International Journal of Chemical Science
www.chemicaljournals.com
Online ISSN: 2523-2843
Received: 13-02-2026, Accepted: 16-03-2026, Published: 31-03-2026
Volume 10, Issue 1, 2026, Page No. 61-65

Recombination dynamics through the ionic complex in system $Krcs^+ + R^-$, where R=F, Cl, Br and J

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Abstract
Results of trajectory simulation of dynamics of an ionic recombination through a complex of the form $KrCs^+ + R^- \rightarrow CsR + Kr$, where R=F, Cl, Br and J are presented. The most important dynamic characteristics, such as excitation function, distribution of impact parameters and internal energy of the formed molecule are received. Calculations show inverse population of vibration energy levels of the formed molecule while rotation energy corresponds to equilibrium distribution. Influence of mass of halogen on dynamics of interaction is analyzed. The most probable mechanisms of a recombination for various values of collision energy are offered.

Keywords: Trajectory model, potential energy surface, recombination probability, collision energy, impact parameter, internal energy

Introduction

The dynamics of the many gas-phase processes that take place in molecular lasers, low-temperature plasmas, reactions in the upper atmosphere and ionosphere, combustion, etc., are of enormous scientific and practical importance, primarily determined by the concentration of charged particles that make up the system under study. This makes actual the problem of studying in detail the mechanisms of chemical transformations with their participation. Atomic and molecular ions appear and disappear predominantly in the case of collision-induced dissociation (CID) of neutral molecules and ionic recombination.

Collision-induced dissociation has been extensively investigated by many authors mainly in experiments with molecular beams [1-13]. More detailed information on CID processes can be obtained on the basis of mathematical modeling, the adequacy of which to the actual interaction of particles is checked by comparing the calculated characteristics of the process with the results of the corresponding experiments. For systems in which heavy particles interact at not very high energies, the classical and semiclassical methods of trajectory simulation based on the Born-Oppenheimer approximation [14-18] are the most visible and effective [19-32]. As a result of this approach, potential energy surfaces (PES) have been constructed for a number of systems including alkali metal halides, which provide a quantitative agreement between the calculated and experimental data [33-35].

The dynamics of the reverse processes of ionic recombination has been studied much worse, which is due to difficulties in obtaining ion beams of sufficient intensity and recording of final products. This circumstance determines the almost complete absence of experimental dynamic information on ion recombination processes. However, recombination is a process inverse to the CID, and therefore, due to the principle of microscopic reversibility [36-49], it must be controlled by the same potential energy surface. Thus, on the basis of trajectory models correctly describing the CID processes, one can obtain detailed information on the dynamics of the corresponding recombination reactions.

This article presents the results of an investigation of the recombination dynamics through the ionic complex of a heavy cesium ion with halogen ions differing in mass via the reaction $KrCs^+ + R^- \rightarrow CsR + Kr$, where R = F, Cl, Br, and J by the quasiclassical trajectory method.

Potential energy surface and computational procedure

The potential energy surface was constructed as an additive function of three pair potentials, i.e. including the interaction between opposite charged ions of cesium and halogen, as well as two potentials of interaction of the krypton atom with each of these ions [33]. Each of the pair potentials was represented in the form of a truncated Rittner potential [50] and contained an exponential Born-Mayer repulsion wall, inductive and van der Waals terms. The potential of the ion pair in addition to these types of interactions also included the Coulomb potential of attraction.

The motion of the particles participating in the interaction was described by a system of first-order differential equations in the Hamiltonian form. The calculations were performed in the collision energy range from 0,1 eV to 10 eV.

At the beginning of the trajectory, the distance between the center of mass of the ion complex and the negatively charged ion was 250 atomic units so that the influence of the potential on the relative motion of particles at the beginning of the trajectory could be neglected. From the point of view of the computational procedure, this requirement means the constancy of the impulses of the relative motion of the colliding particles at the first steps of integration.

Orientation angles of the axis of the ion complex relative to the line of its approach to the negative ion were chosen by the Monte Carlo method in such a way that all spatial collision configurations were equally probable.

The maximum value of the impact parameter of a negatively charged ion with respect to the center of mass of the ion complex was chosen relatively large and equal to 100,0 atomic units, because at collision energies of tenths of an electron-volt, recombination occurs at values close to this value.

The equations of motion were integrated by the Adams method of the 6th order, the initial steps for which were calculated using the Runge-Kutta procedure. The step of integrating the equations of motion on time was chosen equal to 50 a.u., which ensured the conservation of the total energy and momentum along the entire path of the trajectory no worse than one in the sixth significant digit.

The criterion for the end of the trajectory leading to the formation of a stable molecule is the condition that the distance between its constituent ions does not exceed 30 atomic units, the total energy of this pair is negative, and the distances from both ions of the molecule to the third atom are more than 250 atomic units, and the corresponding paired energies are positive. At the end of the trajectory, in the case of the formation of a molecule, its vibrational and rotational energies are determined.

The recombination probabilities are defined as the ratio of the number of "successful" in the sense of completing the recombination process to the total number of calculated trajectories.

Results and discussion

The most important characteristic of the studied processes is the dependence of the probability of the formation of a stable molecule as a function of the collision energy of the ion complex with the halogen ion. Fig.1 shows the dependences of the recombination probability on the collision energy at interaction of the $KrCs^+$ ion complex with various halogen ions. For all systems considered, the curves are qualitatively identical and are characterized by a rapid decrease in the recombination probability with increasing energy, and at energies above 2,0 eV recombination is practically not observed. At the same time, for the greater part of the calculated energy range, the smaller the mass of the negatively charged ion, the lower the probability of recombination.

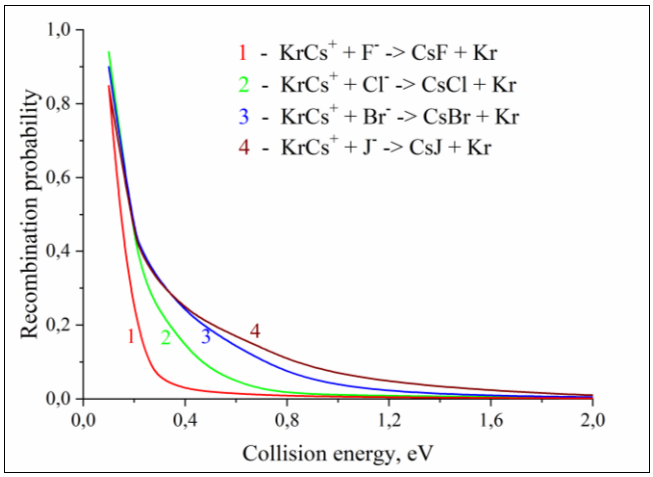


Fig 1: The recombination probability as a function of the collision energy for the process $KrCs^+ + R^- \rightarrow CsR + Kr$, where R = F, Cl, Br and J

For a more accurate understanding of the interaction mechanism, it is necessary to investigate the dependence of the recombination probability on the impact parameter of the bromine ion relative to the center of mass of the ion complex. As can be seen from Fig. 2, the form of the distribution of impact parameters changes with the change in the mass of the halogen ion. The range of values of realized impact parameters for all systems is approximately the same and consist of from 0 to 75 a.u. However, if for fluorine, the lightest of the halogens considered, in the range of 30 a.u. up to 60 a.u. the impact parameters are distributed almost uniformly, then for other systems, the impact parameters near the right-hand boundary of the range are most preferable, and this tendency increases with increasing mass of the halogen ion.

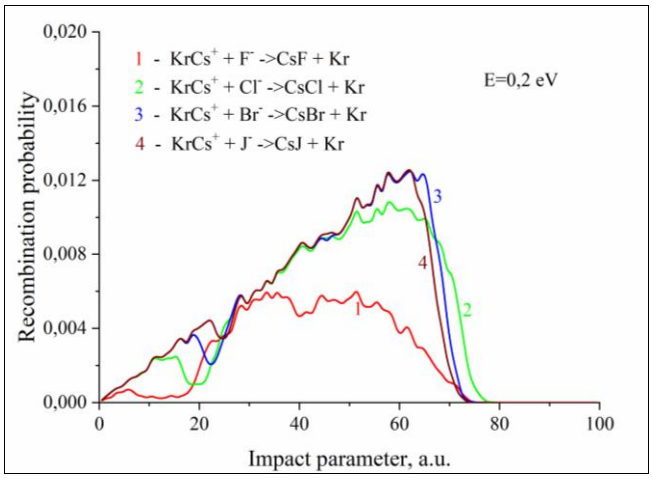


Fig 2: The dependence of the probability of the reaction $KrCs^+ + R^- \rightarrow CsR + Kr$, where R = F, Cl, Br and J, on the impact parameter of the halogen ion relative to the center of mass of the $KrCs^+$ ion complex at a collision energy of 0,2 eV

This allows us to assume that, at low collision energies, the predominant interaction mechanism corresponds to the formation of a new bond between cesium and halogen ions at a considerable distance simultaneously with the cleavage of the cesium ion bond with the krypton atom. Such a mechanism assumes that there is no collision of a halogen ion with a krypton atom, and explains the small scattering energy of the formed molecule and the krypton atom. As an example, Fig. 3 shows the distribution of scattering energy of recombination products at collision energy of 0,2 eV. It is seen that the krypton atom carries away less than 1,0 eV of the total energy of the system, i.e. there is not a deep stabilization of the formed molecule.

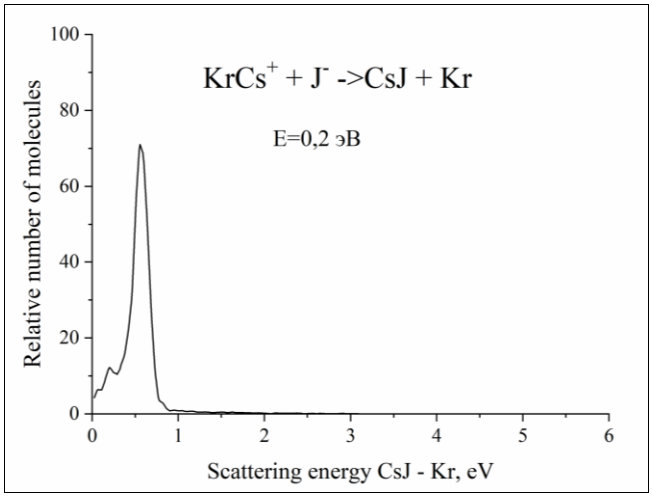


Fig 3: Distribution of the scattering energy of the recombination products in process $KrCs^+ + J^- \rightarrow CsJ + Kr$ at a collision energy of 0,2 eV

Significantly more differences in the distribution of impact parameters for the systems studied are appeared with increasing collision energy. Fig. 4 shows these distributions for energy 1,0 eV. For all systems, the range of impact parameters has become significantly narrower, and the degree of its narrowing is proportional to the decrease in the halogen mass. So, for iodine, the impact parameters are in the range from 0 to 35 a.u. For bromine, the upper limit is reduced to 25 a.u.,

for chlorine to 20 a.u., and for fluorine the maximum value of the impact parameter is 17.5 a.u. This result can be explained by a change in the preferential mechanism of interaction with increasing collision energy. That is, at high collision energies for the stabilization of the molecule, the departing atom must take a considerable amount of energy, which is possible only for small impact parameters, when the incident halogen ion knocks out the atom from the ionic complex.

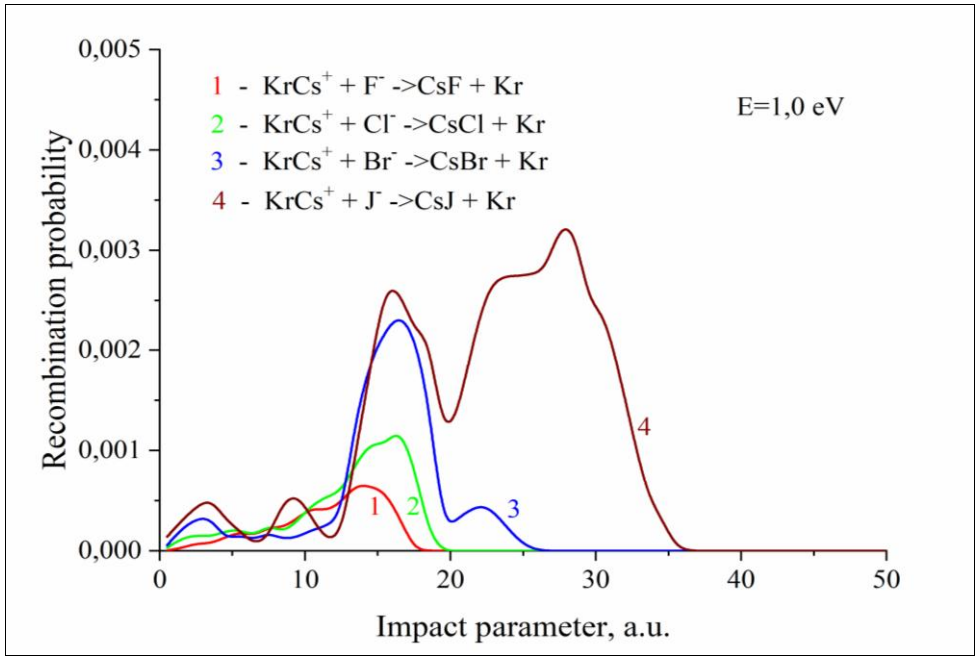
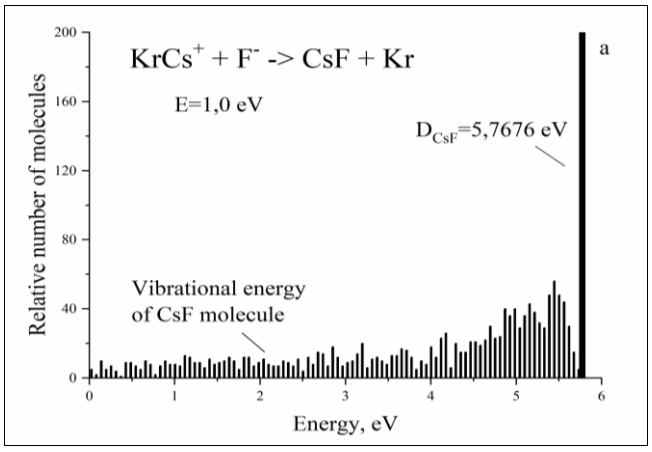
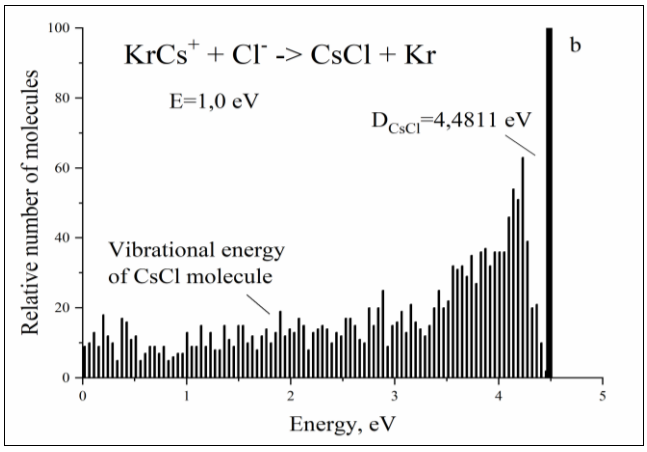


Fig 4: The dependence of the probability of the reaction $KrCs^+ + R^- \rightarrow CsR + Kr$, where R = F, Cl, Br and J, on the impact parameter of the halogen ion relative to the center of mass of the $KrCs^+$ ion complex at a collision energy of 1,0 eV

However, as noted above, in all cases there is not a deep stabilization of the formed molecule, and in the majority of trajectories leading to recombination, the internal energy of the molecule is not much less than the binding energy. Fig. 5 shows the vibrational energy distributions of the resulting cesium halide molecules for all four systems at a collision energy of 1,0 eV. From these distributions it is seen that when the mass of the halogen ion increases, the process of stabilizing the molecules

becomes more difficult, i.e. the relative proportion of molecules in which the vibrational energy is less than half the binding energy in the molecule is significantly reduced. In the case of the heaviest halogen, iodine, practically all the molecules formed have vibrational energy in the range from 3,5 eV to the dissociation energy of the molecule. The rotational energy for all systems is close to the equilibrium distribution and is only a small fraction of the internal energy of the molecule.





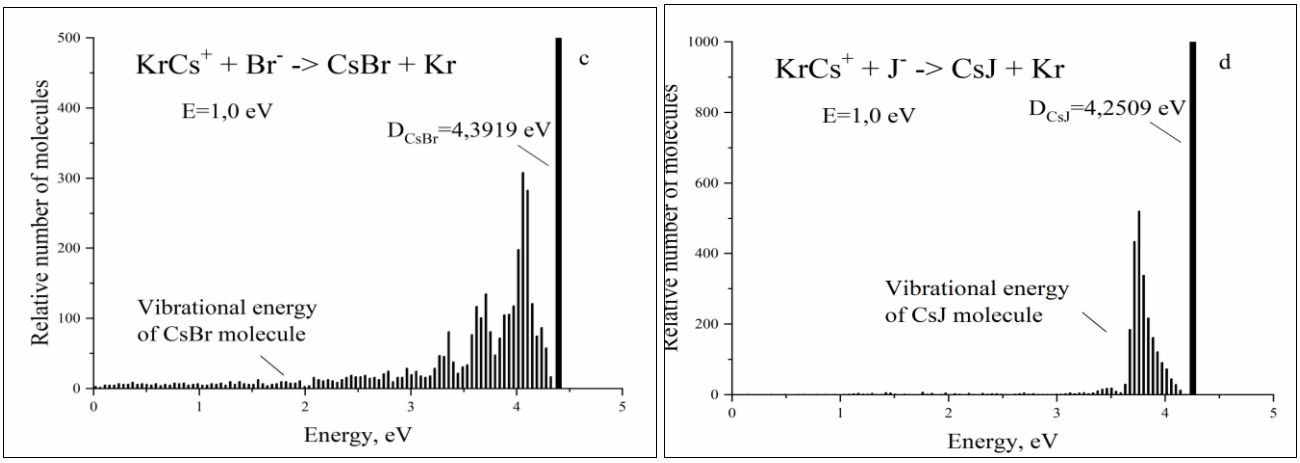


Fig 5: Distributions of the vibrational energy of the resulting molecules of cesium halides in the process $KrCs^+ + R^- \rightarrow CsR + Kr$, where R = F (a), Cl (b), Br (c) and J (d) at a collision energy of 1,0 eV

Conclusion

The principle of microscopic reversibility represents the fundamental basis of trajectory simulation of ion recombination processes and the investigation of the dynamic features of these processes on the basis of a potential energy surface that controls the formation of ion pairs in collision-induced dissociation of molecules with an ionic bond. The revealed features of the investigated recombination processes suggest that this elementary process has a complex dynamic. It is determined both by the structure of the potential energy surface and by the kinematical factors, such as collision energy, impact parameters of the collision, orientation effects, etc. The concept and the modeling method described in the article allow us to study the dynamics of other processes of this type.

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