Unexplained features of capture and ionization for ion–aligned-Rydberg-atom collisions

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Observed but unexplained features, namely, oscillations in the capture cross sections and an unexpected increase in the ionization cross sections at lower velocities, are discussed using classical trajectory Monte Carlo simulated results for ion–aligned-Rydberg-atom collisions. The initial alignment ($m=0$, 1, and 2) dependence of the cross sections shows evidence of ''capture through quasimolecular ion formation,'' identified as the most likely cause for the oscillations. Spatial overlap, in addition to the velocity matching mechanism, is shown to play an important role in the collision process. The unexpected rise in the ionization cross section toward lower reduced velocities is explained qualitatively in terms of the multiple encounter model [Perumal and Tripathi, Nucl. Instrum. Methods B **143**, 429 (1998)].

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INTRODUCTION

The study of ion–Rydberg-atom collisions is still a challenge for theorists as well as experimentalists, owing to its significant characteristics. Theoretically, quantum-mechanical calculations are quite cumbersome due to the proliferation of a large number of channels, and therefore more attention has been focused on alternative classical or semiclassical methods. Experimentally, the selective field ionization technique [1], normally used in ion–Rydberg-atom experiments, is not adequate to resolve densely populated states, and needs further experimental sophistication. Recent experimental developments; in particular, improved laser-optical pumping techniques, stimulated collision studies with the selective Rydberg states [1–4]. This allows one not only to control the initial n and l quantum numbers, but also the magnetic substate m. The understanding of the role of m in Rydberg-atom collisions is an appealing area for investigation both at low as well as high velocities. The alignment dependence of the charge exchange process in Rydberg atoms has been explored much (see, e.g., Refs. [4], [5]). Ionization [6], however, is less studied.

The unexpected oscillations in the charge transfer, excitation, and ionization cross sections at low velocities recently drew the attention of both theorists and experimentalists [4,5,7–11]. It is now clear that these structures are real, but the controversy regarding their genesis and whether they can be explained on the basis of classical mechanics or have a purely quantum mechanical origin still persists. From the quantum-mechanical viewpoint [7], these oscillations appear to be due to the phase interference between inelastic quasimolecular channels. In the classical model, on the other hand, these effects have been explained to arise due to partially resolved contributions of one, three and higher odd swap processes [4] (A swapping process or multiple encounter may be considered as the classical analog of the quantum-mechanical interference phenomenon [7,9]). An intermediate state of a quasimolecular ion (QMI) formed during the interaction and the competition between the final capturing states [5] are also thought to be likely causes for these structures. Although there are several explanations, a precise understanding of these fine structures has yet to be made transparent.

Classical calculations [the classical trajectory Monte Carlo (CTMC) simulation, for example] reproduce these structures [4,5]. It therefore becomes imperative to investigate plausible physical processes in the classical perspective responsible for them. The velocity of the projectile being low in comparison with the orbital electron velocity, the active electron has a chance to move under the influence of both nuclei for an appreciable time. This leads to a trembling motion of an active electron, resulting in a multiple encounter (or swapping) with the projectile more than once. This was effectively confirmed by us in our earlier work [5], based on the multiple peaks appearing in the final n distribution of the capture cross sections. This situation may also be well described by a configuration having an active electron in the field of two ions visualized better as a ''quasimolecular ion,'' with their internuclear separation varying in time [12]. The active electron of this transient quasimolecule undergoes several oscillations (or swapping) before decaying into different final channels. This prolonged interaction may finally end up in capture, excitation, or ionization channels depending upon other kinematic conditions. The competition between these final channels very likely leads to an oscillation in the respective cross sections. Therefore, ''capture through quasimolecular ion formation'' is identified as another channel of capture in addition to other capture mechanisms, i.e., a Thomas double scattering type, mechanism, an Oppenheimer-Brinkman-Kramer mechanism (or momentum matching mechanism), a knock-on-capture mechanism, etc.

It has been found that ''capture through QMI formation'' can be understood better through studies of alignment-dependent collisions. An electron orbit aligned perpendicularly to the projectile motion is a situation in which the condition for the possibility of QMI formation is almost negligible. On the other hand, in a parallel geometry the probability of forming a quasimolecule is the greatest, as the projectile moves in line with the target electron throughout the collision time. Thus structures appearing in the capture

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cross sections due to QMI formation may well be ascertained based on the results obtained separately for these two geometries.

The main objective of the present work is therefore to ascertain the reality behind this type of capture process. In addition, it also aims to explain the unexpected rise in the ionization cross section at low reduced velocities that appears to be an amazing phenomenon. The increases in capture and ionization cross sections in the perpendicular geometry could not be understood in terms of normally known processes; therefore, they ought to be investigated. The cross-section ratio between the two orientations are also determined to obtain further insight into the different mechanisms involved in the capture and ionization processes.

THEORETICAL METHOD

We have used the classical trajectory Monte Carlo simulation method to study these processes. The collision system chosen for the present investigation is

$$\mathrm{Na}^{+}+\mathrm{Na}(n=28,l=2,m=0,1,2)\rightarrow \mathrm{Na}(n'l')+\mathrm{Na}^{+}.$$

The velocity of the projectile is varied from $v^{*}=0.2$ to 2.0 (where $v^{*}=v_p/v_e$, v_p is the projectile velocity, and v_e is the target electron's velocity). The details of the CTMC method were given in our earlier paper [5]; only significant changes are discussed here. The initial orbital quantum number l is specified from the classical angular momentum $l_c=\mathbf{r}\times\mathbf{k}$ and the condition $l\leqslant l_c\leqslant l+1$, where $\mathbf{r}$ and $\mathbf{k}$ are the position and momentum vectors of the electron relative to the target core, respectively. For the preparation of the initial m states, we have introduced the following binning procedure. Instead of generating randomly oriented Kepler orbits, the classical values of orbital angular momentum and orientation were selected by the condition

$$\left(m-\frac{1}{2}\right)\left(\frac{2l_c}{2l+1}\right)\leqslant m_c\leqslant\left(m+\frac{1}{2}\right)\left(\frac{2l_c}{2l+1}\right),$$

where l and m are orbital and magnetic quantum numbers, respectively; the corresponding classical values chosen in the calculations are labeled by the index c. This m-selection procedure is, in fact, a continuation the previous procedures discussed in Refs. [13] and [14]. This binning procedure reproduces the correct quantal distribution of m_l within the n_l sublevels. The two alignments mentioned above, that have been particularly chosen in the present work, are parallel geometry $m=0$ (in which the electron orbit is aligned parallel to the projectile motion) and the perpendicular geometry $m=2$ (in which the electron orbit is aligned perpendicular to the projectile direction) (see Fig. 1). The calculations for the $m=1$ case were also performed for the sake of completeness. 10^6 trajectories were calculated for each v^{*}, which resulted in statistical errors of less than 3%.

RESULTS AND DISCUSSION

In the case of parallel geometry, the projectile moves in the direction of the active electron and, therefore, ''sees''

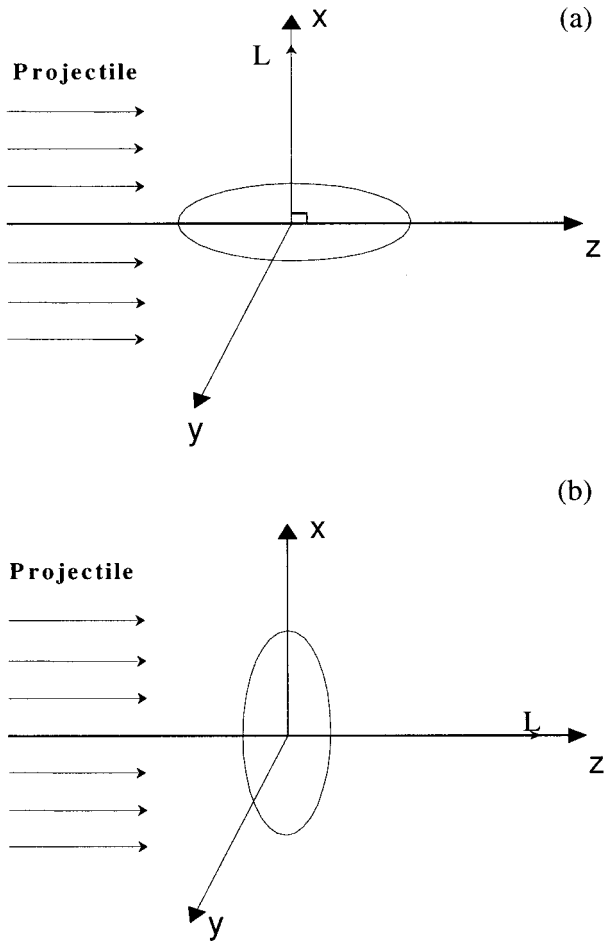

FIG. 1. Schematic diagram of the collision geometry. (a) Parallel geometry ($m=0$). (b) Perpendicular geometry ($m=2$).

only an edge view of its orbit. Hence at lower impact parameters the projectile would be able to significantly perturb the electron, particularly if both of them are on the same side of the target nucleus, paving the way for an easy transfer of the electron [13]. Consequently, because of velocity matching, the probability of charge transfer should increase quite significantly. Interestingly, this is also a situation to be very likely seen in a quasimolecular ion. In the case of perpendicular geometry, the orbital angular momentum vector of the active electron is aligned with the incoming projectile's trajectory. This provides the projectile with a full view of the entire electron orbit. The velocities of the electron and the projectile being perpendicular to each other, the possibility of velocity matching is ruled out. The formation of a QMI in this situation is therefore also not a favorable process. As a result, for this dynamical condition the cross sections should be more or less bereft of any prominent structure in it.

Interestingly, in accordance with the arguments given above it has been noted (see Fig. 2) that structures in the total capture cross sections, which are quite obvious in the case of parallel geometry, are almost lost in the background in the case of perpendicular geometry. It may therefore be inferred that a quasimolecular ion formed as an intermediate state, like a resonance state, provides one of the most plausible mechanisms for the structure arising in the capture cross sec-

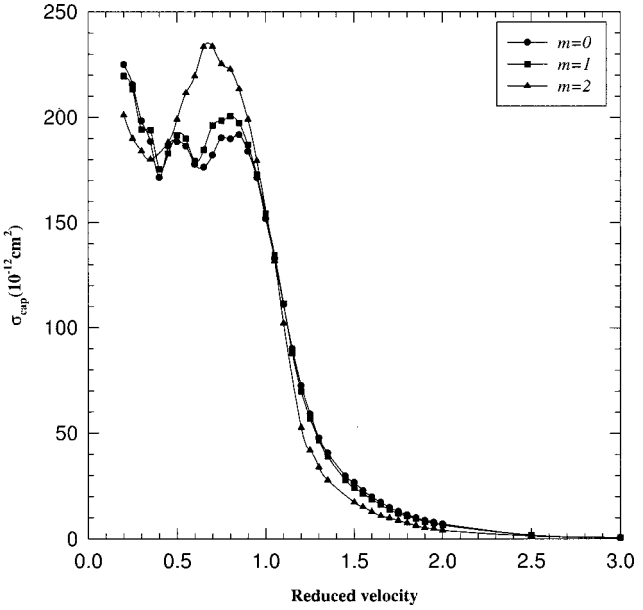

FIG. 2. Charge-transfer cross sections from the initial 24*d* Rydberg state with $m=0$, 1, and 2.

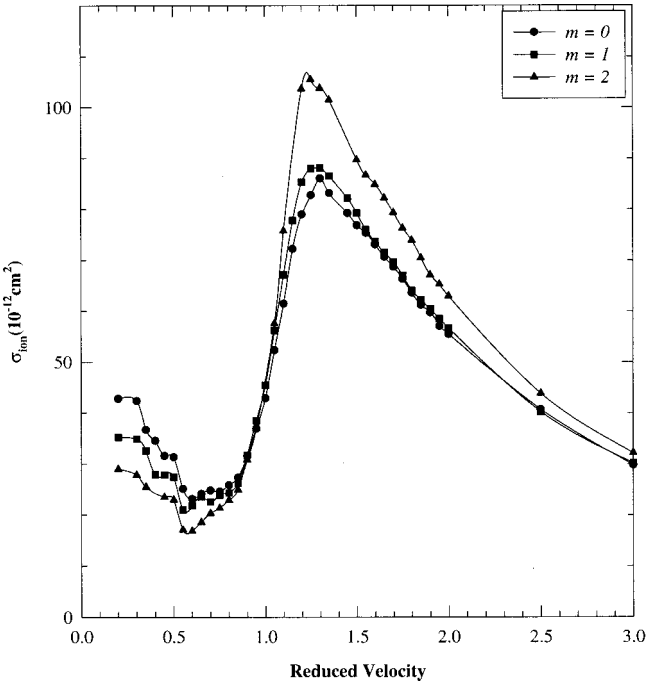

FIG. 3. Ionization cross sections from the initial 24*d* Rydberg state with $m=0$, 1, and 2.

tions in this low-velocity regime. Further, the velocity matching condition being weak, the capture cross section in the case of perpendicular geometry should be less as compared to that of the parallel geometry. However, the results are contrary to this inference (see Fig. 2). This indicates the presence of an altogether different physical process being responsible for the capture rather than the velocity matching mechanism. Careful analyses of the present results of the capture cross section reveal the ''spatial overlap mechanism'' as the most plausible cause of this charge-transfer process. An orbital overlap in the *x* space of the electron cloud and the projectile trajectory will enhance the charge-transfer process even if the velocity matching condition is reasonably weak [15]. The reason for inferring a spatially selective capture mechanism is that for low-*m* values there is an appreciable probability of the target electron residing between the target nucleus and the approaching ion, with the result that the electron may orbit both nuclei during the slow collision. However, for larger *m*'s there is little chance of the electron ever spending time upstream, because the plane of the electron's orbit is approached nearly face on. If velocity matching plays a role in these collisions of aligned states, one would expect that for larger *m* values the capture cross section would decrease, contrary to the results shown in Fig. 2. It is therefore concluded that spatial overlap provides another channel in ion-atom collisions, leading to the capture of an electron.

It may also be noted from Fig. 2 that at $v^*=1.0$, the capture cross sections from the three initial states, viz $m=0$, 1, and 2, are the same, revealing the fact that alignment does not affect the cross section at the velocity matching point. As the velocity increases beyond $v^*=1.0$, the cross section in the perpendicular geometry decreases rapidly as compared to the parallel geometry. This is because, the spatial overlap decreases with the increase in velocity. This is supported by the fact that the same trend is noted at lower velocities (<0.35). In clear contrast to this behavior, cross sections in the case of parallel geometry at lower as well as higher velocities are larger than the perpendicular geometry, which is explained by the prevalence of the velocity matching process.

Alignment-dependent ionization cross sections have also been calculated, and significant features noted (see Fig. 3). Similar to the capture process, the ionization cross section also increases with an increase in the value of *m*. A peak appears at $v^*=1.3$, irrespective of the initial value of *m*. The cross sections at $v^*=1.0$ for all *m* states are the same, showing independence from the alignment. At low reduced velocities, the cross section for $m=0$ dominates that of $m=1$ and 2 whereas, at higher reduced velocities, the cross sections for $m=0$ and 1 are almost the same and are less than that of $m=2$. The most intriguing aspect of the ionization cross section is its unusual rise at low v. This unexpected behavior was also observed by Homan [16], but he did not put forth any reason for its occurrence. In our analysis, we find that the multiple interactions of the active electron with the projectile (swapping) enhance the ionization probability [5]. The electron, after suffering multiple interactions, may end up in an excited state of either the projectile or the target, or may move away from the cores and leave them ionized. This implies that a similar structure appears in the respective cross sections of all three processes (capture, ionization, and excitation). Interestingly enough, similar oscillating structures were very recently observed in Ref. [9] in the ionization cross section for Be^{4+}-H collisions, and in the case of He^{2+}-Li by us in our recent paper [8]. It was shown that oscillations in the ionization cross sections very much resemble the oscillations appearing in the capture and excitation cross sections.

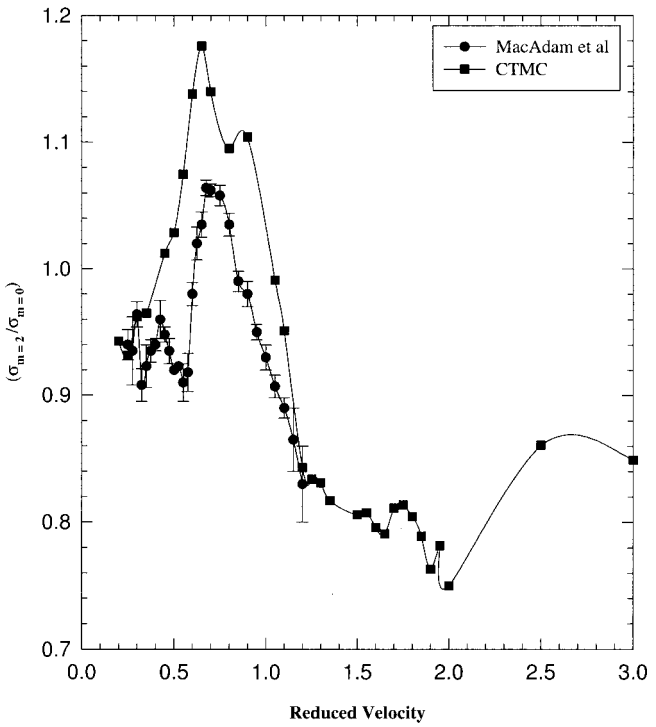

FIG. 4. The capture cross-section ratio between the perpendicular and parallel geometry is plotted along with the experimental results of Ref. [17]. (The CTMC result is adjusted according to the experimental situation to have a better comparison, see the text details.)

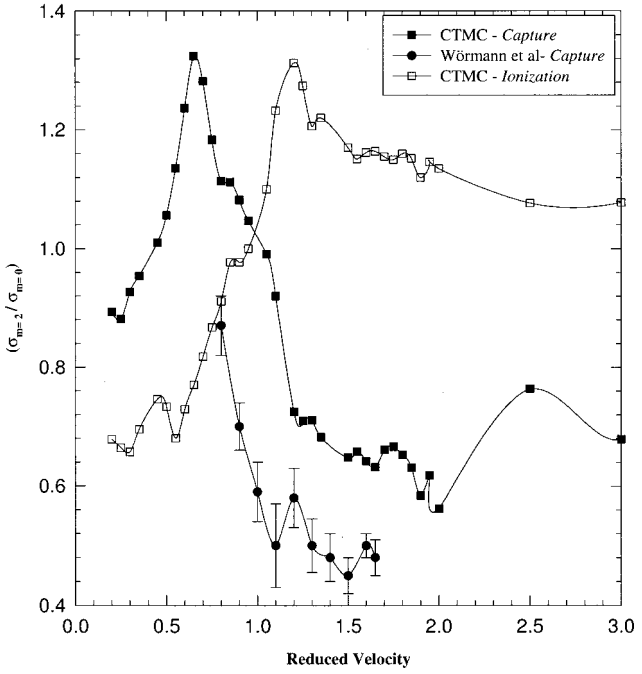

FIG. 5. The cross-section ratio (not the adjusted one) between the perpendicular and parallel geometry for the capture and ionization along with the results of Ref. [3].

In order to understand the mechanisms involved in the capture and ionization processes further, we have determined the cross-section ratio between the two orientations ($\sigma_{per}/\sigma_{par}$). The dependence of this ratio on the reduced speed has been compared with the experimental results of Refs. [17] and [3] (see Fig. 4). The results of Ref. [17] contain a mixture of different sublevels; parallel polarization is a mixture of 40% $m_l=0$ and 60% $m_l=1$, and perpendicular polarization is a mixture of 10%, 30%, and 60% of $m_l=0$, 1, and 2, respectively. In addition, the results of Ref. [17] show the average alignment effect of the projectiles K^+ and Na^+ and targets $n=21$, 24, and 28, whereas the author of Ref. [3] used Ar^+ as the projectile and targets of $n=21-28$. (Note that we have used Na^+ as the projectile and target states of $n=28$). The present CTMC results have been manipulated in the light of the above experimental situation, in order to obtain a meaningful comparison with the experimental results. The CTMC results in the case of capture are in excellent agreement with those of MacAdam [17]. The alignment effect is very much evident from the calculated and measured ratio between $v^*=0.5$ and 1.0. The present as well as the MacAdam's value of this ratio increases with an increase of v^*, and reaches a maximum at $v^*\sim 0.65$. In this phase, the role of spatial overlap dominates the velocity matching condition. With a further increase of v^*, the ratio declines monotonically as a consequence of a decrease in the spatial overlap. At $v^*\sim 1.0$, the ratio is almost unity, showing no effect of alignment at this particular velocity. Beyond $v^*=2.0$, it again increases, which can be understood in terms of the double encounter mechanism (the Thomas double encounter process [18]). Evidence of the Thomas double encounter process was reported recently by Wang and Olson [19] at such low velocities, manifesting a double-peak structure in differential cross sections for ion-orientated Rydberg atom collisions.

The ratio of the pure CTMC capture and ionization cross section (not manipulated) are also plotted separately in Fig. 5 along with the capture cross section ratio of Ref. [3]. The capture ratio shows an excellent agreement with the experimental result of Ref. [3]. Oscillations between 1.0 and 1.6 have been nicely reproduced in the present work; however, the magnitudes differ slightly in both results. The small peaks at 1.2, 1.5, and ~1.6 are also visible in the experimental results, thereby giving credibility to the present work. The cause of this structure is not clear, and in our opinion it may be due to the quasi-Thomas double-scattering mechanism proposed by Wang and Olson [19]. Wang and Olson reported a double-peak structure in the differential cross section at $v^*=1.5$, and suggested the quasi-Thomas double-scattering (QTDS) mechanism to be the reason for it. The present work also reports the same kind of oscillation near $v^*=1.5$, and therefore analogously a QTDS mechanism is identified as the cause of it. It is also interesting to note that these oscillating structures appear in the ionization cross section ratio within the same range of reduced velocities.

In the case of ionization, the cross-section ratio increases exponentially in the low-velocity region, and reaches a maximum at around 1.2. A small oscillation found in the low-velocity regime may result due to the multiple interaction of the electron with the target and projectile cores. At $v^*=1.0$, the ratio becomes unity, which is very similar to the

case for capture, indicating its independence from the alignment effect at the velocity matching point. The ratio declines sharply in its magnitude beyond $v^* = 1.2$. As far as we know there are no experimental results available to compare with this ratio.

CONCLUSIONS

The present theoretical investigations of capture and ionization from aligned Rydberg atoms show clear evidence of electron capture through quasimolecular ion formation. It has also been established that spatial overlap leads to capture in addition to the velocity-matching process. An unexpected rise in the ionization cross section at low velocities has been reported, and explained qualitatively through a multiple encounter model. The cross-section ratios for the two orientations clearly indicate the velocity region in which the different capture mechanisms are involved. We believe that the present work will stimulate experimentalists toward further work in this direction.

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