Cold, dense Rydberg gases produced in a cold-atom trap are investigated using spectroscopic methods and time-resolved electron counting. On the discrete Rydberg resonances we observe large trap losses and long lasting electron emission from the Rydberg gas (>30ms). Our observations are explained by quasi-elastic l-mixing collisions between Rydberg atoms and slow electrons that lead to the population of long-lived high-angular-momentum Rydberg states. These atoms thermally ionize slowly and with large probabilities, leading to the observed effects.

Laser-cooled atoms can be used to study highly excited Rydberg atoms \(^{1}\) at both large densities and low atomic velocities. Due to the low velocity of the Rydberg atoms, ionizing Rydberg-Rydberg collisions that dominate the behavior of hot Rydberg gases \(^{2,3}\) are largely suppressed. Therefore, the interactions between the Rydberg atoms, free electrons and ions result in a variety of novel phenomena that are specific to translationally cold Rydberg gases. Density-dependent effects have been observed in the resonant excitation transfer between cold Rydberg atoms \(^{4}\). A minute increase of the frequency of the Rydberg excitation laser leads to the production of metastable cold plasmas rather than cold Rydberg gases \(^{7}\). At a critical density corresponding to about one atom per atomic volume, Rydberg gases might undergo a Mott transition that would lead to a new kind of metastable matter \(^{6,9}\). The formation of metastable Rydberg matter might proceed through an intermediate phase, in which the Rydberg population accumulates in long-lived high-angular-momentum (high-\(l\)) states \(^{8}\).

In the present paper, we show that in cold Rydberg gases high-\(l\) Rydberg states are efficiently produced by a robust mechanism, which is, in a similar form, also at work in ZEKE (ZERo Kinetic Energy) electron - spectroscopy, a powerful technique that has revolutionized molecular spectroscopy \(^{11}\).

In our periodically cycled experiment, \(^{87}\)Rb atoms are collected and cooled in a magneto-optic trap (MOT \(^{12}\), see Fig. 1) for a time that could be varied between 95ms and 950ms. 1ms after the shutdown of the MOT a 5\(\mu\)s long diode laser pulse (\(\lambda = 780\)nm) resonant with the \(5S_{1/2}, F = 2 \rightarrow 5P_{3/2}, F = 3\) transition is applied. While the 780nm pulse is on, a blue dye laser pulse (\(\lambda \approx 480\)nm, 10ns width, bandwidth \(\approx 15\)GHz, repetition rate 1Hz to 10Hz) excites \(ns\)- and \(nd\)-Rydberg states from the intermediate \(5P_{3/2}\)-level. The maximum photon fluence of one blue pulse easily exceeds the saturation fluence at the photoionization threshold (\(7 \times 10^{16}\)cm\(^{-2}\) at \(\lambda_{\text{ion}} = 479.1\)nm \(^{3}\)). If the dye laser operates with the oscillator only, the broad-band ASE (amplified spontaneous emission) contained in the blue pulse is < 1% of the pulse energy (\(\approx 50\)\(\mu\)J). With the dye amplifiers on, the ASE contains \(\approx 10\%\) of the pulse energy, is about 5nm wide and centered at \(\lambda = 478\)nm, which is above the ionization threshold. The pulsed dye laser is pumped by the 3rd harmonic of a Nd-YAG laser (355nm), a small fraction of which (<1mJ) can be diverted to partially ionize the atomic cloud before the blue laser pulse arrives. The Rydberg excitation causes a reduction of the ground-state population, which reduces the area density of ground-state atoms that we measure with a low-intensity probe laser pulse resonant on the \(5S_{1/2}, F = 2 \rightarrow 5P_{3/2}, F = 3\) transition. A microchannel-plate (MCP) detector located about 10cm from the atomic cloud is used to detect electrons emitted from the Rydberg gas.

FIG. 1. Level scheme (left) and outline of the experimental setup (right).
the observed trap loss is due to a permanent removal of atoms from the trap upon excitation. The removal is due to many blue pulses exciting the same atoms. We have used a simple model of the MOT loading dynamics to estimate the loss fraction \( X \) due to a single Rydberg excitation event. In Fig. 1(b), a floor of \( X \approx 1\% \) is observed between the discrete Rydberg lines, which is due to direct photoionization by the above discussed 10% ASE of the blue pulse. The discrete Rydberg lines peak at an \( X \) of up to 8% above the floor, a value that corresponds to one-third loss of the excited Rydberg atom population. Further, there is no significant change in \( X \) at the continuum threshold. Our observations show that there is a process by which initially bound Rydberg atoms permanently leave the trap with an efficiency that rivals direct optical photoionization.

Two-body ionizing Rydberg-Rydberg collisions could, in principle, cause a trap loss. Based on an ionization cross section given in [1], a Rydberg atom velocity of 0.1m/s, a lifetime of 100\( \mu \)s \((n \approx 40)\), and a Rydberg atom density of \( 5 \times 10^9 \text{cm}^{-3} \) we estimate a collisional ionization probability of \( \approx 0.5\% \) of the excited Rydberg population, corresponding to an \( X \approx 0.13\% \). This figure, obtained for \( n = 40 \), is too small for two-body ionizing Rydberg-Rydberg collisions to be the dominant source of trap loss.

To estimate the importance of thermally induced microwave ionization of the excited \( ns \) and \( nd \) Rydberg states, we have performed rate equation simulations of the population flow among the bound atomic states and the continuum. We use a basis \((n,l)\) of discrete levels up to \( n = 100 \) with all allowed values of \( l \) and the proper quantum defects, and a grid of 10100 continuum states \((\epsilon,l)\) with energies up to \( \epsilon = 130\text{meV} \) and \( l = 0,1,...,101 \). Due to isotropy, we can assume uniform distributions over the magnetic substates and use \( m \)-averaged transition rates [3]. The obtained thermal ionization probabilities for an ideal 300K blackbody spectrum are displayed in Fig. 2.

While direct thermal ionization of the initially excited states does not cause enough ionization to explain the observed trap loss - see Fig. 2 - it produces ions moving at about 1m/s and electrons with about 8meV average kinetic energy; the latter figure results from the rate-equation calculations. Based on Fig. 2 and on the number of excited Rydberg atoms, we estimate that up to \( \sim 10^5 \) electron-ion pairs are created. If the blue laser is used with its amplifiers active, the ionizing ASE of the blue laser pulse adds a significant amount of additional electron-ion pairs (electron energy \( \approx 10\text{meV} \)). As a result, conditions are such that a metastable cold plasma is formed [4]: a fraction of the electrons quickly evaporate, leaving behind a plasma with a net positive charge that acts as an electron trap. If, under our conditions, the initial number of electrons exceeds about 1000, the trap becomes deep enough to retain a fraction of the electrons [4]. The net positive charge causes a slow Coulomb expansion, due to which all trapped electrons eventually evaporate. The electron storage time is thereby limited to of order 100\( \mu \)s, which is long enough for the retained electrons to frequently collide with the main product of the laser excitation - the bound Rydberg atoms floating in the plasma. The collisions initiate a sequence of events we refer to as the ZEKE-effect.

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these collisions, we have numerically solved the time-dependent Schrödinger equation. For a given initial state \( |n_0, l_0, m_0 \rangle \), electron velocity \( v \) and collision parameter \( b \) the calculation yields a final probability \( P(n_0, l_0, v, b) \) of finding the atom in the hydrogenic manifold, i.e. in a state with \( l \geq 4 \). For \( l_0 \neq 0 \), we run the calculation for the allowed values of \( m_0 \) and average the resultant probabilities over \( m_0 \). The cross section \( \sigma \) for a transition into \( l \geq 4 \) is then defined as

\[
\sigma(n_0, l_0, v) = \int_{b=0}^{b=\infty} P(n_0, l_0, v, b) 2\pi b \, db
\]

(1)

For \( l_0 = 0, 1 \) or 2 it is easy to determine an upper cutoff value for \( b \) where \( P \to 0 \). The range \( b < a_0 n^2 \), where the neglected ionizing processes should become dominating \( n \), does not significantly contribute to \( \sigma \).

![Graph 1](attachment://graph1.png)

**FIG. 4.** The ZEKE effect visualized using the Stark map of Rb in the vicinity of \( n = 20 \). The three steps \( A, B \) and \( C \), explained in the text, lead to the production of long-lived Rydberg atoms and time-delayed thermal ionization. The step \( A \) is induced by quasi-elastic collisions between electrons and Rydberg atoms.

![Graph 2](attachment://graph2.png)

**FIG. 5.** Left: Calculated \( l \)-mixing cross sections \( \sigma \) for collisions of Rydberg atoms in the indicated initial states with electrons versus the electron energy. Right: \( l \)-mixing cross sections \( \sigma \) with \( n_{\text{eff}}^2 \)-fits (dotted) for \( s \)- and \( d \) initial states at an electron energy of 4.5 meV versus the effective quantum number.

![Graph 3](attachment://graph3.png)

**FIG. 6.** Rate of detected electrons formed at different delay times between the Rydberg excitation and the counting gate for the indicated Rydberg \( d \)-states. The signal lasts at least 100 times as long as the natural lifetime of the initially excited states, and shares the qualitative features of simulated results (dotted), which show the rates at which a single Rydberg atom would produce a thermal electron. Note that the plasma that initiates the ZEKE effect decays within \( \approx 100 \mu s \), and does therefore not contribute to the displayed data.

Subsequently, while the cloud of high-\( l \) Rydberg atoms produced by the steps \( A \) and \( B \) slowly expands, the atoms decay or thermally ionize on a slow time scale (step \( C \) in Fig. 4). To model the overall dynamics of the Rydberg
population, we have included an initial “plasma phase” in our rate-equation simulations. During that phase, the populations in the \(n\)-manifolds and the nearby non-hydrogenic states are periodically averaged over the allowed \(l\)-values (with weights \(\sim (2l+1)\)); after the “plasma phase” the averaging ceases. The obtained ionization probabilities are displayed in Fig. 5 for 25\(\mu s\) and 500\(\mu s\) long plasma phases. The ionization probabilities are stable against variations of the duration of the plasma phase and are large enough to explain the experimentally observed trap losses.

While in molecular spectroscopy the ZEKE-effect typically occurs for \(n > 100\) \[1\], we observe it down to low \(n\). We believe that the large velocity of the charges that collide with the Rydberg atoms - \(\approx 50000\) \(m/s\) in our experiments - and our high degree of saturation of the \(l\)-mixing process explain this difference.

The discussed model is supported by the results described in the following. Using the MCP detector located near the atom trap, we have measured the thermal ionization rate vs. time (Fig. 3). When we excite discrete Rydberg levels, we find long-lived electron signals that extend beyond 30\(\mu s\) and that only occur if the frequency of the blue laser is resonant with a discrete Rydberg line. The delayed electron signal, which is characteristic for the ZEKE-effect \[1\], is due to thermal ionization of high-\(l\) Rydberg states.

Fig. 4 shows the electron count rate in a time-delayed counting window vs. the wavelength of the blue laser for conditions well below the saturation of the Rydberg transition. The clarity of the ionization threshold in the long-lived electron signal, which is typical for the ZEKE-effect \[1\], shows that the delayed electrons are linked to the initial optical excitation of bound Rydberg atoms. In Fig. 4(a) the blue pulse is generated with the dye laser oscillator only, which has no significant ASE. Therefore, all electron-ion pairs that are created within about 100\(\mu s\) from the Rydberg excitation originate in thermal ionization of the excited \(ns\)- or \(nd\)-Rydberg atoms. Since the \(5P \rightarrow ns\)-photoexcitation cross sections are about six times smaller than the ones of the neighboring \(d\)-states, and since the thermal ionization probability of the \(s\)-states is only half that of the neighboring \(d\)-states (see Fig. 4), the thermal electron yield on the \(s\)-lines is less than one-tenth of the yield on the neighboring \(d\)-lines. Recalling that of order 1000 slow electrons are needed to form the essential cold-plasma electron trap - with some electrons left in it - it follows that there is a wide range of parameters where the ZEKE-signal should occur on the \(d\)-lines, but not on the neighboring \(s\)-lines (Fig. 4), where the \(s\)-lines barely appear, shows one such case.

We have used two methods to force a ZEKE-signal on the \(s\)-lines in cases where it would normally not appear. In Fig. 4(b) we have used the same parameters as in a), except that the blue laser pulse has been generated with a dye-laser amplifier being active. The pulse has then been attenuated to the same pulse energy as in a). The ASE produced by the amplifier creates enough slow electron-ion pairs to form the cold-plasma electron trap, independent of whether the coherent part of the laser excites \(d\) or \(s\) Rydberg atoms. As a result, we observe both \(s\) and \(d\) lines in the ZEKE-signal. In Fig. 4(c), the blue laser pulse is the same as in a), i.e. it has no ASE, but we ionize a small fraction of the atoms by a UV laser pulse that hits the cloud a few ns before the blue laser pulse (see Fig. 4). The electrons produced by the UV pulse have an energy of about 1eV and therefore all leave. The remaining electron-free potential well captures any slow electrons that are subsequently produced. The comparatively few thermal electrons produced on the \(s\)-lines now don’t escape, as in the case of Fig. 4(a), but are trapped and trigger the ZEKE-effect (note the \(s\)-lines in Fig. 4(c)).

In this paper we have shown that dense, cold Rydberg gases in a room-temperature thermal radiation field decay via the ZEKE-effect, which involves the quasi-elastic collisional production of high-\(l\) Rydberg states and unusually slow thermal ionization. The effect hinges on the temporary existence of a cold plasma, which acts as a transient electron trap. The stability of the observed phenomenon makes it likely that it represents a generic decay pattern of cold, dense Rydberg gases. It appears likely that the spontaneous and efficient production of high-\(l\) Rydberg states could aid the formation of condensed Rydberg matter \[2\]. Since it has become apparent that the radiation temperature is one of the most important parameters of the system, we intend to perform future studies in a cryogenic enclosure with variable wall temperature.

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