

## Eth Zürich, Trapped Ion Quantum Information Group

Semester Project

# Spectroscopy of high energy Rydberg states of Magnesium

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#### Abstract

The Rydberg energy states of magnesium atoms for different angular momentum quantum states are measured. Transitions in a magnesium gas cloud are driven using lasers of wavelength 285 nm for a transition into the first excited state, and 375 nm to drive a transition into a Rydberg state. Unexpected states at energies in between the theoretically predicted energy states of different angular momentum are discovered in combination with the expected transitions. Additionally in contradiction to the possible transitions, following the dipole selection rules, angular momentum states are reached which should not be possible: from a p-state to another p-state. This experiment determines the energies of the realized states of Magnesium atoms.

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### 1 Introduction

Magnesium ions can be used to perform quantum state manipulations in a controlled way. The rough procedure is described in the following. With trapped ions quantum states can be generated and quantum information processed. This requires ionization and trapping with lasers. Different properties of ground or excited states can be used to generate certain quantum states. Having full experimental control over the system, qubits are used to perform calculations. A qubit consists of two orthogonal quantum eigenstates. These superposition states enable information processing. [1]

The Rydberg atoms allow to perform a similar procedure. Rydberg atoms have properties similar to ions. In high Rydberg states the electron is further departed from the atom core most of the time. The atom now has strong dipole properties. With the dipole interaction of the atoms, one can work similarly to ions. Rydberg atoms allow analytical treatment similar to the hydrogen atom, adding a quantum defect which affects the energy levels of the atom. Being able to apply the properties of a neutral atom as well as these of ions, allows to combine an extended as well as a narrow range of interactions. These make Rydberg atoms attractive for quantum entanglements. [2]

With Rydberg atoms a so called dipole blockade is used to inhibit transitions into certain collective quantum states of an atom cluster. This results in an extended control other the quantum system in form of a limitation of possible states. Rydberg states have longer lifetimes which makes it easier to work with these quantum states. A realization of quantum information processing using Rydberg state atoms promises an more facile treatment due to a more secure control over the system. [3].

A Rydberg atom is characterized by a high energy quantum state of an atom, as the valence electron is excited into a state of high principal quantum number n. Rydberg atoms can hence be treated in a classical approach with quantum mechanical properties. Rydberg atoms are therefore related to the Bohr atom model given a high quantum number. Classically an electron orbits the atom core at a large distance. From the quantum mechanical perspective this means that the electron is more likely to be found at a position further away from the atom core. Due to the larger distance the effect of the electron-electron repulsion as well as an exact coulomb attraction of all core protons loses its effect. Rydberg atoms can hence be treated equally to the analytically solvable hydrogen atom. [4]

In order to further analyse the properties and experimental possibilities of Rydberg atoms, this spectroscopy experiment with Magnesium atoms was realized. Laser excited magnesium gas into higher quantum states. Split up into different values of the angular momentum quantum number, these states could be sectioned. The energy of different angular momentum was mapped. It allowed to determine the quantum defect parameters for a range of Rydberg states of the atoms. Prime intention was to explore possible transitions in lower as well as higher Rydberg states closer to the ionization limit.

### 2 Quantum Defect and Excitation Theory

Rydberg atoms were first introduced in transitions of the hydrogen atom. Explicitly from the second excited state to higher energy states. The visible spectral lines allowed to identify these transitions. Their frequency was described using the Balmer formula which was later generalized for any transition from an s to an p state. The formula for the frequency of a transition connecting two states of quantum number m and n resulted:

$$\mathbf{h}\nu = \frac{Ry}{(m-\delta_s)^2} - \frac{Ry}{(n-\delta_p)^2}$$

Ry = 13.605 eV is the so called Rydberg constant and the  $\delta$  parameters describe the deviation due to an s and p state: a quantum defect. To analytically determine the Rydberg constant one can exploit the classical correspondence of Rydberg atoms: An electron on a circular orbit, held by the coulomb force, combined with energy conservation yields in  $Ry = \frac{e^4m}{32\epsilon_0^2\pi^2\hbar^2}$ . With e, m the electron mass and charge [4]. In the case of heavier atoms such as magnesium this Rydberg constant needs to be adopted slightly to obtain the correct result because of electron reduced mass.

The wave function of the hydrogen atom can be solved analytically starting from the Schroedinger equation and a Coulomb potential. Due to the spherical symmetry and potential of the form  $V(r) \sim \frac{1}{r}$  this yields an analytically solvable solution. In light of the solution of the hydrogen atom a likewise approach for the Rydberg atom is possible. The energy eigenvalues, frequency with respect to ionization, are known from above approximations  $(m \to \inf)$ :  $E_n = -\frac{Ry}{(n-\delta_l)^2}$ . Again, the potential is spherically symmetric considering the valence electron. The change in nucleus from hydrogen to magnesium leads to a lower potential for for small radii. Hence, the kinetic energy of the valence electron is higher in comparison to hydrogen. Since the spherical component does not differ from the hydrogen atom, the consequence is a change in the radial component, reflected by shortened wavelength and a phase shift of the wavefunction. This phase shift  $\tau$ , dependent on the Rydberg atom, can be described by the quantum defect parameters  $\delta_l = \frac{\tau}{\pi}$ . The resulting wavefunction matches the wavefunction of the hydrogen atom, assessed with additional factors of quantum defect: [5]

$$\Psi_{n,l,m}(\Theta,\Phi,r) = \frac{Y_{l,m}(\Theta,\Phi)[a_l r^{l+1}\cos\pi\delta_l - b_l r^{-l}\sin\pi\delta_l]}{r}$$

 $Y_{l,m}(\Theta, \Phi)$  are the solutions of the spherical Laplace operator, the well known spherical harmonics. n is the principal quantum number, l the angular momentum number and m the angular momentum in direction of the z-axis. The energy eigenstates are given by the Rydberg-Ritz formula [6]:

$$E_{n,l} = \frac{-R_{Mg}}{(n-\delta_l)^2}$$

The defect parameters  $\delta_l$  in the most general form are also dependent on n. As the goal of this experiment is to find approximated parameters for a broad range of Rydberg states this defect parameter can be mathematically expended:  $\delta_l = \alpha + \frac{\beta}{(n-\alpha)^2} + \frac{\gamma}{(n-\alpha)^4}$ . The parameters  $\alpha$ ,  $\beta$  and  $\gamma$  determine the energy states of the magnesium atoms. For any angular momentum quantum number the parameters can be calculated and taken from literature [6]. For optical transitions the 'selection rules' need to be considered. Transitions

are possible if  $\langle \Psi_{n,l,m}^* | \Psi_{n',l',m'} \rangle \neq 0$ .

$$\int \Psi_{n,l,m}^*(r,\Theta,\Phi)\Psi_{n',l',m'}(r,\Theta,\Phi)r^3\mathrm{d}r\cos\Theta\sin\Theta\mathrm{d}\Theta\mathrm{d}\Phi\neq 0$$

This problem is solved using 'Parity inversion'. The Parity operator  $\hat{P}$ , performs an inversion of the coordinate directions. Applying it on the integral, returns the properties of the integral. Odd parity means that the integral is zero whereas even parity leads to a non zero integral. The clue is to only consider the angular part of the wavefunction,  $Y_{l,l}(\Theta, \Phi)$ . The parity on this state has the eigenvalue  $(-1)^l$ , an uneven parity. All other angular momentum states are created by application of the angular momentum operator  $\hat{l}_-$ . This operator has even parity. Since the parity inversion transforms the azimuthal angle  $\Theta$  via  $\Theta \to \pi - \Theta$  the sin has uneven, whereas the cosin has even parity. The resulting condition reflects  $(-1)^l(-1)^{l'}(-1)^1 = 1$  to be stated as follows:

$$l' = l \pm 1$$

When performing an optical transition to a quantum state of principal quantum number n, the angular momentum quantum number needs to be changed accordingly. [7]

With the discrete wavefunction of the Rydberg atom and the selection rule as

derived above, optical transitions can be specified. In a gas at room temperature most atoms are in the ground state. This state of principal quantum number n = 0 is specified with angular momentum l = 0. Departing from this ground state  $|n = 0, l = 0\rangle = |g\rangle$ , the principal quantum number can be excited into any state, assuring that the angular momentum quantum number is increased by one. The resulting transition into the first excited state has the form  $|g\rangle \rightarrow |n = 1, l = 1\rangle$ . An excitation into Rydberg states of high principal quantum number can then be leveled into two different excited states, following the selection rules:  $|n, l = 0\rangle$  and  $|n, l = 2\rangle$ . The states with less angular momentum are more strongly bound and hence require less energy to be excited. These states are further departed from the ionization threshold. As a simplification the excited states will be addressed by their angular momentum quantum number: l = s, p, d for l = 0, 1, 2.

## 3 Experimental Set-up

The spectroscopy experiment was performed on magnesium atoms. Magnesium was heated up in an oven, sublimating individual atoms. These gaseous atoms are trapped inside a vacuum chamber. The magnesium vapour contains three magnesium isotopes in natural abundances of 79.0% <sup>24</sup>Mg, 10.0% $^{25}$ Mg and 11.0%  $^{26}$ Mg [8]. The isotope of interest is the most abundant one with <sup>24</sup>Mg. Magnesium atoms contain 12 electrons. The electron configuration in the ground state is  $1s^2 2s^2 2p^6 3s^2 {}^1S_0$  with two valence electrons. Since only one electron is excited in the experiment, the two valence electrons are of interest and the remaining electron's state does not change. The ground state  $3s^{2} {}^{1}S_{0}$  was excited to reach higher states, following the selection rules for dipole transitions. The first transition is the excitation from the ground state into the first excited state:  $3s^{2-1}S_0 \rightarrow 3s3p^{-1}P_1$ . This excited state is luminous. As further excitation any Rydberg state of principal quantum number n can possibly be reached, with the angular momentum l = 0, 2:  $3s3p \ ^1P_1 \rightarrow 3sns \ ^1S_0$  and  $3s3p \ ^1P_1 \rightarrow 3snd \ ^1D_2$ . Fig. 1 shows a scheme of these transitions. The ionization energy of  $^{24}$ Mg is 7.65 eV [9].



Figure 1: Scheme of possible transitions for the magnesium atom. A range of -1530 to 0 GHz of the ionization limit was examined.

The excitations were performed using two different lasers, operating at different wavelengths. Both lasers were tunable external cavity diode lasers. The first laser operates at 285 nm and excites magnesium from the ground  ${}^{1}S_{0}$  state to the  ${}^{1}P_{1}$  state. The second laser for Rydberg transitions is tuneable over a larger frequency range and operates at around 375 nm. The light of both lasers was sent into the vacuum chamber with the magnesium atoms. A rough diagram of the experimental set-up is provided in Fig. 2.

The light of the 285 nm laser needs to be very stable since the magnesium gas cloud requires continuous excitation to be in the first excited state. The 285 nm transition line of magnesium is close to twice the frequency of a set of 570 nm transition lines of molecular iodine. The laser was then locked to this iodine line to keep the frequency in the desired range [10]. The frequency was stabilized using an iodine set-up. The second laser was tunable in frequency so that the desired transitions up to any Rydberg state of principal quantum number  $n \ge 47$  were possible.

Since the 285 nm laser was locked to the iodine frequency, its frequency was always precisely defined. Any variance could steam from the natural linewidth of the absorption line. The wavemeter could have large calibration errors in the range of about 200 MHz. Such a miscalibration appears in a rather constantly shifted frequency impacting the accuracy of the wavemeter over time. To increase the accuracy and validity of observations in our experiment the wavemeter was calibrated using the known frequency of the 285 nm laser, referenced to the molecular iodine transition. This due to the high precision of the wavemeter states could be assigned relative to known

transitions. The variance due to a systematic calibration error can hence be reduced to the natural line-width adding a little shift over time:  $\Delta \nu = 200$  MHz.

In the vacuum chamber the excitation into the first state by the 285 nm laser was realized and helped to trap the gas using a Magneto Optical Trap (MOT). With the 375 nm laser this gas cloud was then further excited into the Rydberg states. The optics used are only simplified in the scheme whereas operation of the MOT required other optical instruments (e.g. acousto optical modulators, waveplates). The trap used for the vapour corresponds to a Paul-trap [10].



Figure 2: Scheme of experimental set-up with the magneto-optical trap (MOT) in the center and the lasers driving the transitions. The 285 nm laser excites the cloud into the first excited state using the cross-beam method. The 375 nm laser drives transitions of the atoms into the Rydberg states.

A UV sensitive camera allowed to image the transitions of the atoms in the MOT cloud. Since the first excited state of magnesium is luminous, the excited gas cloud emits 285 nm photons which can be imaged onto a camera. When the atoms are excited into a higher energy state, the atoms no longer emit UV photons and the cloud intensity drops. Hence the fractional depopulation of the excited state can be calculated analysing the camera picture data in terms of light counts.

### 4 Measurement Method

The goal of the experiment is the determination of the transition frequencies for certain Rydberg states and their energy levels with respect to ionization energy. The energy level positions were estimated by calculating the corresponding energy eigenstates using quantum defect theory. The quantum defect parameters [6] were experimentally determined from Rydberg states of principal quantum number  $4 \le n \le 40$ , allowing to scan estimate regions for Rydberg states. This allowed to assign certain transitions to Rydberg states.

The measurements were executed with the Magnesium gas in the first excited state. The camera measured the light intensity of the luminous cloud. Fig. 3 shows exemplary for one transition images taken by the camera. The light counts are evaluated using python.

With both lasers turned off a background image provides comparison data which is used to determine the relative light counts caused by the luminous cloud. With only the 285 nm laser exciting the magnesium gas the cloud is the brightest. The 375 nm laser is scanned with a frequency range centered at the estimate frequency. The frequency of this laser is varied in small steps of around 80 MHz. This is done by adjusting the position of the laser grating and diode current, feeding back on the wavemeter measurement. The set-up with a shutter allowed the camera to take two pictures. One shot simply pictured the magnesium gas in the first excited state, luminous, with the shutter closed blocking the 375 nm light. The second shot is performed with the shutter opened, which excited the atoms when the 375 nm laser was resonant with a transition to a Rydberg state. The second image hence contains less light counts if the gas is excited into a Rydberg state. Yet if no transition occurs the image should not change compared to the luminous first excited state state. The image procedure is displayed in Fig. 3a.

The light counts per picture are evaluated comparing the two images as shown in Fig. 3b.  $Z_{\text{off}}$  is the absolute counts of the bright gas cloud.  $Z_{\text{on}}$ corresponds to the light counts with the 375 nm laser acting on the gas cloud. If the transition frequency is hit these counts are smaller, proportional to the number of excited atoms. A transition occurred when the fractional light intensity drop was larger than  $0: 0 \leq Z_{\text{rel}} \leq 1$ . The relative counts  $Z_{\text{rel}}$ calculate as  $Z_{\text{rel}} = 1 - \frac{Z_{\text{on}}}{Z_{\text{off}}}$ . In the following the 'Relative Counts' give an estimate for transition strength occurring in terms of an absorption coefficient. The wavemeter used to determine the exact frequency can have a large systematic miscalibration, leading to large systematic errors in frequency of 200 Mhz as mentioned before. This miscalibration can drift over larger timescales as days. Hence the frequency measurements need to be calibrated. To be more sure about the exact frequency of the 375 nm laser the wavemeter is calibrated using the iodine line of the 285 nm laser as well as the position of the 52d Rydberg state. This allows a higher precision on the offset from the ionization energy. It allows Rydberg states to be assigned to the measured transitions. However for higher energies the different energy states are closer together then the systematic variance of the wavemeter which makes assignments impossible.

The energy to ionization calculates as follows with the laser frequency  $\nu_{\text{laser}}$ :

$$E_{\text{to ionization}} = \nu_{\text{laser}} - \nu_{\text{ionization}} + \nu_{\text{detuning 285 nm}}$$

The laser frequency as well as the frequency of the ionization are calculated only for the 375 nm laser, given the frequency of the first excited state. The detuning of the 285 nm laser is used as a correction to the theoretical ionization frequency  $\nu_{\text{ionization}} = 798041$  GHz.



(a) Picture sequence of the magnesium cloud. First a background picture is taken with which the other light counts are compared. Then the gas cloud is excited into the first state and gets luminous. Afterwards the 375 nm laser is turned on and the gas cloud turns excited into an Rydberg state. This procedure is done for every data point.



(b) For every data point two pictures of the atom cloud are taken and compared. First before and then after exposure to 375 nm light. If the 375 nm laser is resonant with a transition then the fluoresence intensity drops. Comparing the light counts per picture results in the relative extinction of the cloud luminosity.

Figure 3: Measurement Methodology

## 5 Spectroscopy Results

Following the goal of the experiment, the assignment of transitions into Rydberg states, the following table and graph show all measured transitions. The position is scaled with the energy of the state with respect to the calculated ionization energy. The assignment to different energy states is done comparing the data to an energy fit using quantum defect parameters from [6].

Table 1: Energies of all measured transitions and their maximal extinction. The laser wavelength corresponds to the 375 nm laser exciting the atoms into an Rydberg state. Assignments are done using the Quantum Defect model from [6].

Laser	Energy	maximal	
wavelength [nm]	to ionization / h [GHz]	extinction	Assignment
376.37833	-1528.66	0.7	$47 \ {}^{1}D_{2}$
376.34816	-1464.81	0.7	$48 \ {}^{1}D_{2}$
376.34810	-1464.68	0.2	$48 \ ^{1}D_{2}$
376.31991	-1405.01	0.2	$49 \ {}^{1}D_{2}$
376.31986	-1404.92	0.5	$49 \ {}^{1}D_{2}$
376.26824	-1295.63	0.9	$51 \ {}^{1}D_{2}$
376.24466	-1245.69	0.4	$52 \ {}^{1}D_{2}$
376.24466	-1245.69	0.8	$52 \ ^{1}D_{2}$
376.24465	-1245.67	0.1	$52 \ {}^{1}D_{2}$
376.24465	-1245.67	0.5	$52 \ ^{1}D_{2}$
376.24464	-1245.65	0.9	$52 \ ^{1}D_{2}$
376.24464	-1245.65	0.9	$52 \ {}^{1}D_{2}$
376.22226	-1198.24	0.9	$53 \ ^{1}D_{2}$
376.22225	-1198.23	0.9	$53 \ ^{1}D_{2}$
376.20146	-1154.19	0.9	$54 \ {}^{1}D_{2}$
376.20145	-1154.17	0.9	$54 \ {}^{1}D_{2}$
376.20145	-1154.16	0.8	$54 \ {}^{1}D_{2}$
376.20144	-1154.15	0.8	$54 \ {}^{1}D_{2}$
376.18140	-1111.69	0.9	$55 \ ^{1}D_{2}$
376.18135	-1111.58	0.7	$55 \ ^{1}D_{2}$
376.18133	-1111.55	0.8	$55 \ ^{1}D_{2}$
375.18026	-1109.27	0.8	$56 \ {}^{1}S_{0}$
375.81741	-339.85	0.8	$99 \ ^{1}D_{2}$
375.81682	-338.59	0.1	unassigned

375.81561	-336.02	< 0.1	$100 \ {}^{1}P_{1}$
375.81421	-333.05	0.9	$100 \ {}^{1}D_{2}$
375.81090	-326.02	0.8	$101 \ {}^{1}D_{2}$
375.77616	-252.20	0.5	unassigned
375.77575	-251.40	0.8	$115 \ {}^{1}D_{2}$
375.77559	-251.07	< 0.1	$116 \ {}^{1}S_{0}$
375.74990	-196.52	0.9	$130 \ {}^{1}D_{2}$
375.74911	-194.85	< 0.1	$131 \ {}^{1}P_{1}$
375.74848	-193.52	0.9	$131 \ {}^{1}D_{2}$
375.74790	-191.85	< 0.1	$132 \ {}^{1}P_{1}$
375.74710	-190.58	0.9	$132 \ {}^{1}D_{2}$
375.74444	-184.93	0.8	$134 \ {}^{1}D_{2}$
375.74369	-183.33	< 0.1	$135 \ ^{1}P_{1}$
375.74315	-182.19	0.8	$135 \ {}^{1}D_{2}$
375.74244	-180.68	< 0.1	$136 \ ^{1}P_{1}$
375.74188	-179.49	0.8	$136 \ ^{1}D_{2}$
375.73944	-174.31	0.6	$138 \ ^{1}D_{2}$
375.73944	-174.31	0.8	$138 \ ^{1}D_{2}$
375.73944	-174.31	0.8	$138 \ ^{1}D_{2}$
375.73943	-174.30	0.5	$138 \ ^{1}D_{2}$
375.73943	-174.30	0.7	$138 \ ^{1}D_{2}$
375.73877	-172.89	0.	$139 \ ^{1}P_{1}$
375.73877	-172.89	0.1	$139 \ ^{1}P_{1}$
375.73877	-172.89	0.1	$139 \ ^{1}P_{1}$
375.73827	-171.82	0.7	$139 \ ^{1}D_{2}$
375.73826	-171.81	0.7	$139 \ {}^{1}D_{2}$
375.73826	-171.81	0.6	$139 \ {}^{1}D_{2}$
375.73826	-171.80	0.4	$139 \ {}^{1}D_{2}$
375.73825	-171.79	0.8	$139 \ {}^{1}D_{2}$
375.73825	-171.79	0.8	$139 \ {}^{1}D_{2}$
375.73759	-170.40	< 0.1	$140 \ {}^{1}P_{1}$
375.73759	-170.40	0.1	$140 \ {}^{1}P_{1}$
375.73759	-170.40	0.1	$140 \ {}^{1}P_{1}$
375.73710	-169.35	0.7	$140 \ {}^{1}D_{2}$
375.73710	-169.35	0.5	$140 \ {}^{1}D_{2}$
375.73709	-169.32	0.6	$140 \ {}^{1}D_{2}$
375.73709	-169.32	0.8	$140 \ {}^{1}D_{2}$
375.73709	-169.32	0.8	$140 \ {}^{1}D_{2}$

375.73212	-158.77	0.	$145 \ {}^{1}P_{1}$
375.73211	-158.76	0.2	$145 \ ^{1}P_{1}$
375.73201	-158.54	< 0.1	unassigned
375.73167	-157.82	0.3	$145 \ {}^{1}D_{2}$
375.73166	-157.80	0.8	$145 \ {}^{1}D_{2}$
375.73166	-157.80	0.9	$145 \ {}^{1}D_{2}$
375.73165	-157.78	0.9	$145 \ {}^{1}D_{2}$
375.73165	-157.78	0.9	$145 \ {}^{1}D_{2}$
375.73165	-157.78	0.9	$145 \ {}^{1}D_{2}$
375.73157	-157.61	0.2	$146 \ {}^{1}S_{0}$
375.73115	-156.70	0.1	unassigned
375.73110	-156.60	0.1	$146 \ ^{1}P_{1}$
375.73110	-156.59	< 0.1	$146 {}^{1}P_{1}$
375.73110	-156.59	< 0.1	$146 \ ^{1}P_{1}$
375.73108	-156.56	0.	$146 \ ^{1}P_{1}$
375.73106	-156.52	0.5	$146 \ ^{1}P_{1}$
375.73104	-156.47	0.2	unassigned
375.73092	-156.22	0.2	unassigned
375.73092	-156.22	0.	unassigned
375.73065	-155.65	0.8	$146 \ {}^{1}D_{2}$
375.73064	-155.63	0.9	$146 \ {}^{1}D_{2}$
375.73064	-155.62	0.9	$146 \ {}^{1}D_{2}$
375.73008	-154.44	0.1	$147 {}^{1}P_{1}$
375.73007	-154.42	0.2	$147 \ {}^{1}P_{1}$
375.73007	-154.42	0.2	$147 {}^{1}P_{1}$
375.73007	-154.41	0.	$147 \ {}^{1}P_{1}$
375.73002	-154.35	0.3	unassigned
375.72987	-153.99	0.6	unassigned
375.72987	-153.99	0.6	unassigned
375.72986	-153.97	0.7	unassigned
375.72984	-153.92	0.7	unassigned
375.72972	-153.67	0.1	unassigned
375.72972	-153.67	0.1	unassigned
375.72965	-153.53	0.8	$147 \ {}^{1}D_{2}$
375.72964	-153.50	0.9	$147 \ {}^{1}D_{2}$
375.72963	-153.49	0.9	$147 \ {}^{1}D_{2}$
375.72881	-151.74	0.7	unassigned
375.72866	-151.42	0.9	$148 \ ^{1}D_{2}$

375.72410	-141.68	0.6	$153 \ {}^{1}D_{2}$
375.72370	-140.90	0.4	$154 \ ^{1}P_{1}$
375.72323	-139.90	0.8	$154 \ {}^{1}D_{2}$
375.72281	-139.00	0.5	$155 \ ^{1}P_{1}$
375.72239	-138.10	0.7	$155 \ ^{1}D_{2}$
375.72189	-137.04	0.5	$156 \ ^{1}P_{1}$
375.72155	-136.33	0.6	$156 \ ^{1}D_{2}$
375.72124	-135.67	0.2	unassigned
375.71936	-131.68	0.3	$159 \ ^{1}P_{1}$
375.71910	-131.14	0.7	$159 \ {}^{1}D_{2}$
375.71867	-130.20	0.1	$160 \ {}^{1}P_{1}$
375.71864	-130.15	0.5	$160 \ {}^{1}P_{1}$
375.71833	-129.49	0.7	$160 \ {}^{1}D_{2}$
375.71797	-128.73	0.3	unassigned
375.71791	-128.59	0.2	$161 \ {}^{1}P_{1}$
375.71791	-128.59	0.1	$161 \ {}^{1}P_{1}$
375.71721	-127.10	0.2	unassigned
375.71715	-126.99	0.5	$162 \ {}^{1}P_{1}$
375.71520	-122.83	0.2	unassigned
375.71501	-122.44	0.2	$165 \ ^{1}P_{1}$
375.71493	-122.27	0.3	unassigned
375.71466	-121.69	0.3	$165 \ {}^{1}D_{2}$
375.71298	-118.13	0.4	$168 \ ^{1}P_{1}$
375.71232	-116.73	0.4	$169 \ {}^{1}P_{1}$
375.67412	-35.59	0.4	unassigned
375.67383	-34.96	0.1	unassigned
75.673684	-34.66	0.3	unassigned
375.67336	-33.99	0.3	unassigned
375.67285	-32.89	0.3	unassigned
375.67252	-32.18	0.1	unassigned
375.67240	-31.94	0.1	unassigned
375.67226	-31.63	0.2	unassigned
375.67214	-31.39	0.2	unassigned
375.67208	-31.26	0.2	unassigned
375.67142	-29.84	0.2	unassigned
375.67109	-29.15	0.4	unassigned
375.67088	-28.70	0.2	unassigned



Figure 4: Complete acquired data points for transitions at energy of ionization. \$16\$

#### 5.1 Possible Transition

As stated in the above sections, the transitions into Rydberg states correspond to  $n^1S_0$  or  $n^1D_2$  states. Such a transition spectrum is measured for principal quantum numbers 145, 146. The resulting frequencies of these transitions are shown in Fig. 5. The states  $n \ ^1D_2$  and  $(n+1) \ ^1S_0$  are closer in frequency than the different states of one quantum number, hence Fig. 5 presents such a configuration for n = 145.



Figure 5: Expected energies for the 145d and 146s Rydberg states. The lines connecting the data points are to guide the eye.

The experiments intention is to measure such transitions for all Rydberg states. The experimental results illustrated this ambition not to be achievable. Transitions to  $n^1D_2$  states showed the most frequent appearance. In most cases, transitions to the  $n^1S_0$  states were not achieved, denying to measure the corresponding absorption line. Otherwise numerous transitions at other frequencies were discovered. These discoveries contradicted the theoretically not possible transitions to  $n^1P_1$  states or corresponded to energies somewhere in between theoretically calculated states. Fig. 6 illustrates a composition of various measurements showing exemplary exotic transitions in the region of states with Rydberg energy  $146 \leq n \leq 148$ . It visualises that some transitions to the  ${}^1S_0$  states are missing. Additionally, lines without direct correspondence were discovered, for instance right between the energies of  $148{}^1P_1$  and  $148{}^1D_2$ . These exemplary two transitions are characterized in a later section.



Figure 6: Exemplary measured transitions in the region of n = 146 to n = 148. The lines connecting the data points are to guide the eye. The d-states have strong absorption lines, as the p-states can be assigned to weaker absorption lines. Additionally, unexplained strong absorption lines appeared in between.



Figure 7: Lorentzian fit for different energy states. The Lorentzian only gives a rough estimate for the saturated absorption spectrum.

#### 5.2 Transition Characteristics

The transitions did not represent discrete peaks and were characterized as broadened transition regions. Such absorption peaks can roughly be approximated using a Lorentzian function:

$$\mathscr{L}(\nu,\nu_{\frac{1}{2}},\alpha,\delta) = \frac{\alpha}{2} \cdot \frac{\nu_{\frac{1}{2}}^2}{(\nu-\delta)^2 + \nu_{\frac{1}{2}}^2}$$

Indeed, the width of the absorption peaks nurtured additional interest. Since the peaks are saturated the Lorentzian approximation is not accurate and directly connected to the lifetime of the excited state. A rough estimate instead can be done using the saturated intensity from [12]. In reference to Fig. 5 strong absorption lines have a rather large line-width. The properties of this line-width allows to examine properties of the states. Fig. 7 and Fig. 8a prepresent the resulting analyses of properties of the absorption peaks. The functional fits are displayed in Fig. 7 for different energy states. It is clearly visible that an unperturbed Lorentzian only gives a rough estimate of the absorption function.

Fig. 8a shows absorption spectra for different incoming beam powers of the 375 nm laser beam. As stated in [12] the lifetime of a state is connected to the saturated intensity.

$$\tau = \frac{\lambda^3 \cdot 3}{I_{\text{sat}} \cdot c \cdot h \cdot \pi}$$

Since the intensity follows from the incoming beam power and the beam profile, Fig. 8 can give all elements needed for an estimate of the lifetime of the Rydberg states. The saturated intensity  $I_{\text{sat}} = \frac{P_{\text{sat}}}{\pi r^2}$  is set to be at an absorption coefficient of 0.5 or 50%. Fig. 8b shows a logarithmic plot of the incoming beam power, related to the absorption. It follows that the saturation power is 0.73 mW. With a beam radius of about 0.5 cm the estimated lifetime of the transition is:

$$\tau_{\rm Rydberg} \approx 450 \text{ ns}$$





Energy - Ionization Energy [GHz] -12869 (b) Plot of the absorption as a func-(a) Absorption spectrum dependency on tion of the logarythmic power of the beam power. The lines connecting the data laser. The intensity follows from the points are to guide the eye. The power of beam power over area. The saturation the 375 laser was varied to measure the ef- intensity can be found at 50% absorpfect on the absorption strength.

Figure 8: Examination of the saturation intensity and Rydberg state lifetime.

#### 5.3 Diversity of Spectral Lines

The experiments disclosed various spectral absorption lines not always clearly assigned to any Rydberg state. Although the Magnesium cloud only rarely was excited into  $n^1S_0$  states, the  $n^1D_2$  states were reached frequently with only few exceptions. The lowest possible Rydberg states achieved in the experiment are shown in Fig. 9. The d-states were excited frequently, not reaching s-states. Consequently, the d-states could be used as a reference for higher Rydberg states. At higher energies the spectral lines get much closer and as a result more difficult to assign to the correct state.



Figure 9: Multiple transitions for low quantum number

Additionally, two other categories of spectral lines became apparent. The

two most common types of identified irregularities are shown in Fig. 10. In one case, Fig. 10a, an absorption line was visible at an energy in between the  ${}^{1}S_{0}$  and  ${}^{1}D_{2}$  states, corresponding to the energy of the  ${}^{1}P_{1}$  Rydberg state. Following the selection rules for a dipole, such transition should not be possible and the energy not accessible.

With irregular appearance there was another unidentified transition line visible between the  ${}^{1}P_{1}$  and  ${}^{1}D_{2}$  states. Fig. 10b is an example of such a transition pair of both unidentified states of the atom. The transitions close to the  ${}^{1}P_{1}$  state were more common and occurred at about the same position. The other unknown lines however did not appear periodically and at slightly different positions.



(a) One additional transition assigned (b) Two additional transitions without to the p state. The lines connecting the a concrete assignment. The lines condata are to guide the eye. necting the data are to guide the eye.

Figure 10: Unknown transition states

#### **5.4** $n^1P_1$ Correspondence

Since the  $n^1P_1$  states should not be reachable a further examination of these states was realized. The experiment disclosed that although the lines were weaker than other transitions, they did appear regularly. Fig. 11 displays various energy regions of Rydberg states. For each of the examined energy levels, the  $n^1P_1$  state corresponding transitions were achieved, though some with only faint absorptions.



Figure 11: Frequency regions for different principal quantum numbers with transitions assigned to  $n^1P_1$  and  $n^1D_2$ . The lines connecting the data are to guide the eye.  $n^1S_0$  states obey no corresponding absorption.  $n^1P_1$  states are visible as weak absorption lines.

At some point for higher energy states of  $n \ge 157$  only the transitions assigned to the  $n^1P_1$  states were appearing. Fig. 12 shows such a range of states disclosing corresponding energies of possible p-states.



Figure 12:  $n^1P_1$  assignment for high Rydberg energy states.

#### 5.5 High Rydberg states close to ionization

For very high Rydberg states at only a few GHz off the ionization limit it is more difficult to assign states to the discovered transition lines. Two neighbouring states lie within a region of a few hundred MHz. Hence the systematic uncertainty of the experiment makes it rather impossible to assign the correct states to the measured transitions. Fig. 13 shows a measurement for Rydberg states of quantum number n=300 and higher. The calculated energy states for s,p,d states are presented as dashed lines in the background. As visible the calculated states are closer together so that it is not possible to distinguish them. Transitions can not be exactly assigned to any Rydberg state in this energy region.



Figure 13: Rydberg states close to ionization. The lines connecting the data are to guide the eye. The estimated Ryderg energies for s,p,d states are shown in the background to illustrate how close the energy states are together.

## 6 Discussion and Determination of Quantum defect parameters

The measurement results were not expected. Against distinct transitions to the expected states  $n^1S_0$  and  $n^1D_2$ , exotic states of the magnesium atoms occurred. These exotic states showed no regular appearance in strength and position. Indeed energy states corresponded to the  $n^1P_1$  states.  $n^1D_2$  states were located at the expected energies. The  $n^1S_0$  states were missing. Additionally, some transitions were driven with energies not referring to any specific state.

Possibly electric and magnetic fields affected the energy states of magnesium. The atoms interaction with these fields would cause splitting of the energy states in the atom. Interactions with a magnetic field are small and their energy state splitting not resolvable in this experiment [13]. Hence magnetic fields aren't the reason for the unexpected states. Electric fields interact stronger with matter. Accidentally ionized atoms accumulate inside the vacuum chamber and create an electric field which affects laser light as well as the energy states of the magnesium atoms.

The observed breadth of the line-width of the states reflect the lifetime of the excited states. The lifetime is smaller than the measured linewidth in the ns regime. Doppler broadening causes an even greater line broadening. The gas inside the vacuum chamber operates at higher temperatures. Atoms hence move at rather high velocities due to the Maxwell distribution. Applying the relativistic Doppler shift, the absorption spectrum is broadened because of relative changes in light frequency seen from the moving atom.

Table 2: P-state Quantum Defect parameters for measurement data with literature values from [6]. A fit with only measurement data did not have sufficient data to calculate valid variances.

Fit	α	β	$\gamma$	$\delta_E  [\text{GHz}]$
Simple data fit	(0.98)	(505)	(0)	(-0.318)
Extended data fit	$0.84 \pm 0.03$	$466 \pm 63$	$(-2.57 \pm 0.36)10^5$	$-1.44 \pm 0.2$

Table 3: D-state Quantum Defect parameters for both fits: only measurement data and measurement data with literature values from [6]

Fit	α	$\beta$	$\gamma$	$\delta_E  [\text{GHz}]$
Simple data fit	$0.54 \pm 0.03$	$290 \pm 125$	$(-3.09 \pm 1.5)10^5$	$-0.49 \pm 0.17$
Extended data fit	$0.616 \pm 0.001$	$-31 \pm 0.8$	$(-2.47 \pm 0.6)10^4$	$-0.01 \pm 0.08$

With the measured frequencies of the experiment, first hand quantum defect parameters were calculated. Therefore, the data points are fit to the formula of a Rydberg state energy:

$$E_{n,l} = \frac{-R_{Mg}}{(n-\delta_l)^2} + \delta_E$$

The least squares method delivers values for the quantum defect parameter  $\delta_l$ .  $\delta_l$  is expended up to fourth order in a dependency on n to secure a precise fit:  $\delta_l = \alpha + \frac{\beta}{(n-\alpha)^2} + \frac{\gamma}{(n-\alpha)^4}$ . An additional energy offset  $\delta_E$  compensates the convergence of the measured data points with respect to the ionization limit. Exploiting the measurement data for  $n^1D_2$  and  $n^1P_1$  states, which are shown in Fig. 14, delivered two estimations for the defect parameters shown in Table 2 and Table 3. The first calculation used only the data from this measurement and the extended analysis added the calculated states for lower Rydberg states from [6]. For the p-states the measurement data was not sufficient to achieve valid fit parameters. It was not possible to calculate the covariance matrix. Values for the parameters could be achieved and are used in the following discussion: Fig. 15 shows the corresponding deviation of measurement values and calculated Rydberg energies supporting the validity of the fits for the measured data.

For the  $n^1D_2$  states theory matched up with the measured data validating the suitability of the generated model. Exotic and rather unknown states instead need further investigation for characterization.



Figure 14: Energy of assigned Rydberg states as a function of quantum state. The data is used to calculate quantum defect parameters. For the first set of parameters only the measured data is taken into account. For secondary parameters literature values from [6] are added.



Figure 15: Deviation of the measured data points from quantum defect fit. The deviation is determined for both energy fits: only measurement data and extended data with literature values from [6].

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