International Journal of Chemical Science
www.chemicaljournals.com
Online ISSN: 2523-2843
Received: 03-03-2026, Accepted: 03-04-2026, Published: 18-04-2026
Volume 10, Issue 2, 2026, Page No. 37-42

Trajectory simulation of direct recombination probabilities in the Cs$^+$ + Cl$^-$ + Rb$^+$ + J$^-$ system

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Abstract

Based on the principle of microscopic reversibility, this article proposes a trajectory model for the multichannel process of direct four-body recombination of two positively charged and two negatively singly charged ions. The trajectory calculations used a potential energy surface that quantitatively describes the inverse process of collision-induced dissociation of the corresponding diatomic molecules. Key interaction characteristics, such as the recombination probability as a function of collision energy and the ratios of recombination probabilities for individual channels, were obtained. It was found that in all channels in which stable diatomic molecules are formed, their vibrational energy shows an inverted population of energy levels, while the distribution of rotational energy has the form of an equilibrium Boltzmann distribution.

Keywords: Collision energy, potential energy surface, recombination probability, trajectory model

Introduction

The dynamics of many processes of great scientific and practical interest, such as combustion, reactions in the upper atmosphere and ionosphere, the state of low-temperature plasma, and so on, are determined primarily by the concentration of charged particles that make up the system under study. This makes it crucial to thoroughly study the mechanisms of chemical transformations involving them. Atomic and molecular ions are formed and dissipated primarily as a result of elementary reactions of collision-induced dissociation (CID) of molecules and the reverse processes of ion recombination in the corresponding media.

The collision-induced dissociation of diatomic molecules to form atomic and molecular ions has been intensively studied by a number of authors [1, 24] in experiments with crossed molecular beams. In such experiments, conditions of single collisions of reactants are realized, which makes it possible to obtain the most detailed dynamic information on the nature of their interaction. A distinctive feature of recombination processes is the need for stabilization, i.e., the removal of a portion of the internal energy from the resulting molecules. In the simplest case, this presupposes the presence of a third particle. The design of such recombination experiments is associated with the fundamental difficulties of realizing the simultaneous collision of three or more beams at a given point in space at the required moments in time. This circumstance determines the virtually complete absence of experimental dynamic information on ion recombination processes.

A crucial task under these conditions is the development of simple and reliable theoretical models that consider the various mechanisms of the processes under study, their competition, and the conditions under which they occur. One of the most frequently used approaches to constructing such models for the interaction of heavy particles at moderate energies is trajectory simulation of the process under study. Its adequacy to the actual particle interaction is determined, first and foremost, by the accuracy of the potential energy surface (PES) used in the calculations. However, constructing a PES adequate to the process under study is one of the most complex problems in the theory of atomic-molecular interactions. Despite the enormous advances in computing technology over the past decades, accurate PESs based on quantum chemical calculations have so far been constructed only for a few of the simplest systems, consisting predominantly of light atoms. Semiempirical and empirical PESs, containing a number of selectable parameters whose optimal values are determined by comparing the scattering characteristics obtained in the calculations with those that can be measured directly in the corresponding experiments, have become much more widespread in trajectory calculations.

However, as noted earlier, direct dynamic information on recombination is lacking due to significant experimental difficulties. An alternative approach to choosing a potential energy surface for simulation the recombination process is based on the principle of microscopic reversibility [25, 38], which states that two processes proceeding in opposite directions, inverse to each other, are governed by the same potential energy surface. Thus, if we have a potential energy surface that adequately describes the collision-induced dissociation of neutral molecules into ions in a given system, then the recombination process of these ions, which is inverse to the collision-induced dissociation of CsCl and RbJ molecules, also occurs on the same potential energy surface.

Collision-induced dissociation into ions of a pair of CsCl and RbJ molecules has been studied in detail experimentally in crossed molecular beams [22, 24]. In these studies, the excitation functions for the formation of positively charged Cs$^+$ and Rb$^+$ atomic ions were measured. Subsequent trajectory modeling allowed us to quantitatively reproduce these experimental curves. A comparison of the measured and calculated excitation functions is shown in Figure 1.

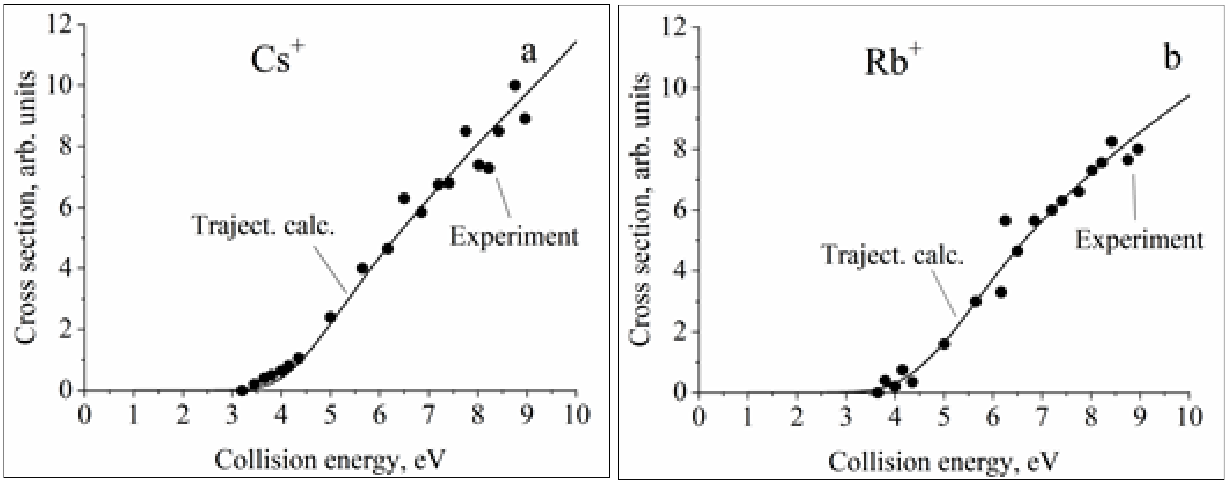

Fig 1: Comparison of experimental (dots) and trajectory calculation-derived (lines) excitation functions of Cs^+ (a) and Rb^+ (b) ions in the collision energy range from 0 to 10 eV.

The good agreement between the measured and calculated excitation functions for both ions across the entire calculated range of collision energies suggests that the PES used in the calculations adequately represents the actual interactions of particles in the system. Therefore, by virtue of the principle of microscopic reversibility, we can use this PES to model the inverse process of four-ion recombination. The article is structured as follows. After this introduction, the structure and parameters of the PES used are briefly described, along with the calculation methodology. This is followed by a section presenting the results of trajectory simulations of four-ion recombination and their discussion. The article concludes with a list of references.

Potential energy surface and calculation technology

The potential energy surface used in the calculations is constructed as an additive function of six pairwise interactions, each of which is described within the framework of a truncated Rittner potential. This model is the basic and most frequently used form of representing the interaction potentials of alkali metal ions and halogens. Using the atomic system of units (e=h=m=1), the truncated Rittner potential [39, 40] has the form:

$$U(R) = E(R) \pm 1/R - (a_1+a_2)/2R^4 - C/R^6 \qquad (1)$$

Where E(R) is the repulsive energy, usually taken in the form of the Born-Mayer model:

$$E(R) = A\cdot\exp(-R/r) \qquad (2)$$

Here, A is the calibration factor and ρ is the repulsive wall stiffness parameter, α_1 and α_2 are the polarizabilities of the interacting ions, C is the dispersion constant, and R is the distance between the ions. The "+" sign before the Coulomb term in expression (1) corresponds to the interaction of like-charged ions, while the "-" sign corresponds to the interaction of ions with opposite charges. The values of the parameters of the pair interaction potentials are given in Table 1.

Table 1. Parameters of pair interaction potentials for the $Cs^+ + Cl^- + Rb^+ + J^-$ system.

Ионная пара	i	A_i	r_i	C_i
Cs^+ - Cl^-	1	136.266	0.6881	138.0
Rb^+ - J^-	2	172.9586	0.7127	200.0
Cl^- - J^-	3	41.5247	1.99	527.18
Cs^+ - Rb^+	4	877.69	0.924	115.678
Cs^+ - J^-	5	179.6108	0.7448	305.0
Rb^+ - Cl^-	6	135.3389	0.6541	92.0

Polarizability of ions: ACS^+=16.48, a_{Cl^-}=24.93, a_{Rb^+}=9.595, a_{J^-}=52.8.

The trajectory simulation method has been discussed in detail in a number of papers [41, 54], and only certain aspects of its specific implementation in the present calculations are noted here. The motion of the particles participating in the interaction was described by a system of first-order differential equations in Hamiltonian form. The initial positions of the ions were calculated using the Monte Carlo method in such a way that all admissible spatial configurations were equally probable. The distances from all ions to the center of mass of the system and the distances between all pairs of colliding ions were set equal to 250 a.u. so that the influence of the potential on their relative motion at the beginning of the trajectory could be neglected. From the point of view of the computational procedure, this requirement implies constancy of the momenta of the relative motion of the ions in the first steps of integration. Then, all ions with identical initial velocities began to move toward the center of mass of the system. Integration of the equations of motion [55, 58] was performed using the sixth-order Adams method, the initial values for which were calculated using the Runge-Kutta procedure, with an integration step of 50 a.u., which ensured that the total energy of the system was preserved throughout the trajectory at a level no worse than 10^{-5}% of its initial value. The trajectories were integrated until one of the possible interaction channels was realized in accordance with the values of the pairwise interatomic distances and energies. The formation of a given group of atoms as a stable product was recorded under the condition that all pairwise distances within a given group did not exceed 30 a.u. and the total energy was negative, while the distances from a given group to other atoms were greater than 250 a.u. and the corresponding energies were positive.

Results and discussion

When studying multichannel chemical reactions, one of the most important and interesting questions is the ratio of the probabilities of the realization of various channels. The complete set of all possible interaction channels in the system $Cs^+ + Cl^- + Rb^+ + J^-$ can be represented by the following scheme, including the formation of both ionic and neutral products:

$$
\begin{array}{lll}
Cs^+ + Cl^- + Rb^+ + J^- & \rightarrow Cs^+ + Cl^- + Rb^+ + J^- & (1) \\
 & \rightarrow CsCl + Rb^+ + J^- & (2) \\
 & \rightarrow RbJ + Cs^+ + Cl^- & (3) \\
 & \rightarrow CsJ + Cl^- + Rb^+ & (4) \\
 & \rightarrow RbCl + Cs^+ + J^- & (5) \\
 & \rightarrow CsCl + RbJ & (6) \\
 & \rightarrow CsJ + RbCl & (7) \\
 & \rightarrow CsClRb^+ + J^- & (8) \\
 & \rightarrow CsClJ^- + Rb^+ & (9) \\
 & \rightarrow CsJRb^+ + Cl^- & (10) \\
 & \rightarrow RbJCl^- + Cs^+ & (11) \\
 & \rightarrow CsClRbJ & (12)
\end{array}
$$

This article analyzes the probabilities of each channel's occurrence, calculated as the ratio of the number of trajectories corresponding to a given channel to the total number of calculated trajectories. The probability of a given channel's occurrence is largely determined, in particular, by the kinetic energy of ion collisions, as well as their initial spatial configuration. Channel (1), in which no chemical transformations occur, has the highest probability of occurrence in this scheme. This channel, however, is of little interest, as it includes a significant number of trajectories in which no real interaction between ions occurs. The dependence of the total probability of occurrence of chemical transformation channels (2)–(12) on the ion collision energy in the range from 0 to 25 eV is shown in Figure 2. As can be seen from the figure, this probability decreases exponentially with increasing collision energy.

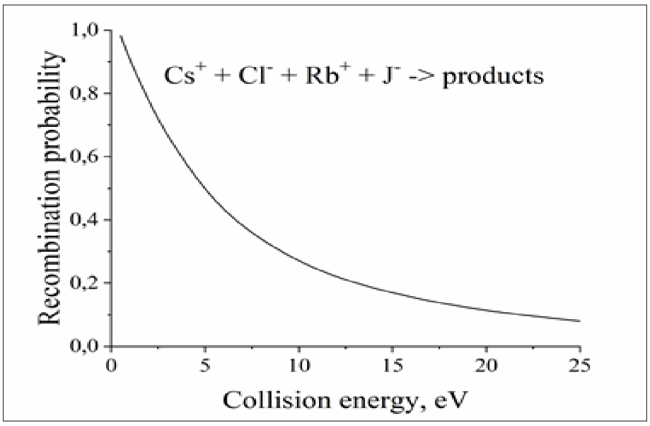

Fig 2: Dependence of the total probability of the realization of chemical transformation channels (2) – (12) on the ion collision energy.

The exact inverse of collisional dissociation into four ions in the CsCl + RbJ system is channel (6) in the above diagram. The probability dependences of these inverse processes are shown in Figures 3 and 4.

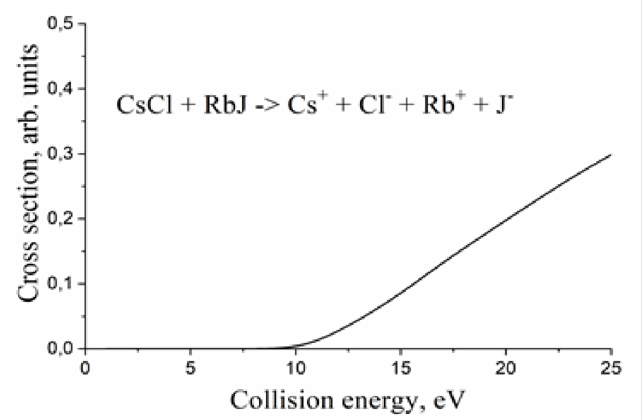

Fig 3: Excitation function of collision dissociation into four ions in the CsCl + RbJ system.

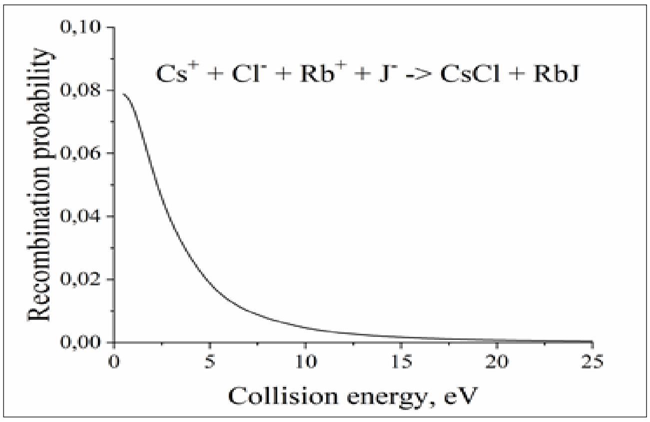

Fig 4: Dependence of realization probability of channel (6) on interaction energy.

In addition to the channel (6), recombination of four atomic ions can lead to the realization of a symmetric channel (7), i.e. the formation of CsJ and RbCl as products. The dependence of the probability of bimolecular recombination on the collision energy of both channels is similar, but at all energies channel (7) shows a slightly lower yield of products (Figure 5).

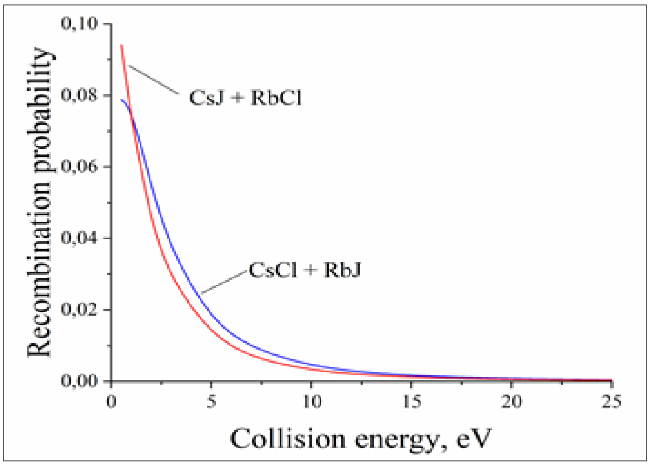

Fig 5: Dependence of bimolecular recombination probability of four ions on their total kinetic energy in symmetric channels of formation of molecular pairs CsCl + RbJ and CsJ + RbCl.

Another group of channels in which only one stable molecule is formed are channels (2) to (5). Figure 6 shows the dependence of the recombination probability of these channels on the total kinetic energy of ions obtained from trajectory calculations. All dependencies are bell-shaped with maxima ranging from 2 to 5 eV. From the figure, a tendency is seen to increase the corresponding maximum probability of the collision energy value with a decrease in the mass of the formed molecule. The maximum value itself also reduces the probability of recombination.

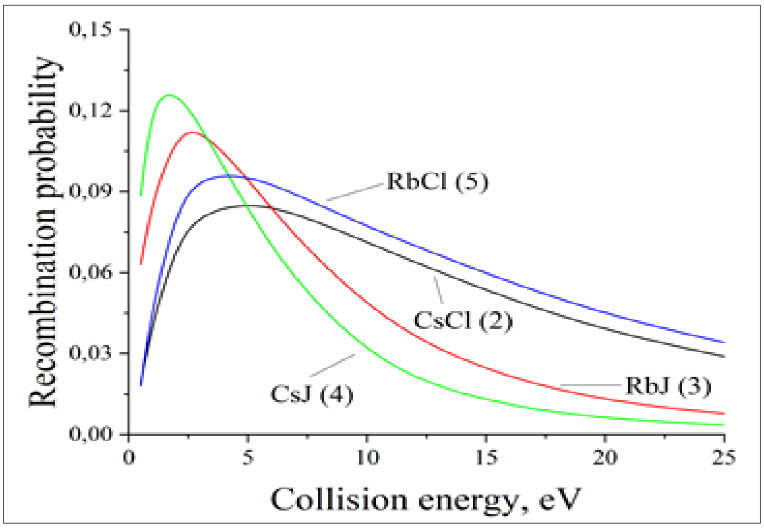

Fig 6: Dependences of the recombination probability of channels (2) - (5) on the total kinetic energy of ions.

It should be noted that in channels (2)–(7), the degree of stabilization of the resulting molecules is low, and the internal energy of the molecules is only slightly lower than their binding energy. Moreover, the vibrational energy exhibits an inverted population of the energy levels, while the rotational energy distribution has the form of an equilibrium Boltzmann distribution. As an example, for channel (2), the internal energy distributions of CsCl molecules are shown in Figure 7.

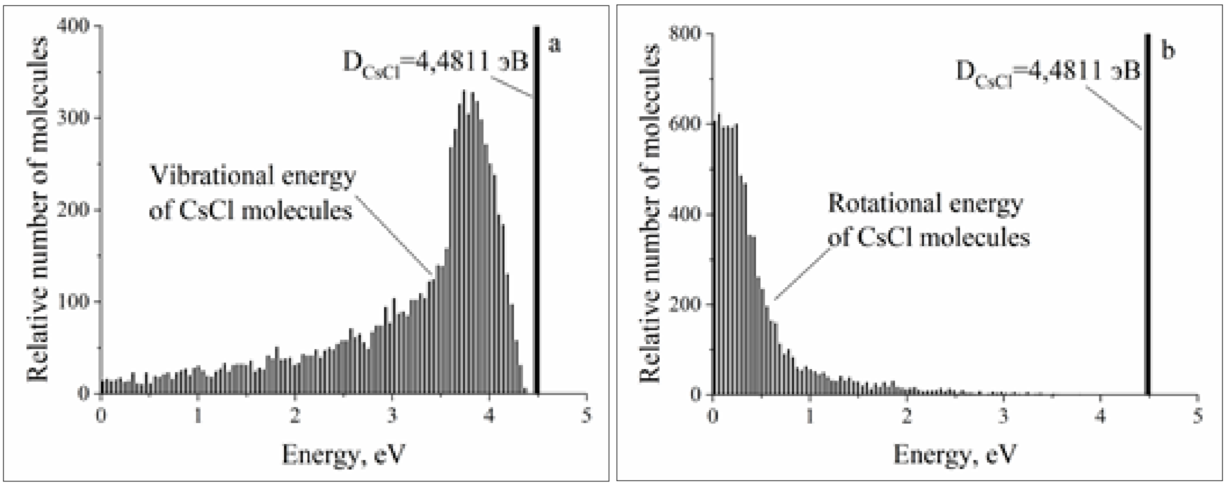

Fig 7: Distributions of vibrational (a) and rotational (b) energies of CsCl molecules formed in channel (2).

Conclusion

The calculations show the complex nature of the multichannel ion recombination process. The principle of microscopic reversibility is a powerful tool for investigating such processes.

Trajectory calculations revealed that channels (2)–(5), in which only one stable molecule is formed, and channels (6)–(7), in which two stable molecules are formed, exhibit significantly different patterns of channel probability dependence on the energy of the colliding ions.

The remaining channels (8)–(12) have extremely low probability of occurrence across the entire calculated range of collision energies, not exceeding $2*10^{-4}$. This is apparently due to the low efficiency of energy extraction by the atomic ion from the significantly heavier triatomic ionic complex, which has many internal degrees of freedom.

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