Lifetimes of ultralong-range Rydberg molecules in vibrational ground and excited states

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Abstract
Since their first experimental observation, ultralong-range Rydberg molecules consisting of a highly excited Rydberg atom and a ground state atom [1, 2] have attracted the interest in the field of ultracold chemistry [3, 4]. Especially the intriguing properties such as size, polarizability and type of binding they inherit from the Rydberg atom are of interest. An open question in the field is the reduced lifetime of the molecules compared to the corresponding atomic Rydberg states [2]. In this paper we present an experimental study on the lifetimes of the $^3\Sigma (5s - 35s)$ molecule in its vibrational ground state and in an excited state. We show that the lifetimes depend on the density of ground state atoms and that this can be described in the frame of a classical scattering between the molecules and ground state atoms. We also find that the excited molecular state has an even more reduced lifetime compared to the ground state which can be attributed to an inward penetration of the bound atomic pair due to imperfect quantum reflection that takes place in the special shape of the molecular potential [5].

(Underline: Some figures in this article are in colour only in the electronic version)
We create the ultralong-range Rydberg molecules in the $^3\Sigma (5s-ns)$ states from a sample of approximately $2 \times 10^6$ $^{87}$Rb atoms at a temperature of $3 \, \mu$K in the ground state $5s_{1/2}$, $F = 2$; $m_F = 2$ via a two-photon transition. The two lasers at 780 and 480 nm are blue detuned by $\approx 400$ MHz from the intermediate $5p_{3/2}$ state. The laser light is generated by two master-slave diode-laser setups at 780 and 480 nm being locked to a passively stable cavity. The 480 nm laser light is generated by frequency doubling the 961 nm light. A schematic diagram of the atomic level structure and the experimental sequence is depicted in figure 1. Due to the curvature of the magnetic field and imperfect polarizations, not only the $m_j = +1/2$ magnetic Rydberg substate is excited but also a small fraction of the $m_j = -1/2$ state. After each laser excitation, we field ionize the created Rydberg atoms and detect the positive ions on a micro-channel plate (MCP). A subsequent transimpedance amplifier converts the ion current into a voltage signal that we record with a PC-digitizer card. In a time-of-flight analysis we observe two separate pulses that have similar spectral shape. We identify these as Rb$^+$ and Rb$^+_2$ ions. To verify this, we have varied the electric ionization field—and thus the electric field during time-of-flight—and recorded the time delay until we detect the two ion peaks (see figure 1(c)). From the geometry of our chamber and of the field plates that field ionize the Rydberg atoms and guide the ions to the MCP, we also calculated the expected time-of-flight for Rb$^+$ and Rb$^+_2$ using the SIMION software package (green curve in figure 1(c)), which is in good agreement with the experimental finding.

In figure 2(b) we show the Rb$^+$ and Rb$^+_2$ signals in the photoassociation spectrum for the 43s Rydberg state. During the excitation, we apply a magnetic offset field of $B_0 = 7 \, \text{G}$. This shifts the magnetic $m_j = -1/2$ substate of the atom by about 20 MHz to the red which is far enough that it does not affect the observation of the molecular states. At a binding energy of $E_B = -5.7 \, \text{MHz}$, we find the vibrational ground state of the ultralong-range Rydberg molecules. Although the potential supports a dimer state which is bound deeper, we denote the state at $E_B = -5.7 \, \text{MHz}$ as the vibrational ground state, since we know from previous experiments that the state with the strongest signal is the most localized one in the molecular potential (for analogy at 35s see figure 3(b)). Apart from the vibrational ground state, we also identify two excited molecular states with lower binding energies than the vibrational ground state at $\Delta = -4.9 \, \text{MHz}$ and $\Delta = -4.0 \, \text{MHz}$ as well as a molecular state with higher binding energy at $\Delta = -7.3 \, \text{MHz}$. At $\Delta = -10.9 \, \text{MHz}$, about twice the binding energy $E_B$, we find a trimer state, where one Rydberg atom binds two ground state atoms.

In a previous investigation we found that the binding energies of the excited molecular states can only be calculated correctly in a non-perturbative approach [5]. We revealed that the p-wave shape resonance leads to an avoided crossing in the molecular potential curve with a deep potential drop near an internuclear separation of $R \approx 1200a_0$. Surprisingly, the excited states are reflected from the potential drop and are therefore located outside this badland (see figure 3(b)). However, the energies of the vibrational ground states $^3\Sigma (5s-ns)(v = 0)$ are well reproduced in an s-wave theory with an effective scattering length $A_{s,\text{eff}} = -18.0a_0$ in the range of $34 \leq n \leq 40$ [2]. In figure 2(a) we give an overview of the energies of the bound states that we have identified in the range $34 \leq n \leq 43$. To illustrate the validity of the effective s-wave calculation with a modified scattering length up to $n = 43$, we also plot the calculated binding energy for an effective scattering length of $A_{s,\text{eff}} = (-18.0 \pm 0.5)a_0$ for the dimer and the trimer states.

In the following part of this paper, we will investigate the reduced lifetime of the $^3\Sigma (5s-35s)$ molecular states. While we found a lifetime of the vibrational ground state of $\tau = 15(3) \, \mu\text{s}$ in a delayed field ionization experiment [2],
Figure 2. Photoassociation of ultralong-range Rydberg molecules. (a) Measured and calculated binding energies for the ultralong-range Rydberg molecules, $E_B$. The solid blue lines are the calculated binding energies for the vibrational ground states assuming an effective s-wave scattering length $A_{\text{eff}} = -18.0 \pm 0.5 \mu$ in. The grey curves are the calculation for the ab initio value of the s-wave scattering length $A_s = -16.05 \mu$ in calculated by Bahrim and Thumm [7]. The red dots mark the line positions that we identify as the vibrational ground state of the dimer or the trimer in the effective s-wave calculation, and the green dots are line positions of vibrationally excited states. (b) Spectrum of the dimer states $^3\Sigma(5s–43s)$ and the corresponding trimer state with magnetic offset field $B_0 = 7 \text{ G}$. At a detuning of $\Delta = -5.8 \text{ MHz}$ from the atomic resonance we excite the molecular ground state $^3\Sigma(5s–43s)(v = 0)$. (c) Photoassociation spectrum of the dimer $^3\Sigma(5s–35s)$ states and the corresponding trimer state with magnetic offset field $B_0 = 1 \text{ G}$. Note the different scaling of the frequency axes in (b) and (c).

Table 1. Lifetimes of $^3\Sigma(5s–35s)$ ultralong-range Rydberg molecules in their vibrational ground state ($\tau_g$) and an excited state ($\tau_e$).

| Peak density of ground state atoms $N$/$\text{cm}^{-3}$ | $3.1 \times 10^{12}$ | $3.5 \times 10^{12}$ | $4.5 \times 10^{12}$ | $5.3 \times 10^{12}$ | $6.6 \times 10^{12}$ | $7.8 \times 10^{12}$ |
|------------------------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| $\tau_g/\mu$s                                       | 33(2)                | 29(2)                | 27.7(14)             | 24.1(11)             | 23(2)                | 22(2)                |
| $\tau_e/\mu$s                                       | 23(3)                | 21(3)                | 20(2)                | 19(2)                | 17(2)                |

we found a lifetime of only $\tau = 6.4(9) \mu$s when we probed the coherent part of the molecular state [8]. However, these results were obtained in different experimental configurations and at different densities of ground state atoms, making it hard to interpret and compare the results. In order to allow for a systematic investigation of the additional decay channels for ultralong-range Rydberg molecules, we have measured the lifetimes of the molecular ground state and the excited state with binding energy $E_B = -17.4 \text{ MHz}$ (see figure 3(b)) for several values of the density of ground state atoms, $N$.

To determine the lifetime of the $^3\Sigma(5s–35s)$ molecular states, we use a delayed field ionization technique (see figure 1(b)). We therefore measure the Rydberg population that is still present when the atoms are field ionized at different times $\tau_d$ after turning off the excitation laser. Since we ramp up the ionization field within 10 ns, we do not only ionize the Rydberg state of interest but also states lying close by. Thus, the lifetimes we measure are not reduced by blackbody-induced decay. To eliminate effects resulting from an off-resonant excitation, e.g. due to drifts in laser frequency, we simultaneously take two spectra in one atomic sample for each delay time of the field ionization. For each frequency, we first photoassociate the Rydberg molecules and measure the Rydberg population after delayed field ionization, and then we re-excite and measure the Rydberg population with zero delayed field ionization as a reference. After fitting the two spectra with Gaussian profiles, we obtain the fraction of the Rydberg population remaining at delay time $\tau_d$ as the ratios of the amplitudes of the two fitted curves.

The measured lifetimes of the vibrational ground state and an excited state of the $^3\Sigma(5s–35s)$ molecules for different densities $N$ are given in table 1. For the sake of readability,
Figure 3. Decay of $3^3\Sigma(5s-35s)$ ultralong-range Rydberg molecules. (a) Decay rate of the molecular ground state $\gamma_0$ (red dots) and the excited state $\gamma_e$ (blue crosses) versus density of ground state atoms $N$. A linear fit of the type $\gamma = \gamma_0 + \alpha N$ yields $\gamma_0 = 2.1(4) \times 10^4$ s$^{-1}$, $\alpha = 3(1) \times 10^{-9}$ cm$^3$ s$^{-1}$ for the ground state and $\gamma_e = 3.3(12) \times 10^4$ s$^{-1}$, $\alpha_e = 3(2) \times 10^{-9}$ cm$^3$ s$^{-1}$ for the excited state, approving the linear scaling in $N$. The measured decay rate of the Rydberg state 35s is $\gamma_{35s} = 1.6(2) \times 10^4$ s$^{-1}$. The inset shows the ion signal of the two states in the spectrum (cf figure 2(b)). (b) Molecular potential curve and wavefunctions for the 35s state. The wavefunction of the vibrational ground state $|g\rangle$ (red) is localized in the outermost potential well. The excited state $|e\rangle$ (blue), however, is spread over several hundred $a_0$ and stabilized by the quantum reflection at the potential drop near $R = 1200a_0$. Since the reflection is not perfect, the excited state can reach the inner region with a rate $\gamma_{inel}$.

we will discuss in the following the decay rates $\gamma = 1/r$. The decay rates $\gamma_0$ of the molecular ground state $|g\rangle$ (red dots) and the decay rates $\gamma_e$ of the excited molecular state $|e\rangle$ (blue crosses) are depicted in figure 3(a) for different ground state densities $N$. The wavefunctions of the two states in the molecular potentials are shown in figure 3(b). We find that the decay rates of both states increase as the density of ground state atoms is increased. We have verified for densities of $5 \times 10^{12}$ cm$^{-3}$ and $15 \times 10^{12}$ cm$^{-3}$ that the decay rate of the bare Rydberg state 35s is independent of the density of ground state atoms at a value of $\gamma_{35s} = 1.6(2) \times 10^4$ s$^{-1}$. It therefore stands to reason that the decay rate of the molecular states consists of two contributions: the atomic decay rate $\gamma_{atom}$, which is present for both molecules and Rydberg atoms and is independent of the density of ground state atoms $N$, and a molecular decay rate $\gamma_{mol}$ which is characteristic for the molecular states and depends on $N$.

To model the $N$-dependence of $\gamma_{mol}$, we employ classical scattering theory. We therefore assume that the molecule dissociates when a ground state atom and the molecule collide. This seems reasonable as an additional ground state atom entering the classical volume $4/3\pi R^3$ disturbs the Rydberg wavefunction and therefore the molecular potential. The rate $\gamma_{col}$ of such collisions in a gas is a well-known problem [9]. In the case where the molecule can be treated at rest compared to the scattering ground state atoms and the density of molecules is much lower than the density of the ground state atoms, the rate is given by [10]

$$\gamma_{col} = N \pi s^2 \bar{v}, \quad (1)$$

Here, $\pi s^2$ is the geometric cross section, which in our case is $\pi (r + R)^2 \approx \pi R^2$, since the bond length $R$ of the molecule is much larger that the size $r$ of the scattering ground state atom. The mean relative velocity $\bar{v}$ of atoms with mass $m$ in a thermal sample at temperature $T$ is $\bar{v} = \sqrt{2/3k_B T/m}$ [11].

Finally, $N$ is the density of the scattering particles and it is reasonable to assume that the density of the scatterers is given by the density of ground state atoms.

By applying these assumptions to (1), the additional decay rate of the molecular state reads

$$\gamma_{col} = R^2 \sqrt{16\pi k_B T/\pi m} N = \alpha_{col} N, \quad (2)$$

where the parameter $\alpha$ accounts for the mean velocity of the ground state atoms and for the scattering cross section. For the decay rate of the molecular ground state $|g\rangle$, we then finally obtain

$$\gamma_e = \gamma_{atom} + \alpha_e N. \quad (3)$$

To compare our model with the experimental results, we fit a linear curve of the type $\gamma_e = \gamma_{0,e} + \alpha_e N$ to the data. For the molecular ground state, we find the best fit for the values $\gamma_{0,e} = 2.1(4) \times 10^4$ s$^{-1}$ and $\alpha_e = 3(1) \times 10^{-9}$ cm$^3$ s$^{-1}$ (red curve in figure 3). The offset decay rate $\gamma_{0,e}$ is close to the value we expect from our model, the atomic value $\gamma_{atom}$. To calculate the theoretical prediction, $\alpha_{col}$, we use the bond length of $R = 1900a_0$. For $^{87}$Rb and a temperature of $T = 3\mu K$, we obtain $\alpha_{col} = 1.2 \times 10^{-9}$ cm$^3$ s$^{-1}$, which is in reasonable agreement with the experimental findings.

Until now we have considered the molecular ground state, where the wavefunction is well confined in the outermost potential well. Fitting a linear curve of the type $\gamma_e = \gamma_{0,e} + \alpha_e N$ for the excited molecular state $|e\rangle$, we find $\alpha_e = 3(2) \times 10^{-9}$ cm$^3$ s$^{-1}$, which is the same as for the molecular ground state. However, the zero-density offset value is $\gamma_{0,e} = 3.3(12) \times 10^4$ s$^{-1}$. To understand this shorter
lifetime, we have to consider a decay process for the excited state that does not occur for the vibrational ground state.

Figure 3(b) shows the vibrational wavefunction of the longer lived molecular state, $|g\rangle$, which is well localized in the outermost well of the oscillating potential. In addition, we find several excited states that are delocalized over the outer potential region and bound only by quantum reflection at the deep potential drop arising from the p-wave scattering resonance of the Rydberg electron–ground state atom interaction [5]. Due to imperfect reflection there is, however, a small probability that these states penetrate to small distances, which ultimately leads to decay of the molecule. On the other hand, this allows us to treat the inner region as an open boundary, such that the excited molecular states can be identified as resonances of an inverted, i.e., inward, scattering process of the two nuclei [5]. From the asymptotic phase shift $\theta(E)$ one obtains the Wigner delay time

$$\tau_{\text{del}} = \frac{d\theta}{dE} \tag{4}$$

whose peak positions correspond to the location of the quasi-bound molecular states and the corresponding peak amplitude gives the characteristic time of exponential decay to small distances and hence decay of the molecule. A list of the calculated lifetimes $\tau_{\text{del}} = 1/\gamma_{\text{del}}$ for $3\Sigma(5s–35s)$ molecules is given in Table 2. For the excited molecular state $|e\rangle$ at $E_B = -16.5\text{ MHz}$, this yields a decay rate of $\gamma_{\text{del}} = 2.5 \times 10^7\text{ s}^{-1}$ and, including our measured lifetime of the atomic state, the calculated total decay rate is $\gamma_e = \gamma_{\text{atom}} + \gamma_{\text{del}} = 4.1 \times 10^7\text{ s}^{-1}$. Our experimental value $\gamma_{0,e} = 3.3(12) \times 10^7\text{ s}^{-1}$ is slightly lower than the calculated value $\gamma_e$, but still matches within the error bar. The agreement in the frame of our simple theoretical model is remarkable and is another strong indication that the binding mechanism of the excited state is based on quantum reflection.

In this paper, we have presented a systematic study of the lifetime of $3\Sigma(5s–35s)$ ultralong-range Rydberg molecules in their ground state and in a vibrationally excited state. We could reveal that the lifetime of both states depends on the density of atoms in the ground state $5S_{1/2}$. The agreement of the experimental results with a classical scattering theory suggests that the reduced lifetime can be explained as a disturbance of the molecular state by the surrounding ground state atoms. The dependence of this reduced lifetime on the temperature $T$ and the density $N$ of the ground state atoms, $\tau_{\text{col}} \propto T^{1/2}N^{-1}$, shows again that the ultralong-range Rydberg molecules are observable only in a narrow window of experimental parameters. If the density is too low, no pairs of ground state atoms are close enough to form the molecules and if the density is too high, they decay too fast to be observed at all.

Moreover, we have found that the decay rate of the excited molecular state is systematically higher than that of the molecular ground state. We have given evidence that this probably results from inward penetration of the bound atomic pair due to imperfect quantum reflection, leading to the dissociation of the molecule. The formation of Rb$_2^+$ in the photoassociation spectra may be a consequence of this process and an investigation of the formation of Rb$_2^+$ might allow a deeper insight into the binding mechanism.

Although the model we have presented has remarkable agreement with the experimental findings regarding its simplicity, this approach should be treated as a fingerpost towards the understanding of the dynamics of ultralong-range Rydberg molecules. We expect that a more sophisticated model based on the ideas we have outlined in this paper will lead to a quantitative understanding of the lifetimes of the molecules. The Ramsey techniques applied to Rydberg molecules recently [8] might prove as a helpful tool in the experimental exploration of the dynamics of the molecules.

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Table 2. Lifetimes of bound states with binding energy $E_B$ due to transmission into the inner region of the molecular potential.

| Binding energy $E_B$/MHz |  $-7.8$ | $-10.7$ | $-16.5$ | $-23.1$ | $-25.9$ |
|--------------------------|---------|---------|---------|---------|---------|
| Wigner delay time $\tau_{\text{del}}$/µs | 8.5 | 26.6 | 40.5 | $\gg \tau_{\text{atom}}$ | 14.7 |
| Decay rate $\gamma_{\text{del}} = \tau_{\text{del}}/10^7\text{ s}^{-1}$ | 11.8 | 3.76 | 2.47 | $\ll \gamma_{\text{atom}}$ | 6.80 |