Rydberg atom formation in ultracold plasmas: non-equilibrium dynamics of recombination

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Abstract. Rydberg atom formation is a source of heating in plasmas. The rate of three-body recombination in an ultracold plasma was measured and electron temperature was derived from it using standard equilibrium recombination rates. With large-scale Monte Carlo and particle-in-cell simulations, we have calculated \textit{ab initio} the rate of excitation, de-excitation, ionization (and recombination) in electron-Rydberg atom collision and investigated the short-time dynamics of three-body recombination in an ultracold neutral plasma. Comparison with observed rates is quite good. Particular attention is paid to the low-frequency microfield effect on Rydberg state cut-off in the plasma.

1. Introduction

The first ultracold plasma was created in 1999 [1] from photoionization of a magneto-optically trapped (MOT) ultracold sample of neutral Xe atoms. Metastable xenon atoms in 5p5(2P3/2) 6s state, produced in a discharge, were collected in a MOT, whose frequency was tuned to the 6s - 6p, 882 nm transition in xenon. The metastable state lives for 43 s. The Xe atoms were cooled to 10 µK with a neutral density of 2 × 10⁹ cm⁻³. The neutral plasma was created using a second pulse at 514 nm to partially ionize the atoms above the first ionization threshold of xenon. Since the ions were created from a nearly frozen gas of neutral Xe atoms, they maintain the temperature Tᵢ = 10 µK of their parent atoms. The liberated electrons carried most of the excess energy in the ionized gas.

Ultracold neutral plasmas (UNP) obtained in table-top experiments are of particular topical interest because of the versatility and the high degree of control of a strongly correlated system, for which several collective and coupled phenomena can be studied. This is possible because the ratio between the interparticle Coulomb energy U and the thermal motion, Γ = \frac{U}{k_B T} > 1. In a UNP, the typical Debye length, over which electric fields are screened is about \lambda_D \sim 5 \mu m, while the spatial extent of the ultracold atomic gas is 200 \mu m. Interested reader is encouraged to consult a recent review devoted to this topic [2].

As the plasma expands and cools down, electrons and ions can recombine into atoms. In a typical high temperature plasma, such as those in lighting sources and astrophysical plasmas, radiative recombination and dielectronic recombination dominate. In a UNP, on the other hand, the most favorable route to recombination is when another electron becomes involved.
in the process, allowing an electron and an ion to form a highly-excited Rydberg state, and carries the binding energy liberated in the recombination process. The rate constant for the steady state TBR has a formidable temperature scaling, \( \alpha_{TBR} \propto T^{-9/2} \). The binding energy of formed Rydberg atoms increases as the UNP expands and the density decreases \([3]\). A TBR rate coefficient \([4]\), which scales as \( n^6 \), with the principal quantum number \( n \), suggests that more atoms are created than observed in such experiments \([3]\), and atoms formed with binding energies within a few \( k_B T \) become thermally equilibrated. Three-body recombination is also the dominant mechanism for forming antihydrogen atoms in strongly magnetized antimatter plasmas \([5]\).

Detailed understanding of electron-Rydberg atom collision is therefore essential not only for understanding the dynamics of UNP, but also for other important plasmas ranging from various astrophysical and early Universe plasmas to laser-produced nano-plasmas and cold glow-discharges. Accurate rate coefficients have been derived from extensive Monte-Carlo calculations \([6]\) for electron-impact transitions, for ionization and for three-body recombination, over a wide range of energies.

The results of \([6]\) show good agreement with the fit formula of Mansbach and Keck (MK) \([4]\) for the rate coefficients, which has been widely used for the last 40 years and provide a solid foundation for the interpretation of current ultracold plasmas. The agreement is however limited to the energy range of validity of MK excellent results, taking into account the limited computational resources of that time. Indeed, significant deviation from the MK rates have been observed for collisions with small energy transfer.

It was demonstrated \([6]\) that the use of corrected rates is critical when an accurate description of the short-time recombination dynamics is required. Long-time and steady state properties seem to be more insensitive to variations in the microscopic rates.

2. Monte Carlo Calculation

Complementary to the variational reaction rate approach used by MK \([4]\), we performed direct classical Monte Carlo trajectory calculation. This method provides the differential rates for transitions in Rydberg atoms from \( \varepsilon_i \) to \( \varepsilon_f \) in collisions with thermal electrons at various impact parameters, according to the formula

\[
\frac{d k(\varepsilon_i, \varepsilon_f; T)}{d\varepsilon_f} = \frac{2\pi b_0}{N \Delta \varepsilon} \sum_{j=1}^{N} \theta(\varepsilon_j - \varepsilon_f, \Delta \varepsilon) b_j v_j e^{b_j/b_0},
\]

Summation includes only trajectories which have a final temperature-scaled energy \( \varepsilon_j \) within a range \( \Delta \varepsilon \) around \( \varepsilon_f \). This is expressed by the step function \( \theta \), which is unity for \( |\varepsilon_j - \varepsilon_f| < \Delta \varepsilon/2 \) and zero otherwise.

The target state is initially sampled from a microcanonical distribution of states with binding energy \( \varepsilon_i \), the impact parameters \( b_j \) are sampled from an exponential distribution \( \propto e^{-b_j/b_0} \), and the velocities \( v_j \) have a Maxwellian distribution with temperature \( T \). The average impact parameter \( b_0 \) is chosen sufficiently large to ensure convergence of the calculated rates, typically few times the size of the target atom.

Compared to the standard impact parameter sampling, the exponential importance sampling yields considerably improved convergence of the Monte-Carlo calculation, allowing us to calculate transition rates over a wide range of initial energies \( 10 \leq n_i \leq 200 \) and temperatures \( 4K \leq T \leq 256K \), by running a total of \( 6 \times 10^6 \) trajectories.

Each trajectory has been run starting with the projectile electron at a large distance from the target Rydberg atom. The convergence with regard to this distance, and the other free parameters, has been carefully controlled and checked. Each trajectory ended when the projectile electron or the Rydberg electron were far enough from the target such that its repulsion energy
with the other electron was smaller than the maximum energy error permitted during the trajectory propagation.

Based on the classical reversibility of the trajectories one can demonstrate that the rates obtained using equation (1) obey a detailed balance relation.

The vast majority of trajectories had little effect in changing the energy of the target Rydberg atom, specially at low impact energy relative to the target energy, although a good number of electron exchange reactions has been observed. This is the reason why a special logarithmic binning procedure has been adopted for counting the rates for various final energies. In this way, there is a large density of bins for final energies close to the initial energy, where there are a lot of trajectories. The size of the bins increases for larger energy transfers for which the data is scarce. This procedure allows us to control the standard deviation of the Monte Carlo results and maintain it uniformly at few percent. The data for ionization is collected into one bin, regardless the energy distribution between the projectile and target electron.

Figure 1 shows the results of Monte Carlo calculation with the rates normalized by the phase space volume of the initial state \((-\varepsilon_i)^2\). There are two kinds of data sets displayed, for fixed temperature of the projectile \(T = 4K\) and initial states with principle quantum number varying from \(n_i = 25\) to \(n = 200\), and for fixed energy of the initial state \(n = 50\) and increasing temperature of the projectile, \(T=8, 16, 32, 64, 128\) and \(256K\). The evident linear feature in this graph corresponds exactly with MK prediction, which has \(k \sim (\varepsilon_f)^{-4.83}\) for de-excitation collisions. However, at low binding energy of the final states the deviation from MK formula becomes evident. The lines in figure 1 show the corrected formula which will be introduced in the next section.

3. Collision Rates

In contrast to the MK rates, the following corrected rates, obtained in [6], describe correctly the results of Monte Carlo calculation over the whole range of initial and final energies and for all temperatures of the projectile:

\[
k(n_i, n_f) = k_0 \frac{\varepsilon_f^\frac{5}{2} \varepsilon_i^\frac{3}{2}}{\varepsilon_>^\frac{3}{2}} e^{-\varepsilon_i - \varepsilon_f} \left[ \frac{22}{(\varepsilon_> + 0.9)^\frac{5}{2}} + \frac{9/2}{\varepsilon_>^\frac{3}{2} \Delta \varepsilon_i^\frac{3}{2}} \right], \tag{2}
\]
from MK formula is the singular $\Delta\varepsilon$ contribution which is responsible for the spikes in rates shown in figure 1. Binary encounter and other approximations [9, 10] had also predicted a singular behavior in the energy transfer for the differential rates, but the crude nature of the approximation made these results questionable. The singularity predicted by them was stronger since the rates diverge as $\Delta\varepsilon^{-2}$ for small energy transfer.

The rates for ionization are obtained directly from the Monte Carlo calculation, in contrast with the corresponding MK rates obtained by extrapolating the excitation rate coefficients close to and across the ionization threshold. The formula which best describes the data also shows important differences compared with the MK rates:

$$k_{\text{ion}}(n_i) = \frac{k_{\text{thr}}(n_i)}{n_i^2 \Lambda^3 \rho_e e^{-\varepsilon_i}} = \frac{11(R/k_B T)^{1/2} k_0 e^{-\varepsilon_i}}{\varepsilon_i^3 + 4.38 e_i^{1.72} + 1.32 \varepsilon_i}, \quad (3)$$

where $\Lambda = (h^2/2\pi mk_B T)^{1/2}$ is the thermal de Broglie wavelength, $\rho_e$ and $m$ are the electron density and mass, respectively, and $k_0$ is the Boltzmann constant.

In contrast to the $n_i^{6.66}$ scaling of the MK TBR rate, equation (3) shows a weaker $n_i^4$ dependence with the principle quantum number, and therefore, by the detailed balance principle, a much smaller initial formation rate of Rydberg atoms.

Figure 2 compares the ionization rates and the three-body rates obtained by the detail balance approximation made these results questionable. The singularity predicted by them was stronger since the rates diverge as $\Delta\varepsilon^{-2}$, for small energy transfer.

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Figure 2 shows that the corrected rates 2 and the MK rates are both in agreement with the results of Monte Carlo calculation, for the range of energy transfer considered by MK. However, the rates at smaller energy transfer are much different. The most important feature missing the rates diverge as $\Delta\varepsilon^{-2}$, for small energy transfer.

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4. Plasma Simulations

How important are the corrections introduced by equations (2) and (3) for understanding UNP dynamics? In order to answer this question we used three test calculations where the MK rates can be swapped with the improved rates, and the comparison of results (between themselves and with the experiment) can provide a direct quantitative assessment about the importance of the corrections. The test calculations are [6]: (1) a steady state master equation calculation for the equilibrium level population, (2) a particle-in-cell UNP simulation to obtain the cloud expansion velocity, and (3) a particle-in-cell UNP simulation to model the Rydberg atom refilling rates.

The first test calculation determines the steady-state distribution of Rydberg levels in a recombining plasma, by adiabatically eliminating the dynamics of excited state populations.
There is no significant difference between the results obtained using the two rates. A kinetic bottleneck marked by a sudden drop in normalized level population appear in both cases at energy \( \sim 4k_BT \). The collisional steady state recombination rate yields the familiar \( \alpha = C_{rec}T^{-9/2} \) law with a coefficient \( C_{rec} = 2.77 \times 10^{-9} K^{9/2} \text{cm}^3\text{s}^{-1} \) about 30\% smaller than the value obtained by MK [4].

For the second and the third test calculation we performed particle-in-cell simulations of UNP introduced in [11] and [12]. Briefly, we employ an adiabatic description of the electron component and a direct particle propagation of the ions, which is coupled to a stochastic treatment for there body recombination and electron-Rydberg atom collision. The corresponding rates for these processes are input parameters in simulations, and can be chosen as the MK rates or the corrected rates.

Recently, absorption imaging of strontium ions was employed to accurately monitor the time evolution of the ion expansion velocity [13]. Detailed comparison with simulations revealed substantial heating due to recombination, which was successfully described using the MK collision rates [13]. Indeed, our simulations show that both the MK and the corrected transition rates yield similar expansion dynamics in agreement with the experiment [6]. This behavior can be understood from well separated timescales for expansion of the plasma and relaxation of highly excited Rydberg states. The initial acceleration of plasma ions normally takes up to several \( \mu \text{s} \) before the onset of considerable expansion, providing sufficient time to develop a quasi-equilibrium distribution of high-Rydberg state populations. As we have shown above, the latter depends only weakly on the details of the individual collision rates, which explains their rather modest effect on the expansion velocity.

The third test calculation proves that the corrections (2) are critical for a correct description of short-time formation of Rydberg atoms. By repeating a sequence of two pulses during the expansion of a xenon UNP the recombination of Rydberg atoms is monitored. The first pulse ionizes Rydberg atoms with \( n \geq 35 \) and while the second pulse, shortly after the first one is used to count the atoms recombined since the application of the first pulse [8].

Figure 4 demonstrates that the MK rates noticeably overestimate the observed recombination rates, while the present rate coefficients yield a much improved description of the observed short-time Rydberg atom evolution. It was previously assumed that the refilling rates are given by the steady state recombination rate coefficient \( \alpha \) and the electron temperature was thus estimated [8]. The resulting temperature evolution was found to be in good agreement with simulations based on the MK rates because of the insensitivity of the long-time plasma evolution to the present rate corrections and of the strong temperature dependence of the coefficient \( \alpha \). However figure 4 demonstrates, that the refilling rate is a sensitive probe of the recombination dynamics and provides clear evidence for the importance of the presented rate improvements.

\[ n_{\text{th}} = \sqrt{R/k_B T} \]
\[ k_0 = n_{\text{th}}^3 \Lambda^3 \rho e k_0. \]
Figure 4. Actual number of recombined atoms (a) and Rydberg atom refilling rate (b), as measured in [8]. Compared to the predictions of the MK rates (dashed lines), plasma simulations based on the present rates (solid lines) yield an improved description of the experimental data (dots).

5. Many-Body Effects
The paricle-in-cell UNP simulations rely on the calculation of the total recombination rates which are divergent in the limit of $n \rightarrow \infty$. In the most simple way, this problem has been solved by introducing a cutoff value at $\varepsilon = 1$. This procedure has been proven to be effective for astrophysical plasma, at much lower temperature and density, and is not valid for UNP conditions. In our simulations the high-$n$ divergence is systematically removed by including field-ionization due to low-frequency ionic microfields [7]. The level population of recombined atoms is weighted with an effective occupation probability $w(n)$, caused by the fluctuating electric fields of the surrounding ions:

$$w(n) = \int P_{\text{Ion}}(F, n) \int_0^F P_{\text{mf}}(F') dF' dF$$

where $P_{\text{mf}}(F)$ is the ionic microfield distribution and $P_{\text{Ion}}(F, n)$ is the ionization field distribution which takes into account the statistical $\ell$ and $m$ distribution inside the $n$ energy shell.

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