Highly excited Rydberg electron as a spectator to an ion-molecule reaction

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We have theoretically studied the conditions of the behavior of a high Rydberg electron as a spectator to an ion-molecule reaction in high Rydberg neutral collisions. Adoption of a circular high Rydberg atom in the initial channel of the high Rydberg neutral collisions ensures the behavior of the high Rydberg electron as the spectator to interaction between an ion core of the high Rydberg atom and an incoming neutral species; i.e., the ion-molecule reaction. This theoretical consideration leads to equivalence between the high Rydberg neutral collision and the ion-molecule reaction with high accuracy. This equivalence gives us a possibility of probing the ion-molecule reaction at low energies without space-charge effects encountered in ion-beam experiments.

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In a high Rydberg atom A^{**} with principal quantum number n, an excited electron in a high Rydberg state moves with a slow velocity $v_n = v_0/n$ around a large orbit with a mean radius $r_n \simeq n^2 a_0$, where v_0 is a mean velocity of the electron and a_0 is a Bohr radius; i.e., a mean radius in the ground state of a hydrogen atom. Actually, if we take, for example, $n = 40$, we have the mean radius $r_{40} \simeq 8.5 \times 10^{-8}$ m and the mean velocity (v_{40}) of the Rydberg electron 5.5×10^4 m/s. For the collision between hydrogen atoms, relative velocity $v_{\rm th}$ at thermal energies is roughly estimated to be 3.1×10^3 m/s. Thus, we have the ratio $v_{40}/v_{\rm th} \approx 20$. Judging from this estimate, we find that the Born-Oppenheimer separation does not hold because it is based on the assumption that the electron moves very fast in comparison with relative motion. Hence, we immediately see that the usual description of atom-atom (molecule) collisions based on potential energy curves at low energies breaks down because of the slow velocity of the Rydberg electron. Therefore, we have to resort to a completely different way of describing slow atom-atom (molecule) collisions.

In 1983, we presented general theoretical aspects on collisions of high Rydberg atoms with neutral species (which, for brevity, we shall refer to as high Rydberg neutral collisions) [1] based on Fermi's model [2]. When the high Rydberg atom A^{**} interacts with the incoming neutral species (B or BC), the Rydberg electron e_R and the ion core A^+ behave as independent scatterers. This arises from the fact that effective ranges of the interaction between the charged particle (e_R or A^+) and the neutral species [B (or BC)] are much smaller than that between the charged particles; i.e., between e_R and the ion core A^+. For the sufficiently high principal quantum number n, we have the following conditions:

$$r[e_R - B\ (\text{or } BC)] \ll r_n, \tag{1}$$

$$r[A^+ - B\ (\text{or } BC)] \ll r_n, \tag{2}$$

where $r[e_R - B\ (\text{or } BC)]$ and $r[A^+ - B\ (\text{or } BC)]$ are the effective ranges of both interactions. This means that these two interactions do not play decisive roles simultaneously in the high Rydberg neutral collisions although they physically coexist.

Under conditions (1) and (2), we can clearly categorize the high Rydberg neutral collisions into the following two extreme cases:

(I) The interaction between e_R and B (or BC) plays a decisive role.

(II) The interaction between A^+ and B (or BC) is important.

In case (I), the Rydberg electron e_R moves slowly, as if it were free, at a peripheral part of the Coulomb potential and interacts with the neutral species B (or BC) impulsively. On the other hand, the ion core A^+ behaves as a spectator except that it gives a momentum distribution to the motion of the Rydberg electron originating from its binding effect by the Coulomb interaction between e_R and A^+. For example, ionization of high Rydberg atoms by collision with polar molecules at thermal energies was understood in terms of energy transfer from molecular rotation to electronic motion [3]. In this case, the binding effect to the Rydberg electron by the ion core was taken into account as a transition form factor of the high Rydberg atom. In some cases, the Rydberg electron can be viewed as an "electron beam" with the momentum distribution originating from the binding effect by the ion core. This is the so-called "free" electron model [1,4]. After establishing the relation between the high Rydberg neutral collisions and the electron molecule collisions (taking proper account of the existence of the ion core as the spectator), one had succeeded in obtaining information on the latter, particularly at low energies from experimental data on the former without space-charge effects encountered in electron molecule collisions at low energies [5–7].

In case (II), in contrast to case (I), the Rydberg electron e_R becomes the spectator while the ion core A^+ interacts with the neutral species B (or BC). Then, the interaction between A^+ and B (or BC) leads to charge transfer or an ion-molecule reaction as pointed out in Ref. [1]. The Rydberg electron automatically follows a positive charge after these collision processes take place. Hence, we can expect a strong correlation between the high Rydberg neutral collisions and these collision processes.

Further, in case (II), the physical situation becomes quite simple in comparison with that in case (I). This comes from the fact that (due to a large mass of the ion core compared with an electron mass) the binding effect gives no appreciable influence over the motion of the ion core. This results from the physical situation that the coordinate of the center of mass

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of the Rydberg atom almost corresponds to that of the ion core. Namely, the Rydberg electron behaves simply as the spectator to the collision between the ion core and the incoming neutral species in the high Rydberg neutral collisions. This also predicts a weak n dependence of cross sections for the high Rydberg neutral collision belonging to case (II) because the Rydberg electron is not directly involved in the collision dynamics [1].

Since 1994, there have been a few (but detailed) experimental works concerning case (II). Chupka and coworkers [8] investigated the molecular Rydberg process $H_2^{**} + H_2 \rightarrow H_3^+ + H + e$ in comparison with the ion-molecule reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$. Strazisar *et al.* [9] studied vibrationally inelastic scattering of the high Rydberg hydrogen atoms from N_2 or O_2 in relation to vibrationally inelastic scattering of H^+ from N_2 or O_2. Wrede *et al.* [10] and Dai *et al.* [11] investigated reactive scattering of the high Rydberg hydrogen atom $H^{**} + D_2 \rightarrow HD + D^{**}$ in comparison with the ion-molecule reaction $H^+ + D_2 \rightarrow HD + D^+$.

In all these experiments, it has been found that the concept of the Rydberg electron as the spectator to the collisions of the ion core with the neutral species in the high Rydberg neutral collisions explains all the experimental findings reasonably and consistently. In particular, Refs. [10,11] studied state-to-state dynamics of reactive scattering of the high Rydberg hydrogen atom with D_2. Further, detailed comparisons of quasiclassical trajectory calculations of the ion-molecule reaction (i.e., $H^+ + D_2 \rightarrow HD + D^+$) [12,13] with the experimental findings [11] were made. These studies show a remarkable resemblance between the results (for example, on the rotational distributions of the product HD) from both the high Rydberg neutral collision and the ion-molecule reaction. All these references [8–11] pointed out the possibility of obtaining information on the interaction between the ion core and the incoming neutral species at low energies from the data on the high Rydberg neutral collisions without the space-charge effects encountered in the ion-beam experiments.

Now, it is worthwhile to examine in more detail the conditions of the Rydberg electron as the spectator in the high Rydberg neutral collision. Here, we focus our attention on the relation between high Rydberg neutral collision (3) belonging to case (II) and ion-molecule reaction (4) as a concrete example,

$$A^{**}(n,\ell) + BC(\beta) \rightarrow AB(\gamma) + C^{**}(n',\ell'), \quad (3)$$

$$A^+ + BC(\beta) \rightarrow AB(\gamma) + C^+, \quad (4)$$

where $n(n')$ and $\ell(\ell')$ are the principal quantum number and the angular momentum of the high Rydberg atom in the initial (final) channel of collision process (3), respectively, and $\beta(\gamma)$ denotes a set of quantum numbers specifying the internal state of the molecule BC (AB) collectively.

Usually, the high Rydberg atoms are experimentally produced from the ground or lower excited states by selective excitation by one- or two-photon absorption. Then, these excited atoms have lower ℓ because of conservation of the angular momentum. The Rydberg electron in an excited orbit with lower ℓ, say, $\ell = 0,1$, or 2, is likely to approach the positive charge, namely, the reaction zone of the ion-molecule reactions because of no centrifugal barrier for the s electron and of a very low centrifugal barrier for the p or d electron. Then, the Rydberg electron with lower ℓ may give an appreciable perturbation to the ion-molecule reaction.

In the present case, the Rydberg electron as the spectator always should be far distant from the positive charge that exists in the reaction zone where the ion-molecule reaction takes place. Hence, initial Rydberg state of collision process (3) should have a higher angular momentum (the most favorably $\ell = n - 1$, namely, the circular state) because the Rydberg electron cannot penetrate into the reaction zone due to the existence of a high centrifugal barrier.

When Ref. [1] was written, there was no experimental method that could efficiently control the angular momentum of the high Rydberg states after their production. Later, experimental methods for the production of the circular high Rydberg state ($\ell = \mid m \mid = n - 1$) were developed, where m is the magnetic quantum number of the high Rydberg state [14–16]. Now, it is experimentally possible to prepare the circular high Rydberg atom in initial channel of collision process (3). In addition to conditions (1) and (2), adoption of the circular high Rydberg atom in the initial channel of high Rydberg neutral collision (3) ensures the behavior of the Rydberg electron as the spectator to the collision of the ion core with the incoming neutral species, namely, collision process (4). In this case, the Rydberg electron keeps collision system (3) as a whole neutral, shields collision process (4) from the outside world, and is quite unlikely to approach the reaction zone due to the existence of the highest centrifugal barrier between the Rydberg electron and the positive charge. Hence, we can expect that this situation naturally leads to the equivalence between collision processes (3) and (4) with high accuracy.

We have already pointed out the weak n dependence of the cross section for high Rydberg neutral collisions (3) belonging to case (II) stated above. Further, we can make the following arguments as to the dependence of collision process (3) on n' and ℓ'. Under condition (2), the whole collision system in collision process (3) looks like a hydrogenic species such as $[(ABC)^+ + e_R]$ even while the ion-molecule reaction is taking place. As collision process (3) proceeds, the Rydberg electron in the circular state as the spectator sees the ion cores; i.e., A^+, $(ABC)^+$, and C^+ successively. Therefore, the energy exchange and angular momentum exchange are quite unlikely to occur between the Rydberg electron and these ion cores due to the existence of the highest centrifugal barrier between them. Hence, the final principal quantum number n' is almost equal to n because relation $E_A(n) \approx E_C(n')$ holds, where $E_A(n)$ and $E_C(n')$ are the energy levels of the high Rydberg atoms; i.e., A^{**} and C^{**}. We can also expect to have $\ell' \approx n' (\approx n)$ because the Rydberg electron remains to be in the circular high Rydberg state during all of the course of collision process (3).

However, state changing processes, i.e., ℓ changing and m changing processes by collisions with residual molecules may take place. The m changing process does not change the behavior of the Rydberg electron as the spectator in the circular state. Experimentally, care must be taken for the ℓ changing processes not to occur. These state changing processes belong to case (I), as discussed above. The state changing processes of the circular high Rydberg atom by collision with rare gas atoms were theoretically investigated based on the "free" electron model [17]. It was found that there is a propensity rule in which

the state changing processes of the circular high Rydberg atom with the rare gas atom occur overwhelmingly between the circular states. This propensity rule originates from the short-range nature of the interaction between the Rydberg electron and the rare gas atom and from a highly anisotropic electron density distribution of the circular high Rydberg state. Once the circular high Rydberg state is prepared as the initial one in collision process (3), the state changing processes of the circular Rydberg states into the Rydberg states with lower ℓ are unlikely to occur. Therefore, the circular high Rydberg states are expected to be stable against the state changing processes by collision with the nonpolar residual molecule such as D_2.

In conclusion, in addition to conditions (1) and (2), adoption of the circular high Rydberg atom in the initial channel of collision process (3) leads to the equivalence between high Rydberg neutral collisions (3) and ion-molecule reactions (4) with high accuracy because of the behavior of high Rydberg electron as the spectator. Therefore, the experimental data on high Rydberg neutral collisions (3) can provide us with a possibility of obtaining quantitative information on ion-molecule reactions (4) at low energies without the space-charge effects encountered in the ion-beam experiments. Our conclusion is based on the theoretical consideration and should be experimentally tested.

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