Development of an Experiment for Trapping, Cooling, and Spectroscopy of Molecular Hydrogen Ions

Dissertation

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Chapter 1

Introduction

In the past few years trapping and cooling of particles has developed into one of the most exciting fields of modern physics. The fundamental work on trapping of atomic particles and on manipulating the motion of atoms, especially with light forces, has been honored with two Nobel-Prices: 1989 for Dehmelt and Paul, as well as 1997 for Chu, Phillips and Cohen-Tannoudji.

However, the past work was mainly restricted to atoms. The experiment described in this thesis transfers the accumulated knowledge on cooling of atoms to molecules. The combination of appropriate experimental methods allows one to trap and to cool molecules and to finally perform spectroscopy of cold molecules with unprecedented precision. This opens up a new field of research, which should be of interest for physics and physical chemistry and will make possible new applications in biology, medicine, and environmental research.

1.1 Quantum Metrology and Fundamental Tests of Physics

The molecular hydrogen ion as the simplest molecule at all – consisting of two nuclei and one electron facilitating the molecular binding – is outstandingly suitable for theoretical calculations which can be compared to experimental data. In addition to $\text{H}_2^+$, its isotopomers $\text{HD}^+$ and $\text{D}_2^+$ have played important roles in the development of molecular quantum mechanics. They are used for the description of many different molecular theories, methods, and approximations. The fact that only one electron exists and thus no interaction between electrons needs to be taken into account, allows the observation of other aspects in molecular structures. Thus the structure and dynamics of the molecular hydrogen ion are probably better understood than those of all other molecules.
The highly accurate spectroscopic measurement of the rotational vibrational transitions in the molecular hydrogen ion can be used for

- the metrology of fundamental constants,
- tests of time invariance of fundamental constants,
- validation of molecular theories,
- to establish a molecular frequency standard based on one of the simplest molecules.

**Metrology**

The measurement of fundamental constants is an important branch in high precision metrology and of outstanding physical interest. On the one hand it is used for the definition of standards, on the other hand the techniques developed here are often transferred to other fields of physics.

The values of fundamental constants given in this thesis are taken from the 1998 adjustment of the fundamental constants [1]. Each value and the corresponding uncertainty is deduced by consideration of several experiments and can thus not be related to a single measurement.

In the past, laser-spectroscopy has already been used successfully for precision measurements of fundamental constants. The Rydberg constant $R_\infty$ is actually the best known fundamental constant with a relative uncertainty of $7.7 \cdot 10^{-12}$. It is deduced from several experiments on the metrology of the hydrogen atom [2].

One set of fundamental constants are the masses of fundamental particles. Generally, it is only possible to measure ratios between two masses; the ratio between the mass of an electron and the proton, $m_e/m_p$, is the most fundamental and is known to a relative uncertainty of $2.1 \cdot 10^{-9}$. The most accurate value of this ratio has been measured using the cyclotron resonance frequencies in a Penning-trap [3].

One goal of our project is the first measurement of $m_e/m_p$ based on laser spectroscopy of vibrational transitions in HD$. Once theory and experiment both achieve an accuracy better than $2.1 \cdot 10^{-9}$, the spectroscopic values of the ro-vibrational transition frequencies of HD$^+$ can be used to obtain a more accurate value of the fundamental constant $m_e/m_p$.

An absolute measurement of the $m_e/m_p$ ratio by measuring the frequency of the molecular transition is not trivial. It has to be done by comparison against other optical frequency standards. The frequency difference between two vibrational levels is given by

$$\Delta \nu_{\text{vib}} = \frac{R_\infty}{c} \sqrt{\frac{m_e}{m_p}} \cdot f\left(\frac{m_e}{m_p}, \alpha, \ldots\right). \quad (1.1)$$
This expression is mainly the Born-Oppenheimer-approximation in higher order, where the function $f$ is only weakly dependent on other quantum numbers. Further improvement of theoretical calculations is required to calculate $f$ to the desired accuracy. Due to the – in terms of molecular theory – relative simplicity of the molecular hydrogen ion, highly precise (and complicated) calculations exist, which shall be significantly improved in cooperation with theorists in Moscow, Sofia and Southampton. Using the Rydberg constant given above, one can extract a new value for the mass ratio of $m_e/m_p$ from a measured value of $\Delta \nu_{\text{vib}}$ with a so far unachieved relative accuracy in the region of $10^{-10}$.

In a second step a more accurate value of $m_e/m_p$ can also be used to find a more accurate value of the fine-structure constant $\alpha$, which is given by

$$R_\infty = \frac{m_e c \alpha^2}{\hbar} \quad \rightarrow \quad \alpha = \sqrt{\frac{2 R_\infty \hbar}{c m_p m_e}}. \quad (1.2)$$

At the moment $\alpha$ is known to a relative accuracy of $3.7 \cdot 10^{-9}$, while $\hbar/m_p$ is known to $5 \cdot 10^{-7}$. Experiments with atom interferometers in Stanford and a proposed satellite experiment (HYPER) which should improve the accuracy of $\hbar/m_p$ significantly.

In addition, if a very high stability of the HD$^+$ transition frequencies can be achieved, precision measurements of physical constants can also be used for fundamental tests of physics and for validity checks of physical theories, e. g. tests of time invariance of fundamental constants. A violation of the time invariance would contradict to the principle of equivalence of the general theory of relativity. However, the theory of relativity is not complete because it lacks quantization. This justifies the tests of fundamental masses as a test of the general theory of relativity. Other theories (e. g. string theories) predict time dependencies of fundamental constants. By measuring upper limits of time variations, those theories can be validated or contradicted (more likely) and perhaps bring us a bit closer to a complete theory.

These kind of tests were already done: The fine structure constant $\alpha$ as an unitless constant provides an ideal physical quantity for a constant time variation test, independently of any possible units time variations. The currently best laboratory determination of the upper bound of the relative time dependence of $\alpha$ consists in a long time (typically several months) comparison of two frequency standards: an electronic transition and the resonance frequency of an optical cavity, which depend on the fundamental constants in a algebraic different way. The electronic transition frequency depends
on the Rydberg energy

\[ \nu_{\text{electronic}} \propto \frac{R_\infty}{c} \propto m_e c^2 \alpha^2, \quad (1.3) \]

while the resonator frequency depends on

\[ \nu_{\text{resonator}} \propto \frac{\hbar}{\text{length}} \propto \frac{\hbar}{a_0} \propto m_e c \alpha. \quad (1.4) \]

The ratio of these two frequencies is proportional to \( \alpha \), and sets an upper limit to the relative time dependence of this constant. The most accurate test so far was done by comparing a microwave-frequency of a hyperfine transition of atomic ions in a Paul trap with the hydrogen maser. The found upper limit for the time dependency of the fine-structure constant is \( |d\alpha/dt|/\alpha < 4 \cdot 10^{-14}/\text{year} \) [4]. For further improvements on this, new oscillators with higher frequency stability need to be developed.

The actual upper limit of a possibly time variance of \( m_e/m_p \) is one order of magnitude lower than the one of \( \alpha \). For the experimental setup of this test an ultra-stable oscillator can be implemented, which is stabilized on a vibrational transition (e.g. of HD\(^+\)). For comparison another oscillator has to be implemented which is based on an electronic transition. The ratio of the frequencies depends on \( m_e/m_p \) only. After consideration of systematic effects and measuring with sufficiently high accuracy, this would yield an improved upper limit on the time variance of the electron-proton mass ratio.

Alternatively, a macroscopic reference oscillator can be applied for the frequency comparison. To this end, we can rely on the knowledge on cryogenic oscillators in our group, which have about the best frequency stability in the world (in the range between 10-1000 s). In this case the time variance of the product \( \alpha \cdot \sqrt{m_e/m_p} \) is tested. However, in combination with the upper limit of \( |d\alpha/dt|/\alpha \) given above, this can be used to improve the accuracy of \( d(m_e/m_p)/dt \).

Validation of molecular calculations

More generally, very high precision measurements on molecules can provide improved tests of molecular theories like molecular quantum electrodynamics (QED) and relativistic corrections. The comparison between spectroscopic measurements and theoretical predictions as a test of molecular theories and calculation methods is of special interest. The targeted accuracies will allow a first test of radiative (QED) and relativistic corrections in molecules. Due to the complexity of the calculations, such kind of tests are preferably performed on the simplest molecule!

Molecular frequency standard

If stable long term operation of the hydrogen spectroscopy is achieved, this is of fundamental interest for the implementation of a frequency standard based on the simplest molecule.
There is also great astrophysical interest in the exact knowledge of the spectral lines of the molecular hydrogen ion. New models in astrophysics predict molecular hydrogen ions in interstellar clouds, but these could not yet be verified. The detection would be simplified if highly precise values of the transition frequencies of low vibrational levels were known. Ultimately, the precise knowledge of the density of molecular hydrogen ions in interstellar clouds would allow a verification of existing models for formation of interstellar molecules.

1.2 Overview of the Project

The homonuclear species \( \text{H}_2^+ \) and \( \text{D}_2^+ \) do not possess electric dipole moments, therefore they cannot exhibit electric-dipole allowed vibrational or rotational spectra. Only the mixed isotope species, \( \text{HD}^+ \), in which the symmetry is broken, exhibits an infrared spectrum of rotational vibrational dipole allowed transitions. Consequently, \( \text{HD}^+ \) has been selected for the experiment.

The theoretical treatment of the molecular hydrogen ion is (to a certain accuracy) much easier than its experimental investigation. Despite its high binding energy and its thermodynamic stability, it is very reactive. Experimentally, the particles need to be separated e. g. from neutral hydrogen. Studies of electronic transitions are difficult: the first exited electronic state is mainly repulsive and higher exited states are more than 11 eV above the ground level, making them hardly accessible for spectroscopy.

Fig. 1.1 schematically shows the experiment.

**Figure 1.1:** “Appetizer”. Schematic view of the experiment. \( \text{HD}^+ \) molecules are confined in a linear rf Paul trap and cooled sympathetically by laser cooled Be\(^+\). High-resolution 2-photon spectroscopy of \( \text{HD}^+ \) is proposed, which can be detected by selective photodissociation, using the ion detector.

The \( \text{HD}^+ \) molecular ions are confined in a linear rf Paul trap.
Compared to a Penning trap the linear rf Paul trap has the main advantage of not requiring any magnetic field, since such a field could be a problem for high resolution spectroscopy. Instead of a classical hyperbolic shaped trap, we will use a linear trap design. This configuration provides more trapped molecular ions in the free-field region, and thus minimizes the influence of second order Doppler shifts.

While trapping of molecular ions is straightforward, the rf motion of the ions causes them to heat up to a temperature as high as several eV, equivalent to more than 10000 K. The corresponding Doppler broadening (first and second order) precludes precise spectroscopic measurements.

It is therefore necessary to cool the particles to mK-temperatures, which we intend to achieve by sympathetic cooling. Another reason for cooling the molecules is to populate the vibrational ground state level \( v = 0 \).

Sympathetic cooling relies on the long-range Coulomb interaction between the molecular ions and the laser cooled atomic ions which are confined in the same trap.

The method of sympathetic cooling is very universal. It should allow to cool nearly any molecular ion: small molecules which are of fundamental interest for physicists as well as large molecules which might be of fundamental interest for biology or chemistry.

It is known that sympathetic cooling works best for minimum mass differences between the interacting particle species. Since HD\(^+\) has only a mass of 3 a.u., we have thus chosen Be\(^+\) as the lightest atomic ion that can be laser cooled.

The light for laser cooling of Be\(^+\) at 313 nm is produced by doubly resonant sum-frequency generation in LBO. The light from a frequency doubled Nd:YAG laser at 532 nm and from a diode laser at 760 nm is resonated in a single bow-tie cavity. The cavity is locked to the Nd:YAG laser, while the diode laser in turn is locked to the cavity. This method transfers the intrinsic high frequency stability of the Nd:YAG laser to the generated UV-light. Output powers > 2 mW are obtained with 1.4 W at 532 nm and 11.5 mW at 760 nm. The system also allows a wide continuous tunability of 16 GHz in the UV, which is required for fast and efficient cooling of the initially hot ions.

Under appropriate conditions the ions form a new state of matter in the trap: at sufficient high cooling rates the ions stop moving around each other and stay in an ordered structure. It was demonstrated, that non laser cooled atomic ions can be added to such an ion crystal (sympathetic crystalization) [5, 6].

The goal of this project is to embed for the first time a significant
number of molecular ions in a laser cooled atomic ion crystal and to cool them sympathetically. These molecules exist in an unique environment. They

- have very low kinetic energies (mK) which is transferred to their inner degrees of freedom,

- are isolated from perturbations by electric or magnetic fields: by the use of a linear radio frequency trap, we can avoid an inherent magnetic field and due to the geometry of the trap the electric field on the axes of symmetry vanishes,

- are free of collisions with walls and interactions with the residual gas can be neglected by working in an ultra-high vacuum of $10^{-10} \text{ mbar}$ or better,

- the distance to the next neighbors in an ion crystal is about 10 $\mu$m,

- the lifetime of the trap is in the region of a couple of minutes due to the high trapping potential of a few eV,

- the ions may be held in interaction with the laser beam for a long time, minimizing transit-time broadening.

- For these reasons, spectroscopy on the molecules can be performed with so far unprecedented spectral resolution ($>1:10^{10}$) which will allow for new fundamental tests of physics and the examination of new or unknown static and dynamic properties of molecules.

In combination with suitable laser sources an ultra-cold ensemble of molecules can lead to spectroscopic measurements with unprecedented spectral resolution.

To avoid the small but, despite of the cooling, still significant 1st order Doppler-broadening, we propose 2-photon spectroscopy of the $(v = 0, N = 4) - (v = 4, N = 4)$ rotational vibrational transition of HD$^+$. In comparison to saturated absorption spectroscopy, the advantage is that all the molecules contribute to the signal. The light needed for the 2-photon transition spectroscopy at 2.8 $\mu$m will be produced by an optical parametric oscillator (OPO), which is developed in other projects of our group.

A difficulty of the spectroscopy is due to the low excitation rate of approximately one per second per molecule, which is not enough to detect a fluorescence signal. In order to get a signal, selective photodissociation will be used. Owing the Franck Condon factor, the cross section depends on the wavelength of the light used for the dissociation and on the vibrational level in which the molecules originate.
1.3 State of Research

1.3.1 State of spectroscopic investigations

Several spectroscopic investigations of the molecular hydrogen ion can be found in the literature. Already in the 60ies the group of Dehmelt demonstrated alignment in Paul traps of the $\text{H}_2^+$ molecular ion in a Paul trap by selective photodissociation and spectroscopy of its radio-frequency spectrum [7].

Wing et al. reported the observation of the infrared spectrum of $\text{HD}^+$ in an ion beam in 1976. Several rovibrational transitions of the lowest vibrational energy levels were measured [8]. Complementary, in the 80ies Carrington and Buttenshaw performed vibration-rotation spectroscopy of the $\text{HD}^+$ ion near the dissociation limit [9, 10]. They used selective photodissociation in the infrared and mass selective detection of the fragments, to detect the vibrational transitions [11]. Hereby they were also able to determine the relative cross sections of photodissociation of $\text{H}_2^+$, $\text{D}_2^+$ and $\text{HD}^+$ [12].

Very recently, in February 2001, a direct measurement of a pure rotational transition in the $v = 19$ level of $\text{H}_2^+$ was reported at $14961.7 \pm 1.1$ MHz, using a modified version of a fast ion beam spectrometer [13]. Recent theory predicts significant electric dipole intensity in forbidden rotation and rotation-vibration transitions involving levels near the dissociation limit. The measurement is consistent with this value.

1.3.2 Theoretical Predictions

The hydrogen molecular ion is the simplest molecule [14], its electronic Hamiltonian is exactly soluble within the Born-Oppenheimer approximation, and its vibration-rotation energies are the most accurately calculated ones of any molecule.

The non-relativistic energies of the lower vibration-/rotation-levels are calculated with variational-algorithms to relative uncertainties of $10^{-15}$. For levels with higher energy the accuracy decreases only slightly [15].

However, already for low accuracies relativistic and QED-corrections have to be taken into account carefully. Relativistic corrections of order $\alpha^2$ of the Breit-equation were calculated [16], and lead to corrections of order of $10^{-5}$, with an uncertainty of $10^{-8}$; more accurate calculations are possible. Vertex-corrections in the order $\alpha^3$ lead to corrections in the order of $10^{-7}$ and could be calculated to $10^{-12}$. To estimate corrections in the order of $\alpha^4$ methods...
are currently being developed [17]. The physics of higher corrections is not yet worked out. Herein the theory will be challenged. In the collaborations mentioned above, progress in the calculations of the hydrogen molecular ion will be pursued.

Today, theory and experiment are in agreement to an accuracy of $10^{-6}$ for the hydrogen molecular ion. However, the last experimental data derive from the year 1976 [8] and are several orders of magnitude less accurate than actual theoretical calculations. Especially the hyperfine structure and QED-effects of the low vibrational levels could not be observed yet.

1.3.3 Trapping and Cooling of Molecules

The particles in the experiments on ion beams have kinetic energies of several thousand eV and a thermal energy distribution. The scanning of the transition frequencies is done by using a spectroscopy laser collinear with the ion beam and shifting the particles resonance frequency via the Doppler-shift, i.e., by changing their mean kinetic energy. Thus, the spectroscopic results are Doppler-broadened and -shifted, and the relative accuracy is only less better than $10^{-6}$. Even if the first order Doppler-shift is eliminated, the short interaction time of the ions with the laser beam would lead to transit time broadening of the same order.

In our project we avoid these types of broadening by trapping and cooling the particles. Furthermore, we plan to eliminate the first-order Doppler-broadening completely by performing 2-photon spectroscopy. The remaining second-order Doppler-broadening is a relativistic effect and independent of the direction of movement: it is proportional to the kinetic energy of the ions and will be seriously reduced by sympathetic cooling of the molecular ions in the trap.

Trapping of cold molecules in a magnetic trap has been demonstrated lately by Doyle et al. at Harvard [18] (→2.1). In their experiment laser ablated paramagnetic molecules are cooled by cold helium buffer gas to a temperature below 1 K and then trapped. This kind of trapping can only be applied on the certain fraction of magnetic molecules. Moreover, the magnetic trap intrinsically comes along with a strong magnetic field, which, for our goal, might harm the applicability for comparison to theory and thus for fundamental tests of the molecular physics.

In our project we use a different approach: molecular ions are stored by an electric alternating current in a rf Paul trap, first demonstrated at [19]. This leads to a stored plasma of ions with a temperature in the region of $\sim 10000$ K. The ion plasma of atomic and molecular ions can be cooled by laser cooling of the atoms and...
Introduction

Laser cooling

Laser cooling of trapped ions was first proposed 1975 by Wineland and Dehmelt [20] and experimentally demonstrated in a Paul trap in 1978 [21]. Temperatures in the sub-mK range have been observed for direct laser cooled atomic ions in Paul traps. A single atomic ion has even be cooled down to the ground state of motion of the trap potential [22].

Sympathetic cooling

The method of sympathetic cooling of atomic ions was first demonstrated by Larson et al. [23]; Baba and Waki shortly reported sympathetic cooling of molecular ions which were ionized from the residual gas and cooled to about 10 K [24].

1.4 In this Work

The fundamentals of ion trapping in a linear rf Paul trap are described in chapter 2, presenting the experimental design and set-up of the trap, the X-UHV environment and the connected peripherals. Chapter 3 reviews various possibilities of cooling; laser cooling of ions in a Paul trap, in particular laser cooling of Be$^+$, and sympathetic cooling of molecules is considered in further detail.

In chapter 4 we present a novel approach for the generation of highly frequency-stable, widely tunable, single-frequency cw UV light suitable for laser cooling of Be$^+$. Sum-frequency generation (SFG) of two solid-state sources using a single cavity resonant for both fundamental waves is employed. Using a highly stable, narrow linewidth frequency-doubled cw Nd:YAG-laser as a master laser and slaving to it the SFG cavity and the other fundamental wave from a diode laser, we generate UV radiation of $>2\text{ mW}$ output power around 313 nm. We obtain a coarse tuning range of 6 nm, a continuous tunability of 16 GHz, a sub-MHz linewidth, a frequency drift below 20 MHz/h, and stable long-term operation. The theory of doubly-resonant SFG is also given.

A detailed concept of ultra-high precision spectroscopy of the HD$^+$ molecule is worked out in chapter 5 and discussed quantitatively. The fundamentals of the molecular theory as well as the spectroscopic techniques, 2-photon spectroscopy in particular, are explained.

The experimental and conceptual work of this thesis is summarized in chapter 6. A final conclusion and a discussion of the future experimental steps is given.
Chapter 2

Trapping Particles

High resolution spectroscopy of atoms and molecules requires a cold confined ensemble of the particles of interest. This allows long interaction times and minimizes the first and second order Doppler shift.

In this chapter a short general overview of different trapping types is given at first. This should motivate our specific choice of trap, the linear radio frequency (rf) Paul trap, which is discussed in (→2.2). The last section of this chapter describes the complete experimental set-up of the trap in an ultra-high-vacuum (UHV) environment and the associated electronics.

2.1 Different Types of Traps

A large variety of neutral atoms can be trapped in magneto-optical traps and optical dipole traps. Unfortunately, those traps are limited to particles with a simple effective two-level electronic structure. In molecules these mechanisms for laser trapping and laser cooling are not applicable, due to the ro-vibrational energy level structure. The lack of a general cooling method has so far prevented trapping of most particles.

Lately cold paramagnetic particles were trapped magnetically by Doyle et al. at Harvard [18]. This type of trap (Fig. 2.1) is also being set up in a newly started project in our group at the university of Konstanz [25].

Laser ablated molecules are collisionally cooled by a buffer gas of cryogenic helium to a temperature below 1 K. They are captured in a strong magnetic quadrupole trap in a $^{3}\text{He}/^{4}\text{He}$ dilution refrigerator. The phase space density of the trapped sample can then be increased by evaporative cooling. This kind of trapping can be applied to neutral paramagnetic molecules and atoms. Proposed applications of this trap include tests of fundamental physics through

Magneto-optical and optical dipole traps

Magnetic quadrupole trap
Figure 2.1: Cryogenic magnetic trap for ultra cold atoms and molecules.

precision spectroscopy on ultracold atomic and molecular samples as well as the production of degenerate Bose and Fermi gases.

However, the spectroscopic applicability for fundamental tests is affected by the strong intrinsic magnetic field of the trap. The influence of the magnetic field leads to large uncertainties in theoretical calculations of molecular energy levels. Additionally, the set-up of a dilution refrigerator with a superconducting magnet represents a major experimental effort.

Ion traps

Charged particles in general can be trapped by electric and magnetic fields. Unfortunately, the electrostatic the Laplace-equation $\nabla^2 \Phi = 0$ (2.1) shows that there is no electrostatic field which has a potential minimum in all three dimensions of space: assume the harmonic potential

$$\Phi \propto (\alpha x^2 + \beta y^2 + \gamma z^2),$$

then the Laplace-equation (2.1) yields $\alpha + \beta + \gamma = 0$. $\alpha$, $\beta$, and $\gamma$ cannot have the same sign simultaneously. Consequently, any electrostatic field ($\neq 0$) is always attractive in at least one direction and thus cannot give electrostatic confinement in all three dimensions.

Penning trap

Nevertheless, in principle there are at least two ways of trapping charged particles. One is found by overlapping of electrostatic and magnetostatic fields, which leads to Penning traps [26, 27]. These traps can confine any kind of ions. Unfortunately, with respect to the pursued fundamental tests of physics, they bring in an intrinsic magnetic field which we like to avoid, as mentioned above.

Paul trap

In this thesis we will focus on the other possibility to trap ions, which is given by the so called Paul trap [19, 26, 27, 28]. These traps use an alternating electrical potential between two electrodes to confine the ions. To explain this dynamic trap potential Paul introduced a mechanical analog: a mechanical realization of a static
saddle potential, as shown in Fig. 2.2, fulfills Laplace’s law. Confinement of an iron ball can be achieved by rotating the saddle potential with a suitable angular frequency which depends on the particles’ mass.

**Figure 2.2:** Mechanical analog to the Paul trap: if the saddle potential is rotated with a suitable frequency, it can confine the particle in its center.

Technically, this is implemented by applying a radio frequency voltage

$$\Phi_0 = U - V \cos \Omega t \quad (2.3)$$

to their hyperbolically shaped electrodes, as shown in Fig. 2.3 (“rf trap”).

**Figure 2.3:** Typical hyperbolic Paul trap.

For usual electrode sizes with $2z_0^2 = r_0^2$ the electrostatic potential is described by a quadrupole field with $\alpha = \beta = 1$, $\gamma = -2$ (2.2), which in cylindric coordinates is given by

$$\Phi = \Phi_0 \frac{r^2 - 2z^2}{r_0^2 + 2z_0^2} \quad \text{(with } r^2 = x^2 + y^2). \quad (2.4)$$

Depending of the sign of the charge this gives confinement either in the $xy$-plane or in $z$-direction only.

If one applies a rf voltage as in (2.3), the attracting potential starts cycling between the two electrodes and one could expect that the
time averaged potential vanishes. This is true for a homogeneous field distribution. However, in the time averaged inhomogeneous quadrupole field a small mean force remains, which is directed towards the field strength minimum i.e. to the center of the trap. The equations of motion can be solved analytically [28]. They lead to stability diagrams, which show regions of stable trajectories of the particles depending on their charge/mass ratio and the applied voltages and the size of the trap.

Compared to the types of traps mentioned before, due to the absence of magnetic fields and strong coupling of ions by the Coulomb force to external electric fields, the Paul trap minimizes disturbances of the inner structure of the trapped particles. In our experiment we use a linear Paul trap, which will be described in detail in the next section. It is slightly different from the hyperbolic set-up just described, which brings in further improvements for applications dealing with ultra high resolution spectroscopy.

2.2 Trapping Ions in a Linear Paul Trap

The linear Paul trap [29] uses a combination of radio frequency and static electric potentials to create a potential which can trap any type of charged particles, including atomic ions as well as molecular ions and also macroscopic particles. The arrangement of the electrodes is shown in Fig. 2.4.

![Figure 2.4: Linear Paul trap.](image)

In comparison to the hyperbolic Paul trap described above, the linear Paul trap confines more ions at less mean kinetic energy. That is explained by the linear symmetry: while in the hyperbolic set-up there is just a single point in the trap center where the rf
field vanishes for all $t$, for the linear set-up this is the case along its whole symmetry axis (see rf heating (\(\rightarrow2.2.4\))). With respect to spectroscopy, this leads to less Doppler broadening and thus to better accuracy of spectroscopy.

In the following the physics of the rf trap are described in more detail.

2.2.1 Equation of Motion in a Two-Dimensional Quadrupole

Confinement in the $xy$-plane of the trap is produced by the rf voltage, which is applied, in opposite phases, to the two orthogonal pairs of the trap electrodes (Fig. 2.5).

![Figure 2.5: Quadrupole field in the $xy$-plane of a linear Paul trap.](image)

The resulting electric field is a two-dimensional quadrupole field, as given in (2.2), with $\alpha = 1$, $\beta = -1$, $\gamma = 0$:

\[
\Phi = \Phi_0 \frac{x^2 - y^2}{2r_0^2}.
\]

(2.5)

Now we consider an ion of mass $m$ and charge $Q$, in an rf voltage as in (2.3) is applied to the electrodes. The equations of motion in the field (2.5) are given by

\[
\ddot{x} + \frac{Q}{mr_0^2}(U - V \cos \Omega t) \, x = 0,
\]

(2.6)

\[
\ddot{y} - \frac{Q}{mr_0^2}(U - V \cos \Omega t) \, y = 0.
\]
With the definition of some handy dimensionless parameters
\[ \tau = \frac{\Omega t}{2}, \quad a = a_x = -a_y = \frac{4QU}{mr_0^2 \Omega^2}, \quad q = q_x = -q_y = \frac{2QV}{mr_0^2 \Omega^2} \] (2.7)

one rewrites the equations of motion (2.6) as
\[ \partial^2 u + (a_u - 2q_u \cos 2\tau) u = 0, \quad u = x, y, \] (2.8)

which can be identified as the generalized form of the Mathieu differential equation.

Its general solution can be written as
\[ u(\tau) = \alpha' e^{\mu \tau} \sum_{n=-\infty}^{n=\infty} C_{2n} e^{2in\tau} + \alpha'' e^{-\mu \tau} \sum_{n=-\infty}^{n=\infty} C_{2n} e^{-2in\tau}, \] (2.9)

where the constants \( \alpha' \) and \( \alpha'' \) depend on the starting conditions \( u_0, \dot{u}_0 \) and \( r_0 \), while \( C_{2n} \) as well as the characteristic coefficient \( \mu \) depend on the parameters \( a \) and \( q \) only.

The characteristic coefficient \( \mu \) determines whether the Mathieu equation gives stable or unstable solutions. A solution is called stable if the amplitude of \( u \) – which describes the particle’s trajectory – stays finite for \( \tau \to \infty \). \( \mu \) is only depended on the parameters \( a \) and \( q \), not on the initial values.

- If \( \text{Re}(\mu) \neq 0 \), one of the factors \( e^{\pm \mu \tau} \) diverges and the trajectory is unstable.
- Suppose \( \mu \) is purely imaginary: \( \mu = i\beta \). If \( \beta \) is not an integer, the results are periodic, stable trajectories. Integer \( \beta \)s set boundaries between stable and diverging solutions. In the Mathematica 4 software the characteristic values \( a \) for these even(odd) Mathieu functions of \( n \)th order and parameter \( q \) can be obtained by the functions \( a = \text{MathieuCharacteristicA}(B)[n, q] \). The resulting regions of stable parameter pairs \( (a, q) \) are shown in Fig. 2.6.

Only those pairs \( (a, q) \), for which stable trajectories in \( x \) and \( y \) dimension are found, lead to stable trapping. Experimentally the region with lowest voltages is the easiest to access. This first stability region is shown on the right-hand side of Fig. 2.6. The diagram shows that stable trapping without rf voltage (i. e. \( q = V = 0 \)) is not possible. On the other hand, if a pure rf voltage is applied (i. e. \( a = U = 0 \)) stability is given for all ions with
\[ q < q_{\text{max}} = 0.908 \] (2.10)
\[ \Leftrightarrow m > m_{\text{min}} = \frac{2QV}{0.908 r_0^2 \Omega^2}. \]
2.2 Trapping Ions in a Linear Paul Trap

Figure 2.6: Stability diagram of the ions in a linear Paul trap. Values \((a, q)\) in the gray shaded areas lead to stable trajectories in either \(x\) or \(y\) direction. For stable trapping both axes need to be stable. An enlargement of the first stability region is shown on the right-hand side.

In this case the trap works as a high-pass mass filter.

Fixed values of the voltages \(U\) and \(V\) lead to a mass independent value of \(a/q = 2U/V\). For a given ratio \(U/V\) all masses hence lie on a straight working line in the \((a, q)\)-diagram, as drawn in the right-hand side of Fig. 2.6. Only those masses with \(q_1 < q < q_2\) are trapped. By scanning \(U\) and \(V\) with fixed ratio \(U/V\) one brings in one mass after another into the stability region. This operation of the two-dimensional quadrupole is known as quadrupole mass spectrometry.

2.2.2 The Pseudopotential

In the previous section a criterion for the stability of the particles’ trajectories was deduced from the equations of motion in a 2-dimensional quadrupole field. In this section a time averaging of the quadrupole field is performed, which leads to a quantitative understanding of the trapping potential which is named pseudopotential.

To find an expression for the pseudopotential an one-dimensional motion of the ion in the applied electric potential is considered [30, 31, 32]. The potential consists of two components: a static component \(U_F(x)\) and an oscillating component \(U_f(x)\), which give rise to a static force \(F(x)\) and an oscillating force \(f(x,t)\), respectively,

\[
\begin{align*}
F(x) &= -Q \frac{dU_F(x)}{dx} \quad (2.11) \\
f(x,t) &= -Q \frac{dU_f(x,t)}{dx} = f_0(x) \cos(\Omega(t - t_0)) \, . \quad (2.12)
\end{align*}
\]
where \( x = X(t) \).

On time scales longer than \( 1/\Omega \) the particle will move in a smooth path which is the secular motion \( S(t) \). The force \( f(x, t) \) adds an oscillation at the frequency \( \Omega \) to the path \( S(t) \) which is named micromotion \( M(S, t) \). The trajectory of the particle is thus given by

\[
X(t) = S(t) + M(S, t). \tag{2.13}
\]

Assume that the amplitude of the micromotion is small compared to the amplitude of the secular motion \( S \gg M \), while the velocity of the micromotion is fast compared to the velocity of the secular motion \( \dot{S} \ll \dot{M} \). \( M \) can then be considered as perturbation to \( S \), and the equation of motion

\[
m\ddot{X} = F(X) + f(X, t) \tag{2.14}
\]

can be expanded in \( M \) around the path described by \( S \)

\[
m\left( \dot{S} + \dot{M} \right) = F(S) + f(S, t) + \]

\[
M \partial_x (F(x) + f(x, t)) \bigg|_{x=S} + \]

\[
\frac{1}{2} M^2 \partial^2_x (F(x) + f(x, t)) \bigg|_{x=S} + \]

\[\mathcal{O}(M^3).\]

Using only the first order in \( M \) and assuming that the large and rapidly oscillating terms on each side are dominating and therefore approximately equal, we obtain

\[
m\ddot{M} \approx f(S, t), \tag{2.16}\]

which can be integrated by using \( f(x, t) \) from (2.12)

\[
M(S, t) \approx \frac{1}{m\Omega^2} f_0(S) \cos (\Omega (t - t_0) + \pi). \tag{2.17}\]

The micromotion \( M \) is oscillatory with the frequency of the force \( f \), but with a phase difference of \( \pi \), and an amplitude depending on the coordinate of the secular motion.

**Energy of the micromotion**

The mean kinetic energy of the micromotion becomes

\[
\overline{K}_{\text{micro}}(x) = \frac{f_0^2(S)}{4m\Omega^2}. \tag{2.18}\]

An expression for the slow secular motion \( S(t) \) is found by averaging first order of (2.15) over one period \( T = 2\pi/\Omega \) of the micromotion. The fast oscillating terms containing \( M, \dot{M}, \) and \( f \) disappear, except for \( M \partial_x f(x, t) \big|_{x=S} \) which contains a \( \cos^2 \):

\[
m\ddot{S} = F(S) + \frac{1}{T} \int_0^T M \partial_x f(x, t) \big|_{x=S} \, dt. \tag{2.19}\]
2.2 Trapping Ions in a Linear Paul Trap

Using $f$ and $M$ from (2.12) and (2.17) this results in

$$m \dot{S} = F(S) - \frac{1}{2m\Omega^2} f_0(x) \partial_x f_0(x) \bigg|_{x=S},$$

(2.20)

which, expressed in the potentials defined in (2.11) and (2.12), can be written as

$$m \ddot{S} = -\partial_x \left( QU_F(x) + \frac{Q^2}{4m\Omega^2} \left( \partial_x U_f(x) \right)^2 \right) \bigg|_{x=S}.$$  (2.21)

This equation shows that the particle – when time averaged over the fast oscillations – in addition to the assumed static potential $U_F$ feels another quasi-static potential raised by $U_f$, which is the so called pseudopotential

$$\Psi(x) = \frac{Q^2}{4m\Omega^2} \left( \partial_x U_f(x) \right)^2.$$  (2.22)

Because of the quadratic dependence on both $Q$ and the potential derivative, the pseudopotential will repel the particle from regions with high amplitudes of the oscillatory field, independent of the sign of the particles’ charge:

The ion in an oscillating field is a low field seeker.

We note that the pseudopotential is also equal to the mean kinetic energy in the micromotion given in (2.18).

With the definition of the pseudopotential the secular potential can be written as

$$\Psi_{sec}(x) = QU_F(x) + \Psi(x).$$  (2.23)

The derived potentials (2.22) and (2.23) can be easily generalized to three dimensions.

The time dependent electric potential of the two-dimensional quadrupole field in our trap (Fig. 2.5) is given by

$$\Phi(x, y, t) = \frac{V}{2r_0^2} \left( x^2 - y^2 \right) \cos(\Omega t).$$  (2.24)

With (2.22) the corresponding pseudopotential of the two-dimensional quadrupole field yields

$$\Psi(x, y) = \frac{Q^2 V^2}{4m\Omega^2 r_0^4} (x^2 + y^2).$$  (2.25)

A trapped ion will be lost if it reaches the electrodes, so the the pseudopotential depth is

$$\Psi_0 = \Psi(r_0) = \frac{Q^2 V^2}{4m\Omega^2 r_0^4} = \frac{QV}{8} q.$$  (2.26)
Resulting secular potential of the quadrupole field

The secular potential of the two-dimensional quadrupole field, which in addition to the pseudopotential takes also the electrostatic potential $U$ into account, is given by

$$\Psi_{\text{sec}}(x, y) = \frac{Q^2V^2}{4m\Omega^2r_0^4}(x^2 + y^2) + \frac{QU}{2r_0^2}(x^2 - y^2), \quad (2.27)$$

with in $x$ and $y$ direction different secular potential depths of

$$\Psi_{\text{sec},0} = \frac{Q^2V^2}{4m\Omega^2r_0^4} \pm \frac{QU}{2}. \quad (2.28)$$

Finally we find a secular oscillation frequency

$$\omega_{\text{sec}} = \sqrt{\frac{2\Psi_{\text{sec},0}}{mr_0^2}} = \sqrt{\frac{Q^2V^2}{2m^2\Omega^2r_0^2} \pm \frac{QU}{mr_0^2}} = \frac{\Omega}{2}\sqrt{\frac{q^2}{2} \pm a}. \quad (2.29)$$

In this section the potential in the $xy$-plane of the trap was considered. To achieve confinement in all dimensions a trapping force in the $z$ direction of the trap needs to be added which is discussed in the following section.

### 2.2.3 Longitudinal Confinement

Confinement of the ions in $z$ direction can be achieved by electrostatic fields. To this end, the potential at both ends has to be raised by a certain amount compared to the potential in the center of the trap. Different electrode setups (pin electrodes on the axis, ring electrodes, etc.) have been demonstrated [33]; to provide best optical access – especially along the axis of the trap – we decided to use a set-up with galvanically separated endcap electrodes. Therefore each of the four electrode rods is divided into three electrically isolated segments. If an electrostatic potential of $\Phi_{\text{ec},0}$ is applied to the eight endcap electrodes a static trapping potential as shown Fig. 2.7 is achieved.
2.2 Trapping Ions in a Linear Paul Trap

The electric field distribution was simulated with finite elements using the Simion 6 software. We find that the longitudinal potential for our specific trap dimensions (which are discussed in section 2.3) has steep walls (compared to the trap length). While the potential on the axis in the endcap region reaches approximately $\Phi_{ec,0}$ it drops rapidly down to a nearly flat potential of 0 in the center region. The motion of the ions in longitudinal direction can rather be considered as motion between hard walls than motion in a harmonic potential. The trap depth in longitudinal direction is $Q\Phi_{ec,0}$.

However, the electric field of the endcap electrodes has also components in the $xy$ direction which have to be considered with respect to the secular potential. The field caused by the endcap electrodes in the center region of the trap is plotted in Fig. 2.8.

We find that the influence of the endcap electrodes is greatly suppressed, even though there is a small potential variance among different radial directions (e.g. $x$ and $xy$). For different trap set-ups (i.e. those with shorter center electrodes [32]) this influence has to be taken into account in the secular potential (2.27) such as the static voltage $U$. In our case the endcap potential does not influence the motion in the $xy$ plane of the trap significantly.

Before the dimensions and voltages of the trap will be discussed, in the next section an intrinsic rf trap heating mechanism needs to be mentioned.

### 2.2.4 Radiofrequency (rf) Heating

A heating mechanism called *rf heating* occurs, when ion–ion or ion–residual-gas collisions happen in trapping regions of strong rf field.
The collisions mainly transfer kinetic energy from the micromotion (i.e. energy of the rf field) to the secular motion of the other particle. This brings the ions out of phase with the rf field, the energy cannot be given back to the rf field, but new micromotion energy will be gained from the field. In this sense the ions are heated up by the rf field.

If more than one ion are trapped, the Coloumb interaction will couple the individual ion motions and the space charge effects will change the potentials in the trap. The coupling is strongly dependent on the trap parameters and ion temperature as well as the number of trapped ions. The dynamics of a closely coupled ion plasma in the trap is highly non-linear. Due to the fast rf frequency on the one hand and the long range coulomb interaction on the other hand computer simulations are extremely time consuming and restricted to only a few particles.

In a linear Paul trap the rf field along the \( z \)-axis vanishes and so does the micromotion (2.18). Ions which move far off the \( z \)-axis gain a considerable kinetic energy due to the micromotion. One advantage of the linear trap design is that the trapping space with low rf field is spread along the \( z \) axis instead of a single point in space for the hyperbolic trap design. For this reason the linear Paul trap can store more ions at less kinetic energy. Therefore the mean second order Doppler broadening in a linear trap of length \( L \) compared to that in a hyperbolic trap of characteristic size \( R \) is reduced by a factor [34]

\[
\frac{5R}{3L} \ll 1 .
\]  

(2.30)
Since the rf heating increases with the distance from the trap axis, the heating effect is stronger for particles far off the axis. Particles will be lost if they are heated above the trap depth. Thus the rf heating limits the maximum extension of the ion cloud in transverse direction.

By the rf heating and due to Coulomb coupling of the ions motions the cloud is heated up to a temperature in the order of the trap depth. These energies of typically a few eV correspond to ion temperatures in the order of 10,000 K. A quantitative description of the energy distribution in the trap requires complicated models of interacting particles as described in [35], or a description of the brownian motion in the ion cloud [36, 37, 38], or a quantum motion description as in [39].

With respect to the spectroscopy, the Doppler broadening needs to be reduced in an efficient way by a cooling mechanism. Before the cooling mechanism is discussed in chapter 3 the following sections in this chapter explain the experimental set-up of the trap in detail.

### 2.3 Experimental Set-up of a Linear Paul Trap

In this section the experimental set-up of the trap, the UHV environment, the trap electronics, the sources for the atoms and molecules, the devices for detection, and lots of auxiliary components are described in detail.

#### 2.3.1 The UHV Environment and Components

The experiment takes place in an UHV environment. The complete set-up consisting of a vacuum chamber, connected pumps, residual gas analyzer, and mounting to the optical table was designed using CAD and is shown in Fig. 2.9.

The vacuum system is designed to achieve extreme ultra-high-vacuum (XUHV) in the $10^{-11}$ mbar region or below. This is especially important since we trap light particles like HD$^+$ or Be$^+$, which are typically lost after a single collision. The interaction of the trapped particles with the residual gas then drops to below 1 per 100 s. Disturbances on this time-scale will neither affect the particles lifetime in the trap nor the precision of high resolution spectroscopy.

The chamber was custom made by Vacuum Generators according to our specifications. Detailed drawings of the chamber are given in Fig. 2.10.
Figure 2.9: CAD designed UHV set-up. The chamber is drawn grey, the pumps and valves blue, the optical table violet, the holder red, elastic parts cyan, the residual gas analyzer pink.

UHV Chamber

The main body of the chamber consists of a 200 mm diameter, 486 mm long tube. After fabrication the chamber was heat treated at 850° for 1 hour to reduce the hydrogen concentration in the stainless steel (316LN, 316L, \( \mu_r < 1.005 \)) and leak checked to be better than \( 1 \cdot 10^{-10} \) mbar/ls. The inner walls of the chamber are mechanically polished.

The chamber is mounted on a holder in a position that the main operating plane of the chamber is 75 mm above the level of the optical table, which is the general beam height of the whole optical set-up. Sand is used to fill the steel carriers of the mount to damp vibrations. The vacuum set-up of the trap is hung down from the
2.3 Experimental Set-up of a Linear Paul Trap

Figure 2.10: CAD Drawing of the UHV Chamber according to our specifications by Vacuum Generators. All dimensions in mm.

DN200CF top flange. The electronic feedthroughs connecting the trap electrodes are also inserted in the top flange, so the trap set-up can be taken out in one piece for assembly. It will be described in more detail in (→2.3.2).

The chamber design includes many flanges. In the operating plane optical access is possible every 45°. Two orthogonal axes have large DN100CF flanges on short ports providing a large access angle, e. g. for detection. Several other axes are provided for future experimental set-ups. Components such as ion gauges, the electron gun, leak valves, etc. can be attached to any of the DN40CF flanges. For ease of use the chamber has tapped flanges and silver-plated screws.

Two pumps are connected to the chamber from below the table. The DN200CF bottom flange is adapted to an ion pump which has an integrated titanium sublimation pump (type Varian, VactIon Plus 300, noble diode, the nominal pumping speed of the ion pump is 260 l/s without titanium sublimation). Due to the weight of the pump, the pump sits on suspension elements mounted on an adjustable plate.

A small turbo molecular pump (type Varian, V70LP, the nominal speed is 600 l/s).

---

1Technical remark: on the M8 screws, a torque of 25 Nm is applied. On the M6 screws, the torque should be 13 Nm. However, if a tap should ever be damaged beyond, there is clearance to put a nut between the flange and the wall of the chamber...
pumping speed is 70 l/s) is attached to a DN63CF flange via an all-metal right angle valve, in series with a membrane pump. Pumping is started by the turbo- and membrane-pump. When the pressure drops below $10^{-5}$ mbar the ion pump can be started. Due to the finite compression ratio of the turbo-pump the right angle valve needs to be closed when the pressure drops below $10^{-8}$ mbar.

With a clean UHV set-up and if the chamber was carefully vented with nitrogen, the chamber can be pumped down to the low $10^{-11}$ mK-region within half a day. The UHV system is designed for a bakeout temperature of at least 300°C, except for the flange of the turbo pump that needs to be cooled to stay below a temperature of 120°C, and the electronics of the residual gas analyser, which have a maximum temperature of 70°C.

**Bakeout temperatures**

**Vacuum analysis**

For vacuum analysis a pressure gauge (type Varian, UHV-24p) using controller of type Granville-Phillips 350) is attached. Due to the small shape of this ion gauge it has a low x-ray limit of $6 \cdot 10^{-12}$ mbar. Furthermore a residual gas analyzer (type Vacuum Generators, Smart IQ+100D) is attached. It is used for more detailed vacuum analysis, leak checking, and to control the bakeout procedure.

**Leak valve**

An all-metal leak valve (type Vacuum generators, ZVLM263R) is attached for defined gas inlet, e.g. HD. It allows reproducible leak rates down to $1 \cdot 10^{-11}$ mbar l/s and can be used as inlet for molecules in gas phase (e.g. H$_2$, HD) as well as for buffer gas inlet of He to cool the ions in the trap. If sympathetic cooling is performed, the molecules are added to a laser-cooled atomic ion cloud in the trap. This process requires low partial pressure and low leak rates in order to avoid destruction of the trapped ion cloud. Further details about cooling in the trap are given in chapter 3. Since recently, a motorized version of the leak valve is available. As soon as loading of the trap becomes computer controlled, the valve should be replaced with the motor driven version.

**Peripherals**

When peripheral components are (re-)attached to the chamber, it is often necessary to pump away the air inclusions in the connecting volume before opening a valve to main chamber. Therefore two auxiliary valves (type Nupro) are provided on a welding flange, which is inserted between the right angle valve to the chamber and the turbo pump. If the turbo pump is disconnected from the chamber with the right angle valve, it can be used to pump out other volumes via the two auxiliary valves without disassembling.

**Viewports**

The window material of the viewports has to be chosen with respect of the light to be transmitted. The cooling light at a wavelength of 313 nm requires fused silica (suprasil) windows. If a spectroscopy laser is added (1.4 µm or 2.8 µm) they need to be replaced with sapphire windows. However, for the beginning of the experiment
and the work presented in this thesis, we have installed less expensive suprasil windows (type MDC, AR coating from Ferroperm), which have an additional advantage of no birefringence compared to sapphire. Other window materials (e. g. fluoride) are only barely suitable for use in UHV, because their thermal expansion coefficient is very different compared to the one of the steel housing, and thus restricts the bakeout to low temperatures and very slow temperature changes.

2.3.2 Set-up of the Trap

To reach the goal of high resolution spectroscopy of molecular ions the linear rf trap should fulfill the following requirements.

- Trap a large number of ions to increase the spectroscopy signal to noise ratio.
- Cool the ions to temperatures down to the 1 Kelvin region or below to reduce the second order Doppler shift sufficiently.
- Allow good optical access to the particles in axial direction for the cooling and spectroscopy laser beams as well as in transverse direction for fluorescence imaging of the laser-cooled ion cloud.
- Provide a quadrupole field with sufficient precision.
- Trap atomic masses 1-9 at a moderate rf voltage and frequency.
- Use XUHV compatible construction and materials for the trap.

The trap designed and built up in this work matches all these requirements and is photographed in Fig. 2.11.

Construction, Dimensions, and Parameters

There is a large number of applications for ion traps and a similarly large variety of trap designs [40]. The dimensions of existing quadrupole traps are quite diverse: there are miniature quadrupole traps which trap single or only a few ions which have a very strong trapping potential and a characteristic size of 100 μm [41], there are traps with diameters of several centimeters [26, 42].

A large trapping region is required to trap many ions. Luckily, a large trap also simplifies the optical access into the trap and
Figure 2.11: Experimental set-up of the linear Paul trap. The trap electrodes are made of oxygen free copper, isolated with Macor™ spacers and finally mounted within two stainless steel side plates. The trap is situated on a big base plate which is mounted on the top flange of the chamber (all stainless steel, V4A). The electron multiplier (→ 2.5.2) also comes into view above the trap.

Construction of the linear Paul trap

The trap consists of four electrode rods having a round cross-section. Each rod is divided into three galvanically separated segments (→ 2.2.3). The electrodes are mounted between stainless steel side plates, which have slits to allow optical access along the trap's z-axis. The trap set-up is placed on a base plate which is clamped to four rods mounted on the top flange of the chamber. The base plate (140x92 mm without clamps, outer trap dimensions 77x40 mm) allows the mounting of additional optics, the beryllium source (Be⁺ will be used as laser-cooled species), and other components.

The chosen dimensions and parameters of our trap are given in Tab. 2.1. Fig. 2.12 shows the first stability regions and the pseudopotential trap depths for the relevant particles at the given parameters.

<table>
<thead>
<tr>
<th>trap size</th>
<th>trap parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_0$</td>
<td>$Ω$</td>
</tr>
<tr>
<td>4.32 mm</td>
<td>$2π \cdot 6.25$ MHz</td>
</tr>
<tr>
<td>$2r'$</td>
<td>$V$</td>
</tr>
<tr>
<td>9.9 mm</td>
<td>600 V</td>
</tr>
<tr>
<td>$L$</td>
<td>$U$</td>
</tr>
<tr>
<td>40.0 mm</td>
<td>0 V</td>
</tr>
<tr>
<td>$L_{cc}$</td>
<td>$Φ_{cc,0}$</td>
</tr>
<tr>
<td>13.0 mm</td>
<td>5 V</td>
</tr>
</tbody>
</table>

Table 2.1: Sizes and parameters of the linear rf trap (see also Fig. 2.4) The values given here are also valid for all other plots and calculations in this work unless otherwise noted. **Left:** Most important sizes. **Right:** Typical electrical voltages.

Construction of the trap’s electrodes

The electrode rods consist of many parts, the technical drawing of
2.3 Experimental Set-up of a Linear Paul Trap

![Diagram showing stability regions and pseudopotential trap depths for relevant particles and parameters.](image)

**Figure 2.12:** First stability regions and pseudopotential trap depths for the relevant particles and for the parameters as given in Tab. 2.1. The approximation of the pseudopotential depth (2.26) is not valid for high \( q \) values near the boundary of the stability region and thus has to be treated carefully.

A single rod is shown in Fig. 2.13. Technical details of the construction were taken over from a linear rf trap which is used in the group of Prof. Werth in Mainz, working with calcium ions [43]. The design of this trap was originally developed in Japan [44]. However, sizes, proportions, mounting, etc. were adjusted to match our specifications.

To avoid virtual leaks, all elements have little holes on their backsides or extra space left open on their fittings.

The electrodes are made of oxygen free copper electrodes, which is XUHV compatible and a good conductor. However, during assembly in air atmosphere, the electrodes seemed to adopt an oxide layer changing their color slightly. Although this effect disappeared after bakeout, we currently prepare a new set of gold plated electrodes out of polished stainless steel. A clean, polished surface of the electrodes is very important to avoid field disturbances due to roughness or due to electrostatic charges on the electrodes that would lead to increased rf heating.

For the same reason the construction of the electrode rods uses overlapping electrode segments. This makes sure that no electrostatic charge on the isolators influences the trapping region. The isolation rings are made of Macor™ and slide on a stainless steel rod which serves as inner carrier of the construction.

Round cross-section of the trap electrodes leads to deviations from an ideal quadrupole field, which in turn cause an inhomogeneous secular potential that increases the heating effects and the loss rate of the trap, but hyperbolic electrodes are technically not feasible and would affect the transverse optical access to the trap. The

---

Round cross-section of the electrodes
Figure 2.13: Technical drawing of the construction of the electrode rods, some detailed views, and the left side plate for the mounting of the four electrode rods. All dimensions are in mm.

Round electrodes we use in our trap have an optimized ratio between electrode diameter and electrode distances of \( r'/r_0 = 1.1468 \) [45] (see also Fig. 2.4, and Fig. 2.5). This is obtained by expanding the electrical field near the axis and choosing the ratio \( r'/r_0 \) so, that the next term after the quadrupole term (12-pole) vanishes.

We estimate that the given trap should confine about \( 10^4 \) ions.

### 2.3.3 Electrical Power Supplies to Drive the Trap

The operating parameter region of the rf voltages is about

\[
\Omega/2\pi = 3 \ldots 12 \text{ MHz}, \quad V = 0 \ldots 1000 \text{ V}, \quad U = 0 \ldots 200 \text{ V}.
\]

Fig. 2.14 shows the wiring of the required electrical components.

**RF power supply** The rf signal is generated using a function generator (type SRS),
and amplified in a 15 W rf power amplifier (from Amplifier Research). This signal is resonantly enhanced in a transformer. The choice of the diameter and number of windings of the coils determine the resonance frequency and amplitude of the circuit. For the circuit resonant at $\Omega = 2\pi \cdot 6.25$ MHz, we use 3 windings having a diameter of 12 mm on the primary side, and 170 windings at a diameter of 10 mm on the secondary side. The coil length is 140 mm. We achieved a maximum rf amplitude of about $V = 600$ V.

The coil and the printed circuit (pc) board are located in a copper housing to keep the rf radiation away from other sensitive instruments in the lab (additionally chokes and ferrite rings were required to conserve sensitive signals). On the pc-board the dc- and rf voltages are added in bias-tee like circuits. Additional reduction of stray fields and capacitances is also achieved by the center symmetric design of the pc-board, which has a grounded plane on its backside. The copper box is mounted directly above the vacuum feedthroughs to reduce capacitances associated with cable lengths.

Other resonance frequencies can be obtained by changing the coils’ length, diameter and number of windings. High rf voltages requiring a resonant enhancement of the rf voltage is desired e. g. to be able to purge other ions except of $\text{Be}^+$ of the trap. For the resonant setup the only remaining free experimental parameter is the rf amplitude, not the rf frequency which is fixed to the circuit’s resonance.
Radiation and capacitances complicate the measurement of the rf voltage applied to the electrodes. We installed two shielded rf voltage dividers directly on the pc-board in the copper housing as indicated on position M1 and M2 in Fig. 2.14. Their readout has the following calibration: 1 V on the oscilloscope gives 208 V on M1 and 602 V on M2, respectively; the differences arise due to different cable length and adjustable capacitances.

**DC power supply**

The dc power supply allows individual correction of each electrode by ±10 V. This permits, on one hand the setting of the endcap potential $\Phi_{ec,0}$, and on the other hand the compensation of field imperfections due to electrostatic charges or contact potentials on the electrode surfaces. Those occur due to the strong electron flux of the electron gun (→2.4) and due to oxide layers or Be particles on the electrodes’ surfaces. In addition the dc voltage $U = 0 \ldots 200$ V can be added symmetrically to increase the potential of the one half of electrodes by $U/2$ and lower the other half by $-U/2$. This makes another parameter available for mass selective trapping (Fig. 2.12).

Fig. 2.15 shows a computer simulation of a single particle in our trap, to give an impression of the ion’s motion in the trap.

![Figure 2.15: Simulation of the rf trap with dimensions and voltages as given in the text.](image)

The simulation was done with the computer software *Simion*. However, at the present state of computer performance, the fast rf voltage and the complex dynamics in an ion cloud do not allow simulations of a whole cloud on a sensible time scale.

### 2.4 Loading Ions into the Trap

Due to the high trap depth of a Paul trap compared to optical, magnetical, and magneto-optical traps, loading of a Paul trap does not require pre-cooling of the particles. The trap depth of the order of 10000 K is usually much higher than the kinetic energy of the generated ions. However, the strong rf potentials of the trap
2.4 Loading Ions into the Trap

Electrodes also prevent ions to be introduced into the trap from outside. To load the trap the ions need to be produced in the trapping region via ionization of the corresponding neutral particle species.

On one hand this requires an efficient ionization process in the trapping region. This can be provided by electron impact ionization, which is described in section 2.4.1, or by photo-ionization. On the other hand it requires particle sources which provide sufficiently high neutral particle densities in the trapping region. For the inlet of gases (e.g., HD) a leak valve is connected to the chamber as already described in section 2.3. The partial pressure of the gas in the chamber will determine the loading rate. The solid-state particles like beryllium, which are to be laser-cooled and then sympathetically cool the molecular ions, need a somewhat more advanced source. This is described in section 2.4.2 and following.

2.4.1 Electron Gun

The ions are generated by electron impact ionization of the neutral particles’ species. Therefore an electron gun (Kimball, type Electron-Flood-Gun-8) is attached to the chamber. The electron beam crosses the trap diagonally, orthogonal to the beam of the evaporated beryllium particles which runs along the other diagonal. A schematic view of this operating plane in the UHV chamber is shown in Fig. 2.16.

Fig. 2.17 shows the power supply that was developed to provide the required voltages for acceleration and shaping of the electron beam.

The gun can produce electrons with energies between 50 and 1500 eV. The typical current of the electron beam is about 100 \(\mu\)A with a diameter of a few mm. The functionality of the gun can be checked by watching the fluorescence light of a phosphor plate placed in beam on the opposite side of the trap. More detailed characteristics of the electron beam are found in the manual.

2.4.2 Beryllium Source

A stream of neutral beryllium atoms is produced by evaporation of a beryllium wire. Beryllium has a melting point of 1278°C and is rather brittle in solid state. It is found by the estimation presented below that temperatures of at least 900°C are required to achieve a sufficiently high particle flux. Direct heating of a single thin beryllium by electric current failed, since the wire is not robust enough. Therefore an electrically heated tungsten wire is used as
Figure 2.16: Horizontal cross-section of the experimental UHV set-up.

Figure 2.17: Wiring diagram of the electron gun and the corresponding power supply.

carrier, around which the beryllium is wrapped [46]. The data of this kind of atom source for beryllium are in Tab. 2.2.

For fabrication, we attach the ends of the beryllium and the tungsten wire to each other. Then we slowly start rotating the tungsten wire, while the Beryllium wire is heated with a heat gun. The beryllium wire wraps around the tungsten wire with a covering ratio of about 50%. Finally, one piece of the wrapped wire of about 5 mm length is clamped to two connectors (for the electrical heating) which in turn are fixed in the backside (Macor™) of a stainless
2.4 Loading Ions into the Trap

<table>
<thead>
<tr>
<th>Beryllium Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>diameter of the beryllium wire</td>
</tr>
<tr>
<td>diameter of the tungsten wire</td>
</tr>
<tr>
<td>length of the wrapped tungsten</td>
</tr>
<tr>
<td>distance oven – center of trap</td>
</tr>
<tr>
<td>covering ratio of the wire surface</td>
</tr>
</tbody>
</table>

*Table 2.2: Data of the beryllium source.*

Steel housing. The housing serves as shielding to prevent the evaporated beryllium from contaminating the whole chamber, and has a small aperture (shaped as a nozzle with a rectangular cross-section) pointing to the trap center. It can be seen in the left-hand part of Fig. 2.18.

Figure 2.18: Left: Final experimental set-up of the UHV inlet, containing the trap, with 12 silver wires leading to the electrodes, the beryllium source diagonal before the trap and the phosphor plate right diagonal behind the trap, and a shielded electron multiplier on top of the trap, Right: UHV chamber with the rf trap electronics in a copper shielding on top, a CCD camera on the right of the chamber, and some optics on the table around the chamber.

To estimate the particles’ flux we consider the vapor pressure of beryllium [47]. The equilibrium vapor pressure in a closed cavity at a given temperature is given by

\[ 0 = \dot{N} = \dot{N}_{\text{evaporate}} - \dot{N}_{\text{stick}} = A \kappa - A \frac{N}{V} \langle v \rangle s, \]

where \( \kappa \) the number of evaporated particles per surface area and time, \( N \) the number of particles, \( V \) the volume of the cavity, \( A \) the surface of the surrounding walls, \( s \approx 0.1 \) is the probability
that a particle hitting the wall gets stuck again, \( \langle v \rangle = \sqrt{\frac{2kT}{\pi m}} \) is the mean velocity of the particles in one direction (Gaussian energy distribution).

Using the ideal gas equation \( pV = NkT \) with (2.31) we find

\[
\kappa = p \cdot s \cdot \sqrt{\frac{1}{2kTm\pi}}. \tag{2.32}
\]

To predict the loading rate into the trap, we have a closer look at the ionization process in the following paragraph.

### 2.4.3 Loading Rate for Be\(^+\)

The loading rate of beryllium atoms into the trap is calculated as

\[
\dot{N}_{\text{load}} = N_{\text{Be}}(T) \cdot \dot{n}_e \cdot \sigma, \tag{2.33}
\]

where \( N_{\text{Be}}(T) \) is the number of beryllium atoms in the loading region, \( \dot{n}_e \) the number of electrons per area and time crossing the region and \( \sigma \) the cross-section of electron impact ionization. The loading region is the volume where conditions for ionization and trapping are present simultaneously, which we estimate to be 18 \( \times \) 1 \( \times \) 1 mm.

The cross-section of electron impact ionization of beryllium can be found in [48]. Although the maximum cross-section is given at electron energies of about 50 eV with \( \sigma \approx 46 \cdot 10^{-18} \text{ cm}^2 \), we work at electron energies of about 1 keV and \( \sigma \approx 12 \cdot 10^{-18} \text{ cm}^2 \). Lower energy electrons are strongly influenced by the rf field of the trap and mostly do not reach the loading region. However, observation of the electron beam on the phosphor screen shows that even the 1 kV electron beam gets diffused by the rf field after passing the trap. For a safe estimation, from the observation of the fluorescence on a phosphor, we assume that only 1% of the total electron gun’s flux is passing the trap at the correct location.

Taking all the data of the set-up given above, we find the loading rate as plotted in Fig. 2.19.

From the plot we see that temperatures of at least 900 °C are required to achieve acceptable loading times for a number of at least \( 10^3 \ldots 10^4 \) beryllium ions. These temperatures are reached when the wire, watched with a bare eye, glows in a red color. This is achieved at a heating current of about 1.5 A. The switching time of the beryllium source is on a scale of 1 s. The functionality of the source was also proven by “coating” a glass plate in front of the source with beryllium. Under normal operating condition the evaporative consumption of the beryllium wire can be neglected and the set-up seems to be quite robust: there is no experimental data of the wire lifetime yet!
2.5 Detection of the Trapped Particles

The detection of the ions has many purposes: it can provide information about which ion species and the number of ions is trapped, and about the shape and dynamics of the ion cloud.

The goal of the proposed experiment is the spectroscopy of sympathetically cooled molecules.

The detection should allow the characterization of the ion cloud containing laser-cooled beryllium ions and sympathetically cooled molecular ions. We expect to confine up to $10^5$ ions in the trap, including a fraction of at least some percent (→3.3) of sympathetically cooled ions. With sufficiently strong laser cooling (Chap. 3), the ions will stay in an ordered structure called an ion crystal, in which the sympathetically cooled ions appear as dark spots in the structure.

A promising way to detect the low excitation rates with high sensitivity in molecular spectroscopy of $\approx 1/s$ (→5.2.2), is the detection by selective photodissociation, i.e. the mass-selective detection of the fragments. This kind of detection can be performed using an ion multiplier and driving the trap as mass spectrometer (→2.5.2).

The following sections describe the different detection methods and their applicability to our requirements. In chapter 3 of this thesis the cooling process is discussed. The spectroscopy of molecules is considered in chapter 5.

2.5.1 Fluorescence Detection with a CCD Camera

Using a CCD camera, fluorescence detection of laser-cooled ions yields the measurement of the total number of ions in the trap.

**Figure 2.19:** Loading rate of beryllium into the trap by electron impact ionization.
as well as the observation of the dynamics in the ion cloud. Furthermore, if the ions are cooled down and remain in an ordered structure, the scattering rate of an atomic dipole transition usually allows even single ions to be recorded.

As already shown in Fig. 2.16 and on the right-hand side of Fig. 2.18 a CCD camera (PCO, type Sensicam) is placed in a transverse direction to the trap. Two different lens set-ups (Fig. 2.20) provide a full view of the cloud for measuring the number of ions and a detailed view for resolving single ions.

![Imaging with the CCD camera.](image)

Figure 2.20: Imaging with the CCD camera.

The peltier-cooled CCD chip provides VGA resolution (640(H) × 480(V) pixels) and has a size of 6.336 mm × 4.752 mm with a pixel size of 9.9 µm × 9.9 µm. The dynamic range of the camera is 12 bits, and the dark count rate is 0.1 e−/s-pixel. Additional features of the camera are external asynchronous triggering, pixel binning (for better signal/noise ratio), an internal memory in the camera to store a series from 10 to 100 images (depending on the recorded image size), and the unique feature that the glass covering of the CCD chip is left off so that there’s is still a significant quantum efficiency to detect UV light (Fig. 2.21).

![Quantum efficiency of the CCD camera.](image)

Figure 2.21: Quantum efficiency of the CCD camera.
The UV quantum efficiency is of interest since the laser cooling transition of the beryllium ion is at 313 nm. The transition has a linewidth of $\gamma/2\pi = 19.4$ MHz. More details on this are given (→3.2.2). However, the glass usually used for camera objectives (and CCD coatings) absorbs wavelength below 350 nm (e.g., BK7). There are only a few high-cost commercial quartz-glass objectives available. For our purpose, we can use a comparably low-cost achromatic triplet lens system (type special optics, 54-17-29), once in front of the camera with a self designed mount for focusing, and second, as an option, as a collimation lens in the UHV. The fabrication of the UHV lens was slightly modified to avoid virtual leaks, and anodizing, glue, cement, and stickers were omitted, of course. These lenses have a focal length $f_{\text{eff}} = 30.9$ mm, an aperture of 17 mm, and thus $F = f/\text{aperture} = 1.8$. They are optimized for the wavelength 313 nm, the diffraction limited spot size, when focusing a collimated beam, is

$$2.44\lambda F = 1.4 \mu m,$$

which is considerably smaller than e.g. the pixel size of the CCD chip.

Using only the lens on the camera and placing the camera directly behind the viewport of chamber (distance lens – trap 160 mm) the image width is about 25 mm, with a resolution of 40 $\mu$m and a focusing depth of 1 mm. Going further back the whole trap can be imaged. This set-up can be used to measure the total ion number and to watch the dynamics of the cloud.

Using additionally the vacuum lens, one covers a large solid angle and produces a bright image at a high resolution. The image width decreases to a few millimeters, giving a resolution in the $\mu$m region and the focal depth drops to about 1 $\mu$m. This set-up is suitable for resolving ion crystal structures, where the typical spacing is in the order of 10 $\mu$m.

The expected scattering rate of laser-cooled beryllium is $\approx 10^7$ s$^{-1}$ (Fig. 3.2, Chap. 3). Depending on the lens set-up, this leads to $10^4 \ldots 10^5$ photons/s hitting the CCD surface. To find the corresponding increase of the camera’s pixel values this number has to be multiplied by the quantum efficiency of the CCD-chip shown in Fig. 2.21 and the number of ions in the trap, of course. A more detailed discussion of the scattering rate and the cooling process is given in chapter 3.

Molecules in general do not provide a closed and strong transition for fluorescence detection, due to their ro-vibrational level structure. The sympathetically cooled molecules will hence appear as dark sports on the CCD image. Performing spectroscopy of the molecular ro-vibrational levels (→5.2.2), the expected excitation rate of about $\approx 1/s$ is to weak for a detection with a CCD camera.
2.5.2 Detection with an Ion Multiplier

Although the detection of the ions with an ion multiplier is destructive, it is of high interest, since it opens up possibilities to efficiently detect weak signals from molecular spectroscopy using photodissociation as proposed in (→5.2.6).

However, extraction of the ions out of a linear Paul trap is more challenging than one would expect on the first view.

Using a hyperbolic Paul trap, efficient extraction was demonstrated by [42]: the ions could be extracted through a mesh in the top electrode which was put on an attractive acceleration potential and were detected with a secondary electron multiplier. Different ion species could be distinguished by time-of-flight measurement. Hereby, what is important to know, is that the phase of the rf field when switching of the trap has carefully to be taken into account, since the micromotion leads to different starting conditions for the time of flight measurement.

In the linear trap design, ions could be extracted easily in longitudinal direction by opening the potential of one endcap. However, the starting conditions of the ions along the long axis are very different, making time-of-flight measurement quite impossible. Information about the ions’ masses would thus require an additional set-up of a mass spectrometer.

From our simulations we found, that there is no static potential configuration to be applied to the trap electrodes (of the linear trap), that would efficiently guide the ions in transverse direction out of the trap without loosing many ions on the electrodes. The idea of a mesh electrode was taken into account, where the ions could be pulled through. Constructing and fabricating an electrode still stable but as transparent as possible and having a smooth surface (to not disturb the quadrupole field) turns out to be a questionable challenge and was finally rejected.

The dynamics of the rf trap provide a much more elegant way of mass selective detection.

Using the mass selective trapping parameters $a, q$ as in a quadrupole mass spectrometer, designated species can be kicked out of the trap. However, these species are kicked out in all directions of space and are mainly lost on the electrodes. Furthermore, there are additional loss mechanisms coming up limiting the trap’s lifetime, when the trap is driven in the mass selective regime [49].

A highly mass selective ($m/\Delta m = 800$) method of extraction of ions by secular excitation was demonstrated by [50]. This method relies on parametric excitation of the oscillation of the ions in the secular potential. As before, this method is not suitable for the efficient
2.5 Detection of the Trapped Particles

detection but it can be used to remove a certain ion species without affecting the other ions.

Highly efficient detection due to the decrease of the rf amplitude was demonstrated by [51]. The entrance dynode of an electron multiplier is placed near the trap having an attractive potential. By slowly (0.1-1 s) decreasing the rf amplitude of the trap, the trapping potential is lowered and the ions can escape to the electron multiplier. This was demonstrated with nearly 100 % detection efficiency. According to (2.26) the potential depth is mass dependent. Thus the heavier ions escape first, when decreasing the rf amplitude $V$. Scanning the rf potential enough slowly, the time-of-flight effects can be neglected.

In the experimental set-up a secondary electron multiplier (type Balzers, SEV217) is mounted on an extra plate clamped on the four rod leading to the top flange. The entrance slit is placed only a few millimeters above the trap (Fig. 2.11, and Fig. 2.18 (left)). The potential of the entrance dynode is $-3.5$ kV, the 17 following dynodes produce a gain of $10^8$. The signal is picked up using an UHV compatible coaxial cable (type Ceramaseal) and connected to a BNC-connector on the top flange. However, despite of the shielding of the multiplier, first experimental tests have shown that the rf voltages of the trap influence the output signal of the multiplier. Unfortunately, the shape and typical length of an ion signal is on a similar scale as the oscillations induced by the rf wires. For final use of the multiplier, further improvement on the shielding and electronics for accurate discrimination are still required.
Chapter 3

Cooling of Trapped Ions

Ions in Paul traps gain kinetic energies of several thousand Kelvin due to radio frequency (rf) heating (→2.2.4). These temperatures cause large Doppler shifts and broadenings. In order to perform spectroscopy with the aimed at resolution of $\Delta \nu / \nu \leq 10^{-10}$, cooling of the ions is strongly needed. Additionally, at such high temperatures the ro-vibrational levels of e. g. the HD$^+$ ion are occupied almost uniformly, making the detection of inner excitation essentially impossible (→5.2.5), (→5.2.6).

The following section briefly reviews different possibilities for cooling in Paul traps. Then we focus on the applied mechanism of Doppler laser cooling of the beryllium ion and on the mechanism of sympathetic cooling of molecules. We also have a closer look at various properties of a cooled ion plasma; e. g. at sufficiently high cooling powers the ions cloud performs a phase transition from the cloud state into a crystalline state.

3.1 Different Ways of Cooling

There is a large variety of cooling methods available. The progress in recent physics towards and beyond a Bose-Einstein-Condensate – first observed in 1995 [52, 53, 54] – is mainly the result of finding and applying appropriate cooling mechanisms. Cold ensembles of particles open up the field for a great variety of new physics. The cooling mechanisms are mainly applied to atoms, so far. The goal of our project is to use appropriate cooling methods to prepare a cold ensemble of molecules and thus make the molecules accessible to high resolution spectroscopy of so far unachieved precision.
Buffer gas cooling

Buffer gas cooling in principle is a very general mechanism and suitable to cool all kinds of particles. A cold gas is let into the chamber containing hot ions and by collision the hot ions thermalize at a lower temperature. The final temperature is given by the temperature of the buffer gas. Of course, cooling to the Kelvin region requires a cryogenic experimental set-up.

In rf traps however, mechanical effects lead to the fact that cooling is possible only if the coolant’s mass is lighter than the mass of the cooled ion [55, 56]. If the coolant is heavier then the cooled particle, the collision between the particles results in a large phase shift in the motion of the light ion and the rf-trapping-field, which in turn leads to rf-heating of the ion instead of cooling. Cooling of light molecules like HD$^+$ would thereby require a buffer gas like cryogenic $^3$He or hydrogen, leading to an expensive experimental set-up.

Buffer gas cooling is best applicable on magnetic traps such as the quadrupole trap which lack the rf heating of a Paul trap. The use of buffer gas in Penning traps in general is prohibitive because the magnetron motion is metastable and any collision tends to move ions outward until they are lost from the trap.

Resistive Cooling

Resistive cooling is a nice mechanism to cool ions in ion traps. The oscillating ion induces image charges in the electrodes of the trap which, in turn, cause an oscillating current to flow through a resistor. The resistor can be realized by a resonant circuit at the secular frequency of the ion. The final temperature limit is given by the temperature of the resistor. However, this set-up is preferably used in Penning traps, since in a Paul trap the cooling rate is weak compared to the rf heating process.

Laser Cooling

The introduction of laser cooling was one of the most significant steps in the development of ion traps for spectroscopic uses. It is essentially a quick and efficient way of taking energy out of the motion of the ions via their interaction with laser light and can reduce their effective temperature to well below 1 K [57, 58].

Laser cooling in Paul traps can be applied either to the ion species of interest or to a second species of ion held in the trap at the same time. These cold ions cool the second ion species by collisions in a process known as sympathetic cooling [23]. In our experiment
we apply Doppler laser cooling to cool Be$^+$, while the molecules are cooled sympathetically. Different from buffer gas cooling, the principle of sympathetic cooling also allows lighter particles being cooled by heavier ones. Doppler laser cooling is introduced in section 3.2 in more detail, and sympathetic cooling in section 3.3.

Laser cooling in ion traps has been applied to only a few ion species so far. The reason for its limited application is that it requires a resonance transition which can be reached by a continuous wave laser and an ion ionic level structure which allows the ion to cycle many times between the ground state and the resonance level in a short time. Electronically excited molecules usually decay to many different ro-vibrational levels, and ro-vibrational transitions in molecules typically have very long lifetimes. For these two reasons laser cooling in general is not applicable to molecules.

Long before laser cooling was invented, Dicke realized that if a radiating particle is confined to a region of dimension much less than the wavelength of the radiation, the first order Doppler effect disappears: the Lamb-Dicke regime [59]. If the motion is harmonic, the usual Doppler profile is replaced by a carrier with a series of sidebands spaced at the oscillation frequency of the particle inside the trapping potential. However, it is very difficult to achieve confinement to a region of dimension much less than an optical wavelength. It was realized that the only way that this could be achieved would be in a miniature Paul trap with strong laser cooling. The first trap of this type was built by the group of Toschek [21]. For the situation where the motional sidebands are resolved, the optimum laser frequency for cooling is equal to that of the first lower sideband and this is then referred to as optical sideband cooling [60, 61]. Single atomic ions can be cooled down to the quantum-mechanical ground state of the trap potential [22]. A large trap like ours, which in contrast can trap a whole cloud of ions, would require prohibitively large rf voltages to generate sufficiently steep walls for tight confinement.

### 3.2 Doppler Laser Cooling

The cooling method used in our project is called Doppler laser cooling. This is applied to atomic beryllium ions, which in turn cool molecular ions by sympathetic interaction.

The next section shortly reviews the atom-laser interaction to introduce the basic theory of Doppler laser cooling. The following section describes the optical transitions of the beryllium ion in terms of laser cooling in further detail.

Doppler laser cooling is based on a combination of the recoil of the
atom (or ion) when scattering a photon from a laser beam and the Doppler effect. A graphical illustration is shown in Fig. 3.1.

\[ |e\rangle \rightarrow |g\rangle \quad mv \quad hk \]

(1)

\[ |e\rangle \rightarrow |g\rangle \quad mv-hk \]

(2)

\[ |e\rangle \rightarrow |g\rangle \quad mv-hk \]

(3)

**Figure 3.1:** Graphical picture of one cycle of Doppler laser cooling. (1) An atom is travelling towards a laser beam. Due to the Doppler effect, the atomic transition frequency is red-shifted from the frequency of the light. (2) The atom absorbs the photon and recoils due to the photon momentum. (3) The atom decays to the ground state by spontaneous emission. The average recoil over many cycles vanishes.

Doppler cooling takes place when an atom moves in a laser field of frequency \( \omega_L \) that is slightly red-detuned from the atomic transition frequency \( \omega_A \), i.e. \( \omega_L < \omega_A \). Then, due to the Doppler shift \( k \cdot v \) the atom preferably absorbs photons when it is moving against the laser beam, i.e. resonance occurs if \( \omega_A - kv = \omega_L \). The atom which absorbs a photon gets a photon momentum \( h k = h \frac{\omega}{c} \) in the direction of the laser beam. Thus, an atom moving against the beam is decelerated by the photons recoil while an atom in the same direction as the laser is not accelerated by the same amount, since their frequencies are off resonance and absorption gets less probable. After absorption the atom decays to the ground state by spontaneous emission and is ready for the next absorption cycle. Since spontaneous emission is isotropic in space, the average photon recoil over many cycles cancels to zero.

### 3.2.1 Doppler Laser Cooling Reviewed

**Semiclassical model**

A quantitative understanding of the process of Doppler laser cooling can be attained from the semiclassical model [62], which treats internal states of the ion with a quantum mechanical two-level model and the ion motion as classical motion.
The electric field \( \mathbf{E}_L(r, t) \) of the light wave is assumed to come from a laser beam with frequency \( \omega_L \), wavevector \( \mathbf{k}_L \), amplitude \( \hat{E}(r) \) and polarization vector \( \mathbf{e}_L(r) \):

\[
\mathbf{E}_L(r, t) = \mathbf{e}_L(r) \hat{E}(r) \cos (\omega_L t + \mathbf{k}_L \mathbf{r}) .
\]  

(3.1)

The atom is treated as a closed two level system with a ground level \( |g\rangle \), an excited level \( |e\rangle \) with a lifetime \( 1/\Gamma \), and a dipole transition between these levels of frequency \( \omega_A \).

We assume the atomic dipolemoment \( d \) along \( z \). The operator of the atomic dipolemoment is then given by

\[
d = d \mathbf{e}_z (|e\rangle \langle g| + |g\rangle \langle e|), \text{ where } \langle e|d|g\rangle = d \mathbf{e}_z = \langle g|d|e\rangle .
\]  

(3.2)

The interaction energy between atom and light wave then results in

\[
V_{AL} = -d \mathbf{E}_L(r, t) = \hbar \Omega_R(r) \cdot \mathbf{e}_z \cdot \mathbf{e}_L(r),
\]  

(3.3)

with the Rabi-frequency defined as

\[
\Omega_R(r) = -\frac{d}{\hbar} \hat{E}(r) \mathbf{e}_z \cdot \mathbf{e}_L(r),
\]  

(3.4)

which determines the interaction strength.

The force operator of the laser field on the atom is \( \mathbf{F}(r) = -\nabla V_{AL} \).

Further calculation yields the mean light pressure force

\[
F_{lp} = \hbar \mathbf{k}_L \Gamma_{sc},
\]  

(3.5)

where \( \Gamma_{sc} \) describes the photon scattering rate

\[
\Gamma_{sc} = \frac{\Gamma}{2} \frac{\Omega_R^2/2}{(\Delta \omega - \mathbf{k}_L \cdot \mathbf{v})^2 + \Gamma^2/4 + \Omega_R^2/2},
\]  

(3.6)

with the detuning \( \Delta \omega = \omega_L - \omega_A \) between the laser light and the atomic transition frequency.

For the discussion of the dynamics of the light pressure we expand (3.5) around \( v = 0 \), define the \( z \)-axis by the direction of the laser beam and have a closer look at the force component

\[
F_z(v) = F_{z,0} + \alpha v_z + O(v^2)
\]  

(3.7)

where

\[
\alpha = \hbar k_l^2 \frac{S}{(S+1)} \frac{\Delta \omega \Gamma}{\Omega_R^2/2},
\]  

(3.8)

\[
S = \frac{\Omega_R^2/2}{(\Delta \omega - \mathbf{k}_L \cdot \mathbf{v})^2 + \Gamma^2/4} = \frac{I/I_{sat}}{1 + 4(\Delta \omega - \mathbf{k}_L \cdot \mathbf{v})^2/\Gamma^2},
\]  

(3.9)

\[
I_{sat} = \frac{2\pi^2 \hbar c \Gamma}{3\lambda_A^2}.
\]  

(3.10)
Here $\alpha$ can be identified as the damping coefficient of a friction force, $S$ as the saturation parameter, and $I_{sat}$ as saturation intensity. The Rabi-frequency can be related to the saturation intensity by $\Omega^2_R = \frac{\Gamma^2}{2I_{sat}}$.

$F_z(v)$ has a term with a constant pressure force $F_{z,0} = F_z(v = 0)$ and a $v$-dependent friction force as depicted in Fig. 3.2, left-hand side. The right-side plot in Fig. 3.2 shows the behavior of the damping coefficient $\alpha$ as a function of detuning.

**Figure 3.2:** Light pressure force of a single laser beam. For input parameters see Tab. 3.1. **Left:** Friction force (expressed as scattering rate) of an atom as a function of the Doppler-shift $k_L \cdot v$ of a particle for a red laser detuning of $\Delta\omega = -\Gamma/2$. **Right:** Damping coefficient $\alpha$ as a function of the laser detuning $\Delta\omega$.

<table>
<thead>
<tr>
<th>Parameters of the Plots</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>0.5 mW/mm$^2$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>313 nm</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>$2\pi \times 19.4$ MHz</td>
</tr>
</tbody>
</table>

**Table 3.1:** Parameters of the plots.

The sign of the damping coefficient follows the sign of the detuning $\Delta\omega$. This leads to cooling of the atomic motion for red detuning $\Delta\omega < 0 \Rightarrow \alpha < 0$ and to heating for $\Delta\omega > 0 \Rightarrow \alpha > 0$. The maximum cooling rate at sufficiently high laser intensities ($S \lesssim 1$) is achieved at a detuning $\Delta\omega = -\Gamma/2$ where $\alpha = -\frac{\hbar k^2}{4}$. This can be understood as maximum gradient of the cooling force at $v = 0$, compare Fig. 3.3.

The axes of the plots in Fig. 3.2 and Fig. 3.3 can be understood as follows: a Doppler shift of $k_L \cdot v = 1 \Gamma$ corresponds to a velocity of about $v \approx 6$ m/s for the Be$^+$ ion. A scattering rate $\Gamma_{sc} = 1$ recoil/s can be translated in a force of about $F \approx 2.1 \times 10^{-27}$ N.
Doppler Laser Cooling in a Paul Trap

In a Paul trap cooling can be achieved with a single red-detuned laser beam. Despite the force offset $F_{z,0}$ which pushes the ions slightly to one end of the trap, the comparably strong potential of the Paul trap still confines the ions. The ion will loose some of its kinetic energy while moving towards the laser beam. Although one laser beam cools only one direction in space, the ions are cooled in all dimensions for two reasons: if more than one ion is present in the trap, the Coulomb interaction will couple the ions motion and thus make it possible to cool all translational degrees of freedom. Additionally, as soon as the cooling laser is not exactly aligned to the $z$-axis of the trap or orthogonally, all motions in the trapping potential are affected directly by the laser-cooling beam.

However, two counter-propagating laser beams can be used to cancel the static force offset $F_{z,0}$, as shown in Fig. 3.3. This leads to a symmetric shape of the ion cloud and increases the efficiency of the cooling process.

![Graph showing light pressure force of two counter-propagating beams as a function of the Doppler-shift $k_L \cdot v$ for three different values of laser detuning $\Delta \omega$. See Tab. 3.1 for input parameters and text for further information.]

One beam laser cooling is also known from the Zeeman-Slower, where the Zeeman-shift of a magnetic field is used to keep the atom on resonance while slowing down from a fast velocity. Two counter-propagating beams in each dimension of space are known from optical molasses or from the magneto-optical trap, where –
additional to the velocity dependence of the light force – the atoms are repelled to one distinguished point of space (zero magnetic field) due to the level shift of the Zeeman-effect in the applied magnetic field [63].

**Scanning the Laser**

While switching the sign of the detuning $\Delta \omega$ changes the force from cooling to heating, the magnitude of the detuning needs to be chosen carefully with respect to the initial temperature of the ions on the one hand, and with respect to the desired final temperature on the other hand.

A large red detuning is required for efficient cooling of hot ions in order to achieve sufficiently high scattering rates at large Doppler-shifts. As the temperature of the ions cools down, the Doppler-broadening decreases, and the laser needs to be scanned towards the atomic resonance in order to maintain efficient cooling. Therefore, especially in a Paul trap where the initial temperatures are as large as 10000 K, a large continuous tuning range of the cooling laser is required. In the case of cooling of beryllium, which unfortunately is a light particle, and thus has a large velocity at 10000 K, cooling of the hottest ions requires initial detunings of a few 100 $\mu$, i. e. several tens of GHz. Without detuning the laser frequency the required saturation intensity would be increased by a factor of $100^2$.

We will now look for the optimum detuning to achieve the lowest final temperature possible.

**Doppler Cooling Limit**

When considering low temperatures at which $k_L \cdot v \ll \Gamma$, the cooling force can be expressed by the friction force (3.7). We consider the case of two counter-propagating laser beams. The cooling force is then given by $F_{\text{cool,2beam}} = 2\alpha \dot{z}$, and the equation of motion is $m \ddot{z} = 2\alpha \dot{z}$. Multiplying by $\dot{z}$ yields an expression for the derivative of the kinetic energy $K = \frac{1}{2}mz^2$, $\dot{K} = m \ddot{z} \dot{z}$ of

$$K_{\text{cool}} = \frac{4\alpha}{m}K.$$  \hspace{1cm} (3.11)

The kinetic energy damping rate is proportional to the kinetic energy, so for red detuning of the laser the kinetic energy will decay exponentially, and the ions’ motion will be cooled.

However, if a heating process is present, the equilibrium temperature is found when the cooling rate balances the heating rate. The low-temperature limit can be found by considering the only fundamental heating process caused by the randomness of absorption.
3.2 Doppler Laser Cooling

and spontaneous emission recoils. The randomness of the photon recoils makes the ion undergo a random walk in momentum space, and this momentum diffusion will have a heating effect on the ion motion. The emission and and absorption recoils will both add a positive kinetic recoil energy \( \varepsilon = \frac{\hbar^2 k^2}{2m} \) to the ion motion, and for weak excitation of the ion, both laser beams contribute with equal heating rates [64]. This gives a total heating rate of

\[
\dot{K}_{\text{heat}} = 4\varepsilon \Gamma_{sc} .
\]  

(3.12)

With (3.8) we can calculate the steady state energy at low temperatures

\[
\dot{K} = \dot{K}_{\text{heat}} + \dot{K}_{\text{cool}} \Rightarrow
\]

\[
K(t \to \infty) = \frac{\hbar \Gamma}{2} \left( \frac{1 + 2\Omega_R^2 + 4(\Delta \omega)^2}{-4\Delta \omega} \right) .
\]  

(3.13)

This leads to a theoretical minimum temperature \( T = K/k_B \), called the Doppler cooling temperature at \( \Delta \omega/\Gamma = 1/2 \) and \( \Omega_R^2 \to 0 \) of

\[
T_D = \frac{\hbar \Gamma}{2k_B} .
\]  

(3.14)

Doppler cooling limit

3.2.2 Doppler Laser Cooling of Be\(^+\)

Now we will consider the properties of the \(^9\)Be\(^+\) ion in more detail with respect to Doppler laser cooling. As already mentioned, the beryllium ion was chosen because it is the lightest atomic ion that is suitable for laser cooling and therefore qualifies best for sympathetic cooling of light molecules (\( \rightarrow 3.3 \)).

The atomic data of the beryllium ion are collected in Tab. 3.2.

<table>
<thead>
<tr>
<th>Atomic data</th>
<th>Cooling transition data</th>
</tr>
</thead>
<tbody>
<tr>
<td>symbol</td>
<td>(^9)Be(^+)</td>
</tr>
<tr>
<td>configuration</td>
<td>( 1s^2\ 2s^1 )</td>
</tr>
<tr>
<td>nuclear spin</td>
<td>( I = 3/2 )</td>
</tr>
<tr>
<td></td>
<td>( ^2S_{1/2}(F = 2) \leftrightarrow ^2P_{3/2} )</td>
</tr>
<tr>
<td>wavelength</td>
<td>( \lambda = 313.1327 ) nm</td>
</tr>
<tr>
<td>linewidth</td>
<td>( \Gamma = 2\pi \cdot 19.4 ) MHz</td>
</tr>
<tr>
<td>Doppler temperature</td>
<td>( T_D = 0.47 ) mK</td>
</tr>
<tr>
<td>saturation intensity</td>
<td>( I_{\text{sat}} = 83 ) mW/cm(^2)</td>
</tr>
<tr>
<td>recoil velocity</td>
<td>( v_{\text{recoil}} = 0.14 ) m/s</td>
</tr>
</tbody>
</table>

Table 3.2: Data of the Beryllium Ion.

With a closed 1s shell and a single electron in the 2s shell and with an atomic mass of 9 a.u. the beryllium ion is the lightest hydrogen-like atomic ion. Therefore it has a relatively simple level scheme which is sketched in Fig. 3.4.
Cooling of Trapped Ions

Laser cooling is performed on the $^2S_{1/2}(F = 2) \leftrightarrow ^2P_{3/2}$ transition. The nuclear spin $I = 3/2$ leads to a hyperfine splitting of the energy levels. The $^2S_{1/2}$ ground state shows a splitting of $\Delta \nu_{\text{HFS}} = 1.250 \text{ GHz}$, while the hyperfine splitting of the excited states vanishes in the natural linewidth of the levels. The excited $^2P_{3/2}$ state generally can decay into either hyperfine levels of the ground state, so optical pumping to the upper hyperfine level of the ground state takes places. This requires a “repumping” laser beam, at a frequency detuning of $\Delta \nu_{\text{HFS}}$ from the main beam.

Taking Advantage of the Polarization

The required intensity of the repumping beam is determined by the branching ratio of the spontaneous emission from the $^2P_{3/2}$ level, the polarization of the incident light, and the initial population of the ground state levels.

The strength of the dipole coupling of two sub-states is described by the square of the Clebsch-Gordan coefficient, which is determined by the magnetic quantum numbers and the laser polarization, as shown in many text books [65, 66]. Only some coefficients are non-zero and hence reflect the selection rules for the change in the magnetic quantum numbers. The selection rules for the hyperfine transitions under consideration are:

$$\Delta F = 0, \pm 1, \quad (3.16)$$
$$\Delta m_F = 0, \pm 1 \ (\pi, \sigma^\pm \text{ polarized light}). \quad (3.17)$$

We calculated the relative oscillator strength of all related transitions as shown in Fig. 3.5. Racah-algebra [67, 68, 69] was used to
expand the matrix elements

\[ \langle d \rangle = \langle F, m_f | C_q^{(1)} | F', m_f' \rangle \]  

into computable $3j$ and $6j$ symbols.

**Figure 3.5:** Relative squared oscillator strength $\langle d \rangle^2$ of the $^2S_{1/2}(F = 1, 2) \leftrightarrow ^2P_{3/2}(F = 0, 1, 2, 3)$ transitions (normalized to 60 for decay, and to 120 for excitation, respectively).

The ground state splitting of 1.25 GHz is small compared to room temperature, so one can assume an equal initial population of all sub-states of the ground state. Then, using the calculated oscillator strength one can compute the following branching ratios. The probability of finding the beryllium ion after an excitation and emission cycle in a $F = 2$ state when using $\pi$ polarized light is 62.5%, not very different from the probability of 60% when using $\sigma^\pm$ polarization. A particle that is excited from a $F = 2$ state decays with $\approx 80\%$ back to a $F = 2$ state, and similarly for a particle that is excited from a $F = 1$ state and decays back to $F = 1$ with $\approx 70\%$. Looking at these ratios, the repumping beam should have a similar intensity as the main beam.

However, if $\sigma^+$ polarized light is used, after several cycles the ion is pumped to the transition $|F = 2, m_F = 2\rangle \leftrightarrow |F = 3, m_F = 3\rangle$. Decay from the $|F = 3, m_F = 3\rangle$ state to the $F = 1$ is forbidden.
by the selection rules, so no repumping light would be required at all. However, existing polarizing beam splitters are not perfect and residual magnetic fields induce transitions within the excited state like $|F = 3, m_F = 3 \rangle \leftrightarrow |F = 3, m_F = 2 \rangle$ (caused by Larmor precession during the lifetime $\Gamma$). Rough estimations of these effects yield that a repumping light intensity of few percent compared to the intensity in the cooling beam should be sufficient, if circular polarization is used.

It should be mentioned that a coupling strength equal to one is assumed for the saturation intensity given in (3.10). When using polarized light on a specific transition where the coupling strength $\langle d \rangle^2$ is less than 1, the effective saturation intensity is increased by a factor of $1/\langle d \rangle^2$.

### 3.3 Sympathetic Cooling

Sympathetic cooling is a quite recent method. It relies on the long-range Coulomb interaction between laser-cooled atomic ions and any different ion species (atomic or molecular) confined in the same trap. The process of sympathetic cooling is very universal and should be applicable to nearly any ion.

Sympathetic cooling in Penning traps by Coulomb interaction was first demonstrated in 1980 [70]. Laser-cooled $^{24}\text{Mg}^+$ ions sympathetically cooled their simultaneously trapped isotopes $^{26}\text{Mg}^+$ to a temperature of about 0.5 K. Later experiments in Penning traps using laser-cooled $^{27}\text{Be}^+$ ions to cool $^{198}\text{Hg}^+$ [23] and diverse isotopes of $^{112}\text{Cd}^+$ [71].

In rf traps “sympathetic crystallization” was observed accidentally in 1992 [72]. The spatially resolved fluorescence image of an ion crystal of laser-cooled $^{24}\text{Mg}^+$ ions showed dark spots at some crystal positions. These dark spots could be identified as sympathetically cooled ions of different $\text{Mg}^+$ isotopes or ions which were accidentally ionized out of the residual gas. Ions of different types are not excited by the cooling laser and thus appear as dark spots on the fluorescence image.

The first systematic sympathetic cooling of molecules was performed in 1996 [24] using a laser-cooled $^{24}\text{Mg}^+$ ion crystal having a temperature of only some mK. The molecules were ionized out of the residual gas. By electrodynamic excitation of the specific molecular ion’s secular motion, which caused a heating of the whole ion crystal that could be measured, it was verified that the specific ion was added into the crystal. Temperatures of the sympathetically cooled molecules in the region of 7-70 K were reported.
Recent experiments in Århus show the strengths of sympathetic cooling [6, 73]. In an extreme case, one laser-cooled ion maintained order in a 15 ion string. Furthermore, a large ion crystal was created in a linear Paul trap containing several thousand ions of which about 90% were cooled only by sympathetical cooling. The temperature in the crystal was indicated to be below 10 mK, since crystallization was observed only below that temperature for the parameters given [5]. The largest ion crystals consist of more than \(10^5\) ions, where the same large ratio of sympathetically cooled ions should be possible.

### 3.3.1 Mass Dependency of Sympathetic Cooling

The mechanism and quantitative understanding of sympathetic cooling has not yet been explored in detail. Although there are various experiments and theoretical approaches dealing with sympathetic cooling, to our knowledge a general proven quantitative prediction of attainable temperatures is not yet available. However, it turns out that sympathetic cooling works best for minimum mass differences between the interacting particles. To this end, as opposed to buffer gas cooling, sympathetic cooling allows also lighter particles to cool heavier ones. However, the molecule we are interested in, HD\(^+\), has a mass of only 3 a.u. Therefore, we have chosen Be\(^+\) since it is the lightest atomic ion that can be laser-cooled.

The characteristic quantity of the particles in an ion trap is the mass to charge ratio, \(m/Q\). As the characteristic parameter of sympathetic cooling we define the quotient of the mass to charge ratios between the two species, \(\chi\), to be

\[
\chi := \left( \frac{m}{Q} \right)_{\text{cooled}} : \left( \frac{m}{Q} \right)_{\text{coolant}}.
\]

Due to the rf field we can expect that the cooling rate decreases the lighter the cooled ion compared to the cooling ion is ("light" and "heavy" in terms of \(m/Q\)). For better visualization, one can imagine that despite the long-range Coulomb force, heavy particles easily push lighter ones out of phase with the rf trapping field, which in turn leads to rf heating (→2.2.4) of the lighter particles.

The lightest sympathetically cooled molecular ion in the experiments above-mentioned with laser-cooled \(^{24}\text{Mg}^+\) was the \(\text{NH}_4^+\) molecular ion with \(\chi = 3 : 4\). The Århus group in Denmark demonstrated sympathetic cooling of \(\text{Ne}^+\) and \(\text{Ar}^{2+}\) (\(\chi = 5 : 6\)), as well as the crystallization of \(^{24}\text{Mg}^{2+}\) (\(\chi = 1 : 2\)).
In our project we have chosen $\text{Be}^+$ ($m = 9$) to sympathetically cool $\text{HD}^+$ ($m = 3$) leading to $\chi = 1 : 3$.

The specific feasibility of sympathetic crystallization even for values like $\chi = 1 : 6$ was verified by numerical simulations in cooperation with colleagues in Århus (Denmark) for cooling of $\text{D}_2^+$ by two laser-cooled $^{24}\text{Mg}^+$ ions [74], as shown in Fig. 3.6.

![Figure 3.6: Simulation of sympathetic cooling of a single $\text{D}_2^+$ ion by two $^{24}\text{Mg}^+$ ions in a linear Paul trap [74]. The plot shows the axial positions of the particles over the time. The laser cooling beam is applied to the $^{24}\text{Mg}^+$-ions in the axial direction. The $\text{D}_2^+$ ions are coupled by the Coulomb force. Transverse stability parameters are $q_{^{24}\text{Mg}^+} = 0.056$, $q_{\text{D}_2^+} = 0.335$, $q \propto Q/m$ (2.7).](image)

The three particle simulation of sympathetic cooling starts with hot ions at $t = 0$. After about 100 ms the particles stop interchanging their positions; sympathetic crystallization ($\chi = 1 : 6$) takes place. During the 300 ms cooling period, the cooling laser is scanned from a detuning $\Delta \omega = -10 \Gamma$ for efficient cooling of the initially hot ions down to $\Delta \omega = -\Gamma/2$ to finally reach the lowest possible temperature $T_D$ (3.15). The distance between the ions in the crystal depends on the trap parameters. The simulation shows a distance of slightly more than 50 $\mu$m. Typical values are in the region of 10 $\mu$m. At the end of the cooling sequence the ions’ positions are shifted somewhat off the trap’s center. This is a feature of the light pressure given in Eq. (3.5) when cooling with a single beam.
3.3.2 Two-Component Ion Plasma

The trapped ions are an example of a non-neutral two-component plasma, where the pseudopotential creates the confining potential. Typical particle densities of these “ion crystals” are on the order of \((10 \, \mu m)^{-3}\). The pseudopotential depth \((2.26)\) is mass dependent, therefore heavier particles (Be\(^+\)) are weaker bound than lighter ones (HD\(^+\)). The light molecules thus crystallize near the center of trap, while the heavier species are arranged in a shell around the center of the trap. Near the center of the trap the amplitude of the rf field \((2.24)\) vanishes, hence the molecules near the trap center have a lower kinetic energy due to less micromotion and the influence of the rf field on the molecular levels is decreased. Both of these effects are beneficial with respect to the spectroscopy of the molecules.

Another effect should be mentioned which occurs in a two-component plasma when cooling with a single beam where only one component is being laser-cooled. The static light pressure \(F_{z,0}\) \((3.7)\) pushes the resonant particles to the opposite end of the trapping potential. This effect begins when the hot ion cloud is cooled and continues even in the ion crystal, where the resonant particles interchange their positions with non-resonant particles in a kind of diffusion process \([75, 32]\).

3.4 Specification of the Cooling Laser

Doppler laser cooling of Be\(^+\) (see Tab. 3.2 for atomic data) requires an ultraviolet laser light source at a wavelength of 313 nm.

The required laser power is determined by the saturation intensity of the atomic transition and the area of the cross-section of the cloud (typically a few mm\(^2\)). Thus, a power of a few mW is sufficient to saturate the transition.

The linewidth of the laser should be smaller than the linewidth of the atomic transition (19 MHz) in order to avoid scattering of blue detuned \((\Delta \omega > 0)\) photons at small detunings like \(\Delta \omega = -\Gamma/2\), in order to avoid degrading the temperature limit \(T_D\).

A continuous tunability of some GHz will be required for efficient cooling of initially hot ions.

Repumping from the metastable upper hyperfine level requires laser light with a frequency shift of 1.25 GHz relative to the main light. A power on the order of a few percent of that of the main beam is required.

Chapter 4 explains the laser system which fulfills these requirements and was built to laser cool ionic beryllium in a linear rf trap.
Chapter 4

UV Laser Source

High-resolution spectroscopy of atoms, ions and molecules often requires practical cw single-frequency lasers emitting in the UV. In our particular case cw light at a wavelength of 313 nm for laser cooling of Be$^+$ is required as specified in the previous chapter.

Dye or solid state lasers emitting this wavelength directly are not available. The shortest wavelength generated by recently developed laser diodes is still in the region of slightly below 400 nm. Nonlinear processes such as second-harmonic generation (SHG, frequency-doubling) or sum-frequency generation (SFG) are required to generate UV laser light at that wavelength. However, conversion efficiencies of this type of nonlinear processes are usually pretty small, which necessitates high powers of the fundamental waves or employment of resonant cavities.

The traditional solution is a single-frequency dye laser resonantly frequency-doubled to the UV [76]. Although such a system is effective and tunable, it is also expensive and hard to maintain. Frequency doubling of light from a laser diode is not feasible due to the weak powers available at the 626 nm wavelength.

In a few cases, the all-solid-state approach has been employed, where a fixed-wavelength solid-state-laser emitting in the near IR (e. g. Nd:YAG at 946 nm or 1064 nm) is frequency-quadrupled in two resonant second-harmonic steps [77]. While this simplifies the source aspect, the spectral coverage is very specific, and is only applicable in particular cases.

Theoretical treatment, simulation, and experiments of doubly resonant sum-frequency mixing in an external resonator were described in 1997, generating 355 nm radiation [78].

In 1988 a laser source at 589 nm based on doubly resonant sum-frequency mixing in a monolithic lithium niobate resonator was demonstrated [79].

Very recently the development of a tunable single-frequency UV
source was reported, based on a Ti:Sapphire laser resonantly frequency doubled in a cavity and then sum-frequency mixed with a diode laser in another cavity [80]. Although this leads to high output powers, the approach is too expensive for the many applications where the power requirement is at the level of a few mW.

Our approach:

In our experiment we use a novel approach to the generation of highly frequency-stable, widely tunable, single-frequency cw UV light suitable for high resolution spectroscopy [81]. Our approach is flexible in terms of UV spectral coverage, avoids the disadvantages of dye lasers, and the costs associated with the use of a Ti:Sapphire laser.

The first fundamental laser is a frequency doubled MOPA (master oscillator-power amplifier) Nd:YAG laser at a wavelength of 532 nm. The second laser is an external cavity diode laser running at 760 nm to generate the sum-frequency of 313 nm.

The features of this approach (e.g., large UV wavelength coverage possible using easily available diode lasers, narrow linewidth, wide tunability, high frequency stability) should make it of significant interest to spectroscopists. We remark that an alternative to the Nd:YAG laser used here would be resonantly frequency-doubled monolithic Nd:YAG lasers [82, 83].

In the first section of this chapter the theory of SFG is reviewed in general. The following section gives the specific experimental details of our implementation of the doubly-resonant SFG set-up designed for the generation of light suitable for laser cooling of trapped \( \text{Be}^+ \). In the last section the results are discussed.

4.1 Theory of Sum-Frequency Generation

Nonlinear optics:

Sum-frequency generation is an application of nonlinear optics, the branch of optics which takes advantage of the nonlinear response of atoms and molecules to optical radiation fields. While theory is well-developed for SHG, this is not the case for SFG (geometry theory, optimization).

4.1.1 Nonlinear Interaction

Polarizing a dielectric medium:

In any real atomic system, the polarization \( P(r, t) \) induced in a dielectric medium is not proportional to the optical electric field \( E(r, t) \), but can be expressed in a Taylor series expansion, wherein the quantity of higher order terms typically decreases

\[
P = \varepsilon_0 \chi E + P_{NL}, \quad \text{with} \quad P_{NL} = 2\varepsilon_0 d E^2 + 4\chi^{(3)} E^3 + \ldots \quad (4.1)
\]
\( \chi \) is the linear susceptibility, while \( d = \frac{1}{2} \chi^{(2)} \) and \( \chi^{(3)} \) are the second-order and third-order nonlinear (NL) optical susceptibilities, respectively; their values are determined by the dielectric properties of the medium. \( \varepsilon_0 \) and \( \mu_0 \) are the permittivity and the permeability of vacuum, respectively.

When applying sufficiently strong electric fields the polarization of the medium contains oscillatory terms with the double, triple, etc. frequency of the fundamental wave. This nonlinear optical response gives rise to numerous interesting phenomena and applications [84, 85]. The second-order nonlinearity is responsible for second-harmonic generation, for sum- and difference-frequency generation and for parametric amplification and oscillation. The third-order term figures in such diverse phenomena as third-harmonic generation, Raman and Brillouin scattering, self-focusing, 4-wave mixing, and optical phase conjugation.

For anisotropic media \( \chi, d \) and \( \chi^{(3)} \) are tensors, and the polarization is written as

\[
P_i = \varepsilon_0 \chi_{ij} E_j + 2\varepsilon_0 d_{ijk} E_j E_k + 4\chi_{ijkl} E_j E_k E_l + \ldots ,
\]

where summation over repeated indices are assumed.

Only noncentrosymmetric crystals can possess a nonvanishing second-order susceptibility \( d \). This follows from the requirement that in a centrosymmetric (e. g. isotropic) crystal a reversal of the signs of \( E_j \) and \( E_k \) must cause a reversal in the sign of \( P_i \), so that \( d_{ijk} \equiv 0 \). Therefore, sum-frequency generation is only possible in media with broken symmetry, e. g. in anisotropic crystals. Lack of inversion symmetry is also the prerequisite for linear electro-optic effect and piezoelectricity, so that all electro- and piezo-electric crystals can be expected to display second-order nonlinear optical properties. The similar argument can be used to show that all crystals, as well as liquids and gases, can display third-order optical nonlinearities.

From Maxwell’s equations in a homogeneous dielectric medium and the nonlinear polarization we obtain the nonlinear wave equation

\[
\nabla^2 E - \frac{1}{c_m^2} \partial_t^2 E = \mu_0 \varepsilon_r \partial_t^2 P_{NL} ,
\]

where \( c_m = c_0/n = 1/\sqrt{\varepsilon_0 \varepsilon_r \mu_0 \mu_r} \) is the velocity of light in the medium, \( \varepsilon_r = 1 + \chi \) (in isotropic media) and for the following we assume \( \mu_r = 1 \).

The right hand side of (4.3) is the source of the radiation generated in the crystal. Consider the propagation of two optical fields at frequencies \( \omega_1 \) and \( \omega_2 \)

\[
E_i(r, t) = \text{Re}(E_j(r)e^{i\omega_1 t} + E_k(r)e^{i\omega_2 t}) .
\]
If the medium is nonlinear, then the presence of these field components can give rise to polarizations at frequencies $n\omega_1 + m\omega_2$, where $n$ and $m$ are arbitrary integers. The polarization component at

$$\omega_3 = \omega_1 + \omega_2$$

(4.5)

is the source of a new light wave at the sum-frequency.

### 4.1.2 Propagation of Light in Nonlinear Crystals

For a practical situation we consider a transverse, monochromatic light wave with linear polarization

$$E(r, t) = E(r, t)e^{-ikz}e_x, \quad \text{with} \quad E(r, t) = \vec{E}(r)e^{i\omega t},$$

(4.6)

where the field amplitude $\vec{E}(r)$ is a slowly varying function of $r$. The general wave equation (4.3) can then be simplified to the paraxial wave equation

$$\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + 2ik\frac{\partial}{\partial z} \right) \vec{E}(r) = -\mu_0\omega^2 (P_{NL}^x(r))_x e^{ikz}$$

(4.7)

with the complex nonlinear polarization $(P_{NL}^x(r))_x$.

The Gaussian modes $\vec{E}(r) = E_{mn}\psi_{mn}(r)$ form a complete set of solutions of the paraxial wave equation (4.7) for the case $P_{NL} \equiv 0$.

The general solution can be found by the trial function

$$\vec{E}(r) = \sqrt{\frac{\omega}{n_0}} \sum_{mn} A_{mn}(z) \psi_{mn}(r)$$

(4.8)

of the amplitude $\vec{E}(r)$ as a linear combination of Gaussian modes having the amplitudes $A_{mn}(z)$. Substituting this in (4.7) and integrating over $x$ and $y$ one gets an equation for the amplitudes

$$\frac{dA_{mn}^x(z)}{dz} = -i\mu_0\omega \sqrt{\frac{\omega}{n_0}} \left( \iint_{-\infty}^{\infty} dx dy (P_{NL}^x(r))_x (\psi_{mn}(r))^* \right) e^{ik_0 z}. $$

(4.9)

In $z$ direction the integration runs over the length of the nonlinear crystal (Fig. 4.1). The total power of a light wave (as in (4.8)) is given by the sum over all powers in individual modes

$$P_\omega(z) = \sum_{mn} P_{mn}(z), \quad \text{where} \quad P_{mn}(z) = \frac{\omega |A_{mn}^x(z)|^2}{2\mu_0 c_0}. $$

(4.10)

**Amplitude equation**

Parametric processes are nonlinear interactions which occur in crystals which do not show any resonances at any of the frequencies
4.1 Theory of Sum-Frequency Generation

involved, i. e. the medium is reactive: the power which is sent into the crystal by one wave is to be taken away by other waves. In the case of sum-frequency generation \( \omega_1 + \omega_2 = \omega_3 \) the changes in total power between the input and output planes are related by

\[
\Delta \left( \frac{P_1}{\omega_1} \right) = -\Delta \left( \frac{P_3}{\omega_3} \right) \quad \text{and} \quad \Delta \left( \frac{P_2}{\omega_2} \right) = -\Delta \left( \frac{P_3}{\omega_3} \right). \quad (4.11)
\]

These equations are known as the Manley-Rowe relations. We find that the increase of the photon flux at the sum-frequency \( \omega_3 \) is equal to the decrease of the photon flux in the beams \( \omega_1 \) and \( \omega_2 \). However, the Manley-Rowe relations do not describe the magnitude of the power transferred to the wave at \( \omega_3 \).

4.1.3 Sum-Frequency Generation in \( \chi^{(2)} \) Media

The process of sum-frequency generation is illustrated graphically in Fig. 4.1. The input of two pump waves at \( \omega_1 \) and \( \omega_2 \) generates a new wave at the sum-frequency \( \omega_3 = \omega_1 + \omega_2 \) on the basis of the crystal’s second order nonlinearity \( \chi^{(2)} \).

![Figure 4.1: Illustration of sum-frequency generation in \( \chi^{(2)} \) media. Two pump waves at \( \omega_1 \) and \( \omega_2 \) generate the sum-frequency \( \omega_1 + \omega_2 \) on the basis of the crystal’s \( \chi^{(2)} \) nonlinearity.]

Our primary interest will be in transparent, lossless crystals where the coefficients \( d_{ijk} \) do not depend on the frequencies involved. In the following all the frequency dependencies in \( \mathbf{d} \) are dropped. Since no physical significance can be attached to the interchange of \( j \) and \( k \) (i. e. \( d_{ijk} = d_{ikj} \)), we can replace subscripts \( kj \) and \( jk \) by the contracted indices \( l \) according to

\[
xx \rightarrow 1 \quad yy \rightarrow 2 \quad zz \rightarrow 3 \quad (4.12)
\]

\[
yz = zy \rightarrow 4 \quad xz = zx \rightarrow 5 \quad xy = yx \rightarrow 6. \quad (4.13)
\]

The resulting \( d_{il} \) components form a \( 3 \times 6 \) matrix that acts on the
electric field column tensor to yield $P$ according to

$$
\begin{bmatrix}
P^{(2)}_{\omega_1 + \omega_2} \\
P^{(2)}_{\omega_1 + \omega_2} \\
P^{(2)}_{\omega_1 + \omega_2}
\end{bmatrix} = 2\varepsilon_0 \begin{bmatrix}
d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\
d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\
d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36}
\end{bmatrix} \times
\begin{bmatrix}
(E_{\omega_1})_x (E_{\omega_2})_x \\
(E_{\omega_1})_y (E_{\omega_2})_y \\
(E_{\omega_1})_z (E_{\omega_2})_z \\
(E_{\omega_1})_y (E_{\omega_2})_z + (E_{\omega_1})_z (E_{\omega_2})_y \\
(E_{\omega_1})_z (E_{\omega_2})_z + (E_{\omega_1})_x (E_{\omega_2})_x \\
(E_{\omega_1})_x (E_{\omega_2})_y + (E_{\omega_1})_y (E_{\omega_2})_x
\end{bmatrix}
$$

(4.14)

For practical reasons the axes of the coordinates are chosen to coincide with the symmetry axes of the crystal. Then, due to the crystal's symmetry, often specific tensor elements $d_{ij}$ disappear.

In practice one specific $d_{ij}$ coefficient is dominant because of its magnitude and because of the phase matching condition (4.1.4) and the polarizations of the fundamental waves $\omega_1$ and $\omega_2$ are chosen accordingly. If the coefficients $d_{11}$, $d_{12}$, or $d_{13}$ are used, the polarization of the fundamental waves is along the same crystal axis. This is called type I-interaction. Other orientations where the fundamental waves have projections onto two axes (e.g. $(E_{\omega_1})_x \neq 0 \neq (E_{\omega_1})_y$) are called type II-interaction.

**Type I-interaction**

We now consider type I-interaction and drop the indices. Then we find the following fundamental equations of parametric interaction for the nonlinear polarization

$$
P^{(1)}_{\omega_1}(r) = 2\varepsilon_0 dE_{\omega_1}(r) E^*_\omega_1(r) 
$$

(4.15)

$$
P^{(2)}_{\omega_1}(r) = 2\varepsilon_0 dE_{\omega_1}(r) E^*_\omega_1(r) 
$$

(4.16)

$$
P^{(3)}_{\omega_1}(r) = 2\varepsilon_0 dE_{\omega_1}(r) E^*_\omega_1(r) ,
$$

(4.17)

where $P_{NL}$ and $E$ are the Fourier component amplitudes,

$$
E_\omega(r) = \tilde{E}_\omega(r)e^{-ik_\omega z}, \quad k_\omega = \frac{n_\omega \omega}{c_0} .
$$

(4.18)

The modes of each wave follow the amplitude equation (4.9), where $\psi_m^{\omega}$ are the base functions of the mode $\omega$ and can be chosen differently for each mode. Applying the polarization amplitudes $P_{NL}$
from Eqs. (4.15)-(4.17) in the amplitude equation (4.9) we get
\[ \frac{dA_{3}}{dz} = -i \kappa e^{i \Delta k z} \int \int dx \, dy \, A_{\omega_1}(r) A_{\omega_2}(r) \left( \psi_{mn}^{\omega_3}(r) \right)^* \] (4.19)
\[ \frac{dA_{1}}{dz} = -i \kappa e^{-i \Delta k z} \int \int dx \, dy \, A_{\omega_3}(r) A_{\omega_2}^*(r) \left( \psi_{mn}^{\omega_1}(r) \right)^* \] (4.20)
\[ \frac{dA_{2}}{dz} = -i \kappa e^{-i \Delta k z} \int \int dx \, dy \, A_{\omega_3}(r) A_{\omega_1}^*(r) \left( \psi_{mn}^{\omega_2}(r) \right)^* \] (4.21)
with \[ \kappa := \frac{d}{c} \sqrt{\frac{n_{\omega_1} n_{\omega_2} n_{\omega_3}}}, \]

the total field amplitudes \( A \), and the phase mismatch expressed by the wave vectors
\[ \Delta k = k_3 - k_1 - k_2. \] (4.22)

The phase mismatch determines whether the integral is constant (i.e. independent of \( z \)), or whether the amplitude of the generated wave is enhanced or inhibited. The inverse phase mismatch
\[ L_c = \left| \frac{\pi}{\Delta k} \right|, \] (4.23)

is called coherence length and is thus a measure of the maximum crystal length that is useful in producing sum-frequency power. The indices of refraction \( n_{\omega} \) are polarization dependent.

We now assume Gaussian TEM\(_{00}\) modes in the pump waves. We obtain
\[ \tilde{E}_{\omega_1,2}(r) = \sqrt{\frac{\omega_{\omega_1,2}}{n_{\omega_1,2}}} A_{00,1,2}^{\omega_1,2}(z) \psi_{00}^{\omega_1,2}(r). \] (4.24)

For simplicity we set \( A_{\omega_1,2} = A_{00,1,2}^{\omega_1,2} \). From (4.19) we get
\[ \frac{dA_{mn}^{\omega_3}(z)}{dz} = -i \kappa e^{i \Delta k z} \cdot O_{mn}(z) \cdot A_{\omega_1}(z) A_{\omega_2}(z) \] (4.25)

with the overlap integral
\[ O_{mn}(z) = \int \int dx \, dy \, \psi_{00}^{\omega_1}(r) \psi_{00}^{\omega_2}(r) \left( \psi_{mn}^{\omega_3}(r) \right)^*, \] (4.26)

which is a function of \( z \) only.

In the simplest case of weakly focused collimated beams (which however is not very realistic and will be corrected in \((\to 4.1.5))\), the overlap integral is independent of \( z \): \( O_{mn}(z) \equiv O_{mn} \). To further simplify the analysis, and yet retain its validity for the majority of the experimental situations where the defacto conversion efficiencies are small, we assume the following: the amount of power lost from the input beams by conversion is negligible, so that the amplitudes of the pump waves remain approximately constant \( A_{\omega_1,2}(z) \approx A_{\omega_1,2}(0) =: A_{\omega_1,2} \). Thus we can integrate (4.25) when
only the pump waves $\omega_1$ and $\omega_2$ are sent through the crystal and $\omega_3$ is generated exclusively in the nonlinear crystal ($A_{mn}^{\omega_3}(z = 0) = 0$, Fig. 4.1):

$$A_{mn}^{\omega_3}(L) = \frac{-i}{c} \sqrt{\frac{\omega_1 \omega_2 \omega_3}{n_{\omega_1} n_{\omega_2} n_{\omega_3}}} \cdot \mathcal{O}_{mn} \cdot A_{\omega_1} A_{\omega_2} \frac{e^{i \Delta k L} - 1}{i \Delta k}. \quad \text{(4.27)}$$

**Power of the generated sum-frequency mode**

Using (4.10) we can now find the power of the generated sum-frequency mode

$$P_{mn}^{\omega_3} = 2 \frac{d^2 \mu_0}{c_0} \frac{\omega_3^2}{n_{\omega_1} n_{\omega_2} n_{\omega_3}} |\mathcal{O}_{mn}|^2 P_1 P_2 L^2 \text{sinc}^2 \left( \frac{\Delta k L}{2} \right), \quad \text{(4.28)}$$

which is proportional to $L^2$ and is dependent on the phase mismatch $\Delta k L = L(k_3 - k_2 - k_1)$ as shown in Fig. 4.2.

![Figure 4.2: Plot of the phase mismatching dependence of the generated sum-frequency power on $\Delta k L$ (as in (4.28)). The maximum is achieved at phase matching $\Delta k L = 0$.](image)

**Transverse Gaussian field distribution**

Now we take the Gaussian transverse profile of the field into account

$$\psi_{00}(r) = \sqrt{\frac{2}{\pi}} \frac{1}{w_0(1 - i\tau)} \exp \left( -\frac{x^2 + y^2}{w_0^2(1 - i\tau)} \right), \quad \text{(4.29)}$$

with $\tau := \frac{z - z_0}{z_R}$,

where $z_0$ is the location of the focus, $z_R = \pi w_0^2 n/\lambda$ the Raleigh range, and $w_0$ the beam waist in the location $z_0$. As mentioned above, the longitudinal focusing is neglected: $L \ll z_R$ hence $\tau \approx 0$. The term $\psi_{00}^{\omega_1} \psi_{00}^{\omega_2}$ within the overlap integral (4.26) then yields

$$\psi_{00}^{\omega_1}(r) \psi_{00}^{\omega_2}(r) = \sqrt{\frac{2}{\pi}} \frac{1}{w_0^{\omega_1} w_0^{\omega_2}} \exp \left( -\frac{x^2 + y^2}{w_0^{\omega_1} w_0^{\omega_2} / (w_0^{\omega_1} + w_0^{\omega_2})} \right)$$

$$= \sqrt{\frac{2}{\pi}} \frac{w_0^{\omega_3}}{w_0^{\omega_1} w_0^{\omega_2}} \psi_{00}^{\omega_3}(r). \quad \text{(4.30)}$$
Besides of the pre-factors, the transverse beam profile of the generated sum-frequency beam is again equal to a new TEM$_{00}$ mode having a waist of

$$w_{0 \omega_3} = \frac{w_{0 \omega_1} w_{0 \omega_2}}{\sqrt{w_{0 \omega_1}^2 + w_{0 \omega_2}^2}}. \tag{4.31}$$

Using the orthogonality relations of the Gaussian modes we find

$$\mathcal{O}_{mn} = \sqrt{\frac{2}{\pi}} \frac{w_{0 \omega_3}}{w_{0 \omega_1} w_{0 \omega_2}} \delta_{m0} \delta_{n0}. \tag{4.32}$$

We see that for the choice of $w_{0 \omega_3}$ according to (4.31), no higher order modes will be generated in the sum-frequency wave.

We have a closer look at the situation of perfect phase matching $k_3 = k_2 + k_1 \Rightarrow \text{sinc}^2(\Delta k L/2) = 1$, $n_{\omega_3} \omega_3 = n_{\omega_1} \omega_1 + n_{\omega_2} \omega_2$ and equal Rayleigh ranges of the two pump waves $z_R = z_{R \omega_1} = z_{R \omega_2}$ (where $z_{R \omega} = \frac{\pi n_{\omega} w_{\omega}}{\lambda_{\omega}}$), which is the case for doubly-resonant sum-frequency generation. Then the total power in the generated sum-frequency beam is

$$P_{\omega_3} = P_{\omega_3}^{00} = 2 \frac{\mu_0 d^2}{\pi \varepsilon_0} \frac{\omega_1 \omega_2 \omega_3}{n_{\omega_3}^2} L \left( \frac{L}{z_R} \right) P_1 P_2. \tag{4.33}$$

This is valid for $L/z_R \ll 1$.

Eq. (4.33) indicates that high intensities in the pump beams and a long crystal length are advantageous to achieve high powers at $\omega_3$. However, unlimited increase of the crystal length and reduction of the beam waist would contradict the assumption $L \ll z_R$. A more comprehensive analysis is presented (→4.1.5).

### 4.1.4 Phase Matching

The function $\text{sinc}^2(\Delta k L/2)$ in (4.28), Fig. 4.2 causes an oscillation of the generated sum-frequency power along the interaction length. This can be interpreted as follows. In the entrance plane of the crystal all three waves have matching phases. The interaction via $d$ is optimal and the power in $P_{\omega_3}$ is increased. During propagation all three waves have different indices of refraction and their phases start mismatching. After the coherence length $L_c = \left| \frac{\pi}{\Delta k} \right|$, (4.23), the phase is inverted and destructive interference takes place, the power in $P_{\omega_3}$ is decreased.

Phase matching

$$\Delta k = 0. \tag{4.34}$$

is required to circumvent this effect. This can be fulfilled if all wave vectors (i.e. the phase velocities in the crystal) are adjusted...
Bandwidth

The width of the sinc^2 phase matching curve for a specified parameter (such as temperature $T$ of the crystal, wavelength $\lambda$ of the light, length $L$ of the crystal or angle $\theta$, $\varphi$ of the crystal orientation) is called phase matching bandwidth of the parameter.

Energy & momentum conservation

In the photon picture of sum-frequency generation where two photons having the energy $\hbar \omega_1$ and $\hbar \omega_2$ generate a new one of the sum-energy $\hbar \omega_3 = \hbar \omega_1 + \hbar \omega_2$ (energy conservation), the phase matching condition can be understood as momentum conservation:

$$\hbar \mathbf{k}_3 = \hbar \mathbf{k}_1 + \hbar \mathbf{k}_2.$$  \hspace{1cm} (4.35)

One distinguishes between collinear (scalar) phase matching where $\mathbf{k}_1 || \mathbf{k}_2 || \mathbf{k}_3$ and vectorial phase matching where $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$ form a triangle.

Dispersion

Typically, when the crystal is transparent over the whole relevant spectral region, the crystal shows normal dispersion, i.e. the index of refraction is increasing with $\omega$ increasing: $dn/d\omega > 0$. Thus it is non-trivial to fulfill the phase matching condition.

Birefringence

A solution is found by taking advantage of the birefringent properties of the crystal, when the laser beams are polarized along different axis of the crystal. The fields then couple via the off diagonal elements of $d_{ij}$.

In general we have two options to fulfill the phase matching condition [84].

- If the different temperature dependence along the crystal axis is used, we talk about non-critical phase matching.

- We talk about critical phase matching, if the angles $\theta$ and $\varphi$ between the optical axes of the crystal and the direction of the incident pump waves are adjusted to fulfill the phase matching condition. However, this method causes a walk-off effect between the sum-frequency beam and the fundamental beams, which limits the effective interaction length and conversion efficiency.

Phase matching in uniaxial crystals

We now consider critical phase matching in uniaxial crystals. Biaxial crystals are much more complicated, but the practically relevant situations can often be reduced to the uniaxial situation, like in our case of LBO (→4.3).

Index ellipsoid

The index ellipsoid of a negative uniaxial crystal is shown in Fig. 4.3.

The crystal has an optical axis in $Z^1$ direction. A light beam (wave vector $\mathbf{k}$) propagating along the optical axis experiences the index

\footnote{We note that the variable $Z$ in this thesis denotes two quantities: the direction of propagation of the light field and the optical axis. The context should clarify which quantity is being denoted.}
4.1 Theory of Sum-Frequency Generation

![Index ellipsoid of an uniaxial crystal. In the \((X,Y)\)-plane LBO, which is biaxial, can be treated like an uniaxial crystal (see Fig. 4.4).](image)

of refraction \(n_o\) - independent of its the polarization. In the general case, we consider the principal plane spanned by the optical axis \(Z\) and the wave vector \(k\). Rays with polarization orthogonal to the plane are called ordinary \((o)\) and have the unique index of refraction \(n_o\), while those rays with polarization within the plane are called extraordinary \((e)\) and have a \(\mu\) dependent index of refraction

\[
\mu^e(\theta) = n_o \sqrt{\frac{1 + \tan^2 \theta}{1 + (n_o/n_e)^2 \tan^2 \theta}},
\]

where \(n_e\) is the index of refraction of an extraordinary ray propagating orthogonal to the optical axis \(Z\). In uniaxial crystals the angle \(\phi\) in the \(xy\)-plane is not of relevance. Crystals where \(n_e < n_o\) are called negative, those with \(n_e > n_o\) positive uniaxial.

To fulfill the phase matching condition for sum-frequency generation in uniaxial crystal one needs to find an appropriate choice of ordinary and extraordinary rays in a way that

\[
k_3^{(o,e)} = k_1^{(o,e)} + k_2^{(o,e)} \to n_3^{(o,e)} \omega_3 = n_1^{(o,e)} \omega_1 + n_2^{(o,e)} \omega_2.
\]

If more than one solution is found, the solution coupled to the larger tensor element \(d_{ij}\) is preferentially used. The interaction is named according to the polarizations applied, e.g. \(oee\) for ordinary rays \(\omega_1\), \(\omega_2\) and an extraordinary ray \(\omega_3\). Further equations for the different types of phase matching are found in [86]. The temperature and the orientation of the crystal can be used for fine adjustment.

The \textit{walk-off angle} of the extraordinary ray depends on the angle \(\theta\) between the wave vector and the optical axis of the crystal and is given by [86]

\[
\rho(\theta) = \pm \arctan \left( \frac{n_o}{n_e} \right)^2 \tan \theta \mp \theta,
\]

where the upper signs apply to negative uniaxial crystals, the lower signs to positive uniaxial crystals.

Walk-off angle
4.1.5 Gaussian Beams

In section 4.1.3 the calculation of the overlap integral $O_{mn}(z)$ was simplified by the assumption of collimated beams ($L \ll z_R$), which led to a $z$ independent expression $O_{mn}$. Later on it was noted, that high intensities in the pump beams are advantageous with respect to the generated sum-frequency power, which contradicts the assumption. In this section we will drop that simplification and treat the case of realistic Gaussian beam profiles. This leads to the Boyd-Kleinman integral [87], derived from the theory of second-harmonic generation with Gaussian beams, and allows the determination of the optimal focusing geometry.

We consider $z$-dependent Gaussian TEM$_{00}$ modes in the pump beams according to Eqs. (4.24, 4.29). The generated light wave may also contain higher order ($mn$) modes. The overlap integral is then given by

$$O_{mn}(z) = \left( \frac{2}{\pi} \right)^{3/2} \frac{1}{w_{0\omega_1}(1 - i\tau_1)} \frac{1}{w_{0\omega_2}(1 - i\tau_2)} \frac{1}{w_{0\omega_3}(1 + i\tau_3)} \times \right. \left. \int \int \exp \left( -\frac{x^2 + y^2}{w_{0\omega_1}^2(1 - i\tau_1)} - \frac{x^2 + y^2}{w_{0\omega_2}^2(1 - i\tau_2)} - \frac{x^2 + y^2}{w_{0\omega_3}^2(1 + i\tau_3)} \right) \cdot \mathcal{H}_m \left( \frac{\sqrt{2}x}{w_3(z)} \right) \mathcal{H}_n \left( \frac{\sqrt{2}y}{w_3(z)} \right) dx \, dy , \quad (4.39)$$

where $\tau_i = (z - z_{0\omega_i})/z_{R\omega_i}$ and $\mathcal{H}_i$ are the Hermite polynomials.

Considering doubly resonant SFG

In the set-up of doubly resonant sum-frequency generation the two fundamental waves are resonated in the same cavity. Consequently these waves have the same location of the foci $z_{0\omega_1} = z_{0\omega_2} \equiv z_0$ and identical Rayleigh ranges $z_{R\omega_1} = z_{R\omega_2} \equiv z_R$, and from that follows $\tau_1 = \tau_2 \equiv \tau$. By choosing $z_{R\omega_3} = z_R$, $z_{0\omega_3} = z_0$, and $\tau_3 = \tau$ as the basis values of the generated beam $\omega_3$ the exponent in the integral simplifies to

$$-\frac{x^2 + y^2}{1 + \tau^2} \left( w_{0\omega_1}^{-2} + w_{0\omega_2}^{-2} + w_{0\omega_3}^{-2} - i\tau(w_{0\omega_1}^{-2} - w_{0\omega_1}^{-2} - w_{0\omega_2}^{-2}) \right) . \quad (4.40)$$

Assuming good phase matching $n_{\omega_1}\omega_1 + n_{\omega_2}\omega_2 \approx n_{\omega_3}\omega_3$ and using $z_R = \pi w_0^2 n/\lambda = w_0^3 n\omega/2c_0$ and the specific choice for the basis values of $\omega_3$ we find $w_{0\omega_1}^{-2} + w_{0\omega_2}^{-2} \approx w_{0\omega_3}^{-2}$. The exponent further simplifies to

$$\frac{x^2 + y^2}{1 + \tau^2} \frac{2}{w_{0\omega_3}^2} = -\frac{2(x^2 + y^2)}{w_{\omega_3}^2(z)} \quad (4.41)$$

where $w_{\omega_3}^2(z) = (1 + \tau^2)w_{0\omega_3}^2$.

Using the orthogonality relation of the Gaussian modes we find that the light generated by doubly-resonant SFG by TEM$_{00}$ fundamental waves does not contain higher modes.
The overlap integral finally yields

$$O_{mn}(z) = \sqrt{\frac{2}{\pi}} \frac{w_{0\omega_3}}{w_{0\omega_1} w_{0\omega_2}} \frac{1}{1 - i\tau} \delta_{m0} \delta_{n0}.$$ (4.42)

To find an expression for the generated SFG power, the amplitude equation (4.9) needs to be integrated over $z$. Assuming constant amplitudes of the fundamental waves over $z$, the integral

$$I_{mn} \equiv \frac{1}{L} \int_0^L dz \, O_{mn}(z) e^{i\Delta k z}$$ (4.43)

can be rewritten as

$$|I_{00}|^2 = \frac{4}{\pi} \left( \frac{w_{0\omega_3}}{w_{0\omega_1} w_{0\omega_2}} \right)^2 \frac{z_R}{L} h,$$ (4.44)

where $h$ is the Boyd-Kleinman factor, analogous to that known from the theory for the second harmonic generation using Gaussian beams [87]:

$$h \equiv \frac{z_R}{2L} \left| \int_{r(z=0)} \frac{e^{i\Delta k z_0 \tau}}{1 - i\tau} d\tau \right|^2.$$ (4.45)

Replacing in (4.28) the term $|O|^2 \text{sinc}^2$ by $|I_{00}|^2$, we find the generated sum-frequency power

$$P_3 = E_{SFG}^{NL} \cdot P_1 \cdot P_2 \quad \text{with} \quad E_{SFG}^{NL} \equiv \frac{4 \mu_0}{\pi c_0^2} \frac{\omega_1 \omega_2 \omega_3}{n_{\omega_3}^2} \cdot h \cdot L.$$ (4.46)

Here we have defined the effective nonlinearity of sum-frequency generation $E_{SFG}^{NL}$. As a test we compare it to the degenerate case of frequency-doubling described in [88] and find the relation $E_{SFG}^{NL} = 4E_{SHG}^{NL}$. This is physically reasonable, since the power $P_0$ in the fundamental wave in SHG is distributed over the two fundamental waves in SFG: $P_1 = P_2 = P_0/2$. Thus $P_1 P_2 = P_0/4$ which explains the factor of 4.

The Boyd-Kleinman integral (4.45) takes on a maximum value $h = 1.07$ at the optimal ratio between Rayleigh range and crystal length of $z_{R\text{opt}} = L/5.7$ [87]. Interestingly, the optimum is for a small phase mismatching $\Delta k L \neq 0$. This can be understood as the best compromise between high intensity and a large interaction region: on the one hand, a small focus (small Rayleigh range $z_R$) yields a high intensity, but on the other hand the radius of curvature of the wavefront increases rapidly with the distance from the focus (4.54), which leads to phase mismatching. The phase matching condition ($\Delta k L = 0$) is only valid in the unrealistic situation of collimated beams. The phase dependence of the Boyd-Kleinman integral
factor is nevertheless still in good agreement with the \( \text{sinc}^2 \) function, and is hence often used for a general description.

Neglecting any losses in the input beams, the optimum location of the focus is in the center of the crystal; deviations in the range of \( \pm L/10 \) are negligible.

### 4.2 The Idea of Doubly Resonant SFG

Eq. (4.46) shows that the generated sum-frequency power is proportional to the power of the fundamental waves in the nonlinear medium: \( P_{\omega_1+\omega_2} \propto P_{\omega_1} \cdot P_{\omega_2} \). Consequently high pump powers lead to high conversion efficiencies.

By placing the crystal in a optical cavity resonating both pump waves, the generated power of the sum-frequency is increased proportionally both enhancement factors of the pump waves. The achievable enhancement factors of the cavity for doubly-resonant SFG depend on

- the overlap of the incident light mode with the cavity mode: \textit{mode matching},
- the losses in the resonator,
- and the transmissions of the incoupling mirror: \textit{impedance matching}.

In a doubly-resonant set-up the resonance condition for both waves has to be fulfilled. For the first wave this is achieved by adjusting the cavity length \( U \) of our ring cavity (i.e. the optical length of one round-trip) to \( U = N_1 \lambda_1 \), where \( N_1 \) can assume any integer value\(^2\).

The resonance condition of the second wave is fulfilled by adjusting the frequency of the second wave to fit the cavity: \( U = N_2 \lambda_2 \). The sum-frequency is then given by

\[
\omega_3 = \omega_1 + \omega_2 = \left( 1 + \frac{\omega_2}{\omega_1} \right) \omega_1 = \left( 1 + \frac{\lambda_1}{\lambda_2} \right) \omega_1 = \left( 1 + \frac{N_2}{N_1} \right) \omega_1.
\]

(4.47)

Two control circuits, described in (\( \rightarrow \)4.6.2), keep the cavity and the second fundamental wave on resonance, and thus hold \( N_1 \) and \( N_2 \) constant. The whole system is then stabilized to the frequency \( \omega_1 \), and frequency tuning of the sum-frequency output can be achieved by tuning the fundamental wave \( \omega_1 \). This was experimentally verified and is shown in (\( \rightarrow \)4.8).

\(^2\)The cavity length is named \( U \), since \( L \) is already assigned to crystal length
Higher output powers, especially at low input powers, could be achieved by resonating the sum-frequency wave, too. However, this would rather complicate the stabilization circuits and degrade the possibilities of frequency tuning and was thus not pursued in our project.

4.3 The Crystal

The selection criteria of the crystal are a high nonlinearity on the one hand and a low absorption loss on the other. In our project we have chosen lithium triborate (LiB$_3$O$_5$, LBO). The characteristic data of LBO found in the literature are collected in Tab. 4.1.

<table>
<thead>
<tr>
<th>Crystal Class</th>
<th>Negative Biaxial Orthorhombic, mm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparency Region</td>
<td>155 nm – 3.2 µm</td>
</tr>
<tr>
<td>Linear Absorption Losses [89]</td>
<td>$\alpha = 0.31$ % /cm @ 350 nm</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 0.035$ % /cm @ 1064 nm</td>
</tr>
<tr>
<td>Indices of Refraction</td>
<td>$n_X = n_Y = n_Z =$</td>
</tr>
<tr>
<td>@ 760 nm</td>
<td>1.5703 1.5971 1.6121</td>
</tr>
<tr>
<td>@ 532 nm</td>
<td>1.5785 1.6065 1.6216</td>
</tr>
<tr>
<td>@ 313 nm</td>
<td>1.6070 1.6387 1.6545</td>
</tr>
</tbody>
</table>

Table 4.1: Characteristics of LBO. The indices of refraction were calculated from the empirical found Sellmeier equation [86].

Compared to other nonlinear crystals LBO shows a significantly greater nonlinearity than KDP or KTP. BBO (Beta-Barium Borat) in which phase matching for the desired sum-frequency generation is also possible, shows a slightly higher nonlinearity, but much higher absorption losses which would degrade the enhancement factors of the cavity in the doubly resonant set-up. Additionally, BBO causes a greater walk-off angle (4.38) than LBO, shortening the effective crystal length. The required powers would thus be not achieved with a BBO crystal. With respect to the experimental stability, the phase matching of LBO is less sensitive with respect to angular misalignment.

Unfortunately, periodically poled (PP) materials like PP lithium tantalate, which reach extremely high conversion efficiencies using quasi phase matching [90], cannot be used for sum-frequency generation of 313 nm: on the one hand they are strongly absorbing in the UV spectral region, on the other hand there is no technology available to produce the required short poling periods.

In addition to what was already mentioned, LBO is a mechanically robust, non-hygrosopic material, that can be well machined, which
allows a good quality of the crystal’s facets. These reasons and the good experience in neighboring laboratories (dealing with SHG) led to the choice of LBO.

**Degradation observed**

After several weeks of operation degradation of the conversion efficiency was observed. Placing the crystal in an oxygen atmosphere avoided this. A similar observation was reported from the neighboring lab, but it is not yet clear, whether the dry atmosphere or the oxygen is of relevance.

**Refractive indices for a biaxial crystal**

The angular behavior of the refractive indices for a biaxial crystal is represented by two superimposed three-dimensional ellipsoids in momentum space. The surface of these overlapping ellipsoids is known as the “normal surface” and, in general, has four points of intersection. The lines that go through the origin and two of the points are known as the optical axes. Fig. 4.4 shows one of the optical axes.

**Figure 4.4:** Normal surface of shown for the biaxial crystal LBO. The sum-frequency generation is performed in the xy-plane, where LBO behaves like an uniaxial crystal.

**Optical axis**

Light propagation along the optical axis has a unique phase velocity regardless of polarization. The group velocity \( v_g = \nabla_k \omega(k) \) which represents the flow of electromagnetic energy – is, however, undefined in this direction, because the two shells of the normal surface degenerate to a singular point. If one draws unit normal vectors perpendicular to the normal surface at that singular points in infinitesimal neighborhood, these vectors form a surface of a cone. Therefore, the flow of electromagnetic energy will take the form of a cone. This phenomenon is known as conical refraction [84].

**Principal plane**

The beams propagating in a principal plane \((X, Z), (X, Y), \) or \((Y, Z)\) with polarization perpendicular to that plane behave in a manner similar to that of the beams propagating orthogonally to the main optical axis of uniaxial crystal and have constant indices
of refraction (circles) \( n_Y \), \( n_Z \), or \( n_X \), respectively. The refraction indices for the in-plane polarization exhibit an elliptical behavior. Unlike uniaxial crystals, where circle and ellipse always touch, in the biaxial crystal the circle and ellipse may cross (like in the \((X, Z)\) plane in Fig. 4.4) or stay separated.

In the \((X, Y)\) plane \((\theta = 90^\circ)\) LBO behaves like an uniaxial crystal with \( n_o = n_Z \) and

\[
n^e(\varphi) = n_Y \sqrt{\frac{1 + \tan^2 \varphi}{1 + (n_Y/n_X)^2 \tan^2 \varphi}}, \tag{4.48}
\]

where \( \varphi \) is the angle in the \((X, Y)\) plane (compare (4.36)). With the data given, we can now fulfill the phase matching condition (4.37) in this plane for ooe type I interaction and find the critical angle of phase matching

\[
\varphi = 54.10^\circ \quad \text{where} \quad n^e(54.10^\circ; 313 \text{ nm}) = 1.6177. \tag{4.49}
\]

The corresponding walk-off angle due to birefringence is \( \rho = 1.2^\circ \).

Assuming the spot size (beam diameter) on the order of 100 \( \mu m \), the interaction length is limited to about 15 mm. The chosen cut of the crystal is illustrated in Fig. 4.5. Other types of interaction, as well as interaction in other planes, cannot fulfill our specific phase matching condition.

The ooe type-I interaction strength in the \((X, Y)\) plane is given by the \( d_{32} \) coefficient reduced by the factor \( \cos \varphi \). The effective nonlinear coefficient is

\[
d_{ooe} = d_{32} \cos \varphi \approx 0.5 \cdot 10^{-12} \text{ m/V} \tag{4.50}
\]

where \( d_{32} \approx \pm 0.85 \text{ pm/V} \) [86, 89].

With (4.33) we can determine the effective nonlinearity

\[
E_{NL}^{\text{SFG}} = 0.092 \frac{\%}{\text{cm W} \cdot L \cdot h}. \tag{4.51}
\]
We will now estimate the phase matching bandwidth \((\rightarrow 4.1.4)\) of the temperature. The behavior of the index of refraction in the range \(T = 20\ldots65\, ^\circ\text{C}\) and \(\lambda = 400\ldots1000\, \text{nm}\) is

\[
\frac{dn_X}{dT} \cdot 10^6 = -1.8, \quad \frac{dn_Y}{dT} \cdot 10^6 = -13.6, \quad \frac{dn_X}{dT} \cdot 10^6 = -6.3 - 2.1\, \lambda, 
\]

where \(\lambda\) = \(\mu\)m and \(\frac{dn}{dT}\) = \(K^{-1}\). One can estimate the bandwidth of the temperature using the \(\text{sinc}^2\left(\frac{kL}{2}\right)\) function, and finds \(\Delta T_{\text{FWHM}}/L \approx 17\, ^\circ\text{C/cm}\). This is considerably larger than the usual temperature drifts in our laboratory(!); a temperature stabilization of the crystal is hence not required.

The crystal (Fig. 4.5) which is used in our experiment, was ordered with the following specifications \(\varphi = 54.10^\circ\), \(\theta = 90^\circ\), \(L = 15\, \text{mm}\), cross-section \(3 \times 3\, \text{mm}^2\) from the company Photox. The crystal has planar facets providing perpendicular incidence of the light beams. A crystal cut under Brewster angle was discussed to avoid the reflection losses on the surfaces, and possibly correct the astigmatism of a ring-resonator. But it turned out that a proper overlap of the two pump beams (due to refraction) in a Brewster cut crystal cannot be achieved. Therefore a crystal with perpendicular facets was ordered and subsequently coated by the company Dünnschicht-Technik Tafelmeier with a triple antireflection coating. The data of the coating are listed in Tab. 4.4.

### 4.4 The Laser Sources

As mentioned before, our approach (Fig. 4.12) is based on doubly resonant sum-frequency mixing of a high-power, single-frequency, doubled Nd:YAG laser (532 nm) and a tunable diode laser. The latter can be an external cavity laser (ECL) or distributed feedback (DFB) laser, and is thus of modest cost. The high power of the Nd:YAG laser (more than 10 W single-frequency power at 532 nm are commercially available at present) ensures that the sum-frequency power attains a level useful for a wide range of applications.

#### 4.4.1 The 532 nm Laser

The first fundamental laser is a master oscillator-power amplifier (MOPA) Nd:YAG laser, which is single-pass frequency-doubled in a 60 mm long periodically poled lithium niobate crystal. The setup of this laser is shown in Fig. 4.6. It was built up as part of the diploma thesis of Dennis Weise [91].
A diode laser pumped Nd:YAG master-laser (type Lightwave 122) is sent into a power amplifier unit (type Lightwave 126) which itself is diode pumped, too. The maximum achieved infrared output power at 1064 nm is 10.4 W.

The output of the MOPA system is single pass frequency doubled in a SHG stage using PPLN. We achieved the highest conversion efficiency of 42% with 8 W of Nd:YAG light at 1064 nm producing 3.2 W of green light at 532 nm required for the SFG. The achievable output power is strongly dependent on the local quality of the periodically poled crystal. Usual powers available for the sum-frequency generation are between 1 W and 3 W. After several weeks of operation we observed degradation of the PPLN crystal in the SHG stage.

The generated frequency doubled light inherits the excellent spectral properties of the Nd:YAG master laser to a high degree: the linewidth is about 10 kHz, the free running frequency drift less than 20 MHz/h, and the mode quality is TEM$_{00}$, $M^2 < 1.1$.

Due to the non-resonant set-up of the frequency doubler, modu-
lition of the master laser is transferred to the 532 nm light. The master oscillator can be frequency modulated via a piezotransducer on the Nd:YAG crystal, which is later used for the frequency lock of the SFG cavity to the 532 nm light (→4.6).

**Tunability**

By changing the temperature of the Nd:YAG crystal the master laser can be frequency tuned without mode-hops by 8 GHz. Since the SFG cavity is locked to the 532 nm wave, and the second fundamental laser is locked to the cavity, the frequency tuning of the master laser controls the tuning of the UV light (→4.8), and in the same way, the frequency stability is transferred to the UV light (→4.9).

### 4.4.2 The 760 nm Laser

**External cavity diode laser**

The second laser is a 760 nm external cavity laser (type TUI Optics, DL100).

The used laser diode (type Specdlas-F760) has a free-running nominal output power of 40 mW. Due to the optical feedback from the grating into the laser diode, the output power of the system should be limited to below half of the free-running power. Usual experimental output powers are in the region of 12 mW.

**Output power**

Furthermore, the optical feedback guarantees a small linewidth of about 1 MHz.

**Spectral properties**

Modulation of the diode laser can be achieved by modulating the diode current and is used to lock the laser to the cavity (→4.6).

The system is build up in Littrow configuration: the first diffraction order reflection from the grating is sent back into the laser diode. This set-up of an external cavity represents a wavelength sensitive optical feedback.

**Tunability**

The angle of the diffraction grating gives a coarse tuning range of 6 nm. Selection of the closest longitudinal mode of the laser diode to the desired frequency is achieved by adjusting the temperature of the diode by a peltier element and the diode current. The angle of the diffraction grating and the cavity length is then varied with a piezo to tune the frequency of the mode more accurately.

Control of the grating via a piezoelectric transducer (with a feed-forward to the diode current) allows a mode-hop free tuning by up to 15 GHz. Additionally, a direct control of the diode current via a field-effect transistor connected parallel to the laser diode gives a high closed loop bandwidth of 200 kHz, which provides a stable lock onto the cavity and allows stable long term operation of the SFG stage (→4.7), and a large continuous tuning range (→4.8).
4.5 Set-up of the Cavity

As mentioned above (→4.2), the SFG output power is increased by enhancing the power of the two pump waves in a doubly resonant cavity. The concept and set-up of this cavity is described in this section.

The cavity should comply with the following criteria

- The cavity’s geometry and the mirror’s reflectivities should maximize the SFG output power, taking the available pump powers into account.
- The cavity has to simultaneously resonate the TEM$_{00}$ mode of both fundamental waves.
- The sum-frequency output is to be used for laser cooling of Be$^+$, requiring a continuous tunability by several GHz at stable output power.
- For the purposes of the experiment the system should provide stable long term operation.

4.5.1 Geometry

An optical resonator – optical counterpart of an electronic resonant circuit – confines and stores light at certain resonance frequencies. It may be viewed as an optical transmission system incorporating feedback; light circulates or is repeatedly reflected within the system, without escaping. The simplest resonator comprises two parallel mirrors between which light is repeatedly reflected with little loss [92].

In a linear resonator arrangement the light is reflected back on itself, which causes a standing light wave (“standing wave resonators”). In contrast, ring resonators have a fixed round trip orientation of the travelling light wave (“running wave resonators”). A ring cavity possesses some advantages compared to the linear cavity: sum-frequency is generated in only one direction and the incoupling mirror does not retroreflect onto the input beam. A typical set-up of a ring cavity is shown in Fig. 4.7.

Because of its shape, this kind of ring cavity arrangement is named “bow-tie cavity”. The cavity mode possesses two foci, a wider one in the incoupling beam $w_i$, and a tighter one between the two curved mirrors in the center of the crystal $w_c$. The angle $\theta$ is minimized to reduce astigmatism and aberration. Other cavity types were discussed, such with fewer mirrors, or cavities containing a Brewster-cut crystal, but calculations showed that a good overlap of the
pump beams could not be achieved. Therefore we decided to set up a bow-tie cavity, which in the following is discussed in further detail.

The cavity consists of two plane mirrors M1 and M2 at a distance $l$ and two concave mirrors M3 and M4. Mirror M1 is used for incoupling of both fundamental waves; the transmissions of the incoupling mirror are derived in (→4.5.6). Mirror M2 is mounted on a piezoelectric actuator to stabilize the cavity length to the green laser light. The focusing mirrors M3 and M4 have a radius $R_c$, corresponding to a focal length $f = R_c/2$, and the distance between them is $2d$. The total length $U$ of the cavity leads to a free spectral range of $\Delta \nu_{\text{FSR}} = c/U$. The reflection of the two incident beams from the incoupling mirror is used for the stabilization of the cavity to the MOPA, and the diode laser to the cavity (→4.6).

A stable resonator provides a stationary state of the light field (mode) with a Gaussian profile. Ideally, this resonator mode is solely defined by the geometry of the resonator and not by the incident light beam. It is named fundamental mode of the resonator. Fundamental modes of various frequencies (frequency spacing $\Delta \nu_{\text{FSR}}$) are called longitudinal modes. Transverse modes, on the other hand, show a different transverse beam profile and usually only small frequency deviations from the fundamental mode.

The profile of the fundamental mode is found by calculating the propagation of a Gaussian beam in the resonator and the condition that the parameters of the Gaussian beam after one round trip coincide with the starting parameters. In the following we will have a look at the calculation for a Gaussian beam. From that we will derive a criterion for the stability of the cavity mode and explore the details of the fundamental mode.

**Figure 4.7**: Schematic of a bow-tie shaped ring cavity.
4.5.2 Propagation of Gaussian Beams

A laser beam can be described by its frequency, amplitude, mode (e.g. TEM$_{00}$) and the Gaussian beam parameter $q$ given by [93]

$$\frac{1}{q(z)} = \frac{1}{R(z)} - i \frac{\lambda}{\pi n w^2(z)}, \quad (4.53)$$

where $R(z)$ is the radius of curvature of the wavefront, $w(z)$ the spot size, $n$ the index of refraction and $\lambda$ the vacuum wavelength. The q-parameter describes the geometry of a Gaussian beam.

Free space propagation is described by

$$q(z) = q_0 + z \quad w(z) = w_0 \sqrt{1 + \frac{z^2}{R^2}} \quad R(z) = z \left(1 + \frac{z^2}{R^2}\right). \quad (4.54)$$

Here $w_0 = w(z = 0)$ is the beam waist, i.e. the spot size in the location of the focus. $z_R = \frac{\pi w_0^2 n}{\lambda}$ the Rayleigh range, which is the distance from the focus in which the spot size $w(z)$ increases by a factor $\sqrt{2}$.

A general description of the propagation of Gaussian beams is found by the $ABCD$ law for Gaussian beams. There the $ABCD$ ray matrices known from classical ray optics are applied on the $q$ parameter in the following way

$$M = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \quad q' = \frac{A q + B}{C q + D}. \quad (4.55)$$

Here $q$ is the initial and $q'$ the final Gaussian beam parameter after propagation through all optical elements contained in $M = \cdots M_b \cdot M_a$.

The most important ray matrices are collected in Tab. 4.2.

<table>
<thead>
<tr>
<th>Optical Element</th>
<th>Ray Matrix</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free travel through homogeneous medium</td>
<td>$\begin{pmatrix} 1 &amp; d \ 0 &amp; 1 \end{pmatrix}$</td>
<td>$d = \text{distance of travel}$</td>
</tr>
<tr>
<td>Plane dielectric interface</td>
<td>$\begin{pmatrix} 1 &amp; 0 \ 0 &amp; \frac{n_1}{n_2} \end{pmatrix}$</td>
<td>$n_1$, $n_2$ indices of refraction</td>
</tr>
<tr>
<td>Thin lens or mirror of focal length $f$</td>
<td>$\begin{pmatrix} 1 &amp; 0 \ -\frac{1}{f} &amp; 1 \end{pmatrix}$</td>
<td>$f = R/2$ for mirror.</td>
</tr>
</tbody>
</table>

Table 4.2: Some important $ABCD$ ray matrices.
4.5.3 Stability of Gaussian Resonator Modes

To find a stable mode of the resonator, we ask specifically if there is a self-consistent value of \( q \) such that after one complete round trip this value will return to its initial value [94]:

\[
q'(z) = \frac{A q(z) + B}{C q(z) + D} = q(z) .
\] (4.56)

A stable cavity mode is found, if this holds for any value of \( z \) within the resonator and \( M(z) = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \) is the ray matrix of a complete round trip, starting at the specified location \( z \).

Using (4.53) the spot size and radius of curvature at the chosen reference plane can be determined by

\[
w^2(z) = \frac{2\lambda |B|}{\pi \sqrt{4 - (A + D)^2}} \quad R(z) = \frac{2B}{D - A} .
\] (4.57)

Solutions are restricted by real, positive values of \( w^2 \), other values lead to oscillating or exponentially increasing strength of the light field with the distance from the axis. The condition \( w^2 > 0 \) leads to the criterion of geometrical stability

\[
\left| \frac{A + D}{2} \right| \leq 1 .
\] (4.58)

Astigmatism

If the astigmatism due to the angle \( \theta \) on the mirrors is to be taken into account, the light field must be described separately in both transverse displacements (sagittal and tangential plane). In our calculation the following correction of the focal length \( f \) has to be performed [94]

\[
f_{\text{tang}} = \frac{R}{2} \cos \theta \quad f_{\text{sag}} = \frac{R}{2} \frac{1}{\cos \theta} .
\] (4.59)

This leads to slightly different stability regions and to a fundamental cavity mode that is slightly astigmatic for small values of \( \theta \).

4.5.4 Sizing the Resonator

The resonator is build of four stable mirror mounts (type Lees). The minimum distance between two mounts requires \( a_s = 55 \text{ mm} \) (Fig. 4.7). Calculation of the cavity mode shows that the distance \( l \) between the planar mirrors does not affect the beam waists significantly, and was thus fixed to \( l = 100 \text{ mm} \). All other sizes of the resonator (as defined in Fig. 4.7) are collected in Tab. 4.3.

The calculation of the cavity mode can be visualized using Fig. 4.8.
4.5 Set-up of the Cavity

**Specifications of the Cavity**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_i$</td>
<td>$\infty$</td>
<td>Planar mirrors defining the incoupling beam</td>
</tr>
<tr>
<td>$R_c$</td>
<td>100 mm</td>
<td>Curved mirrors defining the crystal beam</td>
</tr>
<tr>
<td>$a_s$</td>
<td>55 mm</td>
<td>Transverse size of the cavity</td>
</tr>
<tr>
<td>$l$</td>
<td>100 mm</td>
<td>Length of the incoupling beam</td>
</tr>
<tr>
<td>$2d$</td>
<td>124 mm</td>
<td>Length of the crystal beam</td>
</tr>
<tr>
<td>$L$</td>
<td>15 mm</td>
<td>Length of the crystal (→4.3)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>13°</td>
<td>Angle of incidence</td>
</tr>
<tr>
<td>$U$</td>
<td>483 mm</td>
<td>Cavity length</td>
</tr>
<tr>
<td>$\Delta\nu_{\text{FSR}}$</td>
<td>620 MHz</td>
<td>Free spectral range</td>
</tr>
</tbody>
</table>

**Sizes of the Cavity Modes**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$w_c$ (μm)</th>
<th>$w_i$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>532 nm</td>
<td>40 μm</td>
<td>152 μm</td>
</tr>
<tr>
<td>760 nm</td>
<td>48 μm</td>
<td>182 μm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam waist in the center of the crystal, tangential plane</td>
<td>$w_{c}^{\text{tang}}$</td>
</tr>
<tr>
<td>Beam waist in the center of the crystal, sagittal plane</td>
<td>$w_{c}^{\text{sag}}$</td>
</tr>
<tr>
<td>Astigmatism in the center of the crystal</td>
<td>5% 4%</td>
</tr>
<tr>
<td>Beam waist in the center of the incoupling beam, neglecting the astigmatism</td>
<td>40 μm 48 μm</td>
</tr>
<tr>
<td>Boyd-Kleinman factor</td>
<td>$\approx 0.25$</td>
</tr>
</tbody>
</table>

Table 4.3: Specifications of the cavity. For definitions see Fig. 4.7, for further explanation see Fig. 4.8 and text.

**Figure 4.8:** Sizes of the beam waists of the cavity mode for both fundamental waves: 532 nm (dashed line) and 760 nm (solid line). $d$ is half the distance between the curved mirrors defining the crystal beam (Fig. 4.7). **Left:** Waists in the center of the crystal. Sagittal plane is drawn with positive sign, tangential plane with negative sign. **Right:** Waists in the center of the incoupling beam, neglecting the astigmatism.

The plots show the dependencies of the beam waists $w_c$ and $w_i$ over the half mirror distance $d$ for both fundamental waves (532 nm and 760 nm). The plot of the spot size $w_c$ in the crystal also shows the difference between the tangential and sagittal plane.

The violation of the stability condition (4.58) manifests itself by the waist $w_c$, with increasing $d$, getting imaginary after a minimum. At
small distances $d$, the stability is limited by the divergence of the waist $w_i$ in the incoupling beam. The plot shows slightly shifted stability regions for the tangential and sagittal plane. The optimal distance is found to be $d_{\text{opt}} = 62$ mm, where stability is present for both planes. On the one hand, this value is the best choice with respect to the astigmatism. On the other hand, it provides the best stability of the resonator against mechanical disturbances: if the cavity would be driven on a steep side of the stability region, small disturbances in the distance $d$ would lead to strong fluctuations in the cavity mode. The mechanical stability is more important than the better Boyd-Kleinman factor, which could be realized by an even smaller waist in the crystal, in the region of 15 µm.

Calculations of this type were also done for different radii of curvature $R_c$ of the mirrors defining the crystal beam, as well as for curved mirrors $R_e$ in the incoupling beam. A sharp focus in the incoupling beam would allow a second crystal being placed in the resonator for future extensions of the set-up. However, a sharper focusing resonator requires reduced distances $d$ and $l$, leading to stronger astigmatism, as long as $a_s$ cannot be reduced.

The following section explains, how the optimal transmission of the incoupling mirror is found and how the laser light is coupled into the cavity.

### 4.5.5 Mode Matching

To “fill” the cavity mode with laser light, the mode of the laser light has to be matched to the cavity mode. The transverse and angular overlap of each beam in the cavity is achieved with a pair of mirrors before the cavity. The longitudinal overlap of the light mode with the cavity mode is achieved with a two-lens system (telescope), which matches the location and size of the waists of each mode.

Rough adjustment of the incoupling can be done by watching the structure of the light mode that is transmitted through any mirrors of the cavity. Fine adjustment is performed by scanning the cavity and watching how well the TEM$_{00}$ is coupled into the cavity compared to other transverse modes. A measure of the incoupling is the intensity of the light reflected from the back of incoupling mirror (→4.5.6) or the intensity of the light transmitted through any other mirror.

When using resonators of high finesses, or very broadband pump lasers, the linewidth of the laser might be larger than the resonance $\delta\nu$ of the cavity; in such case not the complete power of the pump laser could be coupled into the cavity.
4.5.6 Impedance Matching

Impedance matching describes the optimization of the transmission of the incoupling mirror to maximize the energy circulating in the cavity.

The specific choice of the resonator’s dimensions \((l, d, a_s)\) leads to a longitudinal mode spacing, the free spectral range \(\Delta \nu_{\text{FSR}}\) (Tab. 4.3). Due to the losses in the cavity (“resonator lifetime”) the resonator’s resonance width \(\delta \nu\) is non-zero. The ratio between free spectral range and resonance width is called the cavity’s finesse

\[
F = \frac{\Delta \nu_{\text{FSR}}}{\delta \nu} = \frac{\pi [(1 - T)(1 - \alpha)]^{\frac{1}{2}}}{1 - \sqrt{(1 - T)(1 - \alpha)}} \approx \left(\frac{2\pi}{T + \alpha}\right) \quad (T, \alpha \ll 1) \quad (4.60)
\]

Herein \(\alpha\) contains all possible losses e. g. absorption of the crystal, diffraction, conversion, and losses of the mirrors, except that of the incoupling mirror M1 which is described by its transmission \(T\).

The transmission of the incoupling mirror is of essential importance for the optimization of the power circulating in the cavity. Maximum enhancement is obtained, if the round trip losses of the cavity, \(\alpha\), are compensated by the transmission \(T\) of the incoupling mirror. This situation is called impedance matching

\[
T = \alpha. \quad (4.61)
\]

In the situation of optimal mode- and impedance matching, the light from the pump laser reflected on the backside of the incoupling mirror interferes with light escaping from the cavity destructively.

With respect to sum-frequency generation, due to conversion, the losses of the green light depend on the circulating power of the red light and vice versa (4.11) & (4.46). This leads to coupling equations, which are discussed in this section. We will give both, an exact numerical treatment of the equations, and a handy approximation to quickly find the optimal transmissions of the incoupling mirror.

Look at the situation given in Fig. 4.9. We introduce the complex electric field amplitudes given by \(|E_i|^2 = P_i\) and \(|E_c|^2 = P_c\), and the amplitude transmission and reflection coefficients \(|t|^2 = T, |r|^2 = 1 - T\), and \(|r'|^2 = 1 - \alpha\). The circulating electric field amplitude is then described by

\[
E_c = tE_i + e^{i\phi}r'E_c, \quad (4.62)
\]

where \(\phi\) is the phase of the light wave after one round trip.

With \(P = |E|^2\) we find the enhancement factor between the circulating power and the power before the cavity

\[
\frac{P_c}{P_i} = \frac{|t|^2}{(1 - r'r)^2 + 4r'r \sin^2(\phi/2)} = \frac{|t|^2}{(1 - r'r)^2}, \quad (4.63)
\]
Figure 4.9: Schematic situation of impedance matching.

where in the last step resonance was assumed, $\sin(\phi/2) = 0$. Replacing the amplitude variables with those corresponding to the intensity, we find

$$\frac{P_c}{P_i} = \frac{T}{\left(1 - \sqrt{(1 - \alpha)}\sqrt{(1 - T)}\right)^2} \approx \frac{4T}{(\alpha + T)^2}, \quad (4.64)$$

Assuming impedance matching ($T = \alpha$), we find the relation $\frac{P_c}{P_i} = \mathcal{F}/\pi$. However, this is not directly applicable to our situation, where the losses $\alpha$ for the one wave depend on the circulating power of the other wave, and vice versa.

The mirrors of our resonator (Fig. 4.7) were produced by Layertec GmbH. The mirrors M2, M3, and M4 have the same customized HR HR HT coating: high-reflection for the fundamental waves at 532 nm and 760 nm, and high-transmission at the sum-frequency 313 nm. All data necessary to calculate the cavity’s round-trip losses are collected in Tab. 4.4.

<table>
<thead>
<tr>
<th>Internal losses in the cavity</th>
<th>532 nm</th>
<th>760 nm</th>
<th>313 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{HR}$</td>
<td>0.16 %</td>
<td>0.13 %</td>
<td>92.8%</td>
</tr>
<tr>
<td>$R_{HR}$</td>
<td>$\gtrsim$ 99.84 %</td>
<td>$\gtrsim$ 99.87 %</td>
<td></td>
</tr>
<tr>
<td>$R^c_A$</td>
<td>0.6 %</td>
<td>0.14 %</td>
<td>&lt; 2 %</td>
</tr>
<tr>
<td>$R^c_B$</td>
<td>0.75 %</td>
<td>0.09 %</td>
<td>&lt; 2 %</td>
</tr>
<tr>
<td>$\alpha^c$</td>
<td>0.035...0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{NL}^{SFG}$</td>
<td>$\approx$ 0.375/kW</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Data of internal losses in the cavity, i.e. all losses except those of the incoupling mirror. The mirrors were measured in transmission and 13° incidence. The crystal’s reflection at 313 nm could not be measured and is specified by the manufacturer.

As above, we now use the subscripts 1,2 to distinguish different values of a specific variable for the two fundamental waves. With the data from Tab. 4.4 we then find the wavelength dependent loss
rates for our specific cavity

$$\alpha_{1,2} = R^3_{HR,1,2} \left( 1 - R^c_{A1,2} \right) \left( 1 - R^c_{B1,2} \right) e^{-\alpha_{1,2} L}.$$ 

$$\cdot \left( 1 - E_{NL}^{SF} \frac{\omega_{1,2}}{\omega_3} P_{c2,1} \right)$$

$$=: R_{R1,2} \cdot \left( 1 - E_{NL}^{SF} \frac{\omega_{1,2}}{\omega_3} P_{c2,1} \right). \quad (4.65)$$

In this equation, all losses are collected in $R_{R1,2}$, except those of conversion. The loss due to conversion is derived from (4.46) and the fact that for each UV photon one photon from each fundamental wave is required. The latter leads to the factor $\omega_{1,2}/\omega_3$ in the conversion loss term, as also seen from (4.11).

The circulating powers of the fundamental waves in the cavity are now given by the coupled equations

$$P_{c1} = \frac{\kappa_{11}^{00} \cdot P_{i1} \cdot T_1}{\sqrt{1 - \left(1 - T_1\right) \cdot R_{R1} \cdot \left(1 - E_{NL}^{SF} \frac{\omega_1}{\omega_3} P_{c2} \right)}} \quad (4.66)$$

$$P_{c2} = \frac{\kappa_{22}^{00} \cdot P_{i2} \cdot T_2}{\sqrt{1 - \left(1 - T_2\right) \cdot R_{R2} \cdot \left(1 - E_{NL}^{SF} \frac{\omega_2}{\omega_3} P_{c1} \right)}},$$

where the additional parameter $\kappa_{12}^{00}$ quantifies the mode matching of the fundamental laser light with the corresponding TEM$_{00}$ cavity mode. For simplicity we assume $\kappa_{12}^{00} = 1$, and correct the measured laser power before the cavity by the effective incoupling efficiency to determine $P_{i1,2}$.

From (4.46) we see, that the output power of the sum-frequency is proportional to the product $P_{c1} \cdot P_{c2}$. For impedance matching we need to optimize the transmissions of the incoupling mirror $T_{1,2}$ to maximize the product $P_{c1} \cdot P_{c2}$.

In general, the circulating powers can be found by numerical solution of the two coupled equations (4.66). The SFG output $P_3$ can then be calculated. Before quantitative analysis is presented, some handy approximations are derived in the following to evaluate the optimal $T_{1,2}$ analytically without using computers.

**Impedance Matching for Small Losses and Small Internal Efficiencies**

We rewrite the circulating powers (4.66) in the form

$$\sqrt{\frac{T_1 P_{i1}}{P_{c1}}} = 1 - \sqrt{R_{R1} \left(1 - E_{NL}^{SF} \frac{\omega_1}{\omega_3} P_{c2} \right)}, \quad (4.67)$$
and a corresponding expression holds for \( P_{c_2} \) after subscript exchange \( 1 \leftrightarrow 2 \).

The optimum values can be calculated explicitly in the case of small losses \( \alpha_i \ll 1 \) and small internal efficiencies \( E_{NL}^{SFG} P_{c_{1,2}} \ll 1 \), when the square root in equation (4.67) can be approximated.

We define the normalized powers \( \varepsilon_i \) and the function \( f(\varepsilon_1, \varepsilon_2) \) as:

\[
\varepsilon_1 := \frac{\omega_2 E_{NL}^{SFG} P_{1}}{\omega_3 \alpha_1 \alpha_2} \quad \varepsilon_2 := \frac{\omega_1 E_{NL}^{SFG} P_{2}}{\omega_3 \alpha_1 \alpha_2} \quad f := 1 + \varepsilon_1 + \varepsilon_2 + \sqrt{(1 + \varepsilon_1 + \varepsilon_2)^2 - 4 \varepsilon_1 \varepsilon_2}.
\]

Get optimum output power

The optimum output power

\[
P_{3 \text{opt}} = \frac{\omega_2^2}{\omega_1 \omega_2} \frac{\alpha_1 \alpha_2}{E_{NL}^{SFG}} \frac{\varepsilon_1 \varepsilon_2}{f/2},
\]

is emitted when the input transmissions are chosen as follows

\[
T_{1,2}^{\text{opt}} = \alpha_{1,2} \left( \frac{f}{2} - \varepsilon_i \right).
\]

We see that the impedance matched output power \( P_{3 \text{opt}} \) is crucially dependent on the product \( E_{NL}^{SFG} / (\alpha_1 \alpha_2) \). In the regime of low input powers, \( \varepsilon_{1,2} \ll 1 \), we have the simple result

\[
P_{3 \text{opt}} = E_{NL}^{SFG} P_{11} P_{22} / (\alpha_1 \alpha_2),
\]

in the limit of one weak and one strong fundamental wave, say \( \varepsilon_1 \gg 1, \varepsilon_2 \ll 1 \), we have full conversion of the weak wave and find

\[
P_{3 \text{opt}} = P_{1,2} \omega_3 / \omega_2.
\]

Results of Impedance Matching

To evaluate the transmissions of the incoupling mirror we calculate the losses in the cavity by the specification of each optical element given in Tab. 4.4 and find the cavity losses \( R_{532} = 1.9\% \) and \( R_{760} = 0.67\% \). The fundamental laser powers coupled into the cavity are assumed to be equal to their actual values used in the experiment \( P_{532} = 0.88 \text{ W} \) and \( P_{760} = 6.4 \text{ mW} \) (→4.7).

The resulting dependence of the sum-frequency output power as a function of the incoupling mirror transmissions is shown in Fig. 4.10.

The optimal incoupling transmissions are found to be \( T_{532}^{\text{opt}} = 1.88\% \) and \( T_{760}^{\text{opt}} = 1.39\% \), giving a theoretical maximum UV output power of \( P_{313}^{\text{opt}} = 8.1 \text{ mW} \).

Further discussion of the impedance matching and comparison with the experimentally achieved output power follows in (→4.7).
Figure 4.10: SFG output power versus the incoupling mirror transmissions for the assumed pumping power of $P_{532} = 0.88$ W and $P_{760} = 6.4$ mW. The plots shows a point of optimal transmission and a steep drop of the output power for small transmissions. **Left:** 3d plot of the SFG output power ($z$-axis) as a function of the transmissions of the incoupling mirror ($x$ – $y$ plane). **Right:** SFG output power as function of a single transmission of the incoupling mirror, while the transmission of the other fundamental wave is matched for maximum output power.

4.6 Stabilization

The resonance condition in a running wave cavity – like ours – is given by $n \cdot \lambda = U$, where $n$ is an integer value: the cavity length is an integer multiple of the resonated wavelength. This can be achieved either by adjusting the length of the cavity or by tuning the wavelength of the laser. In our doubly resonant set-up, where the resonance condition has to be fulfilled for two waves, we exploit both possibilities of resonance adjustment.

To obtain spectrally pure and frequency-stable 313 nm light suitable for high-resolution spectroscopy, we make use of ultra-narrow linewidth and the high intrinsic frequency stability of the 1064 nm master laser in the MOPA and transfer it to the UV by using the doubly-resonant cavity as a transfer resonator. To this end, the cavity is frequency-locked to the 532 nm laser, and the 760 nm diode laser is frequency-locked to the cavity. This transfers the frequency stability and other spectral properties to the cavity, thus to the red diode laser which is stabilized to the cavity, and finally to the generated sum-frequency light.

4.6.1 Laser Phase and Frequency Stabilization Reviewed

For both frequency locks the phase-modulation technique of Pound, Drever, and Hall phase-modulation technique.
Drever, and Hall [95] is used. The sideband modulation technique allows active stabilization of the laser frequency on a cavity mode or vice versa [96, 97]. The schematic of the set-up is shown in Fig. 4.11.

\[ E(t) = E_0 e^{i\omega_0 t} + \sum_{k=-\infty}^{\infty} J_k(\delta) e^{i(\omega_0 + k\omega_m) t} \]

Herein \( J_k \) are the \( k \)th order Bessel functions and \( \delta \) is the modulation index (modulation depth). The given approximation is valid for small values of \( \delta \), where only the terms with \( k = 0, \pm 1 \) contribute to the electric field. Besides the carrier at \( \omega_0 \), we find two additional sidebands at \( \omega_0 \pm \omega_m \). In our approximation, \( J_0 \approx 1 \) and the intensities of the two sidebands \( |J_{\pm 1}(\delta)|^2 \) are found \( J_{\pm 1}(\delta) \approx \pm \delta/2 \).

The incoupling of the cavity depends on the spatial and spectral matching between the incident pump light and the resonator’s mode. Carrier and sidebands experience different “absorption” in

**Figure 4.11:** Set-up for phase and frequency stabilization with the technique of Pound, Drever, and Hall. The plotted error signal represents actual experimental data obtained with the green laser.

**Modulation**

The laser sent into the cavity is phase modulated at the frequency \( \omega_m \). The electric light field of the laser \( E(t) = E_0 e^{i\omega_0 t} \) is then described by

\[ E(t) = E_0 e^{i\omega_0 t + i \delta \sin \omega_m t} = E_0 \sum_{k=-\infty}^{\infty} J_k(\delta) e^{i(\omega_0 + k\omega_m) t} \]

\[ \approx E_0 \left( e^{i\omega_0 t} + \frac{\delta}{2} (e^{i(\omega_0 - \omega_m) t} - e^{i(\omega_0 + \omega_m) t}) \right) \]
the resonator and obtain different factors $e^{-\alpha_k - i\phi_k}$. The light is detected by a fast photodiode either in transmission (Fig. 4.11) or in reflection (Fig. 4.12) of the cavity. The detected intensity $I_D \propto |E|^2$ at the photodiode is given by

$$I_D \propto E_0^2 e^{-2\alpha_0} \left[ 1 + (\alpha_{-1} - \alpha_{+1})\delta \cos \omega_m t + (\phi_{+1} + \phi_{-1} - 2\phi_0)\delta \sin \omega_m t \right],$$

where we the interference terms between carrier and sidebands cancel each other and terms with $\delta^2$ were dropped.

We see that the phase modulation of the input field gets converted into amplitude modulation in the output.

The RF signal of the photodiode is mixed (electronically multiplied) with the signal of the local oscillator, which is phase-locked to the laser modulation signal, and is then send through a low-pass filter. Sweeping the phase relation between the local oscillator and the modulation signal we obtain either the sine (absorption) or the cosine (dispersion) term. In any case the signal changes its sign when the carrier frequency passes the resonance. Therefore the signal is called error signal and gives direct information whether the carrier is below or above the resonance of the cavity. The error signal is used in a feedback loop to control either the laser frequency or the cavity length to retain resonance.

The phase between the local oscillator and the demodulated photodiode output is chosen to be $\Delta \Phi = 0$: on resonance, the error signal then shows the steepest gradient and thus provides the highest efficiency of the feedback loop. The capture range of the feedback loop is twice the modulation frequency.

### 4.6.2 Set-up of the Feedback Loops

For both frequency locks the phase-modulation technique of Pound, Drever, and Hall [95] is used. The light reflected from the incoupling mirror is spectrally decomposed via a diffraction grating and detected by fast radio frequency photodetectors (type FND100), as shown in Fig. 4.12.

To stabilize the cavity to the 532 nm light, the master oscillator is phase modulated at 3.2 MHz via a piezotransducer mounted on the Nd:YAG crystal. Due to the non-resonant set-up of the frequency doubling, this modulation is transferred to the 532 nm light. Phase modulation of the diode laser frequency is obtained by modulation of the diode current at 20 MHz using a bias-tee input connector directly at the diode laser head.

To achieve stable locks it is important to maximize the bandwidth of the feedback loops for efficient correction of fast disturbances on

---

**RF photodetector**

**Mixer**

**Error signal**

**Modulation frequencies**

**Optimizing gain & bandwidth**
Figure 4.12: Set-up of the lasers and the feedback circuits of the doubly-resonant SFG apparatus. Lenses and waveplates are skipped for simplicity. PD: RF photodiodes (type FND 100).

the one side, and to provide a high gain at low frequencies to compensate slow drifts on the other side. The servos of both frequency locks contain an integrator circuit, which provides high (theoretically infinite) gain to compensate slow (static) drifts.

However, if the gain of the feedback loop is too high above a certain frequency, the feedback loop starts oscillating. The maximal possible bandwidth is limited by the mechanical and electronic properties of the controlled module. A piezoelectric transducer (e.g. either the one that controls the cavity length, or the one that con-
4.6 Stabilization

trols the diode laser frequency via the grating) shows resonances at certain frequencies. The first significant resonance usually limits the maximum bandwidth (unless a notch filter is used to suppress the resonance). Mechanical stabilization of the cavity and adding additional metal plates to the mirror mount in particular helps to shift the first resonances to at least well above 10 kHz. A measurement of amplitude and phase response of our cavity piezo is shown in Fig. 4.13.

![Graph](image)

Figure 4.13: Transfer function of the piezo controlling the cavity length

Apart from the amplitude response, the phase response can be used to judge the behavior more quantitatively. An oscillation of the feedback loop occurs if the total phase shift of the feedback loop at a certain frequency $f_{\text{critical}}$ is more than 180° and the gain at $f_{\text{critical}}$ is higher than 1. Then, any small disturbances at $f_{\text{critical}}$ will be “compensated” by the feedback loop with delay of 180° which causes enhancement instead of suppression of the disturbance, and the loop starts oscillating.

Balancing the piezo mount with heavy weights in our particular set-up could shift the first resonance frequency from 8 kHz to 18 kHz. Furthermore, to damp environmental disturbances the top sides of the cavity mirror mounts are attached to each other via metal bars. Pictures of the cavity before and after mechanical stabilization are shown in Fig. 4.14.

The bandwidth of the integrating cavity length servo is 10 kHz.
Figure 4.14: Pictures of the bow-tie cavity, compare figure 4.7. Since the intensity of the green light (and the human eye’s sensitivity) is considerably higher than the other colors, the path of the light in the cavity appears green. **Left:** Set-up before mechanical stabilization seen from the top. **Right:** Side view after mechanical stabilization.

Two feedback channels acting on the diode laser

The frequency of the diode laser is controlled by two circuits: a slow, integrating channel with high gain at low frequencies acting upon the external grating (bandwidth 3 kHz) (→4.4.2), and a fast channel acting directly upon the current of the diode (bandwidth 200 kHz).

The wiring of the diode laser set-up is rather extensive. The diode laser is controlled by four sources.

- **Main DC supply.**
  To avoid output power noise this source is filtered using a large capacity, and is hence not suitable to add a fast modulation.

- **Phase modulation input.**
  This input is coupled into the diode current using a bias-tee.

- **Fast feedback on the diode current for the frequency lock.**
  This input is attached to the gate of a field-effect transistor, which is connected parallel to the diode. The voltage applied to the gate makes the FET shunt some of the current from the diode.

- **The piezo controlling the external grating.**
  To obtain a wide tunability, the diode current needs to be corrected when the grating is tilted. Therefore a certain amount of the voltage applied to the piezo is fedforward to the diode current. This is achieved via the DC input, since a large bandwidth is not of concern.

More about feedback circuits is found in [68, 98, 99, 100]
The following sections discuss the experimentally measured properties of our SFG set-up, such as the output power, tunability, frequency stability, etc.

4.7 Output Power

The transmissions of the incoupling mirror used in the SFG cavity are

$$T_{532} = 1.8\% \quad T_{760} = 3\%. \quad (4.75)$$

At a first look this might seem to be far off the optimum value given above (~4.5.6), but the discussion below shows that the given values do not degrade the performance of the system significantly.

Measuring the power before the cavity and the transmission through a HR cavity-mirror we found the enhancement factors of the cavity

$$\frac{P_c}{P_i} \bigg|_{532} = 28 \quad \frac{P_c}{P_i} \bigg|_{760} = 46. \quad (4.76)$$

The measurements were performed while the other fundamental wave was not in the cavity, and hence no losses due to conversion occurred, $R_R = \alpha$.

From the enhancement factors given above we find the losses of the cavity using (4.64)

$$R_{R532} = 3.2\% \quad R_{R760} = 2.1\%. \quad (4.77)$$

The experimentally obtained losses in the cavity turn out to be a factor of 2-3 higher than those found by adding the specified losses of all optical components at the design time of the cavity (~4.5.6). The most likely reason for this fact is that the absorption of the LBO crystal is higher than assumed. The antireflection coatings of the crystal were checked with an optical microscope. In the neighboring laboratory working on SHG in LBO it was observed, that the coatings severely degraded due to the high circulating powers – they finally changed to a Brewster angle set-up. Luckily, the coatings of our crystal seem to withstand the circulating powers in our cavity - a Brewster set-up for doubly-resonant SFG is not an option, since a proper overlap of the two pump beams cannot be achieved.

With the fundamental wave powers $P_{532} = 1.4$ W and $P_{760} = 11.5$ mW available before the cavity and incoupling efficiencies of 63% and 56%, respectively, determined by the power of the light reflected on the incoupling mirror, we obtained a maximal measured output power

$$P_{313} = 2.1 \text{ mW}. \quad (4.78)$$
With the values of the real incoupling mirror (4.75) and the measured losses (4.77), the numerical solution of (4.66) yields an expected UV power $P_3 = 2.44 \text{ mW}$, in good agreement with the experimentally obtained UV power.

The incoupling mirror transmission (4.75) and the resonator losses (4.77) show, that the cavity is undercoupled for the 532 nm wave, and overcoupled for the 760 nm wave. The optimum transmissions of the input coupler for the measured losses would have to be $T_{532}^{\text{opt}} = 3.2\%$ and $T_{760}^{\text{opt}} = 2.5\%$, both close to the respective losses $R_{532}$, $R_{760}$. The maximum output power is then $P_{313}^{\text{opt}} = 2.6 \text{ mW}$. We see that the the output power is not strongly dependent on the incoupling transmissions.

Stable long-term operation of the sum-frequency generation could be achieved over 14 h, as shown in Fig. 4.15.

![Figure 4.15: Fundamental powers before the cavity and SFG output power during stable long-term operation. Gray line shows expected drift for the SFG power calculated from the measured powers in the fundamental waves.](image)

The plot shows about 15\% drift of the UV power over the time. The gray line in the bottom plot shows the expected power drift of the SFG output, by multiplying the two fundamental powers. We see that the main reason for the drift is found in the drift of the fundamental powers caused by environmental changes. The small remaining deviations result from changes in the incoupling
efficiency (pointing stability of the fundamental beams) and from instabilities in the SFG set-up.

Due to technical problems with the stability of the crystal in the SHG stage of the MOPA, the long term measurement was performed at different input powers compared to those above.

Fig. 4.16 shows the behavior of the SFG power for variable powers of the fundamental waves.

\[ P_{313} \text{[mW]} \]
\[ P_{313} \text{[W]} \]

\[ P_{532} \text{[W]} \]
\[ P_{760} \text{[W]} \]

**Figure 4.16:** SFG power for variable input powers of the fundamental waves. The solid line shows the SFG power for the actual cavity, while the dashed line assumes optimal impedance matching. **Left:** Expected SFG power for variable green light and fixed power in the red of \( P_{760} = 11.5 \text{ mW} \). **Right:** Expected SFG power for variable red light and fixed power in the green of \( P_{532} = 0.88 \text{ W} \).

The plot shows a slightly less than linear dependence of the SFG power from each fundamental wave (4.46). If one fundamental wave becomes much stronger than the other, the curves show a saturation behavior, which is explained by the depletion effect of the weaker fundamental wave, since for each generated photon one photon of each fundamental wave is required (4.11).

The most effective enhancement of the SFG power would be achieved by replacing the diode laser with a Ti:Sapphire laser. Having 1 W light available at 760 nm the expected SFG output power is in the region of 0.5 W.

A final conclusion is given in (→6).

### 4.8 Tunability of the System

The frequency of the 313 nm sum-frequency is essentially controlled by the frequency of the master laser (frequency doubled to 532 nm), to which the SFG cavity is locked.
With the locking scheme employed (→4.6.2) a frequency change \( \Delta \nu_{532} \) of the “master” wave causes a frequency change

\[
\Delta \nu_{760} = \frac{\lambda_{532}}{\lambda_{760}} \cdot \Delta \nu_{532} = \frac{532.2407}{760.6399} = 0.69973 \cdot \Delta \nu_{532}
\]

(4.79)
of the other fundamental wave (760 nm). Dispersion effects due to the crystal length, crystal temperature changes, and drifts in the two servos can be neglected. The servo errors are estimated to lie well below 1 MHz on time scales of 1 h.

Fig. 4.17 shows a measurement of the response of the locked 760 nm wave to tuning of the master wave.

![Diagram showing frequency tuning of the UV light](image)

**Figure 4.17:** Frequency tuning of the UV light. Frequencies of the master 532 nm light and slave 760 nm light were simultaneously measured with wavemeters. 16 GHz of continuous tuning in the UV are achieved without mode-hops.

From the measurement the tuning of the other fundamental wave is found to be

\[
\Delta \nu_{760} = 0.6997(4) \cdot \Delta \nu_{532},
\]

(4.80)
in agreement with the expected value of 0.69973 of (4.79).

In our specific case, the UV tuning is given by

\[
\Delta \nu_{313} = \Delta \nu_{532} + \Delta \nu_{760} = 1.6997 \cdot \Delta \nu_{532}.
\]

(4.81)

**16 GHz continuous tuning range**

Fig. 4.17 shows that 16 GHz of continuous mode-hop free tuning in the UV. A direct frequency measurement of the UV light could not be performed due to the lack of a suitable wavemeter.
4.9 Frequency Stability and Linewidth

Another important feature of our scheme is the absolute frequency stability and narrow linewidth of the UV light. This is achieved by choosing one of the two fundamental lasers to have high absolute frequency stability and narrow linewidth. By stabilizing the SFG cavity to this wave and the second laser to the cavity, the spectral properties of the first laser are to a large extent transferred to the UV wave.

The low frequency drift of the Nd:YAG laser leads to a correspondingly low drift of the UV frequency. Fig. 4.18 shows the measured Nd:YAG laser frequency drift from which a UV drift rate of less than 20 MHz/hour can be inferred. The locks are very stable and allow uninterrupted operation for many hours, as already shown in Fig. 4.15.

\[\text{Figure 4.18: Frequency drifts of the 532 nm (measured) and UV light (calculated by multiplying with 1.7).}\]

If a higher frequency stability is required, the frequency-doubled Nd:YAG wave can be locked to a hyperfine transition of molecular iodine [98]. A drift rate of less than 200 kHz/hour should then be achievable.

We give the following estimation for the linewidth of the SFG output. In the worst case it should at least not be larger than the instantaneous linewidth of the free-running diode laser in the order of 100 kHz. Since the lock of the diode laser is tight, and given sufficient mechanical stability of the cavity, we expect a reduced linewidth of the diode laser and therefore also of the UV light. Under optimal conditions (stability of the cavity and a high bandwidth of the diode laser lock) the UV light can thus replicate the narrow linewidth of the Nd:YAG laser of about 10 kHz.
4.10 Repumping Light

As noted before (→3.2.2) the Doppler cooling transition in Be$^+$ $^2S_{1/2}(F = 2) \leftrightarrow ^2P_{3/2}$ is not a closed transition. Spontaneous emission to the metastable ground state $^2S_{1/2}(F = 1)$ is possible: repumping light with a red detuning of $\Delta \omega_{\text{HFS}} = 2\pi \cdot 1.250$ GHz to the carrier frequency of $\lambda = 313.1327$ nm is required. Taking advantage of polarization effects and compensating for residual magnetic fields the repumping light intensity as low as a few percent of the main beam should be sufficient.

We have discussed different options to produce the repumping light. A set-up of a second laser system would be too expensive. Much more elegant is the generation of the repumping light by a frequency shifter. Studying the commercially available electro-optical and acousto-optical modulators (EOM/AOM), the specific combination of the UV-frequency and the relatively large modulation frequency has shown that a resonant EOM set-up is the most suitable for our requirements.

The propagation of light in anisotropic crystal media was treated with respect to the sum-frequency generation before (→4.1). It was shown that the normal modes of propagation can be determined from the index ellipsoid. In certain types of crystals, the application of an electric field results in a change in both the dimensions and orientation of the index ellipsoid. This is referred to as the electro-optical effect. A fundamental description of electro-optics (which is in principle similar to the description of propagation in anisotropic media) is found in [84, 68].

4.10.1 Phase Modulation of Light

Electro-optical modulation can be used for a variety of applications. For our purpose we focus on the specific set-up for phase shifting of light propagating through an electro-optic crystal as shown in Fig. 4.19.

The incident beam is polarized parallel to one of the principal dielectric axes, thus no birefringence occurs. The change in the index of refraction due to application of an electric field $E_m$ is described by

$$\Delta n = \frac{1}{2} n^3 r_{ij} E_m,$$  \hspace{1cm} (4.82)

where $n$ is the index of refraction without electric field applied and $r_{ij}$ is the electro-optical coefficient for the particular orientation of the crystal.

The phase shift after passing the crystal of length $L_{\text{EOM}}$ is
4.10 Repumping Light

Input beam

Electro-optic crystal

Phase modulated output beam

Figure 4.19: An electro-optical phase modulator (EOM). The optical polarization is parallel to the electrically induced principal dielectric axis, and remains unchanged. The phase of the light wave is shifted according to the applied voltage $V$.

$$\delta = \frac{\omega L_{EOM}}{c} \Delta n = \frac{\omega n^3 r_{ij} E_m L_{EOM}}{2c}. \quad (4.83)$$

If the bias field is sinusoidal

$$E_z = E_m \sin \omega_m t, \quad (4.84)$$

then an incident optical field $E_{in} = A \cos \omega t$ will emerge as

$$E_{out} = A \cos [\omega t + \delta \sin \omega_m t]. \quad (4.85)$$

Using the Bessel-function identities we can rewrite (4.85) as

$$E_{out} = A \left[ J_0(\delta) \cos \omega t + \right.$$  
$$+ J_1(\delta) \cos(\omega + \omega_m)t - J_1(\delta) \cos(\omega + \omega_m)t +$$  
$$+ J_2(\delta) \cos(\omega + 2\omega_m)t + J_2(\delta) \cos(\omega + 2\omega_m)t +$$  
$$+ J_3(\delta) \cos(\omega + 3\omega_m)t - J_3(\delta) \cos(\omega + 3\omega_m)t + \ldots \right]. \quad (4.86)$$

The optical spectrum of the output beam shows sidebands at both sides of the optical input frequency in a constant spacing of $\omega_m$.

The distribution of energy in the sidebands is a function of the modulation index $\delta$. Fig. 4.20 shows the relative energy in the carrier and the first sidebands.

For $\delta = 0$ we note $J_0(0) = 1$ and $J_{\geq 1}(0) = 0$.

4.10.2 Experimental Set-up of the EOM

The experimentally used EOM was custom fabricated by Leysop LTD using an ADP crystal (Fig. 4.21). The electrical bias field
Figure 4.20: Energy in the carrier and first sidebands as a function of the modulation index $\delta$.

Figure 4.21: Technical drawing of the EOM, side view (top view is a circle). The cavity enhances the electric field for the modulation. The screws on top change the length of the cavity and thus the capacitance of the cavity to allow tuning. The direction of the modulation electric field in the crystal is parallel to the screws. Depending on the specific crystal cut, in our case the change of the refractive index is perpendicular to the electric field, perpendicular to the drawing plane in the direction of propagation of the light, of course. The polarization of the input light has to be horizontal, perpendicular to the electric field.

is enhanced in a microwave cavity surrounding the crystal. The resonance frequency can be adjusted from 1.1 GHz to 1.275 GHz.

It is known that ADP is slightly hygroscopic, which might cause some absorption lines in the UV spectral region arising over the time. This effect has to be kept in mind for the future use; for the time being, the losses of the UV light when passing the EOM are below 10% and, fortunately, no increase has been observed. Other materials like KD*P are less critical in terms of UV absorption, but
a significant modulation depth in this spectral region is available only up to modulation frequencies of 200 MHz.

The modulation frequency $\omega_m = 2\pi \cdot 1.25$ GHz is taken from a microwave synthesizer (Racal Dana 9087). The signal is amplified to 28 dBm of microwave power (Minicircuits ZHL-42).

The characteristic data for the use of the EOM are collected in Tab. 4.5.

<table>
<thead>
<tr>
<th>Characteristics of the EOM device</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>crystal</td>
<td>ADP, (NH$_4$)$_2$PO$_4$</td>
</tr>
<tr>
<td>crystal system</td>
<td>tetragonal 42m</td>
</tr>
<tr>
<td>modulation frequency</td>
<td>$\omega_m = 2\pi \cdot (1.10 \ldots 1.275)$ GHz (resonant)</td>
</tr>
<tr>
<td>transmission</td>
<td>$&gt; 90% @ 313$ nm</td>
</tr>
<tr>
<td>power of driver</td>
<td>28 dBm</td>
</tr>
<tr>
<td>polarization of input light</td>
<td>horizontal (i.e.</td>
</tr>
<tr>
<td>modulation index</td>
<td>$\delta = 0.54 @ \lambda = 313$ nm, $\omega_m = 2\pi \cdot 1.25$ GHz</td>
</tr>
</tbody>
</table>

**Table 4.5:** Characteristics of the EOM device. See text for details.

The modulation index $\delta$ was experimentally measured. To this end, two laser beams of which one was passing through the EOM, were overlapped on the sensitive area of a photodiode and the beat-signal was subjected to spectral decomposition, as shown in Fig. 4.22.

The electric fields of the combined light beams to be

$$E_1 = A \exp \left( i \left( \omega_1 t + \delta \sin \omega_m t \right) \right), \quad E_2 = A \exp \left( i \omega_2 t \right). \quad (4.87)$$
The detected intensity $I = |E_1 + E_2|^2$ then yields

$$I = 2A^2 \left[ 1 + \cos \omega_{\text{beat}} t + \frac{\delta}{2} \left( \cos (\omega_{\text{beat}} - \omega_m) t - \cos (\omega_{\text{beat}} + \omega_m) t \right) \right] ,$$

(4.88)

where higher order sidebands are dropped and $\omega_{\text{beat}} := \omega_1 - \omega_2$. We note that the sideband terms cancel each other if $\omega_{\text{beat}} = 0$. Thus slightly different input frequencies $\omega_1$ and $\omega_2$ are required.

The spectrum analyzer shows a symmetric spectrum centered around $\omega_{\text{beat}}$ and the modulation depth can be determined from the ratio of the intensities $I_{\omega_{\text{beat}} \pm \omega_m} / I_{\omega_{\text{beat}}} = \delta / 2$.

However, the required fast photodiode, input lasers, and other optical components were not available for a direct measurement at 313 nm. Equation (4.83) shows that $\delta \propto 1/\lambda$. The measurement could hence be performed with two Nd:YAG lasers at 1064 nm. The resonance frequency of the EOM-cavity was adjusted to 1.25 GHz with the two screws on top. Temperature does affect the center frequency, so the laboratory is to be kept at a constant temperature to avoid frequent readjustments.

From a measurement of the relative intensities at the beat frequency and in the first side-band the modulation index

$$\delta_{1064} = 0.16$$

(4.89)

is determined. Using (4.83) we finally find

$$\delta_{313} = 0.54.$$ 

(4.90)

The relative light intensity in the repumping beam is then (Fig. 4.20)

$$\left| \frac{J_1(\delta = 0.54)}{J_0(\delta = 0.54)} \right|^2 \approx 8\% ,$$

(4.91)

sufficient for efficient laser cooling of Be$^+$ (→3.2.2).
Chapter 5

Laser Spectroscopy of Molecular Hydrogen Ions

As motivated in the introduction, we propose an experiment aimed at the infrared spectroscopy of vibrational transitions of trapped molecular hydrogen ions. Two-photon spectroscopy will eliminate the first order Doppler shift, and the use of trapped and cooled ions will reduce the transit time broadening and the second order Doppler shift. In combination with suitable laser sources, an ultra-cold ensemble of molecules can lead to spectroscopic measurements with unprecedented spectral resolution. In the case of the HD$^+$ molecule, to avoid the small first order Doppler-broadening, we plan to perform two-photon spectroscopy of the $(v = 0, N = 4) \rightarrow (v = 4, N = 4)$ ro-vibrational transition using a single-frequency cw OPO with an output wavelength of 2.8 $\mu$m. The expected excitation rate is approximately 1/s and can be measured by state-selective photodissociation followed by mass selective extraction from the rf trap.

In the introduction the importance of the hydrogen molecular ion in terms of molecular theories and tests of fundamental physics was emphasized. In this chapter a detailed description for the experimental implementation of high precision spectroscopy of HD$^+$ is given.

5.1 Introduction to the Molecular Theory

The hydrogen molecular cation is the simplest molecule, consisting of two protons and one electron. It provides a unique opportunity for accurate theoretical calculations, which may be compared with experimental measurements.
Because the hydrogen molecular ion has only one electron, electron-electron correlation is not of concern; indeed some might dismiss the hydrogen molecular ion as being irrelevant to this central problem of molecular quantum mechanics. However, theory has concentrated instead on nonadiabatic, relativistic, and radiative effects, all of which must be included in the calculations if experimental results are to be reproduced.

The Schrödinger equation for the hydrogen molecular ion may be solved at many different levels of approximation. In what follows we distinguish between three types of solution:

- **Born-Oppenheimer solution:**
  Solution for motion of the electron in the field of the clamped nuclei,

- **Adiabatic solutions:**
  Coupling between the motion of the electron and the nuclei is taken into account, but only terms diagonal in the electronic states are included.

- **Nonadiabatic solutions.**

Both the Born-Oppenheimer and adiabatic approaches separate nuclear and electronic motion, leading to the concept of electronic potential energy curves and separated electronic states.

The theoretical papers written over the years on the hydrogen molecular ion far outnumber experimental papers. This imbalance reflects the fact that it is easier to study this ion theoretically than experimentally. The project described here shall close the gap. For details of theoretical work, the reader is referred to the reviews by Carrington et al. [10] and Leach et al. [14].

A quick review of the theory of the molecular hydrogen ion in this thesis should motivate the proposed experimental approach of ultrahigh-resolution spectroscopy of the hydrogen molecular ion as the “ultimate goal” of our project.

Although transitions to the first excited electronic state have a large electric-dipole transmission probability, this state of $\text{H}_2^+$ was generally considered to be unbound, so no discrete electronic transitions to it were expected. It is now known that it possesses a very shallow long-range potential minimum that supports three ro-vibrational levels [101]. There are some higher bound electronic states, but transitions to these would require far-ultraviolet photons and the Franck-Condon factors would not be favorable.

Because $\text{H}_2^+$ is homonuclear, an electric dipole-allowed ro-vibrational spectrum does not exist. Consequently, the first high-resolution spectrum of $\text{H}_2^+$ was recorded in the radio frequency [7].
Magnetic-dipole transitions between hyperfine and spin-rotation components were observed.

For HD\textsuperscript{+} electric-dipole transitions are allowed because of the separation of the center of charge and the center of mass. Wing et al. [8] carried out the first ion-beam experiment to measure a number of ro-vibrational transitions between levels close to the minimum of the potential curve. Carrington et al. [9] used a complementary ion-beam method to measure ro-vibrational transitions involving levels close to the first dissociation limit.

### 5.1.1 The Schrödinger Equation

The non-relativistic Hamiltonian of a general $N$-body Coulomb system is

$$
\mathcal{H} = \sum_{i} \frac{-\hbar^{2} \nabla_{i}^{2}}{2m_{i}} - \frac{e^{2}}{4\pi \varepsilon_{0}} \sum_{i=1}^{N} \sum_{j=1 \atop j \neq i}^{N} \frac{z_{i}z_{j}}{r_{ij}},
$$

where $p_{i} = \hbar \nabla_{i}$ is the momentum of particle $i$ with mass $m_{i}$ and charge $e z_{i}$, and $r_{ij}$ is the distance between particles $i$ and $j$.

The hydrogen molecular ion and its isotopomers represent a three-body system consisting of a diatomic molecule with nuclear masses of $m_{1}$, $m_{2}$ and a single electron of mass $m_{e}$. The coordinates are defined in Fig. 5.1.

![Figure 5.1: Coordinates of the molecular hydrogen ion. CM = center of mass, G = geometrical center.](image)

After separation of overall translational motion, the complete non-relativistic Hamiltonian Schrödinger equation of the inner molecular dynamic is given by

$$
\left[-\hbar^{2} \left( \frac{\nabla_{r}^{2}}{2m_{e}} + \frac{\nabla_{R}^{2}}{2\mu_{r}} + \frac{\nabla_{r} \cdot \nabla_{R}}{2\mu_{a}} \right) + V\right] \Psi(r, R) = E \Psi(r, R),
$$

(5.2)
where
\[ V = \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{R} - \frac{1}{r_{1e}} - \frac{1}{r_{2e}} \right), \quad (5.3) \]
\[ \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad \text{and} \quad \frac{1}{\mu_a} = \frac{1}{m_1} - \frac{1}{m_2}. \quad (5.4) \]

### 5.1.2 Quantum Numbers

The coupling of the angular momenta in molecules consisting of light nuclei is described by Hunds case b) of weak spin-coupling, which is visualized in Fig. 5.2. This type of coupling is strictly fulfilled in the case of the 1s\( \sigma \) ground state (\( \Lambda = 0 \), no spin-path coupling) of the hydrogen molecular ion [102].

![Figure 5.2: Coupling of the angular momenta, Hunds case b).](image)

The rotational quantum number \( N \) couples with the projection \( \Lambda \) of the electronic angular momentum \( L \) on the axis of symmetry to a resulting angular momentum \( K \) of the nuclei. In the electronic ground state 1s\( \sigma \) of the hydrogen molecular ion is \( \Lambda = 0 \), thus \( K = N \).

The electron spin \( S \) couples with the \( K \) to the total angular momentum \( J \) of the molecule\(^1\).

In this type of coupling \( K (= N) \), \( S (= 1/2) \), \( \Lambda (= 0) \) and \( J = K + S, \ldots, |K - S| \) represent good quantum numbers.

### 5.1.3 Levels of Approximation

The Hamiltonian (5.2) for an one-electron diatomic molecule may be written as
\[ \mathcal{H} = \mathcal{H}_{BO} + \mathcal{H}_{ad} + \mathcal{H}_{gu}, \quad (5.5) \]
where the various contributions to the Hamiltonian are the Born-Oppenheimer Hamiltonian
\[ \mathcal{H}_{BO} = -\frac{\hbar^2 \nabla_e^2}{2m_e} + V, \quad (5.6) \]

\(^1\)Neglecting the nuclear spin.
the adiabatic energy operator

$$\mathcal{H}_{\text{ad}} = -\hbar^2 \left( \frac{\nabla_r^2}{8\mu} + \frac{\nabla_R^2}{2\mu} \right),$$  \hspace{1cm} (5.7)

and the nonadiabatic energy operator

$$\mathcal{H}_{\text{gu}} = -\hbar^2 \nabla_r \cdot \nabla_R \frac{2\mu_a}{2\mu}.$$  \hspace{1cm} (5.8)

**Born-Oppenheimer approximation**

The simplest approach is to ignore $\mathcal{H}_{\text{ad}}$ and $\mathcal{H}_{\text{gu}}$ in (5.5) and to solve the Born-Oppenheimer problem

$$\mathcal{H}_{\text{BO}} \phi_i(r; R) = E_i(R) \phi_i(r; R)$$  \hspace{1cm} (5.9)

in order to obtain the Born-Oppenheimer potentials and wavefunctions, which depend parametrically on $R$. $t$ designates the electronic state.

Any given value $R$ leads to specific energy eigenvalue $E_i(R)$. Solution of the Born-Oppenheimer equation yields an electronic potential energy curve $U(R) = E_i(R)$ as shown in Fig. 5.3, where any coupling between electrons and nuclei is neglected.

![Figure 5.3: Born-Oppenheimer potentials. Electronic energy as a function of the distance $R$ of the nuclei of the HD$^+$ ion. The enlargement shows the ro-vibrational levels of the bound electronic ground state $1s\sigma_g$. The first exited state state is essentially repulsive.](image)

In a second step the potential $U(R)$ is used in a radial Schrödinger equation for the nuclear motion:

$$\left( -\frac{d^2}{dR^2} + \frac{2\mu}{\hbar^2} (U(R) - E_{vN}) + \frac{N(N+1)}{R^2} \right) \chi_{vN}(R) = 0$$  \hspace{1cm} (5.10)
Ro-vibrational eigenenergies: To determine the ro-vibrational eigenenergies and eigenstates, $E_{vN}$ and $\chi_{vN}(R)$, respectively. $v$, $N$ are the ro-vibrational quantum numbers, respectively, as used in the enlargement of Fig. 5.3.

To solve (5.10) in the first approximation, we model the vibration as in an anharmonic potential, the rotation as a rigid rotator, and allow for coupling between ro-vibrational excitation.

This leads to the equation

$$\frac{E_{v,N}}{\hbar c} = \nu_e \left( v + \frac{1}{2} \right) - x_e \nu_e \left( v + \frac{1}{2} \right)^2 + B_e N(N+1) - \alpha_e \left( v + \frac{1}{2} \right) N(N+1), \quad (5.11)$$

which allows a rough estimation of the ro-vibrational energy levels of HD$^+$. The empirical parameters are given by the frequency of the harmonic potential $\nu_e = 1995$ cm$^{-1}$, the anharmonicity of the potential $x_e = 0.022$, the constant of rotation $B_e = 23$ cm$^{-1}$ and the coupling constant of ro-vibrational $\alpha_e = 0.93$ cm$^{-1}$.

Empirical parameters

Discussion: In the Born-Oppenheimer approximation the energy difference of the vibrational levels in H$_2^+$ is

$$\Delta E_{\text{vib}} \propto \sqrt{\frac{m_e}{m_p}}. \quad (5.12)$$

A high resolution measurement of the vibrational levels can therefore be used to deduce an improved accuracy for the electron-proton mass ratio.

Accuracy: The Born-Oppenheimer approximation simplifies the three-body problem by the assumption that the motion of the nuclei is slow compared to that of the electron (due to their comparably large masses $m_{1,2} \gg m_e$), and that the electron can hence follow the nuclear motion quasi-instantaneously. The Born-Oppenheimer solution can be seen as a first order approximation in the small parameter $m_e/m_p \approx 1/1836$. This also gives the order of magnitude of the relative accuracy of the energy levels to be $1/1836$, corresponding to a few $10 \text{ cm}^{-1}$, which of course is much too inaccurate to improve the current accuracy of $2 \cdot 10^{-9}$ [3] of $m_e/m_p$.

Adiabatic and nonadiabatic calculations

By expressing the eigenfunction of the full Hamiltonian (5.2) as an expansion in terms of the Born-Oppenheimer solutions

$$\Psi(r, R) = \sum_{\ell} F_\ell(R) \phi_\ell(r; R), \quad (5.13)$$
a set of coupled equations $F_t(R)$ is obtained \[14\], which cannot be solved exactly.

If the off-diagonal terms in the electronic state are ignored, a ro-vibrational problem results:

$$
\left( -\frac{\hbar^2 \nabla_R^2}{2\mu} + U_s(R) \right) F_{ad}^s(R) = E_{ad} F_{ad}^s(R) \quad (5.14)
$$

with an effective potential:

$$
U_s(R) = E_s(R) + \int \phi_s^*(r;R) \mathcal{H}_{ad} \phi_s(r;R) \, dr . \quad (5.15)
$$

This is the adiabatic potential, and its use for solving the ro-vibrational problem leads to the next level of approximation, the adiabatic approximation. The adiabatic corrections are diagonal in the electronic state and arise because of the finite masses of the nuclei; they can be thought of as resulting from the response of the nuclei to the instantaneous position of the electron so that the uniformity of motion of the molecular center of mass is maintained, while the electron- and nuclear motions still remain decoupled. Note that for HD$^+$, for which $(1/\mu_a)$ does not vanish, $(1/\mu_a)\mathcal{H}_{gu}$ makes no contribution here because it is entirely off-diagonal in the electronic states.

The relative accuracy of the energy levels in adiabatic approximation is in the order of $(m_e/m_p)^2 \sim 3 \cdot 10^{-7}$, equivalent to $0.01 - 0.1$ cm$^{-1}$.

Nonadiabatic effects can be thought of as allowing for the electrons following the nuclei. For heavy nuclei, this following will be almost complete, but for light nuclei, which move more rapidly, there will be a lag behind the nuclei, and this is also accounted for by the nonadiabatic effects. Because of the factors $1/\mu$ and $1/\mu_a$ in the operators (5.7) and (5.8), respectively, the effects are largest for hydrogen and its isotopes. Due to the off-diagonal terms, the concept of the potential energy as a function of the nuclear distance cannot be applied in the nonadiabatic calculation, and an equation like (5.10) cannot be used to find the ro-vibrational levels, either.

The best nonadiabatic calculations achieve relative accuracies on the order of $5 \cdot 10^{-8}$, equivalent to $0.001$ cm$^{-1}$. See \[10, 14\] for an overview of the large variety of nonadiabatic calculation algorithms.

Recent Calculations

Meanwhile the availability of high performance computers and improved numerical methods allow even better nonadiabatic calculations. In 1993 Moss published a list of all ro-vibrational energy
levels in the electronic ground state of HD$^+$ with a relative accuracy of $10^{-9}$ ($1 \cdot 10^{-4}$ cm$^{-1}$) [103]. Many energy levels in H$_2^+$ and D$_2^+$ are known to the same accuracy [104, 105]. Herein the full non-relativistic Hamiltonian is transformed to an operator similar to that used in scattering problems; then the method of “artificial channels” is applied to achieve the given accuracy.

Scattering theory

Variational methods are also used to calculate the three-body problem. In 1998 Grémaud et al. presented a method which allowed calculation of the energies in H$_2^+$ with a relative accuracy of $2 \cdot 10^{-12}$ [106]. However, values are only given for $N = 0$ and $v = 0, 1$. The vibrational basis of harmonic oscillator functions proved to be too large for all but rotationless levels, and even then only low vibrational levels seem to be adequately treatable.

Variational methods

Recent developments

Very recently, even better calculations have been performed. In beginning of 1999 Moss achieved an accuracy of $10^{-13}$ by his scattering methods [107]. In April 1999 Korobov presented a calculation with an accuracy of $2 \cdot 10^{-15}$ for $E_{H_2^+}(v = 0, N = 0)$ and $3 \cdot 10^{-14}$ for $E_{HD^+}(v = 4, N = 4)$ during his visit in Konstanz [15, 81]. Korobov and Moss will perform calculations of this accuracy for other levels in the near future.

The accuracy of these results is in principle only limited by the number of iterations in the calculation. However, the mathematical error is already much smaller than the systematic error raised by the physical assumptions. For comparison with experiment two other contributions must be included, relativistic and radiative effects, and these are considered below.

Relativistic and Radiative Corrections

Relativistic corrections in the first order $O(\alpha^2) \sim 5 \cdot 10^{-5}$ (where $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}$ is the fine structure constant) are determined by the expectation values of the Breit-Hamiltonian, using the wavefunctions found above [15].

Radiative corrections may be determined in the same way as relativistic corrections, as an expansion in orders of $\alpha$. They describe QED corrections of the bound electron, analogous to the Lamb shift in the hydrogen atom. First order corrections yield contributions in the order of $O(\alpha^3 \ln \alpha) \sim 2 \cdot 10^{-6}$ (Lamb shift) and $O(\alpha^3) \sim 4 \cdot 10^{-7}$ (vertex corrections).

Radiative and relativistic corrected energy levels

Wolniewicz et al. [108] have tabulated a large number of energy levels for H$_2^+$ and HD$^+$ in the electronic ground state. Radiative and relativistic corrections were included to an accuracy of about 0.001 cm$^{-1}$. Moss has tabulated these values to an accuracy of up to 0.0001 cm$^{-1}$, i.e. about 3 MHz, for all bound and quasi-bound states in the electronic ground state of HD$^+$ [103]. Those energy
levels which are of relevance for the aimed spectroscopy on the HD$^+$ ion are collected in Tab. 5.1.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$v = 0$</th>
<th>$v = 1$</th>
<th>$v = 2$</th>
<th>$v = 3$</th>
<th>$v = 4$</th>
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<td>16062.6261</td>
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<td>17746.2960</td>
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<td>15500.2938</td>
<td>13894.8475</td>
<td>12377.5054</td>
</tr>
</tbody>
</table>

**Table 5.1:** Energy levels in HD$^+$, given by their dissociation energies in units of cm$^{-1}$. Radiative and relativistic corrections are included to an accuracy up to 0.0001 cm$^{-1}$ [103].

In the near future Bakalov and Korobov plan to improve the relativistic and radiative corrections to accuracies of $10^{-10}$ and $10^{-11}$, respectively. In these calculations however, terms in the order $O(\alpha^4) \sim 3 \cdot 10^{-9}$ will be excluded. Contributions of this type might be estimated to an accuracy of 2-3 digits, but, for the time being, the complete physical background is not yet developed [15, 109]. This is also the case for contributions of even higher order. In this regime the theory is challenged to establish calculational methods which ensure an overall accuracy of at least $10^{-10}$, which in turn could be used to deduce an improved precision in the fundamental constant $\mu_e/\mu_p$, using the results of the ultra-high resolution spectroscopy.

### 5.1.4 Ro-Vibrational Transitions in the Hydrogen Ion

The transition strength between various ro-vibrational levels is of great importance with respect to the spectroscopy. Additionally, when the molecules are cooled sympathetically, the transition strength is also related to the cooling of the internal degrees of freedom.

Diatomic molecules where the center of charge does not coincide with the center of mass, as in HD$^+$ (charge $Q = e$, containing isotopes of masses $m_1$, $m_2$ separated by a distance $R$) show a permanent electric dipole moment of

$$\mu(R) = Q\frac{m_1 - m_2}{m_1 + m_2} R.$$  \hspace{1cm} (5.16)

Note that this expression is exact within the Born-Oppenheimer approximation and is valid irrespective of the electronic state of the molecule [110].
Ro-vibrational decay times in such molecules are in the range of milliseconds to a few seconds. Clearly, the radiative relaxation of ro-vibrational levels is not feasible for molecules with no dipole moment like H$_2^+$ and D$_2^+$. For example, the lifetime for the quadrupole transition $\Delta N = 2$ from $v = 1$ to $v = 0$ in H$_2^+$ is of the order of $10^6$ s [111]. Correspondingly low are the excitation rates in homonuclear molecules; they are about 8 orders of magnitude smaller than in heteronuclear systems.

For this reason the heteronuclear HD$^+$ molecule has been chosen for spectroscopy instead of H$_2^+$.

**Selection rules**

Symmetry consideration leads to the selection rules for electric dipole transitions in HD$^+$. Within the same electronic state only transitions between states of different symmetry are allowed. The selection rule

$$\Delta J = \pm 1$$

of the total angular momentum can be fulfilled for all rotational transitions with

$$\Delta N = \pm 1.$$  \hspace{1cm} (5.18)

The selection rule for vibrational transitions is

$$\Delta v = 0, \pm 1, \pm 2, \pm 3, \ldots \hspace{1cm} (5.19)$$

$\Delta v = \pm 1$ is the fundamental vibrational transition, which would be also allowed in the harmonic approximation of the potential. The overtones $\Delta v = \pm 2, \pm 3, \ldots$ come into account due to the anharmonicity $x_e$ of the potential (5.11), and the intensities of the overtones decrease according to the ratios $1 : x_e : x_e^2 : \ldots$.

**Transition moments**

In 1976 Colbourn and Bunker reported a theoretical calculation of ro-vibrational transition moments for HD$^+$, HT$^+$, and DT$^+$ [112]. Those of relevance for our experiment are collected in Tab. 5.2.

**Radiative lifetimes**

The radiative relaxation times of ro-vibrational transitions for the electronic ground state of HD$^+$ were calculated by Amitay et al. in 1994 [110].

The radiative lifetime $\tau_{v'N'}$ of a ro-vibrational state is given by

$$\tau_{v'N'} = \frac{1}{A_{v'N'}},$$  \hspace{1cm} (5.20)

where

$$A_{v'N'} = \sum_{v''N''} A_{v'N'\rightarrow v''N''}$$ \hspace{1cm} (5.21)

is the total Einstein coefficient, which in the present case is the sum over all probabilities $A_{v'N'\rightarrow v''N''}$ for spontaneous transitions between
5.1 Introduction to the Molecular Theory

Here the transition probability is in s$^{-1}$ when the energy difference $\Delta E_{v'N'v''N''}$ is in cm$^{-1}$ and $M_{v'N'v''N''}$ in eA [110]. The summation (5.21) is performed over all dipole allowed transitions. Tab. 5.3 shows the lifetimes of some specific levels which are of relevance for the proposed spectroscopy.

<table>
<thead>
<tr>
<th>$v' = 1 - v'' = 0$</th>
<th>$v' = 2 - v'' = 0$</th>
<th>$v' = 4 - v'' = 0$</th>
<th>$v' = 4 - v'' = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N''$</td>
<td>$R$</td>
<td>$P$</td>
<td>$R$</td>
</tr>
<tr>
<td>0</td>
<td>0.0861</td>
<td>0.00111</td>
<td>0.00075</td>
</tr>
<tr>
<td>1</td>
<td>0.0820</td>
<td>0.0943</td>
<td>-0.0109</td>
</tr>
<tr>
<td>2</td>
<td>0.0780</td>
<td>0.0986</td>
<td>-0.0108</td>
</tr>
<tr>
<td>3</td>
<td>0.0741</td>
<td>0.1028</td>
<td>-0.0106</td>
</tr>
<tr>
<td>4</td>
<td>0.0702</td>
<td>0.1071</td>
<td>-0.0104</td>
</tr>
<tr>
<td>5</td>
<td>0.1114</td>
<td>-0.0116</td>
<td>-0.0068</td>
</tr>
</tbody>
</table>

Table 5.2: Electronic ro-vibrational $|e\rangle = |v'N'\rangle \leftrightarrow |g\rangle = |v''N''\rangle$ transition moments $M_{v'N'v''N''} = \langle v'N'\mu |v''N''\rangle$ of HD$^+$. The $R$-branch describes $N' - N'' = +1$, the $P$-branch $N' - N'' = -1$. The matrix elements are given in Debye, where 1 Debye $\approx 3.3 \cdot 10^{-30}$ cm $\approx 0.2$ eA [112].

Compared to typical dipole transitions in atoms, the lifetimes given here are considerably longer. This is explained by the weaker transition moments and the smaller transition frequency in the ro-vibrational spectrum of HD$^+$.

We find that radiative relaxation to the vibrational ground state lasts on the order of 100 ms. At sufficiently low temperatures, one can expect all molecules to be in the vibrational ground state. However, the full rotational relaxation will last one order of magnitude longer, since the transition frequencies are again smaller.

<table>
<thead>
<tr>
<th>$v = 0$</th>
<th>$v = 1$</th>
<th>$v = 2$</th>
<th>$v = 3$</th>
<th>$v = 4$</th>
<th>$v = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N = 0$</td>
<td>140.24</td>
<td>14.61</td>
<td>4.04</td>
<td>1.64</td>
<td>0.823</td>
</tr>
<tr>
<td>$N = 1$</td>
<td>0.059</td>
<td>0.059</td>
<td>0.058</td>
<td>0.057</td>
<td>0.055</td>
</tr>
<tr>
<td>$N = 2$</td>
<td>0.032</td>
<td>0.032</td>
<td>0.031</td>
<td>0.031</td>
<td>0.031</td>
</tr>
<tr>
<td>$N = 3$</td>
<td>0.023</td>
<td>0.023</td>
<td>0.023</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>$N = 4$</td>
<td>0.019</td>
<td>0.019</td>
<td>0.018</td>
<td>0.018</td>
<td>0.018</td>
</tr>
<tr>
<td>$N = 5$</td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 5.3: Lifetime $\tau_{vN}$ in seconds of some selected ro-vibrational levels in HD$^+$ [110].
5.2 High-Precision Doppler-Free Two-Photon Spectroscopy

As motivated previously, the high precision spectroscopy of $\Delta \nu_{\text{ vib}}$ of the ro-vibrational levels of HD$^+$ is of fundamental physical interest. In the following we will describe the ultra-high resolution spectroscopy of these levels based on two-photon spectroscopy.

5.2.1 Principle

Two-photon absorption in atoms and molecules was first realized in 1931 [113]. Suppose that the energy of a photon $\hbar \omega$ is just half of the energy difference $\hbar \omega_{ge}$ between a ground $E_g$ and exited state $E_e$:

$$E_e - E_g = \hbar \omega_{ge} = 2 \hbar \omega.$$  \hspace{1cm} (5.23)

It was found in the 70’s that two-photon transitions can be used to gently suppress the Doppler-broadening of the absorption line [114]. The principle is schematically shown in Fig. 5.4.

![Figure 5.4: Principle of two-photon spectroscopy. Left: Energy levels. Right: The first order Doppler-effect cancels.](image)

We consider a molecule moving at velocity $v$, which can absorb two photons by excitation from $|g\rangle$ to $|e\rangle$. Assume a light field of two counter-propagating laser beams, parallel to the $x$ axis, having frequency $\omega_1^0$ and $\omega_2^0$, respectively. In the molecular center of mass frame the frequencies of the lasers are first order Doppler-shifted to

$$\omega_1 = \omega_1^0 \left( 1 + \frac{v_x}{c} \right) \quad \text{and} \quad \omega_2 = \omega_2^0 \left( 1 - \frac{v_x}{c} \right).$$  \hspace{1cm} (5.24)

**1st order Doppler-effect cancels**

1. We consider a two-photon absorption of one photon out of each beam:

$$\omega_1 + \omega_2 = \omega_1^0 + \omega_2^0 + \frac{v_x}{c} (\omega_2^0 - \omega_1^0).$$  \hspace{1cm} (5.25)
We find that the Doppler-broadening of the two-photon resonance is reduced to the term \((\omega_2^0 - \omega_1^0)\). If the counter-propagating beams have the same frequency \(\omega_1^0 = \omega_2^0 = \omega\), e.g. by retroreflection of a single light beam, the first order Doppler-effect cancels.

### 5.2.2 Excitation Rates

The two-photon excitation is not as weak as one would at first expect from a process of higher order.

- All atoms or molecules participate in the spectroscopy, as opposed to Doppler-free saturation spectroscopy, where only those particles of a specific velocity class are affected.
- The excitation rate can be enhanced by an almost-resonant intermediate state.

The transition rate of two-photon absorption from \(|g\rangle\) to \(|e\rangle\) is derived by second order perturbation theory and given by

\[
\Gamma_{ge}^{(2)} = \frac{1}{\hbar^2 \varepsilon_0 c^2} \frac{P^2}{S^2} \sum_k \frac{\langle e | \mu_{e k} | k \rangle \langle k | \mu_{k e} | g \rangle}{\hbar \Delta \omega_k} \left| \frac{\Gamma_c}{4 \delta \omega^2 + \Gamma_c^2/4} \right|^2
\]

where \(P\) is the laser power, \(S\) is the geometrical cross-section of the beam, \(\hbar \Delta \omega_k = (E_k - E_g) - \hbar \omega\) is the energy defect to the intermediate state \(|k\rangle\), \(\Gamma_c\) is the natural linewidth of the excited state \(|e\rangle\), and \(\delta \omega\) the complete detuning, as shown in Fig. 5.4.

The summation in principle is to be done over all levels of the system [115]. However, if there is a particular level \(|k\rangle\) near to the one-photon resonance, the energy \(\hbar \Delta \omega_k\) is small, and the contribution of this single state dominates.

Furthermore, we find a quadratic dependence on the laser power \(\Gamma_{ge}^{(2)} \propto P^2\). Resonating the spectroscopy laser in a cavity will therefore enhance the excitation rate by the factor of the cavity enhancement squared.

From (5.26) we find the selection rule for two-photon transitions as the product of two one-photon transitions, which for electric dipole transitions yields

\[
\Delta N = 0, \pm 2.
\]

### 5.2.3 Finding a Two-Photon Transition

The criteria for finding an appropriate two-photon transition are as follows.
• The ground state of the spectroscopy is chosen to be the vibrational ground state \( v_g = 0 \) of HD\(^+\), in order to provide a sufficiently high occupation at low temperatures.

• The rotational quantum number \( N_g \) of the spectroscopic ground state shall be small for the same reason.

• The frequency \( \omega \) of the spectroscopy laser will be in the infrared spectral region, covered by the OPO light sources which are developed in our group at the university of Konstanz, and an absolute frequency measurement should be possible by using existing frequency standards.

For the transition \( v_g = 0 \rightarrow v_k = 1 \rightarrow v_e = 2 \) a matching intermediate state cannot be found. However, going to

\[
v_g = 0 \rightarrow v_k = 2 \rightarrow v_e = 4
\]

(5.28)

one finds an enhanced transition for the rotational quantum numbers

\[
N_g = 4 \rightarrow N_k = 3 \rightarrow N_e = 4.
\]

(5.28')

The energy difference between \(|g⟩\) and \(|e⟩\) is

\[
\hbar \omega_{ge} = 7010.0272 \text{ cm}^{-1} \cdot \hbar c = 2 \hbar \omega,
\]

resulting in a required laser wavelength of

\[
\omega = 2\pi \cdot 1.05077664 \cdot 10^{14} \text{ Hz}, \quad \lambda = 2.85305598 \text{ \si{\mu m}}.
\]

The values above are given to the accuracy as derived in Tab. 5.1, using \( c = 299792458 \text{ m/s} \).

The lifetime of the exited state is about 0.018 s (Tab. 5.3), leading to a linewidth of \( \Gamma_e \approx 2\pi \cdot 56 \text{ Hz} \), and \( \Gamma_e/\omega_{ge} \approx 2.7 \cdot 10^{-13} \).

The energy defect is \( \Delta \omega_k \approx 2\pi \cdot 850 \text{ GHz} \). For the spectroscopy laser we assume typical output powers of our OPO laser sources of 100 mW [116] and a cross-section of 1 mm\(^2\), which is about the typical transverse dimension of the ion cloud in our linear rf trap. A power-buildup cavity is not taken into account. Then the excitation rate on resonance is found to be

\[
1 \text{ s}^{-1}.
\]

(5.29)

Even for large ion clouds of \( 10^5 \) molecules fluorescence or absorption detection of such low excitation rates is not feasible. In our project we plan to use selective photodissociation to efficiently detect such weak excitation rates (→5.2.6).
5.2 High-Precision Doppler-Free Two-Photon Spectroscopy

5.2.4 Expected Spectroscopic Accuracy

As shown before (→3.3), sympathetic cooling can produce ion crystals at temperatures of only a few mK. In order to increase the signal to noise ratio we assume a large number of sympathetically cooled molecules compared to laser-cooled atoms in the trap, and hence conservatively assume the temperature of the molecules to be

\[ T = 1 \text{ K}. \]  

\[(5.30)\]

The first order Doppler effect, which fortunately is suppressed by the two-photon spectroscopy, would lead to

\[ \left| \frac{\Delta \omega}{\omega} \right|_{1\text{st order}} = \frac{v}{c} \approx 2.5 \cdot 10^{-7}, \]  

\[(5.31)\]

where \( \Delta \omega = kv \) and \( v \) is the mean velocity of the distribution.

However, the second order Doppler effect still remains, which yields to

\[ \left| \frac{\Delta \omega}{\omega} \right|_{2\text{nd order}} = \frac{1}{2} \frac{v^2}{c^2} \approx 3 \cdot 10^{-14}. \]  

\[(5.32)\]

We find that the aimed accuracy of \( \delta \nu / \nu \leq 10^{-10} \) at these temperatures will not be Doppler limited.

When talking about such high accuracies, it is of course important, to consider systematic errors as well. With respect to the proposed experiment, the specific kind of trap which we use (→2.2) should produce the fewest intrinsic perturbations for the molecules. However, there will still be small effects due to

- the Stark effect raised by the electrical rf trapping potential,
- the influence of the laser light used for cooling and for photodissociation on the molecular transition,
- a Zeeman shift caused by residual magnetic fields, e. g. due to the earth or the attached ion pump,
- a Zeeman shift caused by magnetic fields originating from the electrical rf trapping potential.

These effects, which are estimated to be small, still need to be carefully treated when a high precision value of \( m_e / m_p \) is deduced from a spectroscopic measurement.
5.2.5 Occupation of the Ground State

In this section the temperature-dependent population distribution within the ro-vibrational levels of \( \text{HD}^+ \) is discussed. It is of particular importance to make sure that a large portion of the trapped molecules can contribute to the spectroscopy.

**Hot temperatures**

At temperatures of more than 1000 K (typical for rf traps without cooling (\( \rightarrow 2.2.4 \))) and assuming a thermal density distribution, all ro-vibrational levels are occupied. Due to the \( (2N+1) \) degeneracy of the rotational levels, in the thermal Boltzmann distribution,

\[
\frac{n_{vN}}{n_{00}} = (2N + 1)e^{-\frac{E_{vN}}{kT}},
\]  

(5.33)

where \( n_{vN} \) is the number occupancy, some higher rotational levels have even higher occupation than the lower levels. The spectroscopic excitation of the ro-vibrational level system could not be detected. We see that cooling is strongly required, not only to reduce the line broadening, but also to obtain a spectroscopic signal at all.

**Room temperature**

Cooling the ions down to 300 K, we find an occupational distribution as shown in Fig. 5.5

![Figure 5.5: Thermal density distribution \( n_{vN} \) at 300 K in the ro-vibrational levels of \( \text{HD}^+ \), normalized to the ground state population \( n_{00} \), on logarithmic scale. Left: Vibrational levels. Right: Rotational levels in the vibrational ground state. The spectroscopic ground state \( |0, 4\rangle \) is occupied sufficiently, the exited state \( |4, 4\rangle \) is depleted.](image)

At room temperature nearly all molecules are in the vibrational ground state, the spectroscopic ground state \( |g\rangle = |v_g = 0, N_g = 4\rangle \) is occupied sufficiently and the excited state \( |e\rangle = |v_e = 4, N_e = 4\rangle \) is depleted. For the first experimental spectroscopic attempt a temperature in this region is hence preferable.

**Ultracold temperatures**

As mentioned before the sympathetic cooling process can provide low temperatures in the region of mK (\( \rightarrow 3.3 \)), which will
increase the spectroscopic accuracy. At these temperatures the ro-vibrational excitations relax to the ro-vibrational ground state $|v = 0, N = 0\rangle$. From the relaxation times given in Tab. 5.3 we expect this process to take place on a time scale of a few of seconds. This process should be verified as a first validation of the sympathetic cooling; the measurement can be interpreted as a kind of internal molecular thermometer. The measurement will also assure that the internal degrees of freedom of the molecules are coupled to the sympathetically cooled kinetic energy.

One possibility to actively re-populate the spectroscopic ground state $|g\rangle$ is to drive rotational transitions directly in order to transfer the population from $n_{00}$ to $n_{04}$. Due to the selection rules this transfer will require multiple steps, and the frequencies are in the microwave region between 100 to 500 GHz.

Alternatively, population transfer can be achieved by optical pumping ($\rightarrow$5.3) using a tunable 5 μm infrared laser. The laser drives the transition from $|00\rangle \leftrightarrow |11\rangle$, which, due to the selection rule $\Delta N = \pm 1$, can only spontaneously decay to $|00\rangle$ or $|02\rangle$. In a second step a similar process can pump the population from $|02\rangle$ to $|04\rangle$.

Another very efficient method of population transfer is described by the technique of stimulated Raman scattering involving adiabatic passage (STIRAP) [117], which is sketched in Fig. 5.6.

\[\begin{align*}
|2\rangle & \quad \Delta_1 \\
|1\rangle & \quad \omega_P \\
|3\rangle & \quad \omega_S \\
|4\rangle & \quad \omega_P - \omega_S
\end{align*}\]

*Figure 5.6: Open three-level system coupled by two laser pulses. Levels $|1\rangle$ and $|2\rangle$ are coupled by the pump laser $\omega_P$ and levels $|2\rangle$ and $|3\rangle$ by the Stokes laser $\omega_S$. Radiative decay from level $|2\rangle$ may lead to other states, summarized as level $|4\rangle$.\*

The process is exclusively based on stimulated transitions. Two lasers pulses, a *pump* laser at frequency $\omega_P$ and a *Stokes* laser at frequency $\omega_S$, couple the initial state $|1\rangle$ to the final state $|3\rangle$, to which the population is transferred. The interaction with the Stokes laser pulse begins first, followed by the interaction with the pump-laser pulse. However, overlap of the pulses in time is needed in order to achieve efficient transfer. The sequence of pulses is counterintuitive. The energy difference between state $|1\rangle$ and $|3\rangle$ is equal to the
frequency difference $\omega_P - \omega_S$. Resonant enhancement is achieved if the detuning $\Delta_1$ to an intermediate state $|2\rangle$ is small. The advantage of the STIRAP method compared to other population transfer methods is that STIRAP is exclusively based on stimulated transitions. High transfer efficiencies near to 100 % can be achieved [118].

Due to the selection rule $\Delta N \pm 1$, the STIRAP process cannot transfer the population from $|00\rangle$ to $|04\rangle$ directly. Instead two STIRAP transfers are required, first going from $|00\rangle$ to $|02\rangle$ and in a second step from $|02\rangle$ to $|04\rangle$. Nevertheless, compared to the methods mentioned above, this process will still provide a high transfer efficiency and the required laser light at 1.4 $\mu$m is commercially available by diode lasers.

### 5.2.6 Selective Photodissociation

As already mentioned, excitation rates on the order of $1/s$ (→5.2.3) cannot be detected by fluorescence or absorption.

**Method**

State selective photodissociation however, can be applied to selectively photodissociate (and thereby detect) the exited state $|e\rangle$. Here laser light is used to drive a transition from $|e\rangle$ to the repulsive electronic excited state of HD$^+$. Although the repulsive state is a continuum, the cross-section of photodissociation strongly depends on the wavelength of the laser and the ro-vibrational initial state of the molecule. The cross-section is calculated from the Franck-Condon overlap integral of the wavefunctions of the bound state $|e\rangle$ and the dissociated state.

**Other experiments**

The method of selective photodissociation is well established: Carrington _et al._ [10] used it to detect transitions of the high vibrational states of HD$^+$: The wavelength of the photodissociation for the high vibrational state is in the infrared spectral region. Alheit [42], related to the work of Jefferts [119], demonstrated the selective detection of different hyperfine states using an excimer laser.

**Cross-sections**

A theoretical calculation of all photodissociation cross-sections of the ro-vibrational levels of HD$^+$ using the Born-Oppenheimer approximation is found in the work of Tadjeddine and Parlant [120]. Those cross-sections relevant for our experiment are plotted on the left hand side of Fig. 5.7.

**Quantitative prediction**

Assume a laser radiation of 50 mW/mm$^2$ over 1 s. We can then calculate the fraction $x$ of the molecules dissociated by this amount of radiation. This is shown on the right hand side of Fig. 5.7. From the plot we find that a wavelength of about 266 nm will selectively dissociate the $v = 4$ vibrational state. The states $v = 3, 5$ (which are not of concern) will also be dissociated to a small percentage, but the states $v = 0, 1, 2$ are not significantly affected.
5.2 High-Precision Doppler-Free Two-Photon Spectroscopy

Figure 5.7: Cross-sections for the selective photodissociation of HD⁺.
Left: Cross-section as function of the wavelength λ for the vibrational states \( v = 0, \ldots, 5 \) [120]. Right: Fraction of dissociated molecules for an assumed radiation power of 50 mJ/mm². A wavelength in the region of 260 nm will selectively dissociate the \( v = 4 \) state of HD⁺.

The wavelength of 266 nm can be obtained relatively easily by quadrupling a Nd:Yag laser.

Finally, to measure the spectroscopic excitation, detection of the dissociated fragments is required. As already discussed before, the rf trap can be used as a mass selective detector, using the method of “highly efficient detection due to the decrease of the rf amplitude” [51] (→2.5.2).

5.2.7 The Experimental Cycle

As a detection method, selective photodissociation is destructive. Spectroscopy of this kind requires that the experiment operates in cycles. The cycle for a single measurement is sketched in Fig. 5.8.

Fig. 5.9 schematically shows the experimental set-up for the two-photon spectroscopy of ultra-cold HD⁺ in a linear Paul trap.

The first step of the measurement cycle is to load the trap with beryllium ions. This is achieved by the evaporation of a beryllium wire to generate a beam of beryllium atoms (→2.4.2). In the trapping region the atom beam crosses an electron beam (→2.4.1). There the beryllium ions are ionized by electron impact ionization (→2.4.3).

Doppler laser cooling (→3.2) of Be⁺ is performed using light at 313 nm and a 1.25 GHz detuned repumping beam. The light is generated by of doubly-resonant sum-frequency generation (Chap. 4) through mixing a frequency-doubled Nd:Yag laser with a wavelength of 532 nm and a diode laser with a wavelength of 760 nm. The set-up provides for a large continuous tuning range of 16 GHz

Detecting the fragments

Load Beryllium

Cool Beryllium
which is important for cooling the initially hot ions. It also provides a high absolute frequency stability.

**Load HD**

In the next step HD$^+$ molecular ions are added to the ion Be$^+$ ions in the trap. HD gas is let into the chamber through a leak valve (→2.3). Partial pressures of up to $10^{-7}$ should be possible without disturbing the Be$^+$ ions [121]. Ionization of HD is again achieved by electron impact ionization.

**Sympathetically cool HD$^+$**

The HD$^+$ ions are cooled sympathetically by Coulomb-interaction with the simultaneously trapped beryllium ions (→3.3). Our trap size allows us to trap up to $10^5$ sympathetically cooled molecular ions. Sympathetic cooling occurs on a short time scale on the order of a few ms.

**CCD imaging**

Now the ion cloud or – at sufficiently high cooling rates – the ion crystal, can be characterized by CCD imaging (→2.5.1): the number of ions, extension of the cloud, fraction of sympathetically cooled molecules, temperature can be determined.

**Spectroscopy**

Two-photon spectroscopy is performed using an OPO laser source at a wavelength of 2.85 μm. A power build-up cavity might be used to improve the signal to noise ratio (→5.2).

**Detection**

The two-photon transition to the vibrational level $v = 4$ can be detected by selective photodissociation using laser radiation at 266 nm. This frequency can be easily obtained by quadrupling
5.2 High-Precision Doppler-Free Two-Photon Spectroscopy

![Diagram of experimental set-up](attachment:image.png)

**Figure 5.9:** Schematic of the experimental set-up for two-photon spectroscopy of ultra-cold HD$^+$ in a linear Paul trap. Beryllium and HD ions are generated by electron impact and confined in the trap. Laser radiation (including a repumping beam) at 313 nm cools the Beryllium ions, which in turn sympathetically cool the HD$^+$ molecules. The ion cloud is characterized by CCD imaging. Doppler-free two-photon spectroscopy is performed with a laser at a wavelength of 2.85 $\mu$m, using (optionally) a power-buildup cavity for better signal to noise ratio. The spectroscopy is detected by selective photodissociation with a quadrupled Nd:Yag laser; the fragments are detected by an electron multiplier.

a Nd:Yag laser. Appropriate trapping parameters allow the dissociated fragments to be trapped also – together with the other ions. A mass selective detection scan of the trap can be used to count the fragments using the ion detector above the trap. The spectroscopy signal is determined by the ratio of detected protons+deuterons to the number of HD$^+$ ions.

### 5.2.8 Absolute Frequency Measurement

The extraction of an improved value of $m_e/m_p$ out of the comparison between theory and spectroscopic measurement requires an absolute frequency measurement of the laser frequency. This has to be done with the aimed accuracy of at least $10^{-10}$.

The plan is to use an OPO laser source for the molecular spectroscopy at a wavelength of 2.85306 $\mu$m.

The pump light of the OPO, either Nd:Yag at 1064 nm or green light at 532 nm, can be stabilized to an iodine hyperfine transition (the Nd:Yag pump light needs to be doubled) of the 1110 line at 532.245 nm, which is known to an accuracy of a few kHz [98]. While the idler output of the OPO is used for the spectroscopy, the signal wave is available for a beat measurement with existing fre-
frequency standards. Fig. 5.10 shows a suggested set-up for this kind of absolute frequency measurement. Using a Nd:Yag pump wave, the signal wave at a frequency of 1.69804 μm can be beat directly with the doubled frequency of the methane frequency standard at 3.39223142 μm by Bagayev et al. [122], which has a known accuracy of 500 Hz. This yields a relative overall accuracy of a few times $10^{-11}$ (Fig. 5.10).

**Figure 5.10:** Absolute frequency measurement based on the frequency standards of iodine and methane.

While the frequency measurement shown in Fig. 5.10 is based on the accidental coincidence of the doubled methane frequency and the signal output of the OPO, the recent availability of femtosecond optical laser combs provides a universal tool for highly accurate absolute frequency measurements [123, 124]. This technique is sketched in Fig. 5.11.

**Figure 5.11:** Absolute frequency measurement using a femtosecond optical laser comb.

The frequency comb spans the octave from 1064 nm to 532 nm such that the optical frequencies at 1064 nm and 775 nm can be expressed as an integer multiple of the comb spacing plus small measured offsets (beats). The accuracy of this type of frequency measurement is limited only by the accuracy of the rf frequency standard of at least $1 \cdot 10^{-13}$ or better.
5.3 Single-Photon Experiments

The content of the last section – high-precision two-photon spectroscopy of HD$^+$ – can be seen as the ultimate goal of the experiment, for which this thesis is the foundation.

One important step towards this goal is the characterization of the sympathetic cooling process. Spectroscopic experiments, which deal with single-photon excitation, can be used to measure the temperatures of the sympathetically cooled molecules. Additionally, a method of fluorescence imaging the HD$^+$ ions should be pointed out, which allows direct detection and observation of the molecular ions in the trap.

5.3.1 Excitation Rate

The excitation rate $\Gamma$ from a level $|A\rangle$ to an energetically higher level $|B\rangle$ is given by the photon flux $F = I/(h\nu)$ times the absorption cross-section $\sigma(\nu)$

$$\Gamma = \sigma(\nu) \cdot \frac{I}{h\nu}, \quad (5.34)$$

where the absorption cross-section for a resonant light field is given by

$$\sigma = \sqrt{\frac{\ln 2}{\pi}} \frac{2c}{\Delta\nu_D} \frac{S}{n} \frac{I}{h\nu}. \quad (5.35)$$

Herein $n$ is the density of states of the particles, and

$$\Delta\nu_D = 2\frac{\nu_0}{c} \sqrt{\frac{2kT}{m}} \ln 2, \quad (5.36)$$

the linewidth of an inhomogeneously Doppler-broadened absorption line having a Gaussian shape

$$f(\nu) = \sqrt{\frac{mc^2}{2\pi kT\nu_0^2}} \exp \left[ -\frac{mc^2}{2kT\nu_0^2}(\nu - \nu_0)^2 \right], \quad (5.37)$$

with a center frequency of

$$\nu_0 = (E_B - E_A)/h, \quad (5.38)$$

and

$$S = \frac{8\pi^3}{3hc} \frac{e^{-\hbar cE_A/kT}}{Q} \left( 1 - e^{-\hbar cE_A/kT} / Q \right) |M_{BA}|^2 \quad (5.39)$$

is the transition strength from $|A\rangle$ to $|B\rangle$ where $M_{BA}$ is the dipole matrix element as tabulated in Tab. 5.2, $e^{-\hbar cE_A/kT} / Q$ is the thermal
Boltzmann distribution of the initial state $|A\rangle$, normalized by the partition function $Q$, and the factor $\left(1 - e^{-\frac{h\nu_0}{kT}}\right)$ allows for stimulated emission effects which become important in the far infrared region and at high temperatures [125].

**In practical units**  
Assuming low temperatures such that $kT \ll h\nu_0$ and dropping the distribution term of the initial state, we rewrite in practical units

$$S = 4.16 \cdot 10^{-19} \cdot \left(\frac{n}{\text{cm}^3}\right) \cdot \left(\frac{M_{BA}}{\text{Debye}}\right)^2 \cdot \left(\frac{\nu_0}{\text{cm}^{-1}}\right) \quad (5.40)$$

and

$$\sigma = 9.45 \cdot 10^{-13} \cdot \left(\frac{M_{BA}}{\text{Debye}}\right)^2 \cdot \sqrt{\frac{m/\text{a.u.}}{T/\text{K}}} \quad (5.41)$$

**Some specific excitation rates**  
We can now calculate the excitation rates of the transitions, which are of interest in the next paragraphs. Therefore we assume a laser power of 1 mW, a beam cross-section of 1 mm$^2$, $T = 300$ K, and the matrix elements given in Tab. 5.2.

The overtone excitation for the $|v = 0\rangle \rightarrow |v = 4\rangle$ transition yields $\Gamma \approx 20 \text{ s}^{-1}$ per molecule in the initial state.

The matrix element of the fundamental excitation $|v = 0\rangle \rightarrow |v = 1\rangle$ is more than two orders of magnitude greater. The excitation rate is therefore more than a factor of $10^4$ larger.

### 5.3.2 Fluorescence Imaging of Cold Molecular Hydrogen Ions

Fluorescence imaging of molecules in general is inhibited by two facts.

- Molecules usually do not offer a closed transition, which allows for fast cyclic excitation.
- Low fluorescence rates of the molecules lead to insufficient detection sensitivity.

In this section we point out a way, by which fluorescence detection of the HD$^+$ molecule could still be performed.

The experimental set-up of fluorescence detection using a CCD camera has already been shown for the laser-cooled beryllium ions in Fig. 2.20 (→2.5.1).

Fig. 5.12 shows schematically the optical excitation scheme, which should allow for fluorescence detection of HD$^+$. 
5.3 Single-Photon Experiments

An infrared laser at $\omega_1 = 5.12 \, \mu\text{m}$ drives the transition $|v = 0, N = 0 \rangle \rightarrow |v = 1, N = 1 \rangle$. The lifetime of the excited state is $\tau_{11} \sim 0.06 \, \text{s}$. The selection rules $\Delta N = \pm 1$ allow spontaneous decay only to the levels $|v = 0, N = 0 \rangle$ or $|v = 0, N = 2 \rangle$; pure rotational transitions within $N = 1$ are negligible. By applying a second laser at $\omega_2 = 5.48 \, \mu\text{m}$ resonant on the transition $|v = 0, N = 2 \rangle \rightarrow |v = 1, N = 1 \rangle$, a closed level system is realized. At high excitation rates as derived before ($\rightarrow 5.3.1$), the fluorescence rate will be limited by the lifetime $\tau_{11} \sim 0.06 \, \text{s}$.

A pulsed operating mode is favorable in order to increase the detection sensitivity. The relatively high excitation rate enables the transfer of a large part of the population from $|v = 0, N = 0 \rangle$ to $|v = 1, N = 1 \rangle$ in a time scale short compared to $\tau_{11}$. If the laser is switched on for a short excitation pulse only, the fluorescence detection can happen in the dark phase in order to reduce the background noise. A laser power of only a few $\mu\text{W}$ should be sufficient. Highly sensitive CCD chips in this spectral region are available from astronomical applications (e. g. from Raytheon, indium-antimonid, liquid He cooled, quantum efficiency $> 70\%$ from $1 - 5 \, \mu\text{m}$).

5.3.3 Molecular Thermometer

To characterize the process of sympathetic cooling, it is of great importance to measure the translational as well as the ro-vibrational temperature of the molecules.

The translational temperature can be determined by taking advantage of the first order Doppler-broadening which occur in one-photon spectroscopy (any other broadening effects are comparably small for the trapped ions). The Doppler-broadening (5.36) of the spectral line $\omega_1$ can be measured by fluorescence detection using the

**Figure 5.12**: Fluorescence detection of HD$^+$, based on optical pumping. A closed transition system in the ro-vibrational level structure is obtained by the use of two excitation lasers.
set-up shown in Fig. 5.12. Of course spatial resolution of course is no longer required, which simplifies the fluorescence detection.

**Rotational temperature**

The rotational temperature is found by extending the set-up of Fig. 5.12. The ground state \(|v = 0, N = 0\rangle\) of the given transition scheme can be easily lifted to higher rotational states \(|v = 0, N = 1, 2, 3, \ldots\rangle\). The rotational temperature can then be deduced from the relative fluorescence intensities between the different lines.

Alternatively, one-photon spectroscopy of the transitions \(|v = 0, N = 0, 1, 2, \ldots\rangle \rightarrow |v = 4, N = 1, 2, 3, \ldots\rangle\) at a wavelength of 1.4 \(\mu\)m could be performed, where widely tunably laser diodes are commercially available. We expect excitation rates of 20 \(s^{-1}\) (\(\rightarrow\) 5.3.1). However, the large number of spontaneous decay channels to \(|v = 2, 3, N = 0, 1, 2, \ldots\rangle\) prevents fluorescence detection (and direct laser cooling). Detection should still be possible using selective photodissociation (\(\rightarrow\) 5.2.6).
Chapter 6

Conclusion and Outlook

Figure 6.1: Overview of the apparatus as developed and described in this thesis. The vacuum system (including trap, particle sources, and detectors), as well as the laser source for laser cooling of Be$^+$ (DR-SFG), has experimentally been set up. The laser source for the molecular spectroscopy and for photodissociation, as well as the stabilization of the lasers on iodine has not yet been implemented.

A novel experiment for trapping, cooling, and examining the spectroscopy of the molecular hydrogen ion, HD$^+$ was developed. New experimental concepts for the high precision spectroscopy of cold molecular ions were introduced and quantitatively discussed.

Conceptual work
The ultimate goal of the project is to perform Doppler-free two-photon spectroscopy of cold HD\(^+\) molecules. From the high resolution spectroscopy of the ro-vibrational molecular structure we can obtain improved values of fundamental constants (e.g. \(m_e/m_p\)). Furthermore, tests of the time variance of fundamental constants could be carried out in a different way than tests based on electronic transitions in atoms or on ultra-stable resonators. In addition, molecular theories, like relativistic corrections and radiation corrections (QED), are waiting for an experimental verification. Last but not least, the HD\(^+\) spectroscopy is ideal for establishing an ultimate molecular frequency standard based on one of the simplest molecules.

The desired frequency resolution is at least \(\delta \nu/\nu \leq 10^{-10}\). To this end, the molecules are confined in a linear Paul trap and sympathetically cooled by laser-cooled Be\(^+\) confined in the same trap. This will reduce the transit time broadening and the second order Doppler effect. The first order Doppler effect is eliminated by the use of two-photon spectroscopy. The linear Paul trap avoids the use of a strong intrinsic magnet field, which might affect the spectroscopic applicability for fundamental tests, and stores more ions at less kinetic energy compared to the hyperbolic Paul trap. The spectroscopic excitation rate of approximately 1/s can be detected with high efficiency by selective photodissociation, where the trap serves as a mass spectrometer.

For the Doppler laser cooling of Be\(^+\) a novel approach for the generation of highly frequency-stable, widely tunable, single-frequency cw UV light suitable for high resolution spectroscopy is presented. Doubly resonant sum-frequency generation of two solid-state sources is employed. Based on a frequency-stable solid-state laser and a diode laser as fundamental sources, a frequency-tunable cw UV light with high absolute frequency stability (drift \(< 20\) MHz/hour) and narrow linewidth (\(< 1\) MHz) has been produced with \(> 2\) mW power. The large continuous tuning range of 16 GHz is of particular importance e.g. for laser cooling in rf traps and for resolving hyperfine structure. The advantages of this approach and the large UV wavelength coverage possible using easily available diode lasers, should make it of significant interest to spectroscopists. This work is about to be submitted for publication in *Appl. Opt.* [126].

An ultra-high-vacuum chamber was designed and set-up, providing an ultra-high vacuum pressure (XUHV) in the region of \(10^{-11}\) mbar, reducing the interaction of the ions with the residual gas to less than 1:100 s. This guarantees long trapping times, low temperatures, and undisturbed spectroscopy.

A linear rf Paul trap was constructed and built up which can confine a large number of ions (\(\geq 10^5\)). A CCD camera system...
to watch the fluorescence of the Be\textsuperscript{+} ions, as well as various other peripheral devices (electron gun, beryllium source, electron multiplier) to generate and detect the ions were set up.

Currently we are in the process of confirming the observation of laser-cooled Be\textsuperscript{+} ions and \textbf{optimizing the cooling process}. The next step is to add the molecules to the ion cloud and to \textbf{characterize the process of sympathetic cooling}.

The dynamics of the light \textsuperscript{9}Be\textsuperscript{+} ions in a rf trap, compared to the typically trapped ions (\textsuperscript{24}Mg\textsuperscript{+}, \textsuperscript{40}Ca\textsuperscript{+}), cause unusual requirements on the Doppler laser cooling. The initial energies of a few eV ($\rightarrow$2.2.4) lead to a large Doppler-broadening of the absorption line: the lighter the ion the larger the line broadening; in the case of Beryllium we estimate the absorption line to be larger than 500$\Gamma$, equivalent to 10 GHz. The integrated fluorescence of the hot ions thus drops down, and calculations show, that a fluorescence detection of the hot ion cloud is not possible for the given signal/noise ratio of the CCD-camera.

\textbf{Cooling is required before fluorescence can be observed.}

The common way is to start with a far red detuning and slowly scan towards $\Delta \omega = \Gamma/2$. This should compress the width of the velocity distribution and increase the fluorescence. Measurements of this type were performed and very weak fluorescence light could be recorded, as the laser frequency approached the atomic resonance. However, the signal was very weak and not readily reproducible.

Improvement of the absolute frequency control of the laser set-up is required. To sufficiently cool the Be\textsuperscript{+} ions with the laser power available, several cycles of well defined frequency scans from far red detuning to $\Delta \omega = \Gamma/2$ are required. The UV frequency scan is to be stopped as close as possible to $\Delta \omega = \Gamma/2$: if the scan goes beyond this, the light near the atomic resonance will heat up and blow the ions out of the trap; if the scan stops before this frequency, the temperature will remain quite high. Furthermore, continuous cooling of the ions is required, otherwise rf heating occurs quasi instantaneously. Despite the excellent free-running stability of the developed laser source, the reproducibility of the frequency scan is insufficient for the described situation. \textbf{Stabilization of the master laser} of the SFG set-up on a molecular resonance of iodine is currently being developed, at the new location of the experiment in the group of Prof. Schiller at the University of Düsseldorf. Additionally, a Ti:Sapphire laser is available, which can replace the 760 nm laser diode. \textbf{Increased output power}, >13 mW was already obtained in a first attempt, which enhances the cooling rate as well as the fluorescence rate. These improvements should allow the first CCD pictures of cold ions in the near future.

In the long-term both stabilization and increased output power of the laser are required.
the laser system, will help build an experimental set-up, that reliably cools molecular ions sympathetically via Doppler laser-cooled Be\(^+\). The set-up of the laser sources for the spectroscopy of the HD\(^+\) molecule, either using an OPO source at 2.8 \(\mu\)m (knowledge already available in our group) for the two-photon spectroscopy, or a commercially available diode laser at 1.4 \(\mu\)m for 1-photon excitation is left for the future.
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