

Dynamics of two-stage direct three-body recombination of ions



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ABSTRACT

Single-stage three-body recombination of ions and recombination via intermediate complex formation can be considered as two limiting cases of a general mechanism involving two stages separated by some time interval T , namely, energy removal by the third body and closest approach of the ions. Any of these can occur first. Particular dynamics of nascent molecule stabilization is determined by various kinematic parameters including two collision energies and the lag T . In this paper, recombination dynamics of the Cs^+ and Br^- ions in the presence of the Xe atom is studied by quasiclassical trajectories. If T vanishes (one-stage process), stabilization proceeds chiefly via energy transfer in encounters of Xe with both ions approaching each other. If the energy removal stage is late, dynamics changes drastically, stabilization occurring via interaction of Xe mainly with only one ion. This three-body recombination mechanism may be of considerable importance at low pressures in gas medium.

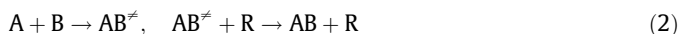
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1. Introduction

The reactions of three-body recombination of atoms, ions, or small radicals determine, to a large extent, kinetics of various gas phase processes such as combustion, oxidation, or explosions. These reactions are also responsible for the properties of natural and artificial non-equilibrium media such as, for instance, atomic, ionic, and molecular interactions in the upper layers of the atmosphere or in low temperature plasmas where the recombination processes control the concentrations of active particles. The studies of these reactions in chemical kinetics have been confined by a phenomenological description of a three-body interaction as of a direct single-stage reaction



or of reactions involving intermediate complexes¹:



or



As is noted in Ref. [3], the literature on chemical kinetics gives preference to the recombination mechanisms that include various intermediate complexes. One of the reasons for this preference is a comparison of the frequencies of double and triple collisions in a gas within the framework of the hard sphere model. Such a comparison implies a considerable predominance of double collisions over triple ones. In fact, in the kinetics literature, there are described several mechanisms of three-body processes. The analysis of these mechanisms in the paper [3] shows that in most cases, at least for atoms and small radicals, recombination proceeding via a collision of all the three particles makes an appreciable or sometimes even prevailing contribution to the total recombination rate. At the same time, the dynamics of triple interactions has been explored quite poorly compared with that of pair collisions. Dynamics of the chemical processes accompanying three-body collisions is of great interest. In particular, dynamics of the ion recombination reactions and especially of reactions of direct three-body recombination of ions is intriguing.

It is hard to find out the actual mechanism of an elementary recombination process while being based just on a formal examination of the termolecular interaction. This mechanism is determined by the specific interaction potentials of the reagents, i.e., by the structure of the potential energy surface (PES). It is in general more difficult to construct the PESs for termolecular reactions than those for bimolecular ones. Moreover, three-body interactions are characterized by a considerably more complicated collection of the kinematic parameters than bimolecular processes (see Section 2 below), and each kinematic parameter has its own distribution function. The absence of suitable experimental dynamical data is also an important reason for an insufficiently complete understanding of the mechanisms of three-body reactions.

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¹ The question of the prevailing mechanism of three-body interactions has a rather long history. While considering the mechanisms of termolecular reactions involving intermediate compounds, Kassel [1] pointed out correctly that the formation of intermediate complexes AB or AR in the processes (2) and (3) could require a three-body collision (like the process (1) requires). Moreover, Kassel's discussion of Tolman's calculations [2] showed that the model of direct termolecular collisions (i.e., the model (1)) could in principle explain the observed rates of third order reactions.

On the other hand, the main dynamical features of three-body recombination can be investigated, to a large extent, on the basis of the principle of microscopic reversibility. This principle enables one to connect two directions of an elementary reaction, for instance, collision induced dissociation (CID) of a molecule and recombination of the dissociation products in the presence of the third body. All the three phenomenological recombination mechanisms Eq. (1)–(3), at least in the case of recombination of atoms or single-atom ions, can be governed by the same PES and proceed independently of each other but with different collections of the kinematic parameters.

Recombination of atomic ions,



is a simple reaction that can be explored by this approach. This is the process reverse to CID of some molecules with an ionic bond [4–6]. However, due to various circumstances, the reaction Eq. (4) has been examined insufficiently.

One of the CID reactions whose dynamics has been studied experimentally in crossed molecular beams best of all is collision induced dissociation of some alkali halide molecules (see e.g. the papers [4–12]) proceeding as a diabatic process with the formation of ionic products:



where e.g. $MX = CsF, CsCl, CsBr, CsI$ or other alkali halides that break up mainly into ions. The cross section of the channel Eq. (6) is much smaller than that of the channel Eq. (5). Besides CID reactions in three-atom systems [4–12], there are also known four-atom systems exhibiting dynamics typical for the diabatic CID processes [13–15].

In Refs. [16–21], we constructed quasiclassical trajectory models for direct three-body reactions corresponding to so-called central [16–18,20,21] and non-central [19] encounters of the recombining ions (see Section 2 below). These models were based on the well determined interaction potentials in the prototypical systems involving the Cs^+ and Br^- ions and the rare gas atom $R = Kr, Xe$ or the mercury atom $R = Hg$. We have revealed [16–21] that three-body recombination exhibits a great manifold of dynamical mechanisms whose occurrence depends on the particular collection of the kinematic parameters of the three-body collision. For instance, the ion recombination probability was shown to depend strongly on both the collision energy of the recombining particles and the energy of the third body (see Section 2 below). Statistically, on the qualitative level, these dependences manifest themselves the same way for central and non-central encounters of the recombining pair. However, from the quantitative viewpoint, the recombination probability in the non-central encounters is about 5–6 times smaller on the average [19]. Both the energies affect considerably the dynamical mechanism of recombination. This can be seen in the opacity functions describing the dependence of the recombination probability on the impact parameter b_R of the third body with respect to the center-of-mass of the recombining pair. For central encounters of the ions at small values of the impact parameter ($b_R < 6$ au), stabilization of the product molecule is achieved by energy transfer to the third body from both the recombination partners [18]. At large impact parameters ($b_R > 6$ au), the nascent molecule stabilizes mainly in the interaction of the third body with one of the recombining ions [18].

These results have been obtained for the recombination reaction model that assumes the simultaneous presence of all the three particles in a small neighborhood of the center-of-mass of the system where the interaction of the particles is sufficiently strong.

This concept corresponds to *single-stage direct* three-body recombination, and the hypothesis of a simultaneous collision of the three particles is in fact the only restriction imposed in the papers [16–21] on the analysis of a three-body collision yielding recombination. However, such an approach to dynamics of three-body recombination—where all the three particles are considered to “arrive” at the strong interaction zone simultaneously—narrows significantly the domain of the conditions under which recombination can happen. This model implies the conclusion (perhaps not always justified) that an effective course of the three-body reaction Eq. (4) requires a sufficiently high pressure in a gas medium [22].

In the present paper, we propose a *more general*, in our opinion, dynamical model of direct three-body recombination by example of the recombination reaction of the Cs^+ and Br^- ions in the presence of the Xe atom. In the framework of this model, one considers three-body collisions with an arbitrary “arrival” time T of the third body with respect to the computed duration τ of the approach of the recombining particles to the center-of-mass of the ion pair. This time is expressed below as the percent amount of τ and can be both positive (in the case where the energy removal by the third body is delayed) and negative (in the opposite case where the energy removal occurs in advance).

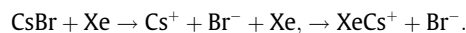
The article is organized as follows. After this introduction, in Section 2, we briefly describe the PES employed (this PES allows one to reproduce quantitatively correctly the CID dynamics in the $CsBr + Xe$ system), the process model we use (due to the presence of the time lag T , this model differs considerably from that in Refs. [16–21]), and the calculation procedure. In Section 3, we present the results of trajectory calculations of dynamics of ion encounters followed by the stage of recombination product stabilization by the Xe atom: this paper studies mainly the consequences of a *delay* of the third body rather than of its coming first (which does not affect statistical dynamics² of the reaction almost of all). The limiting cases of the model with a delay are the phenomenological Schemes (1) and (2). Section 4 is devoted to a discussion of the results obtained, and concluding remarks are given in Section 5.

2. Potential energy surface, model of the process, and trajectory calculation procedure

We explore the dynamics of the three-body recombination



on the PES that governs the two-channel CID process Eqs. (5) and (6)



This PES describes quantitatively correctly the dynamical experimental data obtained in crossed molecular beams and characterizing the excitation functions of the CID reaction products as well as the angular and energy distributions of these products (the differential and double differential cross sections) [10–12]. The same PES was used for our previous studies of the reaction Eq. (7) [16,18–21].

The PES in question is the sum of the three pairwise diatomic interaction potentials and the cross term:

² In the framework of *statistical dynamics*, one considers the dependences of the process probability on some chosen kinematic parameters under averaging over the remaining parameters. On the other hand, if averaging over kinematic parameters is absent or minimal in the calculation procedure at hand, one gets the opportunity to explore *detailed dynamics* of the process [20,21,23].

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