

Reactivity in ion-neutral high density media

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Abstract. The recent development of hybrid traps technology has revolutionized the field of cold chemistry. Recently, new trap configurations have been built in order to explore more involve chemical processes, among them is the three-body recombination involving ions and neutrals. Different ion-neutral-neutral reactions at low collision energies: 0.1 mK - 10 mK, are studied by means of a very recent method for classical trajectory calculations in hyperspherical coordinates for treating three-body collisions [J. Pérez-Ríos, S. Ragole, J. Wang and C. H. Greene, J. Chem. Phys. **140**, 044307 (2014)]. On the other hand a classically derived threshold law is obtained and numerically confirmed. The derived threshold law predicts molecular ions should dominate over molecular neutrals as the most products formed.

1 Introduction

The development of hybrid traps technology has brought the opportunity to study different kinds of chemical reactions involving neutrals and charged particles at cold temperatures ~ 1 mK. Hybrid trap technology relies on the combination of neutral atom traps and ion traps, in order to make a dual trap region where ions and neutrals overlap in space. On the other hand, by switching among different kinds of neutral traps or ion traps configurations, a broad spectra of ion-neutral chemical reactions can be explored. In particular, one interesting hybrid trap configuration is done by an optical dipole trap for neutrals, whereas a four-pole Paul trap is employed for trapping ions [1]. The scheme of this trap is shown in Fig.1, where also it is shown the specific Paul trap configuration employed by Härter *et al* [1], as well as the typical potential that an ion feels in the Paul trap. This hybrid trap configuration allows to study the same ion-neutral chemical reactions in a quite broad range of densities, and hence exploring the reactivity of the reactants as a function of the density.

In cold ion-neutral chemistry, most of the theoretical and experimental efforts have been devoted to the study of charge transfer reactions between ions and atoms, and more recently in molecular ion-atom systems [2]. Here, however we will focus on the study of three-body recombination (TBR) processes. TBR is a non-radiative few-body process in which three atoms collide, and eventually leading to the formation of a molecule as a product state, *i.e.*, $A + A + A \rightarrow A_2 + A$. Nevertheless, in ion-neutral-neutral TBR the reaction has two different channels: first, $B^+ + A + A \rightarrow A_2 + B^+$, and second, $B^+ + A + A \rightarrow AB^+ + A$. These two different reaction channels are studied for $^{87}\text{Rb}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ and $^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$, by means of a recent method based on classical trajectory calculations

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(CTC) in hyperspherical coordinates [3, 4]. On the other hand, it is reported a classical threshold law for ion-neutral-neutral TBR, which is numerically tested, as well as it has been experimentally corroborated [5].

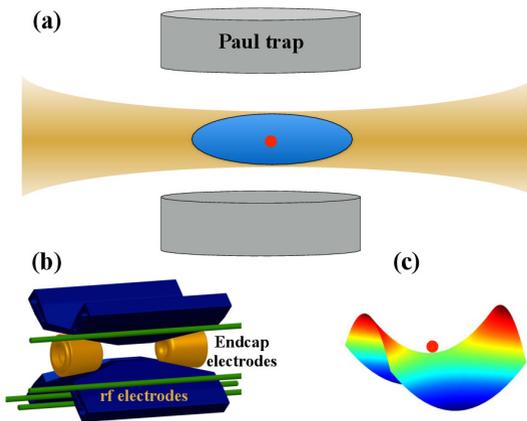


Figure 1. Hybrid trap. Panel (a); schematic representation of a hybrid trap involving a dipole trap for neutrals, represented by the orange beam and a Paul trap for ions, which is pictorially represented by the grey disks. The ultracold cloud of neutrals is represented by the blue ellipse, whereas the ion in this scheme is represented by the red dot. Panel (b): representation of the Paul trap configuration employed in the experimental results discussed here. The blue electrodes are the radio frequency electrodes, the endcap electrodes are DC electrodes to guarantee axial confinement of the ion along the z axis. The green conductors provide extra DC fields to compensate the micromotion of the ion in the Paul trap, which leads to a very high control on the kinetic energy of the ion. Panel (c): typical potential that an ion sees in a Paul trap at a given time.

2 Theoretical Approach

A recently developed method for the calculation of TBR cross sections based on classical trajectories [3] has been adapted for the study of ion-atom-atom recombination. The method relies on mapping the three-body problem into a 6-dimensional space (after separating out the trivial center of mass motion), where the cross section emerges as a generalization of the well-known two-body cross section, since the impact parameter can be defined as a 5-dimensional vector imbedded in the 6-dimensional space [3]. This approach is totally general and in principle it is suitable for solving the N -body problem. The position and momentum vectors in the 6-dimensional space is represented in hyperspherical coordinates [6, 7], which leads to a very efficient sampling of the phase-space.

The validity of a classical approach for ion-neutral-neutral collisions at cold temperatures may be questioned. However, the long-range ion-neutral interaction is dominated by the charge induced dipole moment interaction $-C_4/r^4$, where $C_4 = \alpha/2$, and α is the neutral atom polarizability. This long-range interaction is more attractive than its analog for neutral-neutral interactions, *i.e.*, the van der Waals interaction. Thus, the typical length scale of ion-neutral systems will be larger than its equivalent for neutral-neutral interactions. As a consequence, the energy in which the dynamics will be totally quantal is lower in ion-neutral than in neutral-neutral interactions. A more detailed analysis of this point can be found in [4]. In order to have a more quantitative argument, the angular momentum distributions of the TBR process for $^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ have been calculated at different collision energies, and the results are shown in figure 2. In this figure, it is noticed that even at collision energies $\sim 100 \mu\text{K}$, still many partial waves will contribute to the collision processes. Therefore, classical trajectory calculations might be an adequate approach for describing ion-neutral-neutral three-body recombination.

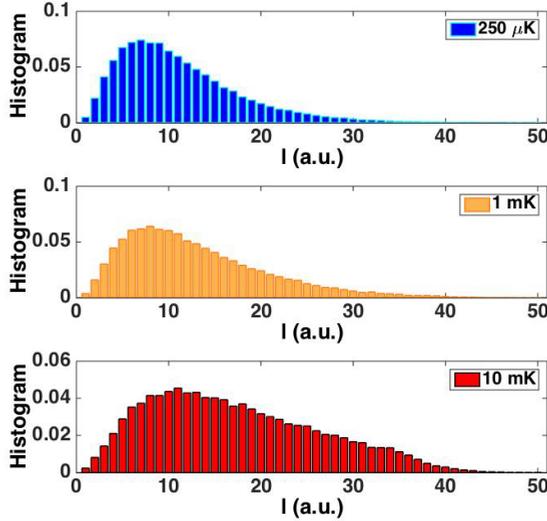


Figure 2. Total angular momentum distribution associated with the TBR for $^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ at different collision energies. The total angular momentum l is given in a.u., whereas the collision energy is given in K.

3 Results

The TBR cross section for $^{87}\text{Rb}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ and $^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ has been computed by running 10^5 trajectories per collision energy. Details about the numerical method employed to solve Hamilton's equations of motion, in conjunction with the sampling of the initial conditions, can be found elsewhere [3]. All of the calculations have assumed that neutral-neutral interactions, as well as ion-neutral interactions occur along one single potential energy curve. Concretely, Rb - Rb collisions are assumed to occur through the $^3\Sigma$ potential, *i.e.*, the spin flip transitions have been neglected [4]. On the other hand, the ion-neutral potential is described by the model potential $-C_4(1 - (r_m/r)^4)/r^4$, where C_4 is taken as $C_4=160$ a.u., and r_m represents the position of the minimum of the potential [4].

Table 1. Classical threshold law for the TBR cross section. A power law dependence of the TBR cross section as a function of the collision energy is assumed and used as a fitting function for the CTC numerical results. The error on the fitting parameters are associated with a confidence interval of 95 %.

System	β (dimensionless)
$^{87}\text{Rb}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$	-1.27 ± 0.13
$^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$	-1.18 ± 0.07
Classical threshold law	-1.25

From a long-range perspective, the ion-atom interaction is of course more attractive than the atom-atom interaction. For any orientation, energy and impact parameter, the collision begins when the trajectories of the atoms start to deviate from uniform motion or free motion. This happens when the interaction potential where the moving atoms are currently located is comparable to the collision energy, *i.e.*, $E_k \approx C_4/r^4$, where E_k represents the collision energy. Let us assume that this value of the

radius defines the maximum impact parameter associated to a TBR event, *i.e.* $b_{max}(E_k) = (C_4/E_k)^{1/4}$. In our formalism the TBR cross section is defined as [3]

$$\sigma(E_k) \propto \int_0^{b_{max}(E_k)} b^4 db, \quad (1)$$

where a unit opacity function has been assumed. Finally, substituting the value of $b_{max}(E_k)$ in Eq. 1, $\sigma(E_k) \propto E_k^{-5/4}$ it is found. This prediction is tested by fitting the CTC numerical results. In particular, the fitting function employed has the form $\sigma(E_k) = \gamma E_k^\beta$, and the results are shown in table 1. In table 1, it is observed that energy scaling law for the TBR cross section numerically obtained for both systems, $^{87}\text{Rb}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ and $^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$, are in a good agreement with the predicted energy scaling law associated with the derived threshold law. This suggests that the derived threshold law is satisfied in different systems under different dynamical conditions. On the other hand, the presented numerical results for $^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ have been corroborated in hybrid trap experiments [5]. The classically derived and numerically confirm threshold law has important implications on the final product state distributions. In particular, it predicts that for ion-neutral-neutral recombination the dominant product state will be the channel associated to molecular ions, *i.e.*, $B^+ + A + A \rightarrow AB^+ + A$.

4 Conclusions

The study of TBR for $^{87}\text{Rb}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ and $^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ has been performed by using a very recent classical trajectory method in hyperspherical coordinates. On the other hand, a classically derived threshold law for ion-neutral-neutral recombination has been obtained and corroborated numerically. Finally, this threshold is consistent with experimental results of the TBR rate for $^{138}\text{Ba}^+ - ^{87}\text{Rb} - ^{87}\text{Rb}$ [5].

Chemistry is maybe one of the most important playgrounds for few-body physics, where many important reactions involve the collision of very few molecules or atoms. However, chemistry has been receiving a very little of consideration by the few-body physics community. The present work is an example of how few-body physics can elucidate some of the intriguing chemical reactions. Therefore, we hope that our work serves as a motivation to go beyond the *apparent* limits of few-body physics.

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