) - \frac{C_1}{r_1^6} - \frac{C_3}{r_3^6} - \frac{\alpha_1}{2} \left(\frac{1}{r_1^4} + \frac{1}{r_3^4} + \frac{r_2^2 - r_1^2 - r_3^2}{r_1^3 r_3^3} \right) \left(1 - \frac{\alpha_2 + \alpha_3}{r_2^3} \right),$$

where A_i and ρ_i are the parameters of the Born–Mayer wall for the interacting particles; C_i are the disperse constants of three pair interactions; and α_1 , α_2 , and α_3 are the polarizabilities of Xe (Ar), Cs^+ , and Br^- , respectively. The PES parameters used here are presented in Table 1.

The histogram dependence of the probability of formation of a stable product of recombination on the collision energies of ions E_i and the ion pair with the third body E_{R} for $\text{R} = \text{Ar}$ is shown in Fig. 1. The histogram for $\text{R} = \text{Xe}$ is qualitatively identical in its structure to the one presented in Fig. 1. Both dependences are characterized by a drastic decrease in the recombination probability at increased ion collision energies, especially in the range of low E_{R} values and a slightly weaker dependence on the energy of the third body.

Table 1. Potential energy surface parameters for the $\text{Cs}^+ + \text{Br}^- + \text{R}$ systems in the atomic unit system

Pair	A_i	ρ_i	C_i
Cs^+-Br^-	127.5	0.7073	87.36
Cs^+-Ar	934.0	0.494	171.5
Br^--Ar	68.3	0.653	178.7
Cs^+-Xe	318.5	0.6494	490.0
Br^--Xe	62.84	0.877	297.3

The polarizabilities are $\alpha_{\text{Cs}^+} = 16.48$, $\alpha_{\text{Br}^-} = 32.46$, $\alpha_{\text{Ar}} = 11.1$, $\alpha_{\text{Xe}} = 27.2$.

The differences between the two histograms are mainly quantitative. First of all, we can note low absolute probabilities of the process, which do not exceed 3.5×10^{-3} for Xe and 1.2×10^{-3} for Ar , e.g., at maxima of the diagrams; this seemingly confirms the important role of the mass of the third body. Note, however, that the use of the mercury atom as the third R body, which is five time heavier than the argon atom, leads to the maximum probability of recombination of $\leq 3.0 \times 10^{-3}$. Thus, the mass of the third body is significant, but it is not the only factor that determines the probability of stabilization of the recombination product.

The similarity of the structures of the recombination probability histograms allows us to compare the presented results on the recombination probabilities p_{ij} for each node ($E_{\text{R}}(i)$, $E_i(j)$) averaged over the energy ranges under study for $E_{\text{R}}(i)$ and $E_i(j)$. The average probability can be determined by the equation

$$S_{\text{M}} = \frac{1}{N} \sum_{i=1}^{10} \sum_{j=1}^{10} p_{ij},$$

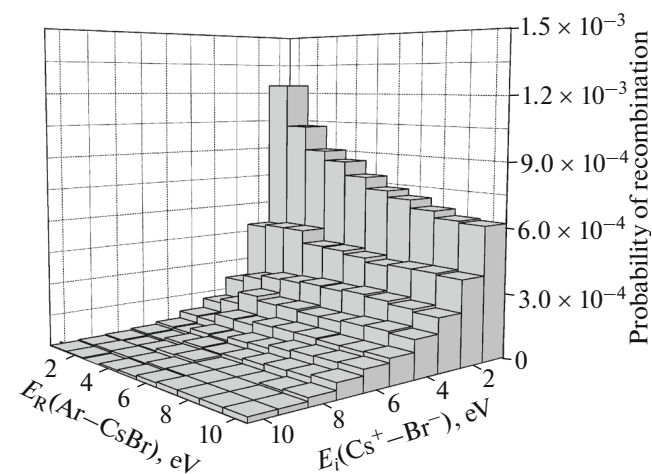


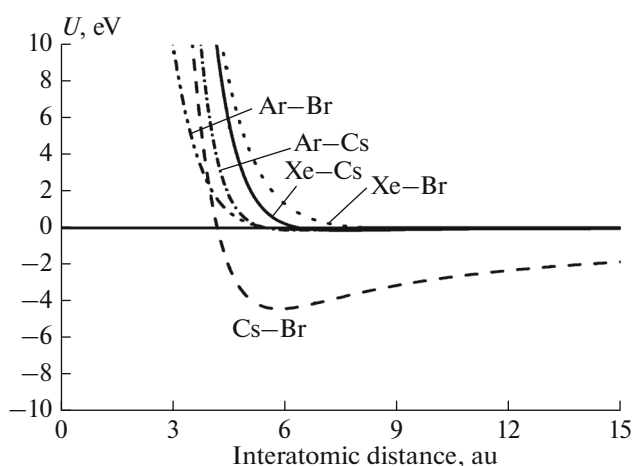
Fig. 1. Dependence of the recombination probability of Cs^+ and Br^- ions on the three-body collision energies in the presence of Ar ($T_{\text{del}} = 0$).

Table 2. Average probabilities S_M of stabilization of CsBr molecules with a mass m_R of the third bodies of 40 and 131 amu

System/ m_R	$T_{\text{del}} = 0$	$T_{\text{del}} = 0.1$	$T_{\text{del}} = 0.2$
Ar–CsBr/40	1.95×10^{-4}	1.22×10^{-4}	0.43×10^{-4}
Ar–CsBr/131	3.35×10^{-4}	2.04×10^{-4}	0.72×10^{-4}
Xe–CsBr/131	5.11×10^{-4}	3.29×10^{-4}	1.23×10^{-4}
Xe–CsBr/40	2.93×10^{-4}	2.16×10^{-4}	0.76×10^{-4}
Hg–CsBr/201	5.25×10^{-4}	3.68×10^{-4}	1.31×10^{-4}

where $N = 100$ is the total number (10×10) of the calculated probabilities p_{ij} . To understand the role of the mass of the third R body, we constructed similar diagrams of recombination probability distribution for the Ar–CsBr and Xe–CsBr systems with the mass of the Ar atom formally replaced by the mass of the Xe atom and vice versa, but using the same PESs. Table 2 lists the average probabilities S_M of the recombination of the Cs^+ and Br^- ions with real and hypothetical masses of the third body. For comparison, the same table gives the S_M values for the delay time of the third body, which is 10 and 20% larger than the initially calculated time with $T_{\text{del}} = 0$, and the corresponding values for the Hg–CsBr system, whose PES differs from those of the systems with $R = \text{Ar}, \text{Xe}$ in its structure.

According to Table 2, the average recombination probability with a zero delay time of the third body ($T_{\text{del}} = 0$) and with stabilization by Xe atoms is 5.11×10^{-4} , which is 2.6 times larger than for Ar atoms ($S_M = 1.95 \times 10^{-4}$). At the same time, the average probability for the Hg atom, whose mass is ~ 1.5 times larger than that of the Xe atom, is 5.25×10^{-4} , which is very close to S_M for the Xe–CsBr system. Also note that the S_M values of this system and Hg–CsBr are close for the other two T_{del} values. Moreover, the function of the

**Fig. 2.** Potential energy curves of the interaction of Cs^+ and Br^- ions and Ar and Xe atoms with ions.

efficiency of the third bodies as excess energy acceptors during recombination was studied in [16, 17] according to the minimum residual energy of the molecule. It was found that the average efficiency of the third bodies in the same ranges of both particle collision energies as those given in the present paper for Xe and Hg coincides almost completely despite the 1.5-fold difference in the masses of these atoms. Both coincidences may be the consequence of the differences in the PES structures of the systems under study.

According to Table 2, the decrease to 40 amu in the mass of the third body in the Xe–CsBr system leads to S_M decreased to 2.93×10^{-4} , which exceeds the above-mentioned $S_M = 1.95 \times 10^{-4}$ for Ar–CsBr. Note that an increase in the mass of the third body in the Ar–CsBr system from 40 to 131 amu leads to the average probability of the process increased from 1.95×10^{-4} to 3.35×10^{-4} , which is smaller than S_M for the interaction of Xe atoms with the recombining ion pair (5.11×10^{-4}). This confirms the higher (relative to argon) energy accepting ability of the xenon atoms. This difference in the recombination probability is evidently caused not only by the greater mass of the Xe atom, but also by other factors. The latter include, e.g., the differences in the structure of the corresponding PESs, which are due to the nature of the interaction of the neutral Ar and Xe atoms with ions.

Figure 2 shows the potential curves that describe the interactions of the $\text{Cs}^+ - \text{Br}^-$, Ar–Cs $^+$, Ar–Br $^-$, Xe–Cs $^+$, and Xe–Br $^-$ pairs of particles. According to Fig. 2, the dependences of the potential energies on the interatomic distances for Xe and Ar atoms and both ions are similar in shape, but strongly differ quantitatively. These peculiarities themselves do not explain the above-discussed differences in the efficiency of both atoms as excess energy acceptors of the recombining pair. However, they should undoubtedly substantially affect the ion recombination probability, in particular, they point to the nature of the lower efficiency of argon as an excess energy acceptor of the formed cesium bromide molecule compared with the efficiency of xenon.

The above differences in the recombination probability evidently reflect not only the dependence of the latter on the mass of the third body and different effects of the PES structure on the efficiency of stabilization by the atoms in question, but also the possibility of other factors that affect the statistical dynamics of stabilization of the excited associate of recombining particles.

One of these factors that significantly affect the probability of a direct three-body recombination is primarily the diversity of possible trajectories on the PES, which lead to stabilization of the product molecules. This factor allows for, e.g., the sequence of third body collisions with ions, the collision configuration at the shortest distances between particles, and some

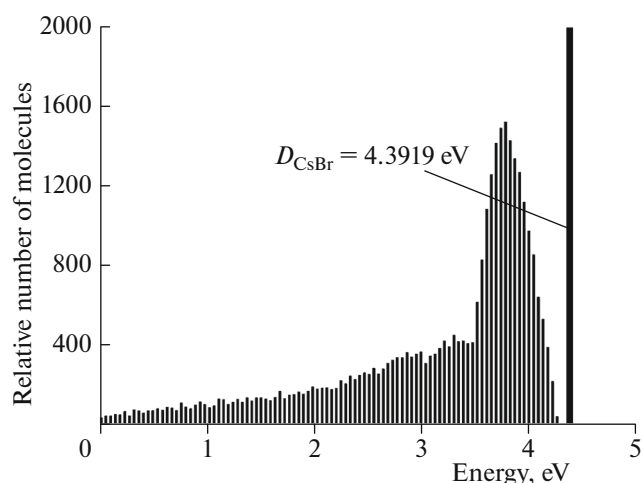


Fig. 3. Vibrational energy distribution in the Ar–Cs⁺–Br[–] system at $E_R = 1$ eV, $E_i = 1$ eV, and $T_{del} = 0$.

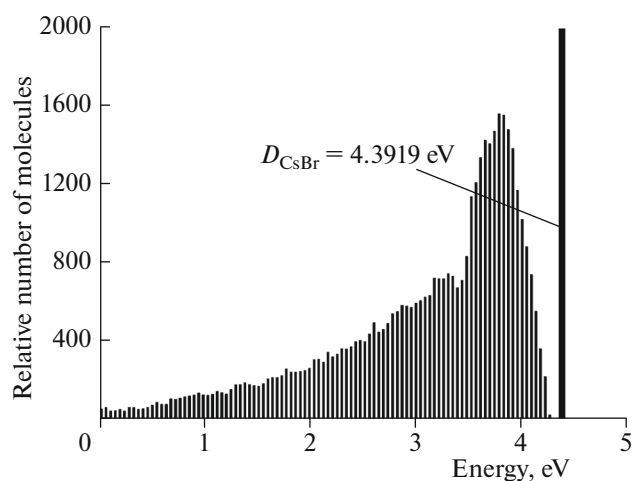


Fig. 4. Vibrational energy distribution in the Xe–Cs⁺–Br[–] system at $E_R = 1$ eV, $E_i = 1$ eV, and $T_{del} = 0$.

other peculiarities of three-body collisions. Each of the systems under study probably has a definite set of the types of these trajectories possessing different weights in the general statistics of recombination calculation. According to the data of Table 2, the Xe–CsBr system has a larger number of statistically significant types of trajectories than the system with an argon atom. This is confirmed by the considerable differences of the above-mentioned functions of the efficiency of Xe and Ar atoms, which represent the dependences of the minimum residual energy of the product molecule on both collision energies [16, 17]. The average efficiency of Ar atoms in the ranges of E_R and E_i under study is 16 times smaller than the average efficiency of Xe atoms.

In statistical dynamics of elementary processes, this should affect the shape of product distributions, of which the most interesting ones are those of the energy evolved in the elementary process. As mentioned above, in excimer lasers, the specific electron energy distribution of ion recombination products is the reason for the formation of a laser medium.

Data on the presence of sufficiently stable electronically excited states of alkali halide molecules are absent (see, e.g., handbook [18]). Therefore, below we consider the distributions of vibrational and rotational energies. The histograms in Figs. 3 and 4 show the vibrational energy distributions in ion recombinations in the presence of Ar and Xe at collision energies $E_R = 1$ eV and $E_i = 1$ eV. As would be expected in view of the similar PES structures, these figures are qualitatively similar and show at least two distributions superimposed on each other: low-energy distribution, which corresponds to the formation of the most stable products, and high-energy one, which reflects the mechanism or mechanisms of recombination with weak stabilization of the salt molecules. The values of the maxima of the distributions approximately correspond to

the dependences of recombination probabilities on both collision energies of three particles. An increase in E_R to 5 eV at $E_i = 1$ eV does not change the bimodal form of the distribution almost at all, markedly decreasing the relative number of vibrationally excited molecules. This decrease is caused not only by the decrease in the recombination probability at these energies, but also by the corresponding peculiarities of the stabilization dynamics. An increase in the ion collision energy E_i to 5 eV at $E_R = 1$ eV leads to a considerably more decreased (compared with the recombination probability) vibration population of both distributions and especially of the low-energy component. For both Ar and Xe, the distributions show that the largest content of vibrationally excited products is observed at energies of ~ 3.5 – 4.3 eV at all values of both collision energies.

Comparing Figs. 3 and 4, we can see that the low-energy distribution for Ar–CsBr has considerably lower intensity. This result is evidently explained by the lower ability of argon to withdraw energy from the recombining pair.

The presence of two vibrational distributions suggests at least two mechanisms of energy withdrawal from the recombining pair. The energy transfer is most effective in the triangular configuration of collision at the maximum approach of particles with the maximum repulsion between the neutral atom and both ions [14–17]. Another mechanism responsible for molecular stabilization can take place in collisions of R with the ions that approached one another to the extent of strong mutual repulsion. If the R atom in this case lies at a sufficiently long distance from both interacting ions and the ion pair has a high repulsion energy, the stabilization can be insignificant. A similar situation takes place in the two-stage process involving the scattering of the repelling ions and subsequent

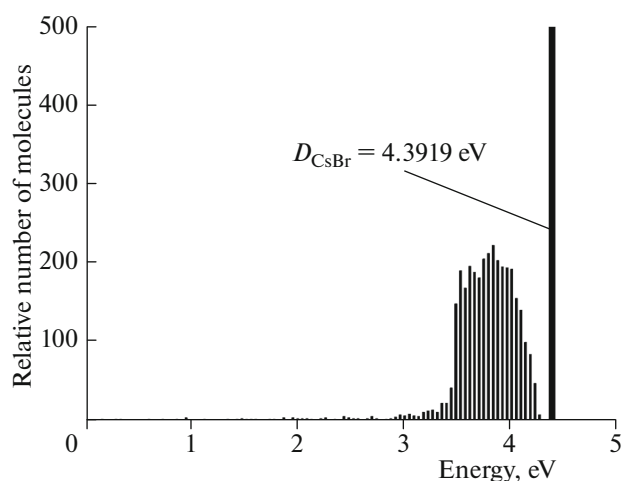


Fig. 5. Vibrational energy distribution in the $\text{Ar-Cs}^+-\text{Br}^-$ system neglecting the strong energy transfer.

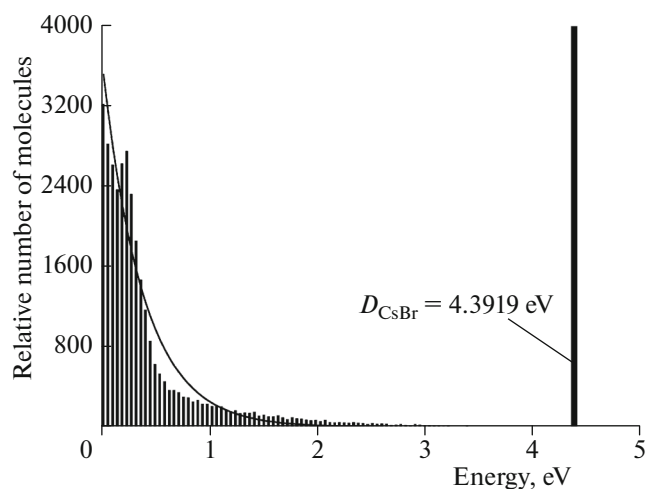


Fig. 6. Rotational energy distribution of recombination products in the $\text{Ar-Cs}^+-\text{Br}^-$ system at $E_R = 1$ eV, $E_i = 1$ eV, and $T_{\text{del}} = 0$.

transfer of some part of energy from one of the ions to the neutral atom. Evidently, each of these brutto mechanisms responsible for its own statistical distribution mode contains a whole group of detailed mechanisms, whose set constitutes the detailed dynamics of the process.

To separate both brutto mechanisms and reduce, if possible, the effect of the first indicated mechanism, 10 or 20% delays of the arrival of the third body to the center of gravity of the ion pair relative to the moment of the arrival of ions were included in the calculation procedure. Figure 5 shows the histogram of the vibrational energy distribution of the products for $R = \text{Ar}$ at collision energies of $E_R = 1$ eV and $E_i = 1$ eV and 20% delay of the arrival of the third body. The vibrational energy distribution of CsBr molecules for $R = \text{Xe}$ has

a similar form, though the high-energy part of the distribution in this case is more pronounced than for $R = \text{Ar}$. Both distributions show that the low-energy component, which corresponds to an effective energy transfer to the third body, vanished almost completely. The high-energy components of the vibrational energy distributions demonstrate a strong vibrational nonequilibrium state of the products. The observed quantitative differences in the obtained vibrational distributions are evidently caused by the difference in the efficiency of the atoms under study as energy acceptors.

The rotational energy distribution of the recombination products in the presence of Ar is presented in the histogram in Fig. 6 and its approximation with an equilibrium distribution corresponding to the temperature 4380 K. This approximation was performed by minimization of the quadratic residuals of the differences of the content of each element of the histogram and the calculated value from the equilibrium distribution at the given temperature. According to Fig. 6, the low-energy component of the histogram is satisfactorily described by the equilibrium distribution, while the high-energy component is described slightly less satisfactorily. In the range 0.5–1 eV in the medium part of the histogram, the coincidence is considerably worse, which possibly suggests different mechanisms of stabilization of the rotationally excited products in different regions of the distribution.

Table 3 lists the temperatures rounded in the last place at which the equilibrium expression most adequately describes the rotational distributions. According to this table, the increase in the ion energy E_i from 1 to 5 eV at $E_R = 1$ eV leads to growth of the rotational temperature of distribution for both inert atoms, for $R = \text{Xe}$ this growth being smaller than for $R = \text{Ar}$. The same table gives the temperatures that approximate the rotational distributions for $R = \text{Hg}$, which have the same dependence on E_i as the dependences for Ar and Xe . The effect of E_R is also the same on the whole for all the three R 's, and the increase in E_R leads to a decrease in the rotational temperature at $E_i = 1$ eV. The increase in E_R to 5 eV entails a decrease in the maximum value of distribution intensity almost twofold for Xe and 1.5-fold for Ar in accordance with the recombination probability ratios for the pairs of collision energies of particles under study. Note that the width of each distribution does not change. An increase from 1 to 5 eV in E_i at $E_R = 1$ eV causes further decrease in the distribution maximum for both third bodies in accordance with the recombination probability distribution, but for Xe the maximum is appreciably higher than for Ar . A transition to the energies $E_R = E_i = 5$ eV does not change the maximum population for both atoms almost at all.

The formation of molecules with high rotational temperatures should be mainly associated with the dynamic peculiarities of the collision of three bodies. The rotation of the recombination products is determined, in particular, by the presence of the impact

parameter of collision of ions b_i and their collision energy E_i . Note that the influence of b_i on the recombination probability is much weaker than the effect of b_R . It can be seen from the rotational energy distributions that this effect extends to energies above 3 eV, though the fraction of molecules with this energy is small. The indicated rotational energy distribution refers to the stabilized products of recombination, and the dynamics of rotational excitation in the general recombination process remains an open question. To determine the mechanism or mechanisms of stabilization of the recombination product via the transfer of rotational energy and their relation to the PES structure, a sufficiently thorough study is required to investigate the detailed reaction dynamics and the peculiarities of the potential energy surface that are responsible for these mechanisms.

One significant kinematic parameter of the collision of three particles that determines the probability of recombination and basically the whole mechanism of the process is the impact parameter b_R of the collision of the ion pair with the third body. Figure 7 shows the dependences of recombination probabilities on the impact parameters of collision of Ar (curve 1) and Xe (curve 2) with the recombining ion pair. Both dependences have almost the same form with maxima at ≈ 4 a.u. for R = Ar and at ≈ 5.5 a.u. for R = Xe. The half-widths of the distributions are close. According to Fig. 7, the ratio of the maxima of these distributions coincides very closely with the ratio of the maxima of the dependences of recombination probabilities (Table 2) on both collision energies. Note that the total widths of distributions also differ insignificantly. The range of impact parameters at which recombination is possible is slightly narrower for Ar than for Xe at rather close positions of the distribution maxima.

The above-mentioned close characteristics of the probability distributions of recombination are evidently the consequence of close similarity between the two PES structures due to the similarity of the potential curves of ion interaction with both neutral atoms. A change in the delay time of the arrival of the third body relative to the moment of ion collision leads to a considerable modification of the forms of the dependences of probability recombination on the impact parameter b_R , which probably suggests changes in the available set of dynamic mechanisms of recombination. The nature of these changes can be determined by investigating the detailed dynamics of the process under appropriate conditions.

The above results of the statistical analysis of recombination of heavy ions in the presence of Ar and Xe atoms show that the differences in the efficiency of these atoms as excess energy acceptors of recombining particles are quantitative but not qualitative. This is just what was expected based on the qualitative similarity of the potential curves of pair interactions presented in Fig. 2 and hence the similar total structure of

Table 3. Temperatures of rotational distributions of the recombination products of Cs^+ and Br^- ions in the presence of the Ar, Xe, and Hg third bodies

E_i , eV	E_R , eV	Temperature, K		
		Ar	Xe	Hg
1	1	4380	4950	4950
1	5	4080	4530	4720
5	1	5140	5370	5700
5	5	5940	5550	5420

potential energy surfaces that govern the processes under study. Thus, the quantitative discrepancies in the recombination probability distributions and in the energy distributions of the products are due not only to the more than threefold excess of the mass of the xenon atom over that of argon atom, but also (with the same analytical expressions for PES) to differences in their structures. These differences in the systems under study determine the diversity of the detailed mechanisms of stabilization of recombination products for each third body and the contribution of these mechanisms to the total efficiency of the third body.

The results of the statistical analysis of the dynamics of the direct three-body recombination show complex relationships of possible dynamic mechanisms of elementary processes or their groups. This situation results from the strong influence of averaging over the sets of initial conditions of the three-body collision on the calculated dynamic characteristics. The statistical dynamics highlights the general issues of process dynamics such as the role of the particle masses and the effect of the structure of the PES or some of its regions, but fails to give an unambiguous answer to

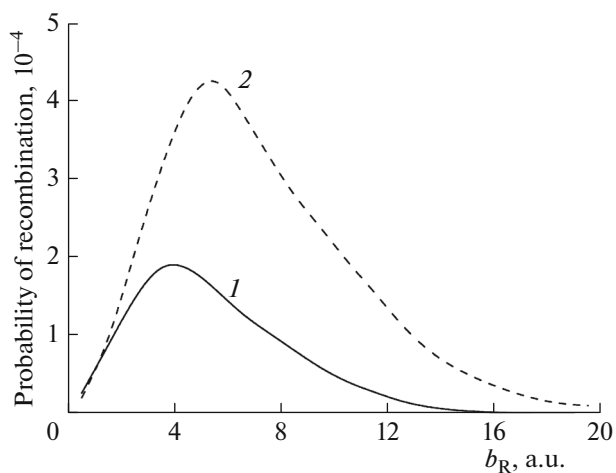


Fig. 7. Dependences of the recombination probability of Cs^+ and Br^- ions on the impact parameter b_R during collision of ions in the presence of Ar (1) and Xe (2) at $E_R = 1$ eV, $E_i = 1$ eV, and $T_{\text{del}} = 0$.

questions about the mechanism and outcome of a particular three-body collision of reagents. The dynamics of each collision is reflected by the trajectory of the representation point on the PES. A transition from the statistical dynamics of the elementary process to its detailed dynamics allows us to correlate the characteristics of the brutto process to the dynamics of each elementary act determined by the structure of the potential energy surface.

ACKNOWLEDGMENTS

We are grateful to M.B. Sevryuk for useful discussions of the paper.

We are also grateful to the Russian Foundation for Basic Research for financial support of this study (project no. 14-03-00201-a).

REFERENCES

1. V. N. Kondrat'ev and E. E. Nikitin, *Kinetics and Mechanism of Gas-Phase Reactions* (Nauka, Moscow, 1974) [in Russian].
2. N. M. Emanuel' and D. G. Knorre, *Course of Chemical Kinetics* (Vysshaya Shkola, Moscow, 1974) [in Russian].
3. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes: The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena* (McGraw-Hill, New York, 1941).
4. H. R. Kaufman and R. S. Robinson, *AIAA J.* **20**, 745 (1982).
5. E. Y. Choueiri, *Sci. Am.*, no. 2, 58 (2009).
6. A. V. Elets'kii, *Sov. Phys. Usp.* **21**, 502 (1978).
7. A. M. Boichenko, V. F. Tarasenko, and S. I. Yakovlenko, *Laser Phys.* **10**, 1159 (2000).
8. A. M. Boichenko and M. S. Klenovskii, *Tech. Phys.* **58**, 744 (2013).
9. F. D. Colavecchia, F. Mrugala, G. A. Parker, and R. T. Pack, *J. Chem. Phys.* **118**, 10387 (2003).
10. J. Pérez-Rios, S. Ragole, J. Wang, and C. H. Greene, *J. Chem. Phys.* **140**, 044307 (2014).
11. E. V. Ermolova, L. Yu. Rusin, and M. B. Sevryuk, *Russ. J. Phys. Chem. B* **8**, 769 (2014).
12. V. M. Azriel, D. B. Kabanov, L. I. Kolesnikova, and L. Yu. Rusin, *Izv. Akad. Nauk, Energet.*, No. 5, 50 (2007).
13. V. M. Azriel, E. V. Kolesnikova, L. Yu. Rusin, and M. B. Sevryuk, *J. Phys. Chem. A* **115**, 7055 (2011).
14. V. M. Azriel and L. Yu. Rusin, *Russ. J. Phys. Chem. B* **2**, 499 (2008).
15. V. M. Azriel, L. Yu. Rusin, and M. B. Sevryuk, *Chem. Phys.* **411**, 26 (2013).
16. E. V. Kolesnikova and L. Yu. Rusin, *Russ. J. Phys. Chem. B* **6**, 583 (2012).
17. E. V. Ermolova and L. Yu. Rusin, *Russ. J. Phys. Chem. B* **8**, 261 (2014).
18. K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979; Mir, Moscow, 1984).

Translated by L. Smolina