Chapter 4

Radium and Barium: Atomic Properties

Laser spectroscopy is an ideal tool for precise determination of atomic system properties. It not only provides information on the electron cloud, but also e.g., the nuclear spin, charge distribution, the magnetic dipole and electric quadrupole moment of the nuclei. In particular, isotope shifts and hyperfine structure depend on nuclear and atomic properties. Their knowledge improves the understanding of the structure of the atom and atomic nucleus. As an example, laser spectroscopy is a precise method for determining mean charge radii of nuclei of radioactive atoms [104]. Other properties, like an EDM, which might have their origin in nuclear forces, can be amplified due to the atomic structure and become visible by precise laser spectroscopy. This is exploited in experiments with different atoms in many searches for an EDM [8].

In order to prepare for an EDM experiment, the atomic and nuclear properties of the atom of interest have to be determined. Thus extensive studies through laser spectroscopy are indispensable. Since radium has been identified as a good candidate for an experimental search for an EDM we develop laser spectroscopy to determine the missing atomic and nuclear properties. In the literature very scarce information is available on the radium atom. Only a few energy levels, transition rates and life times of states of interest for an EDM experiment have been determined so far. The available data as well as the information, which has to be determined is discussed below. Part of the reason is that radium itself is only available in small quantities since most isotopes are short-lived and the radioactivity poses a problem. In the future short-lived isotopes of radium, like $^{213}$Ra with $I \neq 0$, will be available at TRIµP facility [18].
Chapter 4. Radium and Barium: Atomic Properties

Figure 4.1: Level diagram of the radium atom with the wavelengths (vacuum) in nm of the transitions relevant for laser spectroscopy, laser cooling and trapping and for an EDM experiment. Wavelengths are according to [14]. The thickness of the line indicates the strength of the transition.

In section 2.2.3 of Chapter 2 the advantages of radium for searches of electric dipole moments was discussed. Here we give an overview on the available experimental data on radium atom as well as the spectroscopy work that needs to be performed as a precursor for an EDM experiment.

4.1 Radium Atom

The energy level scheme of low lying states of atomic radium is shown in Fig. 4.1. Radium (\(^{226}\)Ra) was discovered in 1898 by M. Curie. Other short lived isotopes were recognized later. The first spectroscopic measurements of radium dates back to 1934. Rasmussen [42, 43] measured the energy levels of radium ion and atom from a discharge lamp using a grating monochromator. The interpretation of these measurements was corrected by Russel [107]. Absorption spectroscopic
4.1. Radium Atom

Figure 4.2: Level diagram of the radium atom with the transition rates calculated by K. Pachucki [105]. The measured value for the $^1S_0 - ^3P_1$ transition by Scielzo et al. [106] is $2.37(12) \times 10^6 \text{s}^{-1}$. The thickness of the lines indicates the strength of the transitions.

measurements of the $^1P_1$ Rydberg series in radium are reported in [108, 109].

The first direct laser spectroscopic measurements on radium were reported in 1983 by Ahmad et al. [104, 110]. They made a systematic investigation of isotope shifts and hyperfine structures of radium atoms and radium ions of the $7s^2 \, ^1S_0 - 7s7p \, ^1P_1$ transition at 482.6 nm. The isotopes were produced at the ISOLDE facility at CERN. The method of on-line collinear fast beam laser spectroscopy was used to obtain the nuclear spins and moments. Later, Wendt et al. [111] continued the measurements on the $7s^2 \, ^1S_0 - 7s7p \, ^3P_1$ transition at 714.3 nm and confirmed the previously evaluated moments. The nuclear magnetic moments of $^{225}\text{Ra}$ and $^{213}\text{Ra}$ were determined to be $-0.7338(15)\mu_N$ and $0.6133(18)\mu_N$ [112], respectively. The nuclear magnetic moment of $^{213}\text{Ra}$, according to theory, is $0.607(12)\mu_N$ [113]. This is in good agreement with experiment. Because of the interest in radium as a good candidate for an EDM measurement the group of R. Holt recently started spectroscopy of radium. They focus on the $^1S_0 - ^3P_1$ intercombination line at 714.3 nm. They determined an absolute frequency of
Table 4.1: Excitation energies of low states in radium. Reference [14] are the experimental values. Reference [114]: ‘a’ is Dirac-Coulomb (DC) and ‘b’ is Dirac-Coulomb-Breit (DCB) excitation energies calculated based on relativistic coupled cluster (RCC) method. Reference [115] is based on configuration interaction method and many-body perturbation theory.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>$7s7p^1P_1$</td>
<td>20716</td>
<td>21156</td>
<td>21148</td>
<td>20450</td>
</tr>
<tr>
<td>$^3P_1$</td>
<td>13999</td>
<td>14072</td>
<td>14096</td>
<td>14027</td>
</tr>
<tr>
<td>$^3P_2$</td>
<td>16689</td>
<td>16855</td>
<td>16855</td>
<td>16711</td>
</tr>
<tr>
<td>$7s6d^1D_2$</td>
<td>17081</td>
<td>17806</td>
<td>17737</td>
<td>17333</td>
</tr>
<tr>
<td>$^3D_2$</td>
<td>13994</td>
<td>13974</td>
<td>13907</td>
<td>13980</td>
</tr>
<tr>
<td>$^3D_1$</td>
<td>13716</td>
<td>13672</td>
<td>13609</td>
<td>13727</td>
</tr>
</tbody>
</table>

that transition of 13999.269(0.001) cm$^{-1}$ by referencing it to the 13999.2459 cm$^{-1}$ line in molecular iodine and they found the lifetime of the $^3P_1$ state to be 422(20) ns [106]. In particular they are using this transition for laser cooling and trapping of radium.

There are several theoretical many body calculations of this multi-electron system. Recently there has been an increased effort by the theoretical community for a better estimation of the transition energies and lifetimes of the states. Various methods are used to calculate the transition energies and lifetimes of the states in radium [105, 114–117]. Generally the calculated excitation energies reported are higher than those from the experiment. The deviation is in between 200 - 400 cm$^{-1}$ for the low excitation energies and increases for the highest levels. The lifetime of the $7s6d$ $^3D_2$ level in radium was calculated [12, 115, 118] to be 3.3 to 15 seconds. However, there is no experimental data to test these calculations. New measurements will help to constrain the atomic wave functions for theoretical calculations and will improve the overall quality of the theoretical predictions.

A prerequisite for a radium EDM experiment are the following measurements: The first and foremost is the knowledge of the energy levels of radium to a GHz accuracy. This is because the energy level diagram shown in Fig. 4.1 is based on the 1934 data [43], which has a limited resolution. Optical spectroscopy has to be carried out on the singlet and triplet $P$ ($7s7p$ $^1P_1$, $7s7p$ $^3P_1$) and $D$-states ($7s6d$ $^1D_2$, $7s6d$ $^3D_{1,2}$) respectively. Especially for an EDM measurement the positions of the $^3D_{1,2}$ levels with respect to the triplet $P$-states play an important role. This is because the actual position of the $7s6d$ $^3D_2$ energy level with respect
4.2. Barium Atom

Barium has a similar atomic structure as radium and we use it as a precursor to develop the laser spectroscopic techniques which we can apply to the radium atom. Our spectroscopic work on barium allowed us to establish the first laser cooling of barium.

Here we describe the spectroscopy of barium. The focus is on the laser spectroscopy of the 6s5d \(^1D_2\) - 6s6p \(^1P_1\), 6s5d \(^3D_2\) - 6s6p \(^1P_1\) and the 6s5d \(^3D_1\) - 6s6p \(^1P_1\) transitions (see Fig. 4.3). We report the first laser spectroscopy studies of these transitions. In particular, we measure the repumping rates and hyperfine structure of these transitions. In addition, we were able to determine for the first time the isotope shift of the metastable 6s5d \(^3D_1\) state. Natural barium with several isotopes was used. This gives access to the isotope dependence of nuclear charge radii.

Barium is an alkaline earth element (group II). Its atomic number is 56 and the electron configuration is [Xe] \(6s^2\) i.e., it has two \(s\) valence electrons. The ground state \(LS\) configuration is \(6s^2\) \(^1S_0\). The natural abundance of barium isotopes with their nuclear spin is given in Table 4.2. The energy levels relevant for spectroscopy and laser cooling are shown in Fig. 4.3. The transition rates shown in Fig. 4.4 are taken from [106, 119, 120].

<table>
<thead>
<tr>
<th>Isotope</th>
<th>(^{138})Ba</th>
<th>(^{137})Ba</th>
<th>(^{136})Ba</th>
<th>(^{135})Ba</th>
<th>(^{134})Ba</th>
<th>(^{132})Ba</th>
<th>(^{130})Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear spin (I)</td>
<td>0</td>
<td>3/2</td>
<td>0</td>
<td>3/2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Abundance %</td>
<td>71.7</td>
<td>11.3</td>
<td>7.8</td>
<td>6.6</td>
<td>2.4</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 4.2: Natural isotope distribution of barium, spin and abundance [121].

to the 7s7p \(^3P_1\) level is crucial for the enhancement of the P and T-odd effects considered in references [12, 13]. This enhancement is due to the very small energy difference of 5 cm\(^{-1}\) between the opposite parity states 7s7p \(^3P_1\) and 7s6d \(^3D_2\). A significant change in the position of the \(^3D_2\) state would severely affect the enhancement.

The other requirement for experiment on parity and time reversal invariance violation in radium is the measurement of the lifetimes of the \(^1D_2\), \(^3D_1\) and \(^3D_2\) states, which reveal information on the electronic wave function at the location of the nucleus. In addition, lifetimes are also important for laser cooling and trapping of radium using \(^1S_0\)-\(^1P_1\) transition and they provide information on the decay rates.
The first excited state of barium is the singlet $6s6p \, ^1P_1$ state. We have measured the lifetime of the $^1P_1$ state using the Hanle effect to be $8.0(5)$ ns in good agreement with the value of $8.2(2)$ ns [122] reported in the literature. This results in a natural line width of $19(1)$ MHz. The transition rate of $6s^2 \, ^1S_0 - 6s6p \, ^1P_1$ transition is $1.19(1) \times 10^8 \, s^{-1}$ [119]. This transition is the only option for laser cooling of barium. Since it exhibits large leak to metastable $D$-states, this is not a closed two level system and we have to use lasers to drive the $D - P$ transitions.

The atomic transitions from the excited $^1P_1$ state, relevant for laser cooling other than the $^1S_0 - ^1P_1$ transition are the $^1D_2 - ^1P_1$ transition at 1500.4 nm, the $^3D_2 - ^1P_1$ transition at 1130.6 nm and the $^3D_1 - ^1P_1$ transition at 1107.8 nm respectively. The wavelengths and transition rates were determined by Fourier transform spectroscopy using a hollow-cathode discharge [119]. The measured transition probabilities of these transitions are $2.5(2) \times 10^5 \, s^{-1}$, $1.1(2) \times 10^5 \, s^{-1}$.
Figure 4.4: Level diagram of barium atom with transition rates for the transitions used in optical spectroscopy of the metastable D-states and in the laser cooling of barium experiment. The experimental transition rates are according to the references [106, 119, 120].

and $3.1(5) \times 10^3 \text{ s}^{-1}$ [119] respectively. To the best of our knowledge there are no direct laser spectroscopic measurements of these transitions reported in the literature.

While using the strong $^1S_0 - ^1P_1$ transition for laser cooling atoms leak into the $^1D_2$, $^3D_2$ and $^3D_1$ states. The branching ratio ($B_r$) into the metastable $D$-states when we use the numbers from Table 4.3.

$$B_r = A_{1\text{leak}}^{-1} = \frac{A_{1P_1,^1S_0}}{A_{1P_1,^1D_2} + A_{1P_1,^3D_2} + A_{1P_1,^3D_1}} \approx 330(30) \quad (4.1)$$

On average an atom in the cooling cycle scatters $B_r$ photons before it decays into one of the metastable $D$-states. This is a constraint for laser cooling.

For simplicity we discuss here the slowing of the atom with a laser beam
<table>
<thead>
<tr>
<th>Upper Level</th>
<th>Lower Level</th>
<th>Wavelength [nm]</th>
<th>$A_{ik} \times 10^8 \text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1P_1$ 8.2(2) ns [122]</td>
<td>$^1S_0$</td>
<td>553.7</td>
<td>1.19(1)$^a$</td>
</tr>
<tr>
<td>8.0(5) ns Our measurement</td>
<td>$^3D_2$ (60 s) [123]</td>
<td>1500.4</td>
<td>0.0025(2)$^a$</td>
</tr>
<tr>
<td></td>
<td>$^3D_1$</td>
<td>1130.6</td>
<td>0.0011(2)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1107.8</td>
<td>0.000003(5)$^a$</td>
</tr>
<tr>
<td>$^3P_1$ 1345(14) ns [106]</td>
<td>$^1S_0$</td>
<td>791.3</td>
<td>0.0030(3)</td>
</tr>
<tr>
<td></td>
<td>$^3D_2$</td>
<td>2723.0</td>
<td>0.0012(1)$^b$</td>
</tr>
<tr>
<td></td>
<td>$^3D_1$</td>
<td>2923.3</td>
<td>0.0032(3)$^b$</td>
</tr>
</tbody>
</table>

Table 4.3: The energy levels, lifetimes in italic, wavelengths (vacuum) and transition rates of the barium atom relevant for our experiments. Experimental transition rates: ‘a’ [119], ‘b’ [120]. Lifetimes from [106,122] are the experimental values and from [123] are the calculated values.

against the velocity direction of the atoms and we assume that the momentum transfer in the emission cycle averages to $\Delta \overrightarrow{p} = 0$. This becomes clear when we look at the velocity change of an atom after scattering $n$ photons

$$v_r = \frac{\Delta \overrightarrow{p}_a}{m_{Ba}} = \frac{n\hbar \overrightarrow{k}_\gamma}{m_{Ba}}, \quad (4.2)$$

where $\overrightarrow{p}_a$ is the momentum of the atom, $n$ is the number of scattered photons and $\overrightarrow{k}_\gamma$ is the photon wave vector and $\hbar = h/2\pi$, $h$ is Planck constant. For barium the velocity changes by $v_r = 0.52 \text{ cm/s}$ due to a single photon kick. Scattering of $B_r$ photons means a fraction of $1/e$ of the atoms are left for cycling while the velocity change is only $1.7 \text{ m/s}$, hardly enough to speak of laser cooling. To achieve further slowing, the atoms have to be pumped back into the cooling cycle. Hence, laser spectroscopy of the $D - P$ transitions, which we are reporting here is a prerequisite to laser cooling.

In the future, the experimental methods which we employed for spectroscopy of the $D$-states in barium can also be applied to radium. There are no experimental data available on the $D - P$ transitions in radium. Such data will not only help for laser cooling but are also indispensable input to improve theoretical many-body calculations, which is needed for an evaluation of a radium EDM experiment.
4.3 Experimental Setup

For the experiment we need an atomic beam source for barium, appropriate lasers, a detection and a data acquisition system. We explain the details of our setup below.

4.3.1 Barium Oven

The design of the atomic beam oven used for barium experiments is similar to the oven used for the Alcatraz experiment [124]. It is adapted from the design of an oven used by the Time and Frequency group of the Physikalisch-Technische Bundesanstalt, Braunschweig, Germany.

The central part of the oven is a stainless steel tube. The base (back end) of the steel tube has a small cavity, which can be filled with the element of interest. To measure the temperature of the oven a thermocouple is attached to the heated cavity. The front end of the cavity is an exit channel of 1 mm diameter and 10 mm length. The stainless steel tube is surrounded by a cylindrical tube made of Al$_2$O$_3$. The Al$_2$O$_3$ ceramic holds a tantalum heating wire, which is thread back and forth through thin holes in the Al$_2$O$_3$ periphery to provide uniform heating. The entire set up of the oven chamber is mounted on a standard CF35 vacuum flange, which has feedthroughs for the heater current and for a thermocouple to measure the temperature of the oven. The temperature of the oven is regulated with a PID controller. It can be heated to 1000°C.

We use two ovens for the barium experiments. One oven is for the spectroscopy of the $^1S_0 - ^1P_1$ transition serving as a frequency reference for the laser cooling experiments. It contains natural barium (with all isotopes). The typical operating temperature of the ovens is around 800 K.

For laser cooling experiments the second oven is filled with isotopically enriched $^{138}$Ba. The enriched barium has $^{138}$Ba - 99.7% in purity supplied by [125] in the form of barium carbonate (BaCO$_3$). To produce a barium beam, finely powdered zirconium as a reduction agent is mixed with the barium carbonate and heated in the oven. The oven was operated for 12 hours at the maximum temperature to transfer the BaCO$_3$ to BaO and CO$_2$ gas.

4.3.2 Vacuum System

The vacuum vessel for barium spectroscopy and cooling experiments consists of a six-way cross and a trap chamber. It is shown in Fig. 4.13. The entire system is maintained at a typical pressure of $1 \times 10^{-9}$ mbar by a 10 l/s (Gamma
Vacuum) ion pump. The inside walls of the trap chamber are coated with SPI conductive carbon paint [126] to minimize the scattered light. Baffling, extension ports and AR coated optical windows are also used to reduce the scattered light seen that causes a background count rate in the detector (a photomultiplier tube or a photodiode).

### 4.3.3 Laser Systems

#### Dye Laser

A Coherent CR-699-21 ring dye laser (see Fig. 4.5) at 553.7 nm was used for spectroscopy of the $^{1}S_0 - ^1P_1$ transition. The CR-699 is a unidirectional, travelling wave, ring dye laser. It provides a single frequency, tunable, stabilized output of several hundred milliwatts of power, capable of scan operation across 30 GHz range. Unidirectional, travelling wave operation of the dye laser is achieved by an optical diode employing the Faraday effect. The diode construction is such that light passing through in one direction undergoes a small polarization rotation and subsequently, reflection losses at the Brewster surfaces in the laser. Light travelling in the opposite direction undergoes no net rotation and hence, less loss per round trip.

The single frequency operation is achieved by the use of three optical elements: A three-plate birefringent filter, a thin etalon and a piezoelectric driven thick etalon.

1. The three-plate birefringent filter has a passive bandwidth of about 380 GHz and its use reduces the laser line width to about 2 GHz.
2. The thin etalon has a free spectral range of 200 GHz, which is sufficient to enforce single longitudinal mode operation.

3. A piezoelectric driven thick etalon with 10 GHz free spectral range allows to select a single mode.

The CR-699 employs active stabilization, which is servo-locked to a temperature stabilized reference cavity. An error signal from the reference cavity is used to adjust the dye laser cavity length by driving a high-frequency piezoelectric mounted folding mirror and a scanning Brewster plate. To scan the laser in the lock mode, the length of the reference cavity is varied, which is accomplished using a galvo driven Brewster plate in the reference cavity. The dye laser line width as quoted by the manufacturer is 1 MHz.

A Coherent Verdi-V10 (10W) diode pumped solid-state DPSS, single frequency, continuous wave laser at 532 nm optically pumps the Pyrromethene 567 dye which is solved in ethylene glycol. The concentration of the dye solution used for optimum performance at 553.7 nm is 1 gram of dye in 1.5 liter of ethylene glycol. We achieved 350 mW single frequency laser output at 553.7 nm with 5 W pump power and a lasing threshold of 3.2 W pump power. At higher dye concentrations the optimum performance is shifted to longer wavelength. The normal operating pressure of the dye circulator is 6 bar. The typical life time of the dye is 200 Wh.

Fiber laser system

The advent of erbium (Er), ytterbium (Yb) or (Er/Yb) doped fiber amplifiers with the development of UV writing of gratings in photosensitized fibers has paved the path for distributed feedback (DFB) fiber lasers.

In the infrared we use three commercial custom built fiber laser systems (KOHERAS) for barium spectroscopy of the $^1D_2 - ^1P_1$ transition (1500.4 nm), the $^3D_2 - ^1P_1$ transition (1130.6 nm) and the $^3D_1 - ^1P_1$ transition (1107.8 nm) and for laser cooling of barium.

The principle of the DFB fiber lasers is shown in Fig. 4.6. The three basic parts of a DFB fiber laser are a semiconductor pump laser, a fiber Bragg grating (FBG) and an active, doped fiber. The ytterbium (1107.8 nm and 1130.6 nm) ytterbium/erbium (1500.4 nm) doped fiber is the gain medium of the fiber laser. The semiconductor diode laser acts as a pump laser at 980 nm for the wavelength output in the range of 1020-1610 nm. The fiber Bragg grating defines a cavity as it is written onto the doped fiber by UV-illumination of the fiber through a phase mask. The wavelength is preselected to within a fraction of a nm. The wavelength
Figure 4.6: Principle and basic components of a DFB fiber laser [taken from KOHERAS brochure]. It consists of a fiber Bragg grating written in an actively doped fiber pumped at 980 nm or 1480 nm with a semiconductor laser.

Tuning is provided by changing the temperature and is limited to about 0.4 nm. An additional advantage is the TEM$_{00}$ output mode from the fiber.

Additionally, the fiber laser can be tuned by a PZT. The tuning range is about 0.3 nm. The fiber laser wavelength can be modulated by modulating either the period of the grating, or the refractive index of the fiber. Both of these parameters are affected by the strain of the fiber. The simplest way of wavelength modulation of a fiber laser is with a PZT that affects the strain on the fiber.

Non-linearity in tuning with PZT is an issue for fiber lasers. When the power of the laser changes, the frequency of the fiber laser tends to drift due to change in temperature of the fiber. To overcome this, power of the fiber lasers are set to the required value and once in thermal equilibrium measurements are taken. The operating temperature and PZT voltages of the three fiber laser systems are given in Table 4.4.

### 4.3.4 Fluorescence Detection System

The detection (imaging) system (see Fig. 4.7) used to detect fluorescence for spectroscopic studies and for laser cooling of barium is a photomultiplier tube (PMT) in photon counting mode. It is a Hamamatsu PMT (R7205-01) with low dark current and high sensitivity at 550 nm. The fluorescence from the radiative decay of the $^1P_1$ state atoms is imaged with a telescopic lens system. It consists
4.3. Experimental Setup

Distributed Feedback (DFB) Fiber lasers

<table>
<thead>
<tr>
<th>Specification</th>
<th>1500.4 nm</th>
<th>1130.6 nm</th>
<th>1107.8 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. Output power</td>
<td>15 mW</td>
<td>90 mW</td>
<td>150 mW</td>
</tr>
<tr>
<td>Linewidth</td>
<td>&lt;48 kHz</td>
<td>&lt;50 kHz</td>
<td>&lt;100 kHz</td>
</tr>
<tr>
<td>Thermal wavelength tuning coefficient</td>
<td>1.25 pm/K</td>
<td>10 pm/K</td>
<td>9 pm/K</td>
</tr>
<tr>
<td>Thermal tuning range</td>
<td>368 pm</td>
<td>300 pm</td>
<td>260 pm</td>
</tr>
<tr>
<td>(25°-55°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piezo wavelength tuning coefficient</td>
<td>3.7 pm/V</td>
<td>3 pm/V</td>
<td>2.6 pm/V</td>
</tr>
<tr>
<td>(0 - 90 V)</td>
<td>493 MHz/V</td>
<td>704 MHz/V</td>
<td>635 MHz/V</td>
</tr>
<tr>
<td>Piezo wavelength tuning coefficient</td>
<td>292(10) MHz/V</td>
<td>410(4) MHz/V</td>
<td>420(4) MHz/V</td>
</tr>
<tr>
<td>(Our Measurement)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature °C</td>
<td>44.7</td>
<td>38.2</td>
<td>41.7</td>
</tr>
<tr>
<td>PZT Voltage (V)</td>
<td>4.6</td>
<td>3.3</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 4.4: Optical specifications of the three fiber lasers provided by the manufacturer KOHERAS. Our measured values of the piezo wavelength tuning coefficient are also shown. Last row is the operating temperature of the fiber lasers for the wavelengths and PZT voltages of the $^{138}$Ba resonances. In section 4.5.2 and 4.6.2 frequency calibration methods for the fiber lasers is described.

of a lens of focal length $f = 30$ mm. The fluorescence is imaged on to a pin hole. The pinhole has a diameter of 1.0(1) mm. From the magnification of the imaging system $34/250 = 1/7$ we estimate the fluorescence from a region with diameter of 7 mm is imaged onto the PMT. After the pinhole a 25.4 mm lens collimates the light again. An interference filter of bandwidth 10 nm with a transmission of $e_{trans} = 45\%$ centered at 550 nm is placed in-front of the PMT.

The output signal from the PMT is fed into a dual bipolar amplifier (LRS 333) to amplify the pulses. A discriminator with a low threshold converts the pulses to logic NIM signals which can be counted by pulse counters (Racal 1999) with variable integration time.

The detection efficiency $\varepsilon$ depends on solid angle $\Omega$, the quantum efficiency of the PMT, $\varepsilon_{PMT}$, and the transmission efficiency of the interference filter, $e_{trans}$, i.e.,

$$\varepsilon = \Omega \cdot \varepsilon_{PMT} \cdot e_{trans},$$  (4.3)
with $\varepsilon_{PMT} = 0.07(1)$, $\varepsilon_{trans} = 0.45(2)$ and a solid angle for the light collection of $\Omega = 5(1) \cdot 10^{-4}$ we get

$$\varepsilon = 1.6(4) \times 10^{-5}. \quad (4.4)$$

We can estimate the atomic flux with the detection efficiency $\varepsilon$, the number of photons detected and the laser beam size. With a laser beam diameter $d$ of 1 mm the PMT count rate was 20 kHz. The fluorescence is detected from atoms passing through the laser and the imaging system selects a region $l$, 7 mm along the laser. The estimated atomic flux $F$ is

$$F = \frac{Countrate}{\varepsilon \cdot d \cdot l}, \quad (4.5)$$

which was about $10^{10}$ cm$^{-2}$s$^{-1}$ for an oven temperature of 550°C at a distance of 60 cm from the oven. In addition, to detect the 553.7 nm fluorescence we use a home built low-noise, high-sensitive and high-gain photodiode amplifier.

### 4.3.5 The Data Acquisition System

In this section, the data acquisition system used to collect and store the data for barium experiments is described. The block diagram of the data acquisition system is shown in Fig. 4.8. The data acquisition system consists of the following parts: frequency counters, a SR245 interface module, a USB-to-GPIB controller module and a computer.

The SR245 ADC module is used to set the voltages for the piezo elements of the dye laser and fiber lasers to scan their frequencies. It has 8 analog I/O chan-
4.4. Spectroscopy of the $^1S_0-^1P_1$ Transition

Figure 4.8: Data Acquisition system for the optical spectroscopy and laser cooling of barium experiments. Computer controlled GPIB is used to set the voltages to the lasers, read the data from the frequency counters and to scan the frequency of synthesizers.

channels with 13-bit resolution over the $\pm 10.24$ VDC full scale range, with 0.05% accuracy.

A USB-to-GPIB controller (ICS Electronics model:488-USB) with a USB interface to the PC is used. It is operated with a Windows XP PC that supports this driver. Programs written in C++ language are used to set the laser frequencies, scan the laser frequencies, scan acousto optic modulators with frequency synthesizers, monitor the frequency lock status of the diode lasers and to count photons.

4.4 Spectroscopy of the $^1S_0-^1P_1$ Transition

The $6s^2 \; ^1S_0 - 6s6p \; ^1P_1$ transition at 553.7 nm is the only transition available for laser cooling in barium. In our experiments it is extensively used for the
sensitive probing of other transitions. Here we give the basic properties of the spectroscopy. In particular we use this transition for frequency stabilization of the dye laser and to measure the lifetime of the $^1P_1$ state and later for the spectroscopy of the $D$-states and laser cooling experiments. Precision spectroscopy of this transition can be found in the literature [121, 127–132].

### 4.4.1 Stabilization of the Dye Laser

The Coherent dye laser nozzle and dye circulator has limitations. The system is instable if operated at pressures higher than 5 bar. The laser output power has fast dropouts on the scale of 10 $\mu$s due to the air bubbles in the dye. This causes problems for frequency stabilization as well as power stabilization. To overcome this the Coherent dye laser nozzle was replaced with a nozzle RDSN 02 from Radiant Dyes. In addition we use a high pressure dye circulator RD1000 CW with an air cushion RDAC 20 from Radiant Dyes. This helped to achieve a more stable operation without fast dropouts of the dye laser. Still we have a slow drift of the laser frequency and power fluctuations at the level of 5%.

To overcome these problems we implemented external stabilization of power and frequency. Power fluctuations can occur due to change in pressure of the dye jet, mechanical disturbances, thermal fluctuations of the laser dye and aging of the laser dye.
4.4. Spectroscopy of the $^1S_0 - ^1P_1$ Transition

![Diagram of split photodiode and frequency signal](image)

**Figure 4.10:** Principle of the Doppler shift method. Making use of the atomic beam divergence the position dependent fluorescence is detected with a split photodiode. Two identical Lorentzian line shapes offset by half their linewidth and the difference between the two Lorentzian line shapes is shown.

The schematic layout of the dye laser power stabilization is shown in Fig. 4.9. The power is regulated by the diffraction efficiency of an acousto optic modulator (AOM) in the light path. The light for the experiment is taken from the zeroth order beam of the AOM. The amount of light is monitored by a photodiode after splitting off a few percent with a beam splitter. From the detected light level we subtract a set point value in a difference amplifier. The resultant signal is an error signal which indicates that the power deviates from the set point. The error signal is used to control the diffraction efficiency of the AOM by controlling the RF power. With the servo loop closed the power stability of the system is improved and the fluctuations are less than 1% of the output power of the dye laser. The fluctuations of the power of the dye laser with power stabilization OFF and ON is shown in Fig. 4.12.

The dye laser is frequency stabilized to the $^1S_0 - ^1P_1$ transition in barium employing a Doppler shift method. The method makes use of the divergence of an
Figure 4.11: $^1S_0 - ^1P_1$ fluorescence from natural barium. The fluorescence is detected with an amplified split photodiode with a sensitivity of 0.2 V/nW. (a) Fluorescence spectrum of the atomic beam when intersected by 553.7 nm laser beam at an angle of 90° from one segment of the split photodiode. The $^{136}\text{Ba}$ peak also contains a $^{135}\text{Ba} F = 5/2$ component. (b) Dispersion-like (error) signal measured from the difference between the two photodiode sections. It is obtained using the Doppler shift method shown in Fig. 4.10. The $^{138}\text{Ba}$ isotope is used for stabilization because it has the largest signal to noise.
4.4. Spectroscopy of the $^1S_0 - ^1P_1$ Transition

Figure 4.12: Fluorescence of the $^1S_0 - ^1P_1$ transition detected by a photomultiplier tube when the dye laser is frequency locked to the $^{138}$Ba resonance with external power stabilization OFF and with external power stabilization ON.

atomic beam. The principle is shown in Fig. 4.10. The barium beam from the oven intersects with the laser beam at a right angle. The fluorescence light is imaged with a 30 mm lens on to a split photodiode with two zones, separated by 0.13 mm distance. The signal from one segment is shown in Fig. 4.11(a). The two signals from the two halves of the split-photodiode are subtracted in a difference amplifier. The difference signal is shown in Fig. 4.11(b). It exhibits a zero-crossing with a high slope, which is used for the dye laser frequency stabilization. It is amplified and fed back to the external scan input of the laser after appropriate integration. The long term drift of the dye laser frequency is minimized by locking to the $^1S_0 - ^1P_1$ transition and a long term frequency stability within 1 MHz is achieved (Fig. 4.12).

4.4.2 $^1P_1$ state Lifetime

Measurement of lifetime $\tau$ of a state gives information about the absolute transition probability of a transition. It is defined as
Figure 4.13: Setup to measure the $^1P_1$ state lifetime in barium. The polarization of the 553.7 nm laser and magnetic field direction are perpendicular to each other. The fluorescence is detected with a PMT perpendicular to the direction of both magnetic field and polarization of the laser.

\[
\tau = \frac{1}{\sum_i A_{ik}} = \frac{\lambda^3}{<i|r|k>^2}, \quad (4.6)
\]

where $i$ is the lower state and $k$ is the higher state. This yields transition dipole matrix elements. Thus, lifetime measurements are important tests as well as input for the computed wave functions and models of the electron distribution in complex atoms like heavy alkaline earth elements.

We used the Hanle effect [133,134] to measure the lifetime of the $^1P_1$ state by measuring the intensity distribution of the 553.7 nm fluorescence in an external homogeneous magnetic field. The polarization of the 553.7 nm laser light is perpendicular to the magnetic field, which is applied perpendicular to the atomic barium beam. We detected the fluorescence at different magnetic fields. Shown in Fig. 4.14 are the measurements for the $^{138}\text{Ba}$ and $^{136}\text{Ba}$ isotopes respectively. Atoms in a homogeneous magnetic field $B = \{0,0,B_z\}$ are excited by the polarized electromagnetic wave

\[
E = E_y \cos(\omega t - kx), \quad (4.7)
\]

the frequency $\omega$ is on resonance with the $^1S_0 - 1P_1$ transition. The field-dependent term falls to half its maximum value at the magnetic fields $B_\pm$ given by
4.4. Spectroscopy of the $^1S_0 - ^1P_1$ Transition

\[
\Gamma = 2\omega_L = 2\frac{g_J\mu_B B_\pm}{\hbar}, \quad (4.8)
\]

where $g_J$ is Lande factor, $\hbar = h/2\pi$, $h$ is Planck constant, $\mu_B$ is Bohr magneton. The full width at the half maximum of the signal ($\Delta B_{1/2}$), $\Gamma = 1/2\pi \tau$, is related to the radiative lifetime through the relation

\[
\tau = \frac{\hbar}{2\pi g_J\mu_B \Delta B_{1/2}}. \quad (4.9)
\]

The Lande factor $g_J = 1$ for the $^1P_1$ state, $\mu_B/\hbar = 1.4$ MHz/G and from the width of the measured depolarization curve, the excited state lifetime is determined. The
results are fitted with a Lorentzian function. From the magnetic field FWHM of the curve was extracted. In Fig. 4.14 the minimum is not exactly at zero magnetic field because of the residual magnetic field due to the magnetization of the the experimental chamber and the earth’s magnetic field. We did not shield any external fields. Using the Eq. 4.9, the lifetime of the $^1P_1$ state was obtained to be 8.0(5) ns, which is in good agreement with the reported value of 8.2(2) ns [122].

4.5 Laser Spectroscopy of Metastable D-states

To conduct laser spectroscopy and to find the transitions we realized an experimental setup that satisfies two requirements. First the production of metastable atoms and second the probing of the population of the metastable states by laser spectroscopy. The layout of the experimental setup is shown in Fig. 4.15.

We provide two separate regions for the interaction with laser beams. In the first section we pump the atoms optically into the metastable states. This is done either by the $^1S_0 - ^1P_1$ transition using the dye laser or the $^1S_0 - ^3P_1$ transition using a diode laser (Fig. 4.15). In the second interaction region we probe the metastable

**Figure 4.15:** Set up for production and detection of barium atoms in the metastable D-states. Region 1 is to populate the metastable states with 553.7 nm or 791.3 nm laser. Region 2 to probe the metastable atoms driven by the infrared lasers by detecting the 553.7 nm fluorescence from the $^1P_1$ state with a PMT.
4.5. Laser Spectroscopy of Metastable D-states

atoms by driving the atom to the \(^1P_1\) excited state with the corresponding laser. The spatial separation of metastable production and probing is advantageous for the suppression of scattered light onto the detector. The transitions are always detected by the fluorescence at 553.7 nm from the \(^1P_1 - ^1S_0\) transition since the visible light is easily detected with a photomultiplier tube. Here we explain the principle and show different methods of frequency calibration of the scanning of the fiber laser with the PZT voltage.

4.5.1 Production and Detection of Metastable Atoms

Conventionally, metastable barium states are populated in a plasma discharge inside the atomic-beam oven [135] or by electron bombardment on the atomic beam [136]. Typically a few percent of the atoms can be transferred to the metastable states. Unlike the above techniques, we use optical pumping and exploit the branching ratio of the \(^1P_1\) and the \(^3P_1\) states to populate the metastable \(D\)-states. The two feasible optical methods are by the \(^1S_0 - ^1P_1\) transition and the \(^1S_0 - ^3P_1\) transition.

When the barium atoms are excited by a laser at 553.7 nm from the \(^1S_0\) state to the \(^1P_1\) state they can also decay to the \(^1D_2\), \(^3D_2\) and \(^3D_1\) metastable states. The ratio of population is 1 : 1/2.3 : 1/80.

The \(^3D_2\) and \(^3D_1\) states can also be populated by driving the \(^1S_0 - ^3P_1\) transition at 791.3 nm. Around 60% of the barium atoms decay to the \(^3D_2\) and \(^3D_1\) states and 40% decay back to the ground state. Cycling the \(^1S_0 - ^3P_1\) transition effectively populates the triplet \(D\)-states with a ratio of 65% in the \(^3D_2\) and 35% in the \(^3D_1\) state. Here we employ a diode laser, which is locked to the ‘a1’ line of the P(52)(0-15) hyperfine transition in molecular I\(_2\) (Chapter 3.3.2).

Detection of the D-P Transitions

For observing the \(D - P\) transitions we use a sensitive indirect method. The fluorescence at 553.7 nm of the \(^1P_1\) state decay to the \(^1S_0\) ground state is detected rather than the fluorescence in the infrared. The advantages of this method are:

1. The laser wavelength of the driving transition is at a different wavelength than the wavelength of the detected photons. It can be separated easily by an interference filter.
2. PMT’s in the visible region have high gain and good quantum efficiency (\(\simeq 10\%\)) and hence provide good signal to noise ratio for single photon counting. The infrared fluorescence from transitions to \(^1D_2\) and \(^3D_{1,2}\) states
is weaker than the fluorescence to the ground state. Detection of fluorescence at 1500.4 nm, 1130.6 nm and 1107.8 nm is difficult with a photodiode and PMT’s in the infrared have very low quantum efficiency and have to be cooled to minimize the dark counts.

3. The possibility to use the $^1S_0 - ^1P_1$ transition to probe the ground state population efficiently. Since we can cycle the $^1S_0 - ^1P_1$ transition we scatter many photons per atom.

4. We can extract quantitative information of repumping of atoms to the $^1S_0$ state for laser cooling experiments.

Based on these considerations we realized the experimental setup for state selective sensitive laser spectroscopy of metastable barium with high signal to noise ratio. The latter is of particular importance in view of planned spectroscopy of radium.
Figure 4.17: (a) $^1D_2 - ^1P_1$ transition detected by 553.7 nm fluorescence with a PMT. The line through the data points is a fit of a Lorentzian function with a linewidth of $31(2)$ MHz, which is greater than 19 MHz. (b) $^3D_2 - ^1P_1$ transition observed by detecting fluorescence at 553.7 nm with a PMT. The line through the data points is a fit of Lorentzian line shape with a line width of $41(2)$ MHz. In both cases the broadening is due to the angle made by the infrared laser beams with respect to the atomic beam. (c) The $^3D_1 - ^1P_1$ transition detected by 553.7 nm fluorescence. In all the three cases metastable D-states are populated by driving the $^1S_0 - ^1P_1$ transition. Since the population of the $^3D_1$ state is 80 times less than the $^1D_2$ state we cannot detect it. For all the plots each data point has an integration time of 1 second.
Chapter 4. Radium and Barium: Atomic Properties

The $^{138}$Ba atoms in the $^1S_0$ ground state are pumped to the $^1D_2$ state with the 553.7 nm laser in resonance with the $^1S_0 - ^1P_1$ transition. After setting the temperature of the fiber laser appropriately we scan the laser by the PZT. The 1500.4 nm resonance detected through fluorescence at 553.7 nm is shown in Fig. 4.17(a). The linewidth of a Lorentzian function fitted to the data is 31(2) MHz. This is larger than the natural linewidth of 19 MHz due to the excited state lifetime. The broadening is due to the alignment of the 1500.4 nm laser beam with respect to the atomic beam.

The steps described for the $^1D_2 - ^1P_1$ transition are repeated to tune the fiber laser to resonance for the $^3D_2 - ^1P_1$ transition at 1130.6 nm. The resonance is shown in Fig. 4.17(b). The ratio of the peak amplitudes of the $^1D_2$ and $^3D_2$ states provide the information on the ratio of population in these states, which is 2.0(3). This is in agreement with the value 2.3(1) reported by Bizzari et al. [119].
Further, comparing the count rate for the $^1D_2$ and $^3D_1$ states we can estimate the ratio of the population in these transitions. Since the count rate is on the order of 800 Hz for the $^1D_2 - ^1P_1$ transition we would expect a count rate of $\approx 10$ Hz for the $^3D_1 - ^1P_1$ transition. With a background rate due to scattered light of the order of 200 Hz we have a $S/N$ of only 0.7. Thus a better experimental configuration was necessary. For this we use a diode laser at 791.3 nm to drive the $^1S_0 - ^3P_1$ transition. Then we populate about 35% of all the atoms in the $^3D_1$ state rather than about 1%.

The experimental setup consists of two diode lasers that are frequency offset locked. One of the diode lasers is frequency stabilized to the 'a1' line of the P(52)(0-15) transition at 791.3 nm in molecular iodine, which is the frequency reference for the $^1S_0 - ^3P_1$ transition in barium. The spectroscopy of iodine was described in section 3.3.2. The frequency offset locking technique of two diode lasers is described in the Appendix A. The diode laser used to populate triplet D-states is frequency offset locked to the diode laser stabilized to iodine. It is tuned to the $^{138}$Ba resonance of the $^1S_0 - ^3P_1$ transition. Between 3-5 mW power from the diode laser is available during the measurements. The fiber laser is scanned with the PZT over the resonance. A typical spectrum is shown in Fig. 4.18.

During the experiments we observed that the passive frequency stability of the fiber lasers is good and we observe a drift of less than 13(2) MHz/h. In order to achieve a higher stability the lasers could be locked to temperature stabilized Fabry-Perot cavities.

Frequency detuning of the repump lasers plays an important role in laser cooling experiments. This is discussed in Chapter 5. The frequency scanning with the PZT voltage of the fiber lasers is calibrated using two methods: In the first method, we used a resonant type electro-optic modulator (EOM) for the 1500.4 nm and 1130.6 nm lasers. The EOM is used for the generation of frequency side bands and its working principle and construction is described in the Appendix C. The lithium tantalate crystal is driven at a frequency of 33.90 MHz. Typical RF power levels used to achieve a modulation index of the order of 1 is 5 dBm.

We detect the side bands by spectroscopy of the metastable states. The side bands observed are shown in Fig. 4.19. From a fit we determine the side band spacing to $84(2)$ mV (1130.6 nm) and $116(3)$ mV (1500.4 nm) for a modulation frequency of 33.9 MHz. We obtain from this measurement a scanning of $404(10)$ MHz/V and $292(10)$ MHz/V respectively.

The second method used to calibrate the fiber laser is the Zeeman splitting of energy levels in a uniform external magnetic field. Here we populated the
Figure 4.19: The spectral width of the (a) 1500.4 nm and (b) 1130.6 nm lasers are broadened by an EOM with modulation frequency of 33.9 MHz. The sidebands are clearly visible in the spectrum and are used to calibrate the tuning of the fiber lasers. The line is a fit taking three sidebands into account.
Figure 4.20: Spectrum of the D-P transitions in an external magnetic field of 65(3) Gauss by detecting the 553.7 nm fluorescence of the $^1P_1$ state. (a) With the detuning of the 1500.4 nm laser. (b) With the detuning of the 1130.6 nm laser. Each data point is taken with an integration time of 1 second. The fit through the data is a Lorentzian function.
(a) Possible transitions from the hyperfine states of the $^{137,135}$Ba isotopes for the $^3P_1 - ^3D_1$ and $^3D_1 - ^1P_1$ transitions. The calculated strengths for each component of all the transitions are given. (b) Possible transitions from the hyperfine states of the $^{137,135}$Ba isotopes for the $^3P_1 - ^3D_2$ and $^3D_2 - ^1P_1$ transitions. The calculated strengths for each component of all the transitions are shown. Strengths are multiplied with a common factor and are given in the smallest possible integer numbers.

$^1D_2$ level with the 553.7 nm laser. An external magnetic field of 65(3) Gauss is applied perpendicular to the $^{138}$Ba atomic beam. The laser is perpendicular to the atomic beam to reduce the Doppler effect. The resulting spectrum when scanning the laser consists out of three peaks (1500.4 nm) based on the selection rules $\Delta J = 0, \pm 1$ (Fig. 4.20). The voltage difference between the three peaks determined from a fit is 0.31(1) V (1500.4 nm) for an applied magnetic field of 65(3) Gauss. The splitting between the peaks is $\mu \cdot B$. With this we get a scanning of 294(20) MHz/V for this laser. In Table 4.4 we give all the calibrations for the fiber lasers. Their values differ significantly from the scanning sensitivity given by the manufacturer.
4.6 Hyperfine Structure of Triplet D-States

4.6.1 Expected Hyperfine Spectrum

The interaction between the electron and the moments of the nucleus results in hyperfine structure for an atom. For isotopes with nuclear spin \( I \), the hyperfine splitting can be written as

\[
\nu = \frac{1}{2} C \cdot A + B \cdot C1,
\]

where

\[
C = F(F + 1) - I(I + 1) - J(J + 1),
\]

\[
C1 = \frac{3C(C + 1) - I(I + 1)J(J + 1)}{8I(2I - 1)J(2J - 1)},
\]

where \( A \) is the magnetic dipole interaction constant, \( B \) is the electric-quadrupole coupling constant, \( J \) is the angular momentum of the electron and \( F \) is the total angular momentum. It is important to know how the isotopes with nuclear spin \( I \neq 0 \) influence the transition strength within the hyperfine states of these isotopes. This plays an important role in laser cooling and trapping because of the optical pumping effects that arise while using polarized light.

For barium isotopes with nuclear spin \( I = 3/2 \) one can find the hyperfine splitting for the triplet \( D \)-states as well as for the singlet and triplet \( P \) state in literature. The hyperfine splitting frequencies of the \( ^3D_1 - ^1P_1 \) transition known from references [121, 135] are given Table 4.5 and for the \( ^3D_2 - ^1P_1 \) transition in Table 4.6. We can use the position of these lines for additional calibration of the fiber lasers. The hyperfine structure splitting is sensitive to the overlap of the electronic wave function with the nucleus. A measurement of the hyperfine structure of the \( P \) and \( D \)-states in radium is needed (for laser cooling as well). This will be important for evaluations of possible EDM.

Transition Strengths: Calculation

The calculation of transition strengths for the triplet \( ^3D_1 \) and \( ^3D_2 \) states to the singlet \( ^1P_1 \) state of barium is presented.

Transition strengths are governed by selection rules and define the probability of the transition occurring. The square of the dipole transition matrix element \( \mu_{eg} \) gives the transition strength. The dipole transition matrix element is given by
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Figure 4.22: Calculated transition strengths of the $^{137}$Ba isotope for the $^3D_1 - ^1P_1$ transition. In the spectrum the transition strengths are normalized to the $5/2 \rightarrow 5/2$ transition. The frequencies are relative to the $1/2 \rightarrow 3/2$ transition.

Figure 4.23: Calculated transition strengths of the $^{137}$Ba isotope for the $^3D_2 - ^1P_1$ transition. In the spectrum the strengths are normalized to the $7/2 \rightarrow 5/2$ transition. The frequencies are relative to the $7/2 \rightarrow 5/2$ transition.
\[ \mu_{eg} = (-1)^{1+L'+S+J+J'+I-M'} \sqrt{(2J+1)(2J'+1)(2F+1)(2F'+1)} \times \left\{ \begin{array}{ccc} L' & J' & S \\ J & L & 1 \end{array} \right\} \left\{ \begin{array}{ccc} J' & F' & I \\ F & J & 1 \end{array} \right\} \left( \begin{array}{ccc} F & 1 & F' \\ M_F & q & M_F' \end{array} \right), \] (4.11)

where \( I \) is the nuclear spin, \( S \) is the spin quantum number and the terms with \( \{ \} \) and \( ( ) \) are Wigner 6j and 3j symbols respectively. The quantum numbers without an accent are ground state terms and with an accent are excited states. \( q \) indicates the polarization of the light with \( q = 0 \) for linearly polarized light and \( q = \pm 1 \) for right and left circularly polarized light. The transition matrix consists of a radial and an angular component. The radial part is the same for all the transitions between two terms in the ground state and the excited state, and is therefore only a numerical factor that determines the absolute value of the coupling.

In the calculation of transition strengths, all the hyperfine transitions of the \(^{137,135}\text{Ba}\) isotopes for the \( (L, S, J) \) \(^3\text{P}_1\) state to \( (L', S', J') \) \(^3\text{D}_{1,2}\) states and \( (L, S, J) \) \(^3\text{D}_{1,2}\) states to the \( (L', S', J') \) \(^1\text{P}_1\) state contain a common factor

\[ A_1 = (2J+1)(2J'+1) \left\{ \begin{array}{ccc} L' & J' & S \\ J & L & 1 \end{array} \right\}^2, \] (4.12)

The transition strengths are equally probable for the different polarization of the light i.e., \( q = M'_F - M_F = 0, \pm 1 \) for the allowed transitions. It is a common factor, which is equal to 1 in equation 4.11 for the purpose of our calculation

\[ \sum_{M_F \rightarrow M_F'} \left( \begin{array}{ccc} F & 1 & F' \\ M_F & q & M_F' \end{array} \right)^2 = 1, \] (4.13)

Hence for the calculation of the transition strengths equation 4.11 reduces to the following

\[ A_1 \times (2F+1)(2F'+1) \left\{ \begin{array}{ccc} J' & F' & I \\ F & J & 1 \end{array} \right\}^2. \] (4.14)

The calculated transition strengths for the \(^3\text{P}_1 - ^3\text{D}_1\) transition and for the \(^3\text{D}_1 - ^1\text{P}_1\) transition for different initial \( F \) values and final \( F' \) values for \( J = 1 \) to \( J' = 1 \) are shown in Fig. 4.21(a). Similarly, the calculated transition strengths for the \(^3\text{P}_1 - ^3\text{D}_2\) transition and for the \(^3\text{D}_2 - ^1\text{P}_1\) transition for different initial \( F \) values and final \( F' \) values for \(^3\text{P}_1 (J = 1) - ^3\text{D}_2 (J = 2)\) and \(^3\text{D}_2 (J = 2)\) to \(^1\text{P}_1 (J' = 1)\) are shown in Fig. 4.21(b).
Table 4.5: The first column gives all the possible transitions of the $^3D_1 - ^1P_1$ based on the selection rules for a dipole transition. The second column gives the frequencies of the transitions known from the hyperfine splitting measurements of the $^3D_1$ and $^1P_1$ states from centroid to centroid [121, 135]. The third column gives the calculated transition strengths that are normalized to the strongest transition. The fourth column consists of the transition strengths from our measurement normalized to the strongest transition. The fifth column gives the ratio of strengths from the measurement and calculation.

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<th>Calculation</th>
<th>Measurement</th>
<th>Ratio [M/C]</th>
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</tbody>
</table>

The transition strengths of the seven transitions shown in Fig. 4.22 are the product of the transition strengths of the $^3P_1 - ^3D_1$ transition and the $^3D_1 - ^1P_1$ transition respectively when the $F = 3/2$ hyperfine state of the $^3P_1$ level is populated. Similarly the transition strengths of the 6 transitions shown in Fig. 4.23 are the product of the transition strengths of the $^3P_1 - ^3D_2$ transition and the $^3D_2 - ^1P_1$ transition respectively when the $F = 5/2$ hyperfine state of the $^3P_1$ level is populated.

4.6.2 Results from the Triplet D-states

To populate the hyperfine levels in the triplet $D$-states we locked the diode laser to the $^1S_0$, $F = 3/2 - ^3P_1$, $F = 3/2$ transition. The selection rules allow to populate
the $F = 1/2, 3/2$ and $5/2$ states of the $^3D_1$ level for $^{137}\text{Ba}$ and $^{135}\text{Ba}$, which is shown in Fig. 4.21(a).

The hyperfine splitting of $^{137}\text{Ba}$ and $^{135}\text{Ba}$ isotopes for the $^3D_1 - ^1P_1$ transition are measured simultaneously (see Section 4.7). The 1107.8 nm laser frequency is scanned spanning the entire hyperfine spectrum of 3 GHz. The measured hyperfine spectrum of the $^3D_1 - ^1P_1$ transition for $^{137}\text{Ba}$ and $^{135}\text{Ba}$ isotopes is shown in Fig. 4.24. All the seven transitions are fitted with a sum of Lorentzian functions of the form

$$F_\nu = C + \sum_{i=1}^{7} \frac{A_i}{1 + \left(\frac{\nu - \nu_i}{T/2}\right)^2}$$

(4.15)

where $C$ represents the background counts, $i$ is the sum of all the hyperfine com-
Figure 4.25: Measured hyperfine spectrum of the $^{137}$Ba isotope for the $^3D_2 - ^1P_1$ transition when frequency of the 1130.6 nm laser is scanned 4 GHz. Each point has an integration time of 1 second. The line through the data points is a fit of a Lorentzian line shape with a line width of 20(1) MHz. The frequency scale is relative to the 7/2→5/2 transition (first peak of the $^{137}$Ba isotope). Here the diode laser is locked to $^{137}$Ba F = 5/2 state of the $^3P_1$ level. In the spectrum the frequencies are relative to the frequency of 7/2→5/2 transition.

Figure 4.26: Calibration of the 1107.8 nm laser. Plotted are the voltages at the peak amplitude of each transition with the frequencies from the hyperfine splitting measurements. The fit is a second order polynomial function.
4.6. Hyperfine Structure of Triplet D-States

<table>
<thead>
<tr>
<th>$^3D_2 - ^1P_1$ transition ($^{137}$Ba)</th>
<th>Relative transition strengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>F→$F'$</td>
<td>Frequency [MHz]</td>
</tr>
<tr>
<td>7/2→5/2</td>
<td>1405.99(21)</td>
</tr>
<tr>
<td>5/2→5/2</td>
<td>-72.42(21)</td>
</tr>
<tr>
<td>5/2→3/2</td>
<td>-283.56(25)</td>
</tr>
<tr>
<td>3/2→5/2</td>
<td>-1096.05(21)</td>
</tr>
<tr>
<td>3/2→3/2</td>
<td>-1307.19(25)</td>
</tr>
<tr>
<td>3/2→1/2</td>
<td>-1584.14(42)</td>
</tr>
</tbody>
</table>

Table 4.6: The first column is the six possible transitions of the $^3D_2 - ^1P_1$ transition based on the selection rules of dipole transition. The second column is the frequency of the transitions from centroid to centroid from the hyperfine splitting measurements of the $^3D_2$ and $^1P_1$ states [121, 135]. The third column is the calculated transition strengths that are normalized to the 7/2→5/2 transition. The fourth column consists of the transition strengths normalized to the 7/2→5/2 transition from our measurement. The fifth column is the ratio of the strengths from the measurement and calculation.

The frequencies of the measured spectrum are plotted relative to the 1/2→3/2 transition. The transition strengths from the calculation, the measurement and their ratios are given in Table 4.5.

A similar measurement was done for the $^{137}$Ba isotope for the $^3D_2 - ^1P_1$ transition at 1130.6 nm. Here the $^3D_2$ sub levels $F = 3/2, 5/2$ and 7/2 (Fig. 4.21(b)) were populated by driving the $^1S_0 F = 3/2 - ^3P_1 F = 5/2$ transition with the diode laser.

The 1130.6 nm laser frequency is scanned by 4 GHz, spanning the entire hyperfine spectrum of the $^{137}$Ba isotope for the $^3D_2 - ^1P_1$ transition. The measured hyperfine spectrum is shown in Fig. 4.25. The analysis is done in the same way as for the $^3D_1 - ^1P_1$ transition.

The measurements are compared to the expected values derived in section 4.6.1 and added to Table 4.6. We observe a discrepancy of relative transition strengths, which can be accounted for by the polarization of the infrared lasers with respect to the direction in which we collect the fluorescence.

**Calibration of Infrared Lasers**

We scan the fiber laser (frequency) with a PZT in terms of voltage. We used the hyperfine structure measurement for the calibration of the scanning of fiber components of the respective isotope, $A$ is the amplitude of each component, $\Gamma$ is the halfwidth maximum and $n_i$ is the center of the hyperfine component.
lasers with the piezo element. In the manual we can find this conversion factor (see Table 4.4).

We determine the PZT voltage at the center of each peak from our measurement. The hyperfine splitting frequencies of the $^3D_1$, $^3D_2$ states for the $^{137,135}$Ba isotopes are known from the Atomic Beam Magnetic Resonance (ABMR) experiment [135, 136]. The hyperfine splitting of the $^{137,135}$Ba isotopes for the $^1P_1$ state are also known [121]. From these, frequencies of the different hyperfine transitions of the $^3D_1 - ^1P_1$ transition are calculated.

The measured PZT voltages at the peak of each resonance are plotted versus the frequencies of the transitions (Fig. 4.26). There is a small deviation from a linear behavior. The quadratic term in the fit shown is the non-linearity in the stretching of the fiber by the PZT. These are reproducible over the voltage range used in the experiments.

The value obtained from the fit for the 1107.8 nm laser is 420(4) MHz/V. The measured conversion factor deviates from the value 635 MHz/V provided by the manufacturer. It is 1.5 times higher than our measurement. The error in our measurement is limited by the resolution of the device used to set the PZT voltage. Similarly, the 1130.6 nm fiber laser was calibrated with the $^3D_2 - ^1P_1$ transition and the value is 410(4) MHz/V.

### 4.7 Isotope Shifts

The isotope shift of an atomic transition frequency between two different isotopes of an atom with mass numbers $A_1$ and $A_2$ is decomposed as a sum of normal mass shift ($\delta \nu_{NMS}$), specific mass shift ($\delta \nu_{SMS}$) and field shift ($\delta \nu_{FS}$) [121]

$$\delta \nu = \delta \nu_{NMS} + \delta \nu_{SMS} + \delta \nu_{FS}$$  \hspace{1cm} (4.16)

The normal mass shift arises due to the reduced mass correction to the energy levels in an atom and is calculated by

$$\delta \nu_{NMS} = \nu \frac{m_e}{m_p} \frac{A_1 - A_2}{A_1 A_2}$$  \hspace{1cm} (4.17)

where $m_e$ is the electron mass, $m_p$ is the proton mass and $\nu$ is the transition frequency. The specific mass shift is caused by the momentum correlations among orbital electrons. This is a constant for all the isotopes and insensitive to the nuclear component. It is derived from the theoretical estimates.

The field shift arises due to the change in the spatial distribution of the nuclear charge between the different isotopes, which is given as
Figure 4.27: In region 1 using 791.3 nm laser with an AOM in double pass configuration different isotopes are populated to the $^3D_1$ state. In region 2 we measured the isotope shift and hyperfine structure with the 1107.8 nm laser by spectroscopy of the $^3D_1-^1P_1$ transition for different isotope pairs.

$$\delta v_{FS} = F \delta \langle r^2 \rangle$$  \hspace{1cm} (4.18)

where $F$ is an electronic factor and $\langle r^2 \rangle$ is the expectation value of the square of charge distribution of the nucleus. This provides information on the overlap of wavefunctions with the nucleus, which for us is of interest for an EDM experiment with the radium atom.

Barium isotopes with nuclear spin $I = 0$ have no hyperfine structure in their ground state and excited state. Due to this, the isotope shift between different isotopes can be derived directly from the measurement. Because of the long term drifts of the fiber lasers with temperature, we have to measure the transition for different isotopes at the same time. To achieve this, 791.3 nm laser light from the diode laser is passed through an AOM at a center frequency of 200 MHz in double pass configuration (see Fig. 4.27). We toggle the frequency to the AOM with a frequency synthesizer by switching fast between the different frequencies for the isotopes. Typical switching times are limited by the HP 8656B synthesizer to about 50 ms. This short switching time allows us to reduce the uncertainty of the
Table 4.7: Isotope shifts of the $^1S_0 - ^3P_1$ transition at 791.3 nm in barium [137].

<table>
<thead>
<tr>
<th>Isotope pair</th>
<th>Isotope shift [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>138-137</td>
<td>-183.4(1.0)</td>
</tr>
<tr>
<td>138-136</td>
<td>-109.2(1.0)</td>
</tr>
<tr>
<td>138-135</td>
<td>-219.9(1.0)</td>
</tr>
<tr>
<td>138-134</td>
<td>-122.3(2.5)</td>
</tr>
<tr>
<td>138-130</td>
<td>-174.7(1.2)</td>
</tr>
</tbody>
</table>

Table 4.8: Hyperfine splitting frequencies of the $^3P_1$ state from atomic beam double resonance measurements from the centroid [138].

<table>
<thead>
<tr>
<th>F state</th>
<th>$^{135}\text{Ba [MHz]}$</th>
<th>$^{137}\text{Ba [MHz]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/2</td>
<td>1535.70(3)</td>
<td>1715.48(6)</td>
</tr>
<tr>
<td>3/2</td>
<td>-1001.23(3)</td>
<td>-1108.98(3)</td>
</tr>
<tr>
<td>1/2</td>
<td>-2604.62(6)</td>
<td>-2928.49(6)</td>
</tr>
</tbody>
</table>

measurement due to slow drifts of the fiber laser frequencies. The experimental resolution of this transition in our experiment is below 2 MHz. The spacing allows us to select the isotope by the frequency of the diode laser. This method applies to all isotopes because the isotope shift is large compared to the linewidth of the transition.

We make use of the known isotope shift and hyperfine structure in the $^3P_1$ level. The isotope shift of barium isotopes for the $^3P_1$ level measured by Grundevik et al. [137] are given in Table 4.7. The hyperfine structure in the $^3P_1$ excited state in barium isotopes with nuclear spin $I = 3/2$ were measured by zu Putlitz [138] with the optical double-resonance technique, using a hollow cathode

Table 4.9: Absolute difference frequencies of the corresponding sub-levels of the $^3P_1$ state for different isotope pairs. The difference frequencies allow for isotope selective population of the metastable D-states. The uncertainties are dominated by the isotope shift measurements of the $^3P_1$ state.

<table>
<thead>
<tr>
<th>F state</th>
<th>Isotope pair</th>
<th>$\Delta \nu$ [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>138-136</td>
<td>-109.2(1.0)</td>
</tr>
<tr>
<td></td>
<td>136-134</td>
<td>-13.1(2.7)</td>
</tr>
<tr>
<td>5/2</td>
<td>137-135</td>
<td>143.3(1.4)</td>
</tr>
<tr>
<td>3/2</td>
<td>137-135</td>
<td>-144.3(1.4)</td>
</tr>
<tr>
<td>1/2</td>
<td>137-135</td>
<td>-360.4(1.4)</td>
</tr>
</tbody>
</table>
4.7. Isotope Shifts

Figure 4.28: Spectra of the $^{138,136}$Ba isotopes. They are taken with 100 msec integration time. The line through the measured data is Lorentzian fit function. The isotope shift between $^{136}$Ba and $^{134}$Ba is -71(5) MHz.

Using optical pumping with lasers allows us to provide a state selective and isotope selective metastable beam. The different frequencies for the population transition, the $^1S_0 - ^3P_1$ transition is well known from previous experimental results on isotopes shifts [137] and hyperfine structure [138]. The relevant data is compiled in Table 4.7 and Table 4.8. In Table 4.9 we give the frequency differences for the same transition in the different isotopes we used.

When the diode laser is toggled between the $^{138}$Ba and $^{136}$Ba isotopes we can determine the isotope shift of the $^3D_1 - ^1P_1$ transition. The spectra obtained from one such a scan are shown in Fig. 4.28. The two resonance spectra are fitted with Lorentzian functions. The linewidth is $0.081(4)$ V ($^{138}$Ba) and $0.090(6)$ V ($^{136}$Ba) and the splitting between the peaks is $0.15(2)$ V. Without isotope selective
Figure 4.29: Isotope shift of $^{136}$Ba and $^{134}$Ba. They are taken with 100 ms second integration time. The line through the measured data is a Lorentzian fit function. In the $^{134}$Ba also $^{136}$Ba isotope is seen. The isotope shift between $^{136}$Ba and $^{134}$Ba is -93(6) MHz.

population of the metastable states the two peaks would overlap and the determination of the line center would require much higher statistics. In addition, we find from the peak intensities the abundance ratio $^{138}$Ba : $^{136}$Ba to 10.0(4) : 1, which is in good agreement with the natural abundance ratio of 10.9 : 1 found in literature [121]. Using the calibration of fiber lasers we get an isotope shift of -71(5) MHz and a linewidth of 34(1) MHz and 38(2) MHz, respectively.

In a similar manner we measured the isotope shift between $^{136}$Ba and $^{134}$Ba isotopes in the $^3D_1$ state. The isotope shift between $^{136}$Ba and $^{134}$Ba of the $^1S_0 - ^3P_1$ transition is just 13.1(2.7) MHz [137]. The narrow intercombination line with natural linewidth of 120 kHz permits still the isotope selective population of the triplet $D$-states. Although our experimental resolution of the transition is on the
### Table 4.10: Fit parameters of the different isotopes for the 6s5d $^3D_1 \rightarrow 6s6p \, ^1P_1$ transition in barium.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Width [V]</th>
<th>Center [V]</th>
<th>Amplitude [Counts/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>138</td>
<td>0.081(4)</td>
<td>4.75(1)</td>
<td>21500(400)</td>
</tr>
<tr>
<td>136</td>
<td>0.090(6)</td>
<td>4.90(2)</td>
<td>2150(80)</td>
</tr>
<tr>
<td>136</td>
<td>0.091(3)</td>
<td>4.75(1)</td>
<td>4070(60)</td>
</tr>
<tr>
<td>134</td>
<td>0.062(4)</td>
<td>4.95(1)</td>
<td>1340(70)</td>
</tr>
</tbody>
</table>

### Table 4.11: Measured isotope shifts between $^{137}\text{Ba}$ and $^{135}\text{Ba}$ for the 6s5d $^3D_1 \rightarrow 6s6p \, ^1P_1$ transition.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\Delta \nu$1 [MHz]</th>
<th>$\Delta \nu$2-$\Delta \nu$3 [MHz]</th>
<th>Isotope shift [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2→3/2</td>
<td>-229.3(3.3)</td>
<td>151.0(0.4)</td>
<td>-78.4(3.3)</td>
</tr>
<tr>
<td>1/2→1/2</td>
<td>-167.3(2.5)</td>
<td>97.8(0.6)</td>
<td>-69.5(2.6)</td>
</tr>
<tr>
<td>3/2→5/2</td>
<td>-143.2(2.6)</td>
<td>62.1(0.3)</td>
<td>-81.1(2.6)</td>
</tr>
<tr>
<td>3/2→3/2</td>
<td>-128.3(4.2)</td>
<td>53.8(0.4)</td>
<td>-74.4(4.2)</td>
</tr>
<tr>
<td>3/2→1/2</td>
<td>-76.2(2.2)</td>
<td>0.7(0.6)</td>
<td>-75.5(2.3)</td>
</tr>
<tr>
<td>5/2→5/2</td>
<td>-6.1(0.6)</td>
<td>-68.5(0.3)</td>
<td>-74.6(0.7)</td>
</tr>
<tr>
<td>5/2→3/2</td>
<td>1.2(1.0)</td>
<td>-76.7(0.4)</td>
<td>-75.5(1.1)</td>
</tr>
</tbody>
</table>

We determined the isotope shift of the $^3D_1 \rightarrow ^1P_1$ transition with the same method. We use the $^1S_0^\rightarrow ^3P_1 \, F = 3/2$ transition for the isotope selective population. The frequency difference is 143.3(1.4) MHz. We take one data point on the one isotope then switch the 791.3 nm laser before we change the laser frequency of the 1107.8 nm laser. The obtained spectra are shown in Fig. 4.29. The linewidth is in good agreement with the $^{138}\text{Ba}$ and $^{136}\text{Ba}$ isotope measurements. From a fit to the data we determine the isotope shift to 0.2(1) V. This converts to a shift of -93(6) MHz for this isotope pair. The ratio in abundances is 3.0(1) : 1 in good agreement with the expectation for natural barium. The appearance of both isotopes in the lower spectrum can be explained by the not perfect isotope selectivity in the population process due to the small isotope shift.

We derived the isotope shift between the $^{137}\text{Ba}$ and $^{135}\text{Ba}$ isotopes for the $^3D_1 \rightarrow ^1P_1$ transition from the measured hyperfine spectrum. For this we used hyperfine splitting frequencies from the centroid for the $^{137,135}\text{Ba}$ isotopes of the $^3D_1$ and $^1P_1$ states respectively. The difference frequencies ($\Delta \nu$1), (see Table 4.11) of...
the seven transitions from the measurement are calculated. Substituting the measured values and difference frequencies of the hyperfine splitting for both states with the relation below, the isotope shift between $^{137}$Ba and $^{135}$Ba isotopes is derived.

$$ IS = \Delta v_1 + [\Delta v_{2,137} - \Delta v_{3,135}] $$

(4.19)

where

$$ \Delta v_{2,137} = [h f s(3D_1) - h f s(1P_1)]_{137} $$

$$ \Delta v_{3,135} = [h f s(3D_1) - h f s(1P_1)]_{135} $$

We get seven values from the different components. The most sensitive ones are the components where the transitions nearly coincide in frequency ($5/2 \rightarrow 5/2$ and $5/2 \rightarrow 3/2$). These data points are less sensitive to the frequency calibration of the fiber laser. The isotope shift between $^{137}$Ba and $^{135}$Ba isotopes is $-75.3(5)$ MHz.

The isotope shifts in the $^3D_1$ state between the even barium isotope pairs and odd isotope pair derived from our measurement are summarized in Table 4.1 2. In the literature such data are analyzed using a King plot [139]. In most cases the King plot will be a straight line. The gradient of the line gives the ratio of field factors for the two transitions and the intercept is related to the difference in specific mass shifts. In Fig. 4.30 we show a King plot for the isotope shift data of the $^1S_0 - ^3P_1$ transition as abscissa and our measured isotope shift data of $^3D_1 - ^1P_1$ transition as ordinate. The values shown for each isotope pairs are the modified shifts ($\delta_M$) for the both transitions, which is given as

$$ \delta_M = \nu_{Meas} - \nu_{NMS} $$

(4.20)

where $\nu_{Meas}$ is the measured isotope shift and $\nu_{NMS}$ is the calculated normal mass shift for each isotope pair. However, there are instances of deviation from a straight line as we observe in our case. This is seen also in Samarium [140]. The deviations may be due to the effects of electron-electron correlation in two electron systems [141]. The nuclear charge radii part may not be prominent. There are no theoretical predictions to compare our results. A theoretical analysis could shed light on this issue.

### 4.8 Metastable D-state Spectroscopy

In this chapter, various techniques employed for the spectroscopy of the metastable $D$-states in barium were established. They are required for barium laser cooling experiments.
Isotope shifts: $^3D_1 - ^1P_1$ transition

<table>
<thead>
<tr>
<th>Isotope pair</th>
<th>138-136</th>
<th>136-134</th>
<th>137-135</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotope shift [MHz]</td>
<td>-71(5)</td>
<td>-93(6)</td>
<td>-75.3(0.5)</td>
</tr>
</tbody>
</table>

**Table 4.12:** Measured isotope shifts for the 6s5d $^3D_1 - 6s6p ~^1P_1$ transition in barium.

**Figure 4.30:** A King plot for the modified measured isotope shifts of the $^3D_1 - ^1P_1$ transition versus the modified shifts of the $^1S_0 - ^3P_1$ transition taken from reference [137].

We use the hyperfine structure measurements of the $^3D_1 - ^1P_1$ and $^3D_2 - ^1P_1$ transitions for the $^{137}$Ba and $^{135}$Ba isotopes for the calibration of fiber lasers. We compared the measured transition strengths and we attributed the observed deviations to the angular distribution of the fluorescence. We report the first measurement of the isotope shifts between $^{138,136}$Ba and $^{136,134}$Ba and odd $^{137,135}$Ba isotopes in the $^3D_1$ level respectively. The techniques developed for the spectroscopy of the metastable $D$-states should be applicable to radium.