VRIJE UNIVERSITEIT

Advancing Precision Ramsey-Comb Spectroscopy through High-Harmonic Generation

ACADEMISCH PROEFSCHRIFT

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Light brings us the news of the universe -William Henry BraggThis thesis was approved by the members of the reviewing committee:

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The cover shows a creative representation of Ramsey-comb spectroscopy in combination with high-harmonic generation. The background shows a warped image of continuum generation in air using a high-power ultra fast laser pulse, which are usually used for high-harmonic generation. A series of four Ramsey-fringes is shown with slightly different colors on the bottom, in which both the phase noise and phase shift becomes larger as function of delay.

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CHAPTER 1

Introduction

1.1 Simple atomic systems

The energy level structure of few-electron systems have been studied in great detail for over more than a century. The comparison between the theoretical description and experimental observations has led to the discovery of several laws of physics. For a large part, these developments have relied on the hydrogen atom, because of its simplicity.

The description of the hydrogen atom was initially based on a comparison that Niels Bohr made between the atom and a planetary system. In contrast to the classical case, he assumed that the electron can only occupy energy states that have a specific discrete energy, labeled with principle quantum number n [1, 2]. The resulting gross energy level structure of the hydrogen atom is schematically shown in Fig. 1.1 and agrees with the state and energy solutions found later for the Schrödinger equation, which emerged from the formulation of quantum mechanics. However, more accurate observations revealed substructure which was not explained by the Bohr model, leading to further extensions of the theory. For example, the relativistic effects described by the Dirac equation [3,4], explained the energy separation of levels with different angular momentum quantum number i, and the coupling between the nuclear spin I and the electron's angular momentum accounted for the hyperfine structure. The experimental observation by Lamb and Retherford of the splitting of the $2S_{1/2}$ and the $2P_{1/2}$ levels in atomic hydrogen [5], i.e. levels with different orbital angular momentum quantum number

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Figure 1.1 – A schematic overview of the first few energy levels in the hydrogen atom. The gross energy structure scales with integer quantum number n and was first obtained by Niels Bohr. A more detailed investigation revealed the splitting of levels through relativistic and QED effects and the coupling between the nuclear spin and the electron's angular momentum gives rise to hyperfine structure (HFS).

l, led to the development of quantum electrodynamics (QED) theory. This effective field theory describes the influence of virtual particles on the energy structure. The two lowest-order contributions are the so-called self-energy term, which describes the emission and re-absorption of virtual photons, and the vacuum polarization term, which describes the creation and annihilation of virtual electron-positron pairs. These two terms form the main contribution to the Lamb shift, which is on the order of a few times 10^{-6} of the total binding energy of the 1S level in hydrogen. The further development of QED theory has been very successful and it has been tested with extremely high precision by comparing experimental observations with theoretical predictions, see e.g. [6,7]. However, the absolute scaling of the energy levels are given

by a set of fundamental constants, of which the value can so far not be derived from theory. For example, the gross electronic structure scales with the Rydberg constant (R_{∞}) and the fine-structure constant (α) determines the size of the fine-structure splitting. Therefore, the accuracy of these tests are determined by three contributions: the accuracy of the theoretical description, the accuracy of the experimental observations and the accuracy of the determination of fundamental constants.

1.1.1 Some experimental considerations

Experimentally the atomic energy structure is probed by observing transitions from one energy level to another. This is typically done by tuning the laser frequency and observing spectral lines when the energy of the photons from the laser matches the energy differences in the atom. From these observations the energy structure can be extracted. The uncertainty of the determination of the transition frequencies can be roughly divided into three categories.

First, the natural line width of the probed transition sets a fundamental limit on the precision of the extracted transition frequency. A typical dipole allowed transition has a natural line width of several tens of MHz, which limits the accuracy on the determination of the line center typically to $\sim 10{\text{-}}100 \,\text{kHz}$. This can be pushed to the level of 1 kHz if the line shape is very well understood, see e.g. [8]. Alternatively, a weakly-allowed transition can be probed (ignoring decay to other levels for the moment). Such a transition has a much narrower natural line width, but is also much weaker, making it typically more difficult to excite. Therefore, the experimental observation of these transitions require more laser power and a longer interaction time with the atom, which is not always available.

Secondly, the accuracy of the absolute frequency of the excitation laser sets a technical limit on the accuracy of the measurement. This has improved tremendously over the past two decades by the invention of the frequency-comb (FC) laser in 2000 [9, 10]. This laser source provides an absolute frequency calibration over a large part of the optical spectrum. The accuracy with which the frequency can be determined is given by the accuracy of the reference, which is typically an atomic clock and can therefore be very high. In traditional spectroscopy it is used

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to stabilize or reference the spectroscopy laser, which, in combination with ultra-stable reference cavities and sophisticated locking schemes, can result in a frequency accuracy of ~ 16 digits [11]. Alternatively, the light emitted from a FC laser can be used directly for excitation. This will be discussed more extensively later in this section.

The third source of uncertainty is caused by systematic effects on the transition frequency due to the motion of the atom, or perturbations of energy levels due to coupling with external fields. Starting with the motional effects, the relatively large velocity of atoms at room temperature can lead to a significant shift and broadening of the observed line through the Doppler effect. By improving upon the control over the atomic motion, the accuracy greatly improves. Techniques used for this purpose vary from atomic beams, which allow for a more controlled motion, to trapping and cooling of atoms [12]. The latter has led to ultra-cold gas samples (of a few hundred nK) [13,14] and virtually Doppler-free measurements [15]. Initially, this technique could only be applied in systems with a very specific energy level structure. But it was quickly extended to a large variety of species through the invention of sympathetic cooling schemes [16]. One can also do this with ions which can be manipulated and trapped with rf-electric fields [17].

Besides the Doppler effect, the energy levels can be perturbed by the interaction with electric and magnetic fields through, respectively, the Stark or Zeeman effect. Even the interaction with the excitation laser itself causes shifts of the extracted transition frequency. This ac-Stark shift is particularly problematic when probing weakly allowed transitions, because of the required high laser power. This is typically one of the leading systematic errors in such experiments. At very high levels of accuracy, e.g. in atomic clock transitions, black-body radiation shifts, relativistic Doppler and the influence from the gravitational redshift become significant, see e.g. [18].

Considering all the sources of error discussed above, the best atomic systems to investigate for tests of fundamental physics: are sufficiently simple to calculate with high accuracy (i.e. they should not have too many electrons), have accessible narrow transitions, can be well controlled and are relatively insensitive to perturbations from the environment.

1.1.2 Interesting spectroscopic targets

In the case of low-Z systems, the binding energy $((Z\alpha)^2(mc)^2)$ is much smaller than the rest energy (mc^2) and it can therefore be treated perturbatively using an expansion around $Z\alpha$. This leads to higher-order scaling of QED contributions with Z and therefore larger effects in heavier atomic systems. However, for high-Z ions, the coupling to the nucleus is strong and perturbations due to the nuclear structure become significant. Although this is interesting to investigate on its own, it does not allow for accurate tests of QED. For this purpose, the low-Z ions are most interesting.

For this reason, the hydrogen atom has served as a benchmark system over several decades. The achieved spectroscopic and theoretical accuracy is unprecedented and has led to the most precise tests of boundstate QED. The highest experimental accuracy has been achieved on the 1S-2S transition. The natural line width of this transition is 1.3 Hz and it requires two photons at 243 nm to induce the transition. Therefore it checks two out of three boxes mentioned above: it is a simple system, it has a small natural line width and the transition is accessible with modern-day laser techniques. However, hydrogen is very light, leading to high velocities and large Doppler effects (but that can be can be canceled to first order by exciting with counter-propagating laser beams). A tremendous experimental effort was made to achieve the extremely high precision of 15 digits on the 1S - 2S transition frequency [7]. The theoretical prediction of the transition frequency is nowhere near as accurate, because it is hampered by the uncertainty in the proton-charge radius (r_p) [19]. A 10-fold improvement on the accuracy of r_p was made by the CREMA collaboration using muonic hydrogen [20, 21], but the result is still under debate, because it is significantly different from the previous accepted value of r_p [22]. A large effort is being made to solve this so called *proton radius puzzle* by performing more measurements in hydrogen [8, 23, 24]. However, other insights might be gained by investigating alternative atomic and molecular systems.

An obvious choice is the He⁺ ion, as it is a simple two-body system in which the finite-size effects are still relatively small. Moreover, the nuclear charge radius of the alpha particle is expected to improve from spectroscopy in muonic He⁺ [25, 26]. In addition, since it is an ion, it

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can be trapped and cooled using rf-electric fields [17], which enables long interrogation times and leads to a suppression of the Doppler shifts. The ⁴He⁺ ion has the same sort of electronic structure as atomic hydrogen, but it does not have hyperfine interactions (because it, at least for ⁴He, does not have nuclear spin) and it is therefore much less sensitive to magnetic field perturbations. These properties make the He⁺ ion seem like the ideal candidate for precision spectroscopy and tests of fundamental physics. However, a significant challenge arises from the higher charge state of He⁺, which leads to an up-scaling of the gross energy structure. As a result, excitation of the 1S - 2S transition requires radiation with 4 times higher frequency than in hydrogen, which lies in the extreme ultraviolet spectral part of the spectrum [27]. In this wavelength range there are no narrow-band cw-lasers, which makes high-precision laser spectroscopy much more challenging.

An interesting alternative to atoms are simple molecules; especially molecular hydrogen has served as a model system. The energy structure of a molecule is much richer than that of an atom, because it can rotate and vibrate. Therefore, the spectrum consists of rotational (i) and vibrational (v) states on top of the electronic structure, as is depicted in the zoom-in of Fig. 1.2. Nonetheless, the theoretical description of the ground state is very well developed and now includes up to the seventhorder QED contributions [28, 29]. It recently led to a calculated value of the dissociation energy (D_0) with a nine-digit accuracy [30]. This benchmark quantity D_0 is the energy required to separate the molecule into two individual hydrogen atoms. Based on the recent theoretical and experimental advances, high-accuracy tests of molecular quantum theory in H_2 was performed [31–33]. In addition, molecules are sensitive to fundamentally different interactions. The coupling between the two nuclei in a simple diatomic molecule enables searches for hypothetical fifth forces at the angstrom length scale [34-36].

The value of D_0 has been accurately determined through a measurement of the ionization potential (I_p) of H₂ [31,33]. This requires a combination of transitions frequencies, of which one possible route is shown in Fig. 1.2. The first transition frequency in this scheme (1) is determined by exciting the molecule from the electronic ground state (X) to the first electronic excited state (EF) with two DUV photons [37]. The second transition frequency (2) is obtained by exciting the molecule from the



Figure 1.2 – A schematic overview of some relevant energy levels in H₂ required to determine the dissociation energy $D_0(H_2)$. The ionization potential $I_p(H_2)$ is determined from the combination of three transitions: (1) the $2 \times 202 \text{ nm}$ X-EF transition, (2) the EF-54p transition at 397 nm and (3) the interval between the $54p - I_p(H_2)$ determined with mm-wave spectroscopy and MQDT. In combination with $I_p(H)$ and $D_0(H_2^+)$, $D_0(H_2)$ can be extracted. The zoom-in shows the rotational substructure.

EF-state to a high-lying Rydberg state (54p) with a single UV photon. The last step (3), from the 54p-Rydberg state to the ionization limit, is determined using a combination of mm-wave spectroscopy and multichannel quantum defect theory [38]. In 2009 the groups of W. Ubachs at the Vrije Universiteit Amsterdam and F. Merkt at the ETH in Zurich combined their results to determine I_p in this manner and extract D_0 with eight digits precision [31], which was in agreement with theory [39]. Note that this determination also requires the values of the dissociation energy of H_2^+ and ionization potential of H, but these values are known with a very high precision.

A new result was published in 2018 based on excitation of the X - GK

transition with two photons 180 nm in Amsterdam and a measurements from the GK to the ionization limit at the ETH. This measurement improved the accuracy of D_0 by more than an order of magnitude [33]. The obtained result is in agreement with latest theoretical work, which has reached a fractional uncertainty of 7×10^{-10} by the accurate evaluation of higher-order QED-contributions [30].

The motivation for the work presented in this thesis is two-fold: we aim to measure the 1S - 2S transition in He⁺ for the first time and to improve the X - EF transition in H₂ for a more accurate determination of D_0 . This requires high-precision spectroscopy at deep ultraviolet wavelengths in the case of H₂ and at extreme ultraviolet wavelengths in the case of He⁺. For this purpose we developed a technique based on a frequency-comb laser, which is very suitable for high-precision spectroscopy at short wavelengths.

1.2 High-precision spectroscopy at short wavelengths

At vacuum (VUV) ($< 200 \,\mathrm{nm}$) and extreme (XUV) ultraviolet (< 100nm) wavelengths the atmosphere and most materials are not transparent and therefore there are few or no suitable laser materials in this spectral range. For this reason, laser spectroscopy techniques at VUV and XUV wavelengths are generally based on pulsed lasers. The relatively easy access to high peak-power from these lasers enables frequency up-conversion from typically near-infrared or visible wavelengths to the VUV or XUV spectral range through nonlinear processes. A commonly used technique is based on amplified nanosecond-pulses, which are upconverted to the deep (DUV) or vacuum ultraviolet using nonlinear crystals and so-called four-wave mixing schemes, see e.g. [40, 41]. This enables relatively high conversion efficiencies $(10^{-5} \text{ in the VUV})$ and, due to the 'narrow' bandwidth of these 'long' laser pulses, traditional methods of frequency-scanning spectroscopy [42]. It has led to accurate studies of several diatomic molecules [43-45] and simple two-electron systems, such as neutral helium, for precise tests of QED [46-48]. The achieved accuracy of these experiments was typically limited by the shift

of the instantaneous frequency through the pulse, known as chirp, caused by the amplification processes. Although there have been significant improvements in this field to compensate for chirp effects [49–51], eventually the relatively large bandwidth (of at least a few MHz) of the laser sets a technical limit. The invention of the frequency-comb (FC) laser has led to the development of several alternative techniques for VUV and XUV spectroscopy, which could in principle lead to much higher spectroscopic accuracy.

A FC laser combines the relatively high peak-power of ultra-short laser pulses with an accurate absolute frequency calibration of the emitted modes. This makes a large part of the optical spectrum accessible for high-precision spectroscopy. With nonlinear processes it is not only possible to generate frequencies at VUV and XUV wavelengths [52,53], but also light at the mid-infrared [54] and THz-regime [55]. The employed nonlinear processes are highly coherent and therefore retain the properties of the FC laser (but can broaden the comb lines through phase-noise multiplication).

1.2.1 Spectroscopy with frequency-comb lasers

The general operation of a FC laser relies on the emission of a highly repetitive train of ultra-short (10-100 fs) laser pulses with a known phase relation (see also Fig. 2.3). The overall width of the spectrum is related to the length of the individual pulses and typically spans between tens and a few hundred nanometers. At first glance, such a large bandwidth does not seem suitable for high-precision spectroscopy. However, due to the highly repetitive nature of the FC laser, the wide spectrum consists of a large number of narrow frequency modes. The absolute position of these so-called comb 'teeth' depends on the pulse repetition time (T_{rep}) and the pulse-to-pulse carrier-envelope phase slip. More specifically, the spacing between each mode is given by the repetition frequency of the laser, while the offset of the first mode in the spectrum, the so-called carrier-envelope offset frequency, depends on dispersion properties in the laser cavity. For a non-zero pulse-to-pulse phase slip, the carrier-envelope offset frequency has a finite value between zero and T_{rep} (typically between 50-300 MHz). For a long time, it

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was impossible to measure, and therefore stabilize, the carrier-envelope offset frequency because of the absence of spectral intensity at these low frequencies. However, in 2000, a new technique was developed at the Max Planck Institute for Quantum Physics (Garching, Germany) in the group of Hänsch and at JILA (Boulder, USA) in the group of Hall, which allowed for a direct determination of this frequency [9, 10]. In combination with the more straightforward methods to measure T_{rep} , it enabled the absolute calibration and stabilization of each mode in the wide frequency-comb spectrum. In 2005 the Nobel prize in physics was shared between R.J. Glauber, J.L. Hall and T.W. Hänsch, where the latter two got it in part for their contributions to the FC laser and the impact it had on science.

Nowadays, the FC is used in a large variety of physics applications. A few examples are: precision spectroscopy, optical atomic clocks, attosecond science calibrations of spectrometers for astro-physics applications and optical sensing (see e.g. [7, 56-65]). In the field of high-precision spectroscopy, it is used in many different ways. In traditional spectroscopic techniques, it serves as a frequency ruler, i.e. the frequency of the spectroscopy laser is compared with the frequency of the nearest FC mode for stabilization and determination of the optical frequency. Especially in the field of optical clocks, this technique, in combination with the development of ultra-stable cavities, has advanced the achieved accuracy tremendously [58, 59]. However, over the last two decades a variety of new techniques have been developed to directly use FC pulses for excitation [62]. This often requires a different excitation scheme or method than for traditional spectroscopy, because a FC laser typically emits 10^6 modes at the same time.

The most straightforward approach for direct FC spectroscopy is to simply measure the fluorescence from a target which is illuminated with FC pulses. By changing either the repetition frequency or the carrierenvelope offset frequency, one can scan over a transition and obtain a spectrum. This technique can be combined with cold samples or counterpropagating laser beams in a two-photon scheme to reduce Doppler effects and achieve a high spectroscopic accuracy [57,66,67]. Such methods are only suitable for isolated transitions, because the signal becomes ambiguous if the multiple comb-modes interact with several transitions. Alternatively one can use two frequency-comb lasers, which are slightly repetition-rate detuned with respect to each other for Fourier-transform spectroscopy [62, 68]. In this case one FC serves as a reference and the other as a probe passing through the sample. A heterodyne beat is used to convert the spectrum to the radio-frequency domain where it enables a measurement of a broad spectrum in a short time. Therefore, this technique is especially interesting in combination with nonlinear conversion to the mid- and far-infrared spectral range, because the complex spectrum of molecular ro-vibrational transitions typically lie in this wavelength range, see e.g. [69, 70]. It has applications in fundamental molecular dynamics, biochemistry and trace gas sensing. The obvious technical disadvantage is that it requires two frequency-comb lasers.

The final approach discussed here relies on two amplified FC pulses for a Ramsey-type excitation [71–73]. This so-called Ramsey-comb method is used in this work and will be described in the following section in more detail.

1.2.2 Introduction to Ramsey-comb spectroscopy

The Ramsey-comb spectroscopy technique is a modified version of Ramsey's method of oscillatory fields [74]. Norman Ramsey used two microwave fields, separated in space to excite molecules in a beam in two different regions and observe a so-called Ramsey-fringe. The consecutive excitation of a superposition state of the ground and the excited state leads to interference of the two contributions. By scanning the frequency of the phase locked excitation fields and recording the excited state population, the phase evolution can be observed, which oscillates with the transition frequency. This fringe pattern leads to an effective reduction of the observed line width, which scales inversely proportional to the delay (and therefore the distance) between the two excitation fields. This allows for a more accurate determination of the transition frequency than in traditional spectroscopy and therefore it is used in atomic cesium clocks on which the SI second is based [75]. For this invention and its use in atomic clocks, Norman Ramsey received half of the Nobel prize in 1989.

An analogous picture can be used for two phase-locked optical pulses, separated in time. The principle of quantum interference from excitation with two laser pulses is illustrated in Fig. 1.3. A resonant laser



Figure 1.3 – The principle of quantum interference. Two phase locked pulses excite the atom into a superposition between the ground and excited state. The phase evolution of this state oscillates with the transition frequency and the two excitation contributions can interfere (a) constructively, transferring the population back into the ground state or (b) destructively, transferring the population into the excited state. The amplitude of the superposition state is dependent on the delay and the phase difference between the excitation pulses and can be measured to observe a so-called Ramsey-fringe.

pulse creates a superposition of the ground and the excited state in an atom. This state will freely evolve with the transition frequency. The second pulse creates a similar state which will interfere with the first. This can be constructive, transferring the population into the excited state, as is depicted in Fig. 1.3(a) or destructive (Fig. 1.3(b)), which transfers the population back into the ground state. The amplitude of the superposition state after the second excitation pulse is dependent on the phase difference and the delay between the two pulses. By measuring this amplitude (i.e. the excited state population) one can observe a Ramsey-fringe, from which the transition frequency can be determined. Note that Fig. 1.3 shows a special case, where the transition frequency is an integer number of the repetition frequency. Because the FC laser emits pulses with a well defined and controlled delay and a known phase relation, it is a very suitable source for Ramseytype experiments. However, a complication arises when the pulses are amplified for efficient up-conversion to short wavelengths. This process introduces a significant and typically unknown, phase shift between the pulses, which leads to a shift of the Ramsey pattern and therefore a systematic shift of the extracted transition frequency. This problem can be circumvented by combining Ramsey fringes at different inter-pulse delay and extracting the transition frequency from the phase *difference* [73]. In this manner constant phase shifts lead to common mode shifts of the Ramsey fringes, as is illustrated in Fig. 1.4, and do not influence the extracted frequency [76].

The spectral overlap between the amplified FC spectrum and the atomic transition is not very high. Therefore, single-photon excitation of narrow spectral lines is generally not very efficient in RCS. However, for two-photon transitions, multiple combinations of comb modes add up to the resonance frequency. Therefore, a large part of the bandwidth of the FC pulses then contributes to the excitation. This leads to a significant enhancement of the excitation probability and enables the interrogation of narrow spectral lines with RCS.

The first demonstration of RCS in the near-infrared was performed on two-photon resonances in rubidium and cesium in a gas cell [73]. Due to the relatively large spectral bandwidth, multiple transitions were excited simultaneously. It was shown that these more complex spectral features could be reconstructed by recording enough Ramsey fringes over a large range of pulse delays. This led to an accurate determination of both the amplitude and the transition frequency of the excited transitions.

The extension of RCS to the deep-ultraviolet was successfully demonstrated on the two-photon $4p^6 \rightarrow 4p^55p[1/2]_0$ transition in krypton [77]. Up-conversion of the amplified FC pulses in nonlinear crystals was used to create light at 212.5 nm (the fourth harmonic of 850 nm). The experiment was performed in an atomic beam using a counter-propagating excitation scheme, which suppressed Doppler effects significantly. The obtained results improved upon the previous determination of the transition by a factor of 34 [71] and the accuracy was mainly limited by the upper-state lifetime. A slight modification of the setup enabled excitation of the two-photon X - EF transition in H₂ at 2 × 202 nm for



Figure 1.4 – Visualization of Ramsey-comb spectroscopy. A series of Ramsey fringes are recorded with frequency-comb pulse pairs. The pulse delay can be changed in integer steps of the repetition time (T_{rep}) . A delay independent optical phase shift leads to a common mode shift of the fringes and does not influence the extracted transition frequency.

tests of molecular quantum theory [78]. This experiment is described in Chapter 4 of this thesis and was a crucial step towards a more accurate determination of the dissociation energy in H_2 [79].

Further extension of RCS to the XUV spectral range for spectroscopy in He⁺ requires high-harmonic generation. The demonstration of RCS combined with HHG is one of the main results in this thesis, and the basic principles of it are briefly discussed in the next section.

1.2.3 Combining direct frequency-comb spectroscopy with high-harmonic generation

The process of high-harmonic generation (HHG) can be understood by the three-step recollision model [80, 81], which describes tunneling, acceleration and recombination of a bound electron in an atom. The three steps are driven by the high electric field of a laser and leads to generation of odd harmonics of the optical frequency. The required regime of tunneling ionization is typically reached for intensities of $\sim 10^{14} \,\mathrm{W/\,cm^2}$ (depending on the atom which is used for HHG). This can be achieved by, for example, focusing a 1 mJ pulse of 100 fs down to $100 \,\mu\text{m}$. In a similar manner (actually using shorter pulses), generation of photons of up to 350 eV (3.5 nm) have been generated [82].

The HHG process is not very efficient, because the probability of recombination is low. Therefore, the interaction region gets significantly ionized during up-conversion and a plasma is created. Although the principle of HHG is very well established and the process has been studied over several decades, the influence of this plasma on timescales relevant to RCS (tens to hundreds of nanoseconds) have not vet been investigated. Nonetheless, successful up-conversion of a full FC pulse train has been demonstrated [52, 53]. The typical FC laser does not emit pulses with energies on the order of a mJ, therefore the peak intensity was boosted in an enhancement resonator and intra-cavity HHG was performed. The first XUV-combs were demonstrated in 2005 and direct excitation with such an up-converted FC was demonstrated in 2012 [83]. However, the advantage of pulse amplification in the Ramsey-comb spectroscopy method allows for much more straightforward techniques of HHG. In 2010 an experiment based on Ramsey spectroscopy with two amplified and up-converted FC pulses already led to an accurate determination of the $1s^2 \rightarrow 1s5p$ transition at 51 nm in neutral helium [72]. This measurement only relied on Ramsey measurements at a limited pulse delay range (based on two consecutive pulses from a FC) and therefore suffered from the aforementioned unknown phase shifts from amplification and up-conversion. These problems due to amplification were mostly solved with the development of the RCS technique, as was already discussed, but the influence from up-conversion with HHG was not yet investigated and this so far hampered further extension of RCS to the XUV spectral range.

When combining RCS with HHG, the plasma generated during upconversion of the first FC pulse influences the phase of the second up-converted pulse. Because of the dynamic evolution of the plasma, this phase shift is dependent on inter-pulse delay and therefore leads to systematic shifts of the extracted transition frequency in RCS. An important part of the work described in this thesis was dedicated to the investigation of these plasma-induced effects on a nanosecond timescale using the atom as a phase detector. This investigation is one of the key pieces of this thesis and it enabled the first high-precision RCS measurement at VUV wavelengths as is described in Chapters 5 and 6.

1.3 Outline of this thesis

The thesis is structured in the following way. Chapter 2 discusses the theoretical framework on which the presented work in this thesis is based. It starts out with a quick overview of some basic physical concepts, such as ultra-fast pulse propagation, after which the techniques of high-harmonic generation and Ramsey-comb spectroscopy are described. The final part of Chapter 2 focuses on the expected consequences of combining these two techniques.

In Chapter 3 an overview of the experimental setup is given. The first part describes the Ramsey-comb laser setup and the most recent improvements that were made. The second part elaborates on the newly developed vacuum setup, which was specifically designed to combine RCS with HHG for high-precision 1S - 2S spectroscopy in He⁺. In this chapter the most important considerations are motivated based on this goal. The vacuum setup was slightly altered for the experiments described in Chapters 5 and 6. A detailed overview of these alterations is given in Appendix A.

Chapter 4 shows the results obtained from RCS on the two-photon $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}(0,0)Q^{1}$ transition in H₂ at 202 nm (the fourth harmonic of 808 nm). The presented fractional uncertainty of 2.5×10^{-11} is two orders of magnitude better than what was achieved in the previous determination [37], and is a crucial step in the improved value of the dissociation energy [79].

Chapters 5 and 6 present the results obtained by combining RCS with HHG. The influence of the HHG process on the RCS method was investigated by tracking the atomic phase evolution of excited xenon atoms. The results presented in Chapters 5 and 6 show that effects from plasma formation are subtle and can be suppressed relatively easily. This enabled high-precision Ramsey-comb spectroscopy on the $5p^6 \rightarrow 5p^58s\ ^2[3/2]_1$ transition in xenon at 110 nm (the seventh harmonic of 770 nm). The presented achieved fractional uncertainty of 3.2×10^{-10} is a four-order of magnitude improvement over the previous determination [84] and is the highest obtained accuracy with a HHG source. This

shows great promise for spectroscopy on the 1S - 2S transition in He⁺ with kHz-level accuracy. Chapter 5 gives a brief overview of the most important results, while a more detailed description of the experimental techniques and results is given in Chapter 6.

Chapter 7 contains a short outlook for further improvements on the system and future experiments which will be conducted. This includes a measurement of the X - EF transition in *para*-hydrogen with a better accuracy than was achieved in Chapter 4 and the first ever measurement of the 1S - 2S transition in He⁺.

CHAPTER 2

Theoretical background

In this chapter, the relevant theoretical background for the work in this thesis is given. The chapter is structured in the following way. It starts with some basic concepts of pulse propagation and pulse trains, after which the principle of the frequency-comb laser is introduced. It continues with the description of several methods of nonlinear amplification and up-conversion, where special attention is paid to the process of high-harmonic generation. After this, the method of Ramsey-comb spectroscopy is explained from some fundamental concepts of quantum mechanics and quantum interference. In the final part a discussion is given on how this technique can be combined with high-harmonic generation for high-precision spectroscopy in the vacuum and extreme ultraviolet range.

2.1 Pulse propagation

The mathematical description of an electromagnetic wave $(E_t(z,t))$ traveling in the z direction can be obtained by solving the wave equation (derived from Maxwell's equations). For the moment, we will neglect the interaction with the medium and consider

$$\partial_z^2 E(z,t) - \frac{1}{c^2} \partial_t^2 E(z,t) = 0, \qquad (2.1)$$

where c is the speed of propagation of light in vacuum and ∂_z and ∂_t are the derivatives with respect to the propagation direction z and time

t, respectively. The solution to this equation is a plane wave which oscillates with angular frequency ω_0 and can be described by

$$E_t(z,t) = E_0 e^{i(\omega_0 t - k_0 z)} + \text{c.c.}, \qquad (2.2)$$

where the wave vector is given by $k_0 = \omega_0/c$ and the amplitude of the electric field is E_0 . This continuous wave is monochromatic, i.e. it contains only a single frequency ω_0 . For a light *pulse*, the electric field consists of a distribution of frequencies, which can be described as a linear combination of monochromatic waves with different angular frequencies ω around a central frequency ω_0 according to

$$E_t(z,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} A(\omega - \omega_0) e^{i\omega t} e^{-ikz} d\omega.$$
(2.3)

Here $A(\omega)$ is the amplitude of the different frequency components of the electric field. The expression in Eq. 2.3 can be recognized as a Fourier integral and therefore the electric field in the frequency domain is straightforwardly given by

$$E_{\omega}(z,\omega) = \mathcal{FT}[E_t(z,t)] = A(\omega - \omega_0)e^{-ikz}.$$
(2.4)

When such an electromagnetic pulse propagates through a dielectric medium, linear dispersion affects the spatial properties of the pulse. In order to obtain these properties, we consider the simple case that z = 0 and one can write

$$E_t(0,t) = A_t(0,t)e^{i\omega_0 t},$$
 (2.5a)

$$E_{\omega}(0,\omega) = A_{\omega}(0,\omega-\omega_0), \qquad (2.5b)$$

where $A_t(0, t)$ and $A_{\omega}(0, \omega - \omega_0)$ are the envelope functions of the pulse in the time and frequency domain, respectively. This expression shows that in the frequency domain, the envelope function is centered around ω_0 , as is shown in Fig. 2.1. Starting from the frequency domain and propagating the envelope in the z direction we obtain

$$A_{\omega}(z,\omega) = A_{\omega}(0,\omega)e^{-ik(\omega)z}.$$
(2.6)

Therefore $k(\omega)$ is a frequency dependent propagation factor. By expanding this factor around the central frequency, we obtain

$$k(\omega) = k_0 + k^{(1)}(\omega - \omega_0) + \frac{1}{2}k^{(2)}(\omega - \omega_0)^2 + \dots, \qquad (2.7)$$

with

$$k^{(i)} = \frac{d^i k}{d\omega^i}\Big|_{\omega_0}.$$
 (2.8)

The electric field in the time domain is obtained by combining Eq. 2.6 with Eq. 2.7 and performing an inverse Fourier transform. This yields

$$E_t(z,t) = A_t(z,t)e^{i(\omega_0 t - k_0 z)},$$
(2.9)

with the envelope function

$$A_t(z,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} A_{\omega}(0,\omega - \omega_0) e^{i[(\omega - \omega_0)t - (k(\omega) - k_0)z]} d\omega.$$
(2.10)

2.1.1 Propagation through a dispersive medium

By taking only the linear dispersion term into account, the evaluation of the integral in Eq. 2.10 becomes

$$A_t(z,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} A_{\omega}(0,\omega-\omega_0) e^{i(\omega-\omega_0)(t-k^{(1)}z)} d\omega$$

= $A_t(0,t-k^{(1)}z).$ (2.11)

This result shows that the overall shape of the envelope remains unchanged, but that the group velocity is given by $v_g = 1/k^{(1)}$ which is unequal to the phase velocity $v_{\phi} = \omega_0/k_0$. Therefore, the phase of the carrier "slips" with respect to the envelope function. This so-called carrier-envelope phase slip is given by

$$\phi_{ce} = \left(\frac{1}{v_g} - \frac{1}{v_\phi}\right)\omega_0 z \tag{2.12}$$

This result is illustrated in Fig. 2.1, where the dotted light gray curve represents the shifted carrier (by ϕ_{ce}) at ω_0 and the dark gray curve represents the envelope function of the pulse in the time domain. The second term of the expansion of the wave vector $k(\omega)$ changes the instantaneous frequency linearly through the pulse. The influence of this term on a Gaussian pulse¹ can be calculated [85] and yields

$$A_t(z,t) = \frac{\tau_0}{\sqrt{\tau_0^2 + ik^{(2)}z}} e^{-\frac{1}{2}\frac{t^2}{\tau_c^2} + i\phi(t)},$$
(2.13)

¹ using the envelope function $A_t(\tau) = e^{-\frac{\tau^2}{2\tau_0^2}}$

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Figure 2.1 – The Fourier relation between the time and frequency domain picture for a laser pulse. The spectrum (right panel) is centered around ω_0 and has a bandwidth $\Delta \omega$, which is inversely proportional to the pulse length τ in the time domain (left panel). For a carrier-envelope phase slip (ϕ_{ce}) of zero, the maximum of the carrier (light gray curve) coincides with the maximum of the envelope function (dark gray curve). For a finite ϕ_{ce} (dotted light gray line) the carrier 'slips' with respect to the envelope function.

where

$$\tau_c = \tau_0 \sqrt{1 + \left(\frac{k^{(2)}z}{\tau_0^2}\right)^2}.$$
(2.14)

The result shows that second-order dispersion leads to a stretching of the pulse length from τ_0 to τ_c after propagation through a medium over a distance z. The added phase term is given by

$$\phi(t) = \frac{1}{2k^{(2)}z} \frac{\tau_0^2}{\tau_c^2} t^2 \tag{2.15}$$

and is thus changing quadratically throughout the pulse. This leads to a change of the instantaneous frequency as a function of time, which is also referred to as 'frequency chirp'.

The influence from higher-order dispersion terms lead to higher-order nonlinear frequency chirp for the even terms and pre- or post-pulses, depending on the sign, for the odd terms. The influence of these higherorder terms grows strongly with the spectral bandwidth of the pulse and they are therefore only relevant for very short pulses. For the work in this thesis only second- and third-order dispersion are relevant, because the bandwidth of the pulses is relatively narrow.

2.1.2 Pulse trains

So far only single pulses were considered. However, regular pulse trains have some interesting additional properties, which are essential for the research described in this thesis. The electric field in the time domain of a train of N pulses with a fixed pulse delay of T_{rep} can be described by [86]

$$E_{tr}(t) = \sum_{n=0}^{N-1} A_t(t - nT_{rep}) e^{i(\omega_0 t - n\omega_0 T_{rep} + n\Delta\phi_{ce})}, \qquad (2.16)$$

where $A_t(t)$ is the envelope function and $\Delta \phi_{ce}$ is the *pulse-to-pulse* carrier-envelope phase slip (Eq. 2.12). The corresponding electric field in the frequency domain can be obtained from the Fourier transform of Eq. 2.16

$$E_{tr}(\omega) = \sum_{n=0}^{N-1} e^{i(n(\Delta\phi_{ce} - \omega_0 T_{rep}))} \int A_t(t - nT_{rep}) e^{i(\omega_0 - \omega_0)t} dt.$$
(2.17)

Using the relation $E(\omega) = \int E(t)e^{-i\omega t}dt$ and simplifying the expression², one obtains

$$E_{tr}(\omega) = A_{\omega}(\omega) \frac{1 - e^{-iN(\omega T_{rep} + \Delta\phi_{ce})}}{1 - e^{-i(\omega T_{rep} + \Delta\phi_{ce})}},$$
(2.18)

from which an expression of the spectral intensity can be obtained

$$I(\omega) = |E(\omega)|^2 = I_0(\omega) \frac{\sin(N(\omega T_{rep} + \Delta\phi_{ce})/2)}{\sin((\omega T_{rep} + \Delta\phi_{ce})/2)}.$$
(2.19)

This equation shows that the spectrum of a train of identical pulses with a constant spacing is described by a equidistant modes. The time and frequency domain representation of several sets of pulses is shown in Fig. 2.2. For two pulses (Fig. 2.2(a)), which are spaced in time by T_{rep} , the spectrum of a single pulse is modulated with a cosine of period $f_{rep} = 1/T_{rep}$. The modulation period decreases as the pulse delay increases (Fig. 2.2(b)) and the 'fringe pattern' becomes more narrow if

²Using the identity $\sum_{n=0}^{N-1} x^n = \frac{1-x^N}{1-x}$



Figure 2.2 – Different sets of pulses and their corresponding spectrum. The envelope of the spectrum is determined by the length of the individual pulses. (a) A set of two pulses leads to a cosine-modulated spectrum. (b) The period of the modulation is dependent on the distance between the pulses, here $4 \times T_{rep}$. (c) An infinite pulse train leads to a spectrum of discrete modes of which the spacing is determined by $T_{rep} = 1/f_{rep}$.

we add more pulses (Fig. 2.2(c)). In the limit of $N \to \infty$, Eq. 2.18 becomes

$$E_{tr}(\omega) = A_{\omega}(\omega - \omega_0) \sum_{n=0}^{\infty} \delta(\omega T_{rep} + \Delta \phi_{ce} - n2\pi).$$
 (2.20)

The spectral amplitude is non-zero for $\omega T_{rep} + \Delta \phi_{ce} = n2\pi$, i.e. the spectrum of a pulse train consists of a comb of infinitely narrow discrete frequencies given by

$$\omega_n = \omega_{ceo} + n\omega_{rep}, \qquad (2.21)$$

where $\omega_{ceo} = \Delta \phi_{ce}/T_{rep}$ and $\omega_{rep} = n2\pi/T_{rep}$.

2.2 The frequency-comb laser

The results obtained in Sec. 2.1.2 naturally lead to a description of the properties of a frequency-comb (FC) laser. The invention of the FC laser [9, 10] has revolutionized the field of precision spectroscopy and has many more applications in other fields of physics, as was discussed in Chapter 1. A general description of the properties of a FC laser is given in this section, while the experimental realization and the specific implementation are discussed further in this thesis (Sec. 3.1.1). A FC laser emits a train of femtosecond-pulses, with a well defined delay and phase relation between each pulse. The final equation obtained in Sec. 2.1.2 describes the spectrum of such a pulse train. It consists of a large number of modes at well-defined frequencies. According to Eq. 2.21, the position of these modes are determined by only two quantities: the repetition time T_{rep} of the laser and the carrier-envelope offset phase slip $\Delta \phi_{ce}$. By converting the modes given by Eq. 2.21 from angular frequencies to 'normal' frequencies ($f = 2\pi\omega$), one obtains

$$f_n = \frac{\Delta\phi_{ce}}{2\pi} f_{rep} + n f_{rep}, \qquad (2.22)$$

which is further simplified by defining $f_{ceo} = (\Delta \phi_{ce}/2\pi) f_{rep}$ to the well known FC spectrum, which is given by

$$f_n = f_{ceo} + n f_{rep}.$$
 (2.23)

The spectrum given by Eq. 2.23 consists of equidistant discrete modes which are spaced by f_{rep} and are offset by f_{ceo} from zero. In a FC laser, the absolute frequency of these modes are fixed by stabilizing both f_{rep} and f_{ceo} to a stable reference. The properties of the frequency-comb laser in the time and frequency domain are illustrated in Fig. 2.3.

A powerful aspect of the FC is that the two frequencies which define the spectrum are typically in the radio-frequency domain and can therefore be stabilized to an ultra-stable reference such as an atomic clock, while the modes themselves are in the optical domain. Therefore, the optical modes can be referenced directly to an absolute frequency standard and be used for accurate optical frequency metrology.

The repetition frequency is obtained from the pulse-repetition time by



Figure 2.3 – The time (upper part) and frequency (lower part) domain picture of the frequency-comb laser. An infinite pulse train with a fixed pulse repetition time T_{rep} and well defined carrier-envelope phase slip $\Delta\phi_{ce}$ leads to a spectrum, which consists of narrow modes with equidistant spacing f_{rep} and offset frequency f_{ceo} . By fixing these two frequencies, the full spectrum is defined and can thus be used as an absolute frequency ruler in the optical domain.

measuring the pulse train with a fast photo-diode. This signal can then be used to stabilize f_{rep} by comparing it with a reference signal and providing active feedback to the cavity length of the laser. For stabilization of f_{ceo} a more sophisticated scheme needs to be implemented, because of the absence of spectral intensity at this frequency. The value of f_{ceo} is measured by interference between modes at different ends of the spectrum in a so-called f - 2f interferometer. This technique is based on spectral broadening through nonlinear processes in a fiber to obtain a spectrum which spans an octave. Details of the experimental realization of the frequency-comb laser are given in Sec. 3.1.1.
2.3 Pulse amplification and up-conversion

The energy of a laser pulse is concentrated in a very short time, so even though a typical frequency-comb laser produces pulses with only a few nJ of pulse energy, the peak power can reach values of a few MW. Parametric amplification can be used to further boost the peak power. In this manner a value of few hundred terrawatts has been realized [87]. This amplification process relies on the nonlinear response of a medium for frequency conversion. In this section, the basic principles of these non-linear phenomena are described in the perturbative regime, from which processes such as second-harmonic generation and parametric amplification are derived.

2.3.1 Nonlinear optics in the perturbative regime

When a light pulse travels through a medium, the high electric field can displace the electrons in that medium, and therefore induce a polarization ($\mathbf{P}(\mathbf{r}, t)$). This acts as a source term in the wave-equation (Eq. 2.1) and leads to the emission of new frequencies

$$\nabla^{2} \mathbf{E}(\mathbf{r}, t) - \epsilon_{0} \mu_{0} \frac{\partial^{2} \mathbf{E}(\mathbf{r}, t)}{\partial t^{2}} = \mu_{0} \frac{\partial^{2} \mathbf{P}(\mathbf{r}, t)}{\partial t^{2}}, \qquad (2.24)$$

where μ_0 and ϵ_0 are the vacuum permeability and permittivity, respectively. At low intensity, the induced polarization scales linear with the electric field and can be written as

$$\mathbf{P}(\mathbf{r},t) = \epsilon_0 \chi^{(1)} \mathbf{E}(\mathbf{r},t), \qquad (2.25)$$

where $\chi^{(1)}$ is the linear optical response susceptibility of the medium. Because the induced polarization is proportional to the electric field, the emitted frequencies will be equal to the frequency of the driving field. At higher intensity, the response of the medium becomes nonlinear and scales with higher orders of the electric field

$$\mathbf{P}(\mathbf{r},t) = \epsilon_0(\chi^{(1)}\mathbf{E}_1 + \chi^{(2)}\mathbf{E}_1\mathbf{E}_2 + \chi^{(3)}\mathbf{E}_1\mathbf{E}_2\mathbf{E}_3 + \dots), \qquad (2.26)$$

where $\mathbf{E}_i = \mathbf{E}_i(\mathbf{r}, t)$ with i = 1, 2, 3.. are the different incident fields (which can be identical) and $\chi^{(n)}$ is the tensor describing the n^{th} -order



Figure 2.4 – Two nonlinear processes in a medium with response χ_2 . (a) In sum-frequency generation, the frequency of the two incident beams are added to generate a wave with frequency $\omega_{sum} = \omega_1 + \omega_2$. According to conservation of momentum the propagation direction is given by $\mathbf{k}_{sum} = \mathbf{k_1} + \mathbf{k_2}$. (b) Similarly, a wave with the difference frequency $\omega_{diff} = \omega_2 - \omega_1$ and wave vector $\mathbf{k}_{diff} = \mathbf{k_2} - \mathbf{k_1}$ can be generated.

susceptibility of the medium.

The polarization direction of the electric field can be inverted by applying the inversion operator on the electric field $I_{op}\mathbf{E} = -\mathbf{E}$ in the individual terms of Eq. 2.26. The same operation can be performed on the induced polarization $I_{op}\mathbf{P} = -\mathbf{P}$. These two operations do not yield the same expression for the even terms unless they are zero, and therefore some interesting conclusions can be drawn: for an inversion symmetric medium only odd terms are non-zero. However, in media which break the inversion symmetry, the second term in the expansion is non-zero. In this term, the response of the medium is dependent on the product of two electric fields (or the square of the field in case of identical fields). Omitting the spatial dependence $(E(t) = 1/2A(t)e^{i\omega_0 t} + \text{c.c.})$, the square of the electric field is given by

$$E^{2}(t) = \frac{1}{4}A^{2}(t)e^{i2\omega_{0}t} + \frac{1}{2}A(t)A^{*}(t) + \frac{1}{4}A^{*2}(t)e^{-i2\omega_{0}t}, \qquad (2.27)$$

where A(t) is the envelope function. The expression shows that the second-order response gives rise to a component at the second harmonic $2\omega_0$ of the driving frequency. For very high peak intensities, the induced polarization of higher-order terms also become significant and higher-harmonics can be created. However, the expansion of Eq. 2.26 does not hold in this strong-field regime, where intensities of $> 10^{13}$ W/cm² are reached. A description of high-harmonic generation requires a different approach, which will be given in Sec. 2.4.

Returning to the perturbative regime, for two input beams with a different driving frequency, ω_1 and ω_2 , and corresponding wave vectors $\mathbf{k_1}$ and $\mathbf{k_2}$, respectively, the second-order term yields

$$E_{1}(\mathbf{r},t)E_{2}(\mathbf{r},t) = \frac{1}{4}A_{1}^{2}e^{2i(\omega_{1}t-\mathbf{k_{1}}\cdot\mathbf{r})} + \frac{1}{4}A_{1}^{*2}e^{-2i(\omega_{1}t-\mathbf{k_{1}}\cdot\mathbf{r})} + \frac{1}{2}A_{1}A_{1}^{*} \\ + \frac{1}{4}A_{2}^{2}e^{2i(\omega_{2}t-\mathbf{k_{2}}\cdot\mathbf{r})} + \frac{1}{4}A_{2}^{*2}e^{-2i(\omega_{2}t-\mathbf{k_{2}}\cdot\mathbf{r})} + \frac{1}{2}A_{2}A_{2}^{*} \\ + \frac{1}{2}A_{1}A_{2}e^{i((\omega_{1}+\omega_{2})t-(\mathbf{k_{1}}+\mathbf{k_{2}})\cdot\mathbf{r})} \\ + \frac{1}{2}A_{1}^{*}A_{2}^{*}e^{-i((\omega_{1}+\omega_{2})t-(\mathbf{k_{1}}+\mathbf{k_{2}})\cdot\mathbf{r})} \\ + \frac{1}{2}A_{1}A_{2}^{*}e^{-i((\omega_{2}-\omega_{1})t-(\mathbf{k_{2}}-\mathbf{k_{1}})\cdot\mathbf{r})} \\ + \frac{1}{2}A_{1}^{*}A_{2}e^{i((\omega_{2}-\omega_{1})t-(\mathbf{k_{2}}-\mathbf{k_{1}})\cdot\mathbf{r})} \\ + \frac{1}{2}A_{1}^{*}A_{2}e^{i((\omega_{2}-\omega_{1})t-(\mathbf{k_{2}}-\mathbf{k_{1}})\cdot\mathbf{r})}.$$

$$(2.28)$$

In the expression, the space and time dependence of the electric field amplitudes A_i have been omitted for readability. Eq. 2.28 contains the second harmonic of both driving frequencies, as expected, but also two new components. Namely, the sum frequency $\omega_{sum} = \omega_1 + \omega_2$ and the difference frequency $\omega_{diff} = \omega_2 - \omega_1$ of the two driving frequencies. Due to momentum conservation, the corresponding wave vectors are given by $\mathbf{k}_{sum} = \mathbf{k}_1 + \mathbf{k}_2$ and $\mathbf{k}_{diff} = \mathbf{k}_2 - \mathbf{k}_1$. This so-called sum- and differencefrequency generation process is illustrated in Fig. 2.4. By using a noncollinear geometry, the generated harmonic beam can be separated from the fundamental.

2.3.2 Parametric amplification

Parametric amplification can be viewed as the reverse process from sum frequency generation: a pump photon (ω_p) is split into a signal photon (ω_s) and an idler photon (ω_i) , where $\omega_p > \omega_s \ge \omega_i$. The combined induced non-linear polarization of a medium for an overlapping pump and signal pulse in a single spatial dimension (z) can be written as

$$P_{NL}(z,t) = \epsilon_0 \chi^{(2)} A_p(t) A_s(t) e^{-i[(k_p - k_s)z - (\omega_p - \omega_s)t]}, \qquad (2.29)$$

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Parametric amplification (seeded)



Figure 2.5 – Illustration of the parametric amplification process. This is a special case of difference-frequency generation where a pump photon ω_p is split into an idler photon $\omega_i = \omega_p - \omega_s$ and a signal photon ω_s , with $\omega_p > \omega_s \ge \omega_i$. By seeding the signal (ω_s), this process can be used to amplify the seed beam.

where A(t) is used to describe the amplitude of the electric field, which is the convention in the field of parametric amplification. A similar expression can be written down for the interaction of the pump and idler field. Because of energy conservation, we can write for the frequencies of the three interacting waves $\omega_i = \omega_p - \omega_s$. Therefore the energy of the pump pulse is transferred to the signal pulse and idler pulse. This process (Fig. 2.5) can be described by a set of coupled wave equations [88,89] according to

$$\frac{\partial A_s}{\partial z} + k^{(1)} \frac{\partial A_s}{\partial t} - \frac{ik^{(2)}}{2} \frac{\partial^2 A_s}{\partial t^2} = -i\chi^{(2)} \left(\frac{\omega_s}{2n_s c}\right) A_p A_i^* e^{-i\Delta kz}, \quad (2.30a)$$

$$\frac{\partial A_i}{\partial z} + k^{(1)} \frac{\partial A_i}{\partial t} - \frac{ik^{(2)}}{2} \frac{\partial^2 A_i}{\partial t^2} = -i\chi^{(2)} \left(\frac{\omega_i}{2n_i c}\right) A_p A_s^* e^{-i\Delta kz}, \quad (2.30b)$$

$$\frac{\partial A_p}{\partial z} + k^{(1)} \frac{\partial A_p}{\partial t} - \frac{ik^{(2)}}{2} \frac{\partial^2 A_p}{\partial t^2} = -i\chi^{(2)} \left(\frac{\omega_p}{2n_pc}\right) A_s A_i^* e^{-i\Delta kz}, \quad (2.30c)$$

where the wave vector mismatch is given by $\Delta k = |\Delta \mathbf{k}| = |\mathbf{k}_p - \mathbf{k}_s - \mathbf{k}_i|$ and the slowly varying envelope approximation $(\partial A/\partial z \ll 2k\partial A/\partial z)$ was used. Eq. 2.30 can be solved numerically, see e.g. [90–93], but some insightful results can already be obtained analytically.

The set of coupled equations can be simplified by making the following assumptions: the intensity of the idler beam is initially zero, the pump intensity is considered constant, i.e. there is no pump depletion, and dispersion is neglected. If we now assume the signal beam is seeded by an input beam $(I_{s,in})$, so that the parametric process works as an

amplifier, the intensity of the signal beam after traveling through a crystal with length L is given by [88]

$$I_{s,out} = I_{s,in} \cosh^2(gL), \qquad (2.31)$$

where the gain coefficient can be written as

$$g = \sqrt{\left(\chi^{(2)}\right)^2 \frac{\omega_s \omega_i}{e\epsilon_0 c^3 n_p n_s n_i} I_p - \left(\frac{\Delta k}{2}\right)^2}.$$
 (2.32)

In the large-gain regime (gL >> 1) Eq. 2.31 can be written as

$$I_{s,out} = \frac{I_{s,in}}{4} e^{2gL}.$$
 (2.33)

The overall gain after propagation over a length L is given by $G = I_{s,out}/I_{s,in}$, which is exponentially dependent on the pump intensity. Therefore a gain of 10^4 can be reached for a pump pulse at 532 nm with a peak intensity of $5 \,\text{GW}/\text{cm}^2$ and a seed pulse at 800 nm traveling through a $5 \,\text{mm} \beta$ -BaB₂O₄-crystal (BBO).

Due to dispersion, in general the phase mismatch is non-zero and the interaction length through the crystal is limited. The group velocity mismatch between the three interacting beams limits the coherent build-up of the seed pulse. However, BBO enables birefringent phase matching [94] for the right combination of polarization and propagation angle with respect to the optical axis. This only works for a limited range of wavelengths, but the phase-matching bandwidth can be increased significantly in a birefringent crystal such as BBO using a non-collinear scheme for amplification [90].

2.3.2.1 The phase influence of parametric amplification

For amplification of frequency-comb pulses, it is important to take the influence of phase-mismatch on the phase evolution of the seed beam into account. The envelope function of the three interacting beams can be written as a time-dependent amplitude and phase $A(t) = a(z, t)e^{-i\phi(z,t)}$. The phase evolution of each beam can be described by a set of coupled

equations according to [90]

$$\frac{\partial \phi_s}{\partial z} = -\chi^{(2)} \frac{\omega_s}{2n_s c} \frac{a_i a_p}{a_s} \cos(\xi), \qquad (2.34a)$$

$$\frac{\partial \phi_i}{\partial z} = -\chi^{(2)} \frac{\omega_i}{2n_i c} \frac{a_s a_p}{a_i} \cos(\xi), \qquad (2.34b)$$

$$\frac{\partial \phi_p}{\partial z} = -\chi^{(2)} \frac{\omega_p}{2n_p c} \frac{a_s a_i}{a_p} \cos(\xi), \qquad (2.34c)$$

where $\xi = \Delta kz + \phi_p - \phi_s - \phi_i$. A solution to this set of equations can be obtained by assuming that the initial idler field is zero and using the Manley-Rowe relations [90]. This yields

$$\phi_s = \phi_s(0) - \frac{\Delta k}{2} \int_0^L \frac{f_D}{f_D + \gamma^2} dz,$$
 (2.35a)

$$\phi_i = \phi_p(0) - \phi_s(0) + \frac{\pi}{2} - \frac{L\Delta k}{2},$$
 (2.35b)

$$\phi_p = \phi_p(0) - \frac{\Delta k}{2} \int_0^L \frac{f_D}{1 - f_D} dz, \qquad (2.35c)$$

where $\gamma = \frac{\omega_p I_s(0)}{\omega_s I_p(0)}$ and the fractional pump depletion is given by $f_D = 1 - I_p(z)/I_p(0)$. The obtained result shows that the phase of the amplified seed pulse is only dependent on the phase mismatch and the intensity of the pump pulse, while the phase of the pump pulse directly influences the phase of the idler beam. For a non-zero phase mismatch, the phase of the seed beam is shifted during amplification from the effect of fractional pump depletion f_D . This shift scales with the crystal length and the magnitude of the phase mismatch.

In addition, self-phase modulation (SPM) of the seed beam and crossphase modulation (XPS) with the pump and idler beams can lead to phase shifts of the amplified seed pulse. This effect is caused by the intensity dependent part of the refractive index, proportional to coefficient n_2 of the gain medium

$$n = n_0 + I(z)n_2, (2.36)$$

where n_0 is the refractive index of the medium in the absence of light. The influence of this effect on the phase of the seed pulse is separated in three parts: the contribution due to SPM of the seed pulse itself, and the coupling through XPM between the seed pulse and both the idler and the pump pulse. The total influence can be calculated using the B-integral [92]

$$B_{tot} = B_{ss} + B_{ps} + B_{is} = \frac{2\pi}{\lambda_s} \int_0^L n_2 \Big(I_s(z) + \frac{2}{3} I_p(z) + 2I_i(z) \Big) dz \quad (2.37)$$

This resulting shift due to this effect can be significant. For a pump intensity of $5.5 \,\text{GW}/\text{cm}^2$ and $n_2 = 4 \times 10^{-16} \,\text{cm}^2/\text{W}$ at 790 nm (BBO) the phase shift of the seed pulse due to SPM and XPM is 160 mrad [92]. In this case, the shift is dominated by the contribution from XPM between the seed and the pump beam.

2.3.2.2 Walk-off effects in parametric amplification

For parametric amplification in a birefringent uniaxial crystal such as BBO, the effect of spatial walk-off has to also be included. Spatial walk-off is caused by the difference in direction of the wave vector \mathbf{k} and the pointing vector \mathbf{S} . The pointing vector defines the direction of energy transport, while the wave vector points towards the direction of propagation. This effect only occurs for waves with extraordinary (e) polarization, i.e. polarization perpendicular to the optical axis, and not for ordinary (o) polarized beams (parallel to the optical axis).

In a birefringent crystal, the pointing vector of *e*-polarized beams are tilted by ρ with respect to the wave vector **k**. The walk-off angle is given by

$$\rho = -\frac{1}{n_e} \frac{dn}{d\theta},\tag{2.38}$$

where θ is the angle between the propagation direction and the crystals optical axis and n_e is the refractive index for the *e*-wave. For an *e*-polarized beam propagating in the *z* direction, the walk-off is equal to $\rho \times z$.

In the parametric amplification process with type-I phase matching $(e \rightarrow o + o)$, both temporal and spatial walk-off of the pump beam occurs. The latter had a significant influence on the experiments performed in Chapters 5 and 6, as will be discussed in more detail later in this thesis, and therefore mainly the influence of spatial walk-off is



Figure 2.6 – A walk-off compensating configuration for optical parametric amplification with type-I phase matching in a uni-axial crystal. The pump beam (e-wave) experiences walk-off, while the signal beam (o-wave) does not. However, the pump-to signal phase transfer still leads to a wavefront tilt of the signal beam. By rotating the second amplification crystal, the walk-off direction is reversed and the effect is compensated. Full compensation is achieved for two identical crystals, which are pumped with equal intensity.

described in this section.

The effect of spatial walk-off can be incorporated in the coupled equations (Eq. 2.30) describing the parametric amplification process according to [95]

$$\frac{\partial A_s}{\partial z} + k^{(1)} \frac{\partial A_s}{\partial t} - \frac{ik^{(2)}}{2} \frac{\partial^2 A_s}{\partial t^2} + \rho_s \frac{\partial A_s}{\partial x} = -i\chi^{(2)} \left(\frac{\omega_s}{2n_s c}\right) A_p A_i^* e^{-i\Delta kz},$$
(2.39a)
$$\frac{\partial A_i}{\partial z} + k^{(1)} \frac{\partial A_i}{\partial t} - \frac{ik^{(2)}}{2} \frac{\partial^2 A_i}{\partial t^2} + \rho_i \frac{\partial A_i}{\partial x} = -i\chi^{(2)} \left(\frac{\omega_i}{2n_i c}\right) A_p A_s^* e^{-i\Delta kz},$$
(2.39b)
$$\frac{\partial A_p}{\partial z} + k^{(1)} \frac{\partial A_p}{\partial t} - \frac{ik^{(2)}}{2} \frac{\partial^2 A_p}{\partial t^2} + \rho_p \frac{\partial A_p}{\partial x} = -i\chi^{(2)} \left(\frac{\omega_p}{2n_p c}\right) A_s A_i^* e^{-i\Delta kz},$$
(2.39c)

where ρ_m , with m = s, i, p, is the walk-off angle for the seed, idler and pump beam, respectively. The added term in Eq. 2.39 leads to a lateral translation in the walk-off direction of the beam as it propagates through the crystal.

Although the signal phase is not directly influenced by the pump phase (Eq. 2.35), the effect of spatial walk-off in the parametric amplification process leads to a pump-to-signal phase transfer. Numerical simulations

have shown that walk-off of the pump beam (*e*-wave) gives rise to a phase slip between the idler beam and the pump beam [96]. Therefore the pump phase is also partly imprinted on the signal phase, i.e. the phase difference between the pump and signal beam. This effect is highly gain dependent and can lead to a significant reduction of the output power of the parametric amplifier and a degradation of the quality of the amplified beam, typically in the form of wavefront tilt [96]. The latter makes the propagation direction of the amplified beam dependent on the pump intensity.

In order to reduce the influence of spatial walk-off on the amplified beam, a walk-off compensating configuration was implemented (see Sec. 3.1.3.2). For a uni-axial crystal, a walk-off compensating configuration can be realized by rotating the crystal along the proper axis [97], as is illustrated in Fig. 2.6 for a positive birefringent crystal. The orientation of the optical axis (OA) of the crystal is shown by the line at the top of the crystal. The lateral translation of the pump beam due to the walk-off effect is compensated in the second crystal by reversing the walk-off direction. Therefore, also the induced wavefront tilt of the signal beam in the first crystal is compensated in the second crystal. Full compensation can be achieved with two equally long crystals, which are pumped by the same intensity.

2.4 High-harmonic generation

The nonlinear response for frequency up-conversion or parametric processes were so far treated using a perturbative approach. However, when the intensity of the fundamental beam becomes higher than 10^{12} W/cm², the purtubative approach breaks down as higher order-terms grow too large. This is the regime in which high-harmonics are created and light at vacuum ultraviolet (VUV) or extreme ultraviolet (XUV) wavelengths are produced. A different theoretical approach is needed in this case, which is explained in this section.

2.4.1 The semi-classical single-atom description of HHG

In this section an intuitive picture of HHG is given on a single-atom level using the semi-classical three-step recollision model [80].

2.4.1.1 The three-step model

The intuitive three-step model (TSM) is illustrated in Fig. 2.7. By focusing a high-power laser pulse in a gas medium, the magnitude of the electric field can become comparable to that inside the atom, and the Coulomb potential can be distorted such that an electron can tunnel out into the continuum. This free electron is then accelerated in the electric field of the laser and gains energy. When the electric field changes direction, the electron is accelerated back towards the parent ion where it can recollide with it. The probability for recombination is generally small and therefore the electron can in principle swing by the parent ion multiple times. However, due to the quantum nature of the process, the electron wave-packet spreads transversely with respect to its direction of motion and the probability of recombination becomes increasingly smaller after each round trip. Upon recombination, the excess energy will be released by the emitting a high-energy photon. This whole process of ionization and recombination can occur twice every optical cycle and is highly phase coherent. For a symmetric medium, such as a gas jet, only odd harmonics of the fundamental frequency are produced.

2.4.1.2 Ionization processes

For the first step in the TSM, the regime of tunneling ionization has to be reached. The dominating ionization process can be identified with the Keldysh parameter (γ) [98]. This parameter is dependent on the ponderomotive energy of the driving field (U_{pon}) and the ionization potential of the atom (I_p) according to

$$\gamma = \sqrt{I_p/2U_{pon}} \tag{2.40}$$

The ponderomotive energy of the field can be expressed as

$$U_{pon} = \frac{q_e^2}{2m_e \epsilon_0 c \omega_0^2} I_{peak}, \qquad (2.41)$$

where q_e is the electron charge, m_e is the electron mass, ω_0 the central angular frequency of the driving field and I_{peak} is the peak intensity



Figure 2.7 – Illustration of the three-step recollision model. An electron tunnels out of the Coulomb potential of an atom at t_1 and is accelerated by the driving field. When the field changes direction the electron is accelerated back towards the parent ion (t_2) and recollides at t_3 . The excess energy is released in the form of a high-energy photon.

of the driving field. If $\gamma >> 1$, the dominant ionization process is multiphoton ionization, while for $\gamma \leq 1/2$ the regime of tunneling ionization is reached. In practice, the latter requires a laser intensity of $\sim 10^{14}$ W/cm², which can be reached by focusing a 100 fs long laser pulse of 1 mJ pulse energy down to 100 μ m diameter.

2.4.1.3 Electron kinetics

The kinetics of a free electron in the laser field can be calculated with the classical equations of motion. The velocity and the position of the electron in a sinusoidal electric field $E(t) = A\cos(\omega t)$ are given by

$$x(t) = \frac{q_e A}{m_e \omega^2} (\cos(\phi_i) - \cos(\omega t) - \sin(\phi_i)(\omega t - \phi_i))$$
(2.42)

and

$$v(t) = \frac{-q_e A}{m_e \omega} (\sin(\omega t) - \sin(\phi_i)), \qquad (2.43)$$

respectively, where ϕ_i is the phase of the driving field at the moment of ionization and A is the amplitude of the driving field. A few examples



Figure 2.8 – Possible electron trajectories after ionization at different values of the initial phase of the driving field ϕ_i . For $0 \le \phi_i < \pi/2$, recombination can occur at two different times, while for $\pi/2 \le \phi_i < \pi$ the electron is driven away from the parent ion.

of possible trajectories for different values of ϕ_i are shown in Fig. 2.8. An electron that is ionized with $0 \leq \phi_i < \pi/2$ can recollide with the parent ion, while those that enter the continuum at $\pi/2 \leq \phi_i < \pi$ get driven away from the ion. The excess kinetic energy of the electron upon recollision depends on the exact trajectory and on the phase of the fundamental field at the moment of ionization. At $\phi_i = 0$ (ionization at a near-zero field), the excess kinetic energy is zero upon recollision. In contrast, the maximum excess kinetic energy of $3.17U_{pon}$ is reached at $\phi_i \approx 0.09\pi$. Therefore, the maximum observable photon energy is given by

$$E_{max} = I_p + 3.17U_p, (2.44)$$

which is known as the cut-off energy.

2.4.1.4 Intensity dependent phase

For each value of $0 < E_{kin} < 3.14U_{pon}$ there are two possible trajectories that recombine with same velocity and therefore lead to the emission of an harmonic photon with the same energy. These two trajectories are the so-called 'short' ($\phi_i < 0.09\pi$) and 'long' ($\phi_i > 0.09\pi$) quantum paths. Emission from the two paths have a different phase, not only because they are emitted at different times, but also because they acquire a different intensity-dependent phase in the continuum. The total phase (ϕ_q) of the field of harmonic order q is given by the sum of these two components [99],

$$\phi_q = q\omega t_r + \frac{1}{\hbar}S(t_i, t_r), \qquad (2.45)$$

where t_r is the time of recombination, and $S(t_i, t_r)$ is the quasi-classical action integral. The action contains the kinetic energy of the electron and the ionization potential of the atom

$$S(t_i, t_r) = \int_{t_i}^{t_r} dt \left(\frac{p(t_i, t_r)^2}{2m} + I_p \right)$$
(2.46)

From Eqs. 2.43, 2.45 and 2.46 it can be seen that the phase is intensitydependent through its influence on the kinetic energy (momentum p), and is different for light produced by the short and long trajectory. The sensitivity of this intrinsic dipole phase to the intensity is much higher for electrons on the long trajectory than those on the short trajectory. This leads to a larger chirp in the harmonics spectrum and a bigger divergence (assuming a Gaussian intensity profile for the fundamental) of the generated harmonic beam from the long quantum path. For this reason, light from the short quantum trajectories is preferred for most applications, including the spectroscopy described in this thesis.

2.4.2 The quantum mechanical description of HHG

The results obtained by the intuitive TSM agree with the full quantum description of this process, which was first formulated by Lewenstein [81]. It is restricted to the regime where the fundamental photon energy is much smaller than the ionization potential, and the ponderomotive energy U_p is comparable to I_p , but below the saturation level. The derivation below follows the description given by Lewenstein and is in atomic units.

For an atom in a laser field $E \cos(t)$, which is linearly polarized in the x direction, the time dependent Schrödinger equation in the length gauge

is given by

$$i \left| \Psi(\mathbf{x}, t) \right\rangle = \left(-\frac{1}{2} \nabla^2 + V(\mathbf{x}) - E \cos(t) x \right) \left| \Psi(\mathbf{x}, t) \right\rangle, \qquad (2.47)$$

where $V(\mathbf{x})$ is the atomic core potential.

The following assumptions are made: for high laser intensities, the tunneling ionization regime is reached and intermediate resonances in the atom play no role. The electron is excited from the ground state $|0\rangle$ to the continuum states $|\mathbf{v}\rangle$, where it is no longer influenced by the potential of the ion. The dipole moment of the excitation to the continuum state is expressed as

$$\mathbf{d}(\mathbf{v}) = \langle \mathbf{v} | \, \mathbf{x} \, | 0 \rangle \,. \tag{2.48}$$

The dipole matrix elements of coupling between continuum states $\langle \mathbf{v} | \mathbf{x} | \mathbf{v}' \rangle$ are partly included and treated exact. From these assumptions the time dependent wave function is expanded as

$$|\Psi(t)\rangle = e^{iI_p t} \Big(a(t) |0\rangle + \int d^3 \mathbf{v} b(\mathbf{v}, t) |\mathbf{v}\rangle \Big), \qquad (2.49)$$

where $a(t) \simeq 1$ is the amplitude of the ground state and $b(\mathbf{v}, t)$ is the amplitude of the corresponding continuum states. The Schrödinger equation for $b(\mathbf{v}, t)$ can be solved exactly and the following solution can be obtained [81]

$$b(\mathbf{v},t) = i \int_0^t dt' E \cos(t') d_x (\mathbf{v} + \mathbf{A}(t) - \mathbf{A}(t')) \exp\left\{-i \int_{t'}^t dt'' \Big[(\mathbf{v} + \mathbf{A}(t) - \mathbf{A}(t''))^2 / 2 + I_p \Big] \right\},$$
(2.50)

where $\mathbf{A}(t) = E \sin(t) \hat{\mathbf{x}}$ is the vector potential of the electric field and d_x is the component of **d** along the polarization axis of the electric field. The component of the dipole moment in the x direction can be obtained by combining Eq. 2.49 and Eq. 2.50 and evaluating $x(t) = \langle \Psi(t) | x | \Psi(t) \rangle$. Introducing the canonical momentum $\mathbf{p} = \mathbf{v} + \mathbf{A}(t)$ this leads to [81]

$$x(t) = i \int_0^t dt' \int d^3 \mathbf{p} E \cos(t') d_x(\mathbf{p} - \mathbf{A}(t')) d_x^*(\mathbf{p} - \mathbf{A}(t)) e^{-iS(\mathbf{p}, t, t')} + \text{c.c.},$$
(2.51)

where $S(\mathbf{p}, t, t')$ is the quasi-classical action given by

$$S(\mathbf{p}, t, t') = \int_{t'}^{t} dt'' \left(\frac{(\mathbf{p} - \mathbf{A}(t''))^2}{2} + I_p \right).$$
(2.52)

Interestingly, Eq. 2.51 describes the three steps of the HHG process discussed in Sec. 2.4.1.1. The first part in the integral $E \cos(t') d_x(\mathbf{p} - \mathbf{A}(t'))$ gives the probability amplitude to excite an electron to the continuum at time t' with momentum \mathbf{p} . The electron is then freely moving in the field of the laser with momentum \mathbf{p} from t' to t and acquires a phase given by the action $S(\mathbf{p}, t, t')$. Note that the influence of the ion is small, but is incorporated through the binding energy I_p in Eq. 2.52, and that the acquired phase is intensity dependent. The last step of the process is described by the term $d_x^*(\mathbf{p} - \mathbf{A}(t))$, which gives the amplitude of recombination of the electron and the ion at time t.

The gradient of the action gives the difference in position of the electron between time t and t' and can thus be expressed as

$$\nabla_{\mathbf{p}} S(\mathbf{p}, t, t') = \mathbf{x}(t) - \mathbf{x}(t') = 0$$
(2.53)

which shows that an electron, which appears in the continuum at time t' returns to the same position at time t. This is not surprising, because it tells us that ionization and recombination occurs close to the nucleus. The integral from Eq. 2.51 is difficult to numerically evaluate because of its highly oscillating behavior. A solution to the integral is obtained at the stationary points using the saddle point method in [81]. The stationary points of the canonical momentum are given by

$$p_{st}(t,\tau) = E(\cos(t) - \cos(t-\tau)),$$
 (2.54)

where the return time $\tau = t - t'$ has been introduced. This provides an expression for the action according to

$$S_{st}(t,\tau) = \frac{1}{2} \int_{t-\tau}^{t} dt'' (\mathbf{p}_{st} - \mathbf{A}(t''))^2$$

= $(I_p + U_p)\tau - \frac{2U_p(1 - \cos(\tau))}{\tau} - U_p C(\tau) \cos(2t - \tau),$ (2.55)

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Figure 2.9 – The energy gained by the electron as a function of recombination time τ and normalized to U_p . The maximum possible energy upon recombination is $3.17U_p$ (dashed line). This energy is reached for $\tau = 4.08$, which is roughly 3/4 of an optical cycle of the fundamental wave.

with

$$C(\tau) = \sin(\tau) - \frac{4\sin^2(\tau/2)}{\tau}.$$
 (2.56)

The action is the integral over the kinetic energy plus the energy acquired through ionization (I_p) and therefore the total kinetic energy gained by the electron at time t is given by $E_k(t) - E_k(t-\tau) = (p_{st} - A(t))^2/2 - (p_{st} - A(t-\tau))^2/2$. In combination with Eq. 2.54 it can be shown that the function $2|C(\tau)|$ is equivalent to the E_k/U_p and thus represents the energy gain of the electron. The value of $2|C(\tau)|$ as a function of τ is plotted in Fig 2.9 and shows that there are multiple recollision times at which a certain kinetic energy is reached. The different peaks represent recombination after multiple re-encounters with the parent ion. On the first round trip, i.e. the first peak, there are two solutions for each value of E_k except the maximum kinetic energy (see the dashes line in Fig. 2.9). This maximum energy of $\approx 3.17U_p$ is only reached at a single recombination time of $\tau = 4.08$. Electrons that recombine at smaller τ are have taken the short quantum paths and those with larger recombination time have taken the long quantum paths. This result is in agreement with the simple semi-classical description given in Sec. 2.4.1.3.

2.4.3 The macroscopic response

The previous sections only described HHG on a single-atom level. However, a significant flux of harmonics is only created if they are generated in phase over an extensive region. These optimal phase-matching conditions are reached if the phase velocity of the fundamental beam in the medium is equal to that of the generated harmonic beam. In the perturbative regime of nonlinear optics, the dispersive properties of the medium are known and static. However, in HHG, the medium becomes progressively more ionized throughout the fundamental pulse and therefore the dispersion properties change while the harmonics are generated. The phase mismatch between the fundamental beam and the q^{th} harmonic is defined as

$$\Delta k = qk_0 - k_q, \tag{2.57}$$

where k_0 is the wave vector of the fundamental beam and k_q is the wave vector of the harmonic beam. There are three main contributions to phase mismatch: gas dispersion, plasma dispersion and the geometrical Gouy phase shift through a focus.

2.4.3.1 The Gouy phase of a focussed Gaussian beam

The contribution of the Gouy phase is determined by the chosen geometry for HHG. In the case of a simple gas jet and a focused Gaussian beam, the Gouy phase in the direction of propagation (z) is given by

$$\phi_{\text{Gouy}} = \arctan(z/z_r) \tag{2.58}$$

where $z_r = \pi w_0^2 / \lambda$ is the Rayleigh length and w_0 is the beam waist of the fundamental beam. The phase mismatch for harmonic order q due to the acquired Gouy phase of the fundamental beam is therefore

$$\Delta k_{\rm Gouy} = \frac{q\lambda_0}{\pi w_0^2}.$$
(2.59)

Here the Gouy phase of the harmonic field is neglected because it is much smaller due to the low divergence of the beam. By adjusting the position of the gas jet with respect to the focus position, the influence of the Guoy phase contribution can be tuned.

2.4.3.2 Dispersion in a neutral gas

The index of refraction for noble gasses (taken at 1 atmosphere) is very close to unity and is usually expressed as $\delta(\lambda) = 1 - n(\lambda)$, which is proportional to the atom density. In HHG the neutral atom density is varying throughout the pulse due to the build up of plasma. The dispersion due to the depletion of neutral atoms is therefore dependent on the ionized fraction (η) . The phase mismatch between the fundamental wavelength and the q^{th} harmonic can be expressed as [82, 100]

$$\Delta k_n = \frac{2\pi q}{\lambda_0} \frac{P}{P_{\text{atm}}} (1 - \eta) (\delta(\lambda_0) - \delta(\lambda_0/q)), \qquad (2.60)$$

where $P/P_{\rm atm}$ is the ratio between the pressure and the pressure at 1 atmosphere. This contribution to the phase mismatch due to the depletion of neutral atoms can be calculated from the refractive index that is usually based on the Sellmeier equations for neutral gasses [101]. The value of this contribution is typically small, because the refractive index for the fundamental wavelength and the q^{th} harmonic are on the order of $\delta(\lambda) \sim 10^{-4}$ and $\delta(\lambda/q) \sim 10^{-6}$, respectively.

2.4.3.3 Dispersion due to plasma formation

The contribution to the phase mismatch from plasma formation itself is divided in two parts: dispersion from the generation of ions and of free electrons in the plasma. The contribution from the ions is usually neglected, because the resonance frequencies scale up at higher charge states. The free electrons, however, have a much bigger influence on the refractive index and can therefore cause significant dispersion. The phase mismatch due to the creation of free electrons is given by [82,100]

$$\Delta k_{\text{plasma}} = \lambda_0 \eta r_e N_{\text{atm}} \frac{P}{P_{\text{atm}}} \frac{q^2 - 1}{q} \approx q \lambda_0 r_e \eta N_{\text{atm}} \frac{P}{P_{\text{atm}}}, \qquad (2.61)$$

where $\frac{q^2-1}{q} \approx q$ for q >> 1, N_{atm} is the atomic number density at 1 atmosphere and r_e is the classical electron radius.



Figure 2.10 – The calculated dispersion from plasma formation and neutral atom depletion in the HHG process as a function of ionized fraction η . The contribution from the generation of ions is neglected. The calculations were performed with a pressure of p = 10 mbar in the interaction region. The critical ionized fraction $\eta_{\rm crit}$ is indicated by the dotted vertical line and is in this case slightly below 2%.

2.4.3.4 Phase matching in HHG

The phase mismatch due to the three aforementioned contributions can be balanced to reach optimal phase-matching conditions. The total phase mismatch is expressed as

$$\Delta k = \Delta k_n + \Delta k_{\text{plasma}} + \Delta k_{\text{Gouy}}, \qquad (2.62)$$

For high harmonics the contribution due to dispersion of the neutral gas is negative. Therefore, it is possible to balance the contribution from the geometrical phase and the gas dispersion. Typically, phase matching is achieved by changing the density of the gas jet and tuning the position of the gas jet with respect to the focus position.

For a certain level of ionization, phase matching can not be achieved, because the contribution from plasma dispersion becomes too big and it can not be compensated by the contribution from neutral atom dispersion. This so-called critical ionized fraction $\eta_{\rm crit}$ is typically on the order of a few percent. Fig. 2.10 shows the calculated dispersion terms for the seventh harmonic of 770 nm, generated in argon and the corresponding critical level. An upper limit for the value of $\eta_{\rm crit}$ can be calculated using

$$\eta_{\rm crit} = \left(1 + \frac{\lambda_0^2 r_e N_{\rm atm}}{2\pi\delta_n} \left(1 - \frac{1}{q^2}\right)\right)^{-1},\tag{2.63}$$

where the geometrical phase is neglected. By reducing the driving intensity or choosing an atom with a higher ionization potential, the ionized fraction can be reduced.

2.5 Ramsey-comb spectroscopy in combination with high-harmonic generation

For high-precision spectroscopy at short wavelengths, the aforementioned methods of nonlinear up-conversion can be combined with spectroscopy techniques. Especially in the VUV and XUV spectral range this requires extremely high peak intensities in order to exploit HHG, while still retaining the accuracy of the spectroscopy laser. For this purpose, the combination of HHG with methods of direct FC spectroscopy is especially suitable. The relatively high peak-power of FC pulses enables frequency up-conversion with HHG, which is a highly coherent process and therefore retains the properties of the initial FC pulses. The work in this thesis is based on the combination of HHG with Ramsey-comb spectroscopy (RCS). This technique is based on two amplified FC pulses that are used in a Ramsey-type excitation scheme. The first part of this section is focused on a description of the RCS method based on the quantum interference effect. In the second part, different aspects of combining RCS with HHG are discussed.

2.5.1 Quantum interference excitation

For a pure two-level system with ground state $|g\rangle$ and excited state $|e\rangle$, the wave function can be written as

$$|\Psi(t)\rangle = \begin{pmatrix} c_e(t)\\ c_g(t) \end{pmatrix}, \qquad (2.64)$$

where c_g and c_e are the amplitudes of the ground and excited state, respectively. The transition frequency is given by the energy separation

2.5. Ramsey-comb spectroscopy in combination with high-harmonic generation

between the states $\omega_0 = (E_e - E_g)/\hbar$. Assuming a pure dipole interaction with dipole moment **d**, the states can be coupled by a laser field $\mathbf{E}(t) = \mathbf{E}_0 e^{i\omega_L t} + \text{c.c.}$. The full Hamiltonian of the system in this case is

$$H_{tot} = H_0 + H_{int}$$

= $-\hbar \begin{pmatrix} -\omega_0/2 & \Omega_R e^{-i\omega_L t} + \tilde{\Omega}_R e^{i\omega_0 t} \\ \tilde{\Omega}_R^* e^{-i\omega_L t} + \Omega_R^* e^{i\omega_0 t} & \omega_0/2 \end{pmatrix},$ (2.65)

where $\Omega_R = \mathbf{d} \cdot \mathbf{E}_0/\hbar$ and $\tilde{\Omega}_R = \mathbf{d} \cdot \mathbf{E}_0^*/\hbar$ are the Rabi frequency and the counter-rotating frequency, respectively. The Hamiltonian is transformed to the time-dependent Schrödinger picture using the unitary transformation matrix

$$U(t) = \begin{pmatrix} e^{-\omega_L t/2} & 0\\ 0 & e^{\omega_L t/2} \end{pmatrix}$$
(2.66)

and the operations: $|\Psi\rangle(t) \to U(t) |\Psi(t)\rangle$ and $H \to -i\hbar U(t)^{\dagger} \dot{U}(t) + U(t)^{\dagger} H U(t)$. This yields

$$H_{tot} = -\hbar \begin{pmatrix} (\omega_L - \omega_0)/2 & \Omega_R + \tilde{\Omega}_R e^{2i\omega_L t} \\ \Omega_R^* + \tilde{\Omega}_R^* e^{-2i\omega_L t} & -(\omega_L - \omega_0)/2 \end{pmatrix}$$

$$\approx -\hbar \begin{pmatrix} \Delta/2 & \Omega_R \\ \Omega_R^* & -\Delta/2, \end{pmatrix}$$
(2.67)

where $\Delta = \omega_L - \omega_0$ and the rotating wave approximation $(2i\omega_L t \text{ phase} terms are neglected})$ was used. A solution for the wave function can be obtained by solving the Schrödinger equation, which reads

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = H_{tot} |\Psi(t)\rangle.$$
 (2.68)

The Hamiltonian is now time-independent and direct integration can be used to obtain a solution

$$|\Psi(t)\rangle = e^{-iH_{tot}t/\hbar} |\Psi(0)\rangle. \qquad (2.69)$$

A more insightful representation of this solution is obtained by rewriting the Hamiltonian as $H_{tot} = \mathbf{a} \cdot \boldsymbol{\sigma}$. Where

$$\mathbf{a} = \begin{pmatrix} Re(\Omega_R) \\ Im(\Omega_R) \\ -\Delta/2 \end{pmatrix}$$
(2.70)

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and σ is a vector holding the Pauli matrices, which is given by

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix}. \tag{2.71}$$

The exponential operator of the Hamiltonian can be expanded according to

$$e^{iH_{tot}t/\hbar} = e^{it\mathbf{a}\cdot\boldsymbol{\sigma}}$$
$$= \sum_{0}^{\infty} \frac{1}{n} (it\mathbf{a}\cdot\boldsymbol{\sigma})^{n}$$
$$= \cos(|\mathbf{a}|t)\mathbf{1} + i\frac{\mathbf{a}\cdot\boldsymbol{\sigma}}{|\mathbf{a}|}\sin(|\mathbf{a}|t)$$
(2.72)

where **1** is the unitary matrix and $|\mathbf{a}| = a = \sqrt{|\Omega_R|^2 + (\Delta/2)^2}$ is the Rabi flopping frequency. The final state population as a function of interaction time with the laser field can be obtained by inserting this expression in Eq. 2.69. Assuming the atom is initially in the ground state and interacts with a square pulse of length τ_p , this yields

$$|\Psi(t)\rangle = \begin{pmatrix} c_e(\tau) \\ c_g(\tau) \end{pmatrix} = \begin{pmatrix} i\Omega_R/a\sin(a\tau) \\ \cos(a\tau) - i\Delta/(2a)\sin(a\tau) \end{pmatrix}$$
(2.73)

Ramsey spectroscopy is based on excitation with two coherent pulses of length τ and pulse delay T. In order to obtain the final state, the free evolution of the atom in between the two pulses $T - \tau$ has to be taken into account. Neglecting spontaneous decay or other perturbative effects, such as the Doppler shifts, the free evolution matrix can be obtained by setting $\Omega_R = 0$ in Eq. 2.72. This yields

$$M_{free} = \begin{pmatrix} e^{-i(T-\tau)\Delta/2} & 0\\ 0 & e^{i(T-\tau)\Delta/2} \end{pmatrix}.$$
 (2.74)

The excited state amplitude after excitation with two delayed pulses is

$$c_e(T+\tau) = i \frac{2\Omega_R}{a} \left[\cos(a\tau) \cos\left(\frac{\omega_0 T - \tau \Delta}{2}\right) - \frac{\Delta}{2a} \sin(a\tau) \sin\left(\frac{\omega_0 T - \tau \Delta}{2}\right) \right].$$
(2.75)

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This expression can be simplified by assuming that the excitation is on resonance, i.e. $\Delta = 0$ and $\omega_L = \omega_0$. The excited state population is then given by

$$|c_e(T+\tau)|^2 = 4\sin^2(\Omega_R\tau)\cos^2(\Omega_R\tau)\cos^2(\omega_0 T/2) \propto 1 + \cos(\omega_0 T).$$
(2.76)

This final result, which was first obtained by N. Ramsey [74], describes an oscillation of the excited state population as a function of pulse delay (or phase difference between the pulses) and is known as a so-called Ramsey fringe.

In general, there can be a phase difference $\Delta \phi$ between the two excitation pulses. This is incorporated in the expression in the following way

$$|c_e|^2 = \frac{A_0}{2} [1 + \cos(\omega_0 T - \Delta\phi)]$$
 (2.77)

where $A_0 = 4 \sin^2(\Omega_R \tau) \cos^2(\Omega_R \tau)$. The excited state population is thus dependent on the time delay and the phase difference between the pulses, which are exactly the two well controlled parameters of a frequency-comb laser. Therefore, Ramsey spectroscopy can be performed with a pair of phase locked frequency comb pulses. This last statement does not hold for *amplified* frequency-comb pulses, which are up-converted using nonlinear processes, because the parametric amplification process is known to introduce a spurious phase shift (Sec. 2.3.2.1). This shift is typically difficult to determine with a high level of accuracy. As a result, this leads to systematic shifts of the extracted transition frequency. Therefore, we developed the method of Ramsey-comb spectroscopy, which combines Ramsey fringes at multiple different pulse delays to determine the transition frequency from the extracted phase difference. Because of the differential nature of RCS, the influence of phase shifts which are common for the individual fringes is suppressed.

2.5.2 Ramsey-comb spectroscopy

In Ramsey-comb spectroscopy multiple pairs of amplified frequencycomb pulses are used to obtain Ramsey fringes at delays with a different integer multiple of the repetition time. For now, we will only consider



Figure 2.11 – The Ramsey-comb spectroscopy technique. A set of Ramsey fringes is recorded at different integer intervals (ΔN) of the repetition time (T_{rep}) . The transition frequency is determined from the relative phase difference between these fringes and is therefore independent of constant phase shifts between the pulses.

excitation of a single transition at frequency f_0 with a pair of resonant FC pulses. According to the expression in Eq. 2.77, an oscillation of the excited state population can be observed by scanning either the delay between the excitation pulses, through the repetition frequency (f_{rep}) of the laser, or the phase directly by changing the carrier-envelope offset frequency (f_{ceo}) . The experiments described in this thesis were performed by scanning the delay between the pulses, because it was technically more convenient. Therefore, the description will be limited to this case only.

For two consecutive FC pulses, the delay is given by the repetition time of the laser ($\Delta t = T_{rep}$). In order to observe the phase evolution of the superposition state, the delay is adjusted in small steps over a limited range δ_t , while the excited state population is measured. The obtained signal as a function of δt is given by

$$S(\delta t) \propto A[1 + \cos(2\pi f_0(T_{rep} + \delta t) + \Delta \phi)]. \tag{2.78}$$

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The phase difference $(\Delta \phi)$ can be expressed as a sum of the known carrier-envelope phase shift $(\Delta \phi_{ce})$ and the unknown phase shift $(\Delta \phi_{amp})$ due to amplification $\Delta \phi = \Delta \phi_{ce} + \Delta \phi_{amp}$. In order to remove this unknown contribution from the amplification process, a series of fringes is recorded at different multiples of the repetition time $\Delta t = NT_{rep}$ as is illustrated in Fig. 2.11. For transitions in the optical domain δt is typically on the order of 0.2 - 2 fs (comparable to a period of the atomic oscillation $\delta t \sim 1/f_{tr}$) while the time step between the individual fringes is given by T_{rep} and is typically on the order of 5 - 15 ns.

The signal which is obtained from a Ramsey-comb scan can be written as a multiplication of a window function (W_t) , which is given by the scan range and the macro-delay step, and the rapidly oscillating Ramsey fringe $(S_{R,t})$

$$S_t = S_{R,t} \cdot W_t. \tag{2.79}$$

For a single transition with frequency f_0 and amplitude A, the Ramsey signal is given by

$$S_{R,t} \propto A \cos(2\pi f_0 \Delta t + \Delta \phi_{amp}). \tag{2.80}$$

For simplicity we have taken $\Delta \phi_{ce} = 0$ and $\Delta \phi_{amp}$ to be constant. For a measurement consisting of n scans taken over a range of NT_{rep} , the window function is given by

$$W_t = \sum_{n=1}^{N} \operatorname{rect}\left(\frac{\Delta t - nT_{rep}}{\delta t}\right).$$
(2.81)

The frequency domain representation of the Ramsey-comb signal is obtained with a Fourier transform of Eq. 2.79 and is equal to a convolution of the Fourier transform of the individual functions $S_{R,t}$ and W_t

$$S_f = S_{R,f} * W_f. (2.82)$$

The Fourier transform of $S_{R,t}$ can be readily obtained and is given by

$$S_{R,f} = \frac{A}{2} [e^{-i\phi_{amp}} \delta(f - f_0)], \qquad (2.83)$$

where the negative frequencies were neglected and the offset of the signal in the time domain was removed. The window function in the frequency



Figure 2.12 – The repetitive nature of Ramsey-comb spectroscopy leads to an ambiguity in the extracted transition frequency modulo the effective mode spacing (T_{rep}) of the measurement. The accuracy of the extracted transition frequency is determined by the maximum delay NT_{rep} .

domain can be written as

$$W_f = \delta t \cdot \operatorname{sinc}(\delta t f) e^{-i(N+1)\pi T_{rep}f} \frac{\sin(N\pi T_{rep}f)}{\sin(\pi T_{rep}f)}.$$
 (2.84)

The resulting signal from Ramsey-comb spectroscopy can be rewritten as several cosine contributions at different time delays and is given by [76]

$$|S_{f}|^{2} = \left(\frac{A\delta t}{2}\right)^{2} \operatorname{sinc}^{2}[(f - f_{0})\delta t] \times \sum_{n=1}^{N} \{2(N - n)\cos[2n\pi T_{rep}(f - f_{0})] + 1\}$$
(2.85)

This result resembles the frequency-comb spectrum as is illustrated in Fig. 2.12 as it consists of several 'modes' which are equally spaced. Due to the sub-sampling of the Ramsey fringes at different multiples of the

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repetition time, the spacing between the modes is given by the repetition frequency $(f_{rep} = 1/T_{rep})$ and therefore the transition frequency can only be determined modulo f_{rep} . The width of the individual modes in the spectrum are determined by the maximum delay between the individual Ramsey fringes NT_{rep} (for an infinitely narrow transition) and the width of the envelope spectrum is determined by the range of the individual scans.

This leads to the interesting result that the spectrum and therefore the extracted transition frequency is not influenced by a *delay-independent* phase shift. This can be explained intuitively by the fact that a common phase shift only leads to an additional phase factor in the frequency domain, which does not influence the spectral intensity. This argument also holds for the ac-Stark shift induced in the atom by the excitation pulses as it simply leads to a constant phase shift as long as the pulse energy is kept constant as a function of delay.

Another interesting result is that the line width of the individual 'modes' in the spectrum are determined by the maximum pulse delay NT_{rep} . Therefore it is clear that the accuracy of the extracted transition frequency can be improved by increasing the inter-pulse delay. Experimental limits to the maximum delay are set by, e.g. the upper state lifetime of the transition (neglecting any other broadening effects), or the technical limitation of the lifetime of the laser gain media in the amplifiers. Although the spectrum of the RCS signal provides some insightful information, the actual transition frequency is extracted from a global fit of the phases of the individual fringes in the time domain (Sec. 2.5.2.3) [76].

2.5.2.1 Delay-dependent phase shifts

So far only the influence from constant phase shifts were included in the description of RCS, while the influence of *delay-dependent* phase shifts can also be incorporated. For the most simple case of a linear shift as a function of delay, the phase can be expressed as

$$\Delta\phi(t) = \Delta t \frac{\phi_t}{T_{rep}},\tag{2.86}$$

where ϕ_t is the magnitude of the shift per time step in units of T_{rep} . Including this into the expression from Eq. 2.80 and Eq. 2.83, the signal transforms to

$$S_{R,t} = A \cos\left[2\pi \left(f_0 + \frac{\phi_t}{2\pi T_{rep}}\right)\Delta t\right]$$
(2.87a)

$$S_{R,f} = \frac{A}{2} \left\{ \delta \left[f - \left(f_0 + \frac{\phi_t}{2\pi T_{rep}} \right) \right] \right\}.$$
 (2.87b)

This result explicitly shows that the modes in the spectrum and therefore the extracted transition frequency are shifted for a finite value of $\Delta \phi(t)$. A detailed characterization of the phase of the pulses is therefore of great importance for the correct interpretation of Ramsey-comb signals for high-precision spectroscopy. A well known example of a delay-dependent phase shift is the carrier-envelope phase slip (Sec. 2.2). Fortunately, this phase can be measured and stabilized to a high level of accuracy in a frequency-comb laser using an f - 2f inteferometer setup (Sec. 3.1.1).

2.5.2.2 Extending RCS to multiple transitions

The large bandwidth of the pulses can lead to excitation of several transitions at the same time. This results in more complicated Ramsey signals, consisting of several cosine contributions. In order to illustrate the consequence of this for the interpretation of RCS signals, excitation of two resonant transitions is considered. In this case, Eq. 2.80 and Eq. 2.83 transform to

$$S_{R,t} = \sum_{k=1}^{2} A_k \cos(2\pi f_k \Delta t),$$
 (2.88a)

$$S_{R,f} = \sum_{k=1}^{2} \frac{A_k}{2} \delta(f + f_k).$$
 (2.88b)

For simplicity, additional phase shifts between the pulses have been neglected. When there is no interaction between the levels (such as the same transition in different isotopes), then in the time domain, the signal

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simply consists of a beating between the two excitation contributions. Using

$$s_{N,k} \coloneqq \frac{A_k \delta t}{2} \frac{\sin(N\pi T_{rep}(f - f_k))}{\sin(\pi T_{rep}(f - f_k))},\tag{2.89}$$

the result from Eq. 2.85 transforms to [76]

$$|S_f|^2 = s_{N,1}^2 + s_{N,2}^2 + 2\cos[(N+1)\pi T_{rep}(f^2 - f_1)]s_{N,1}s_{N,2}$$
(2.90)

where the first two terms $s_{N,1}^2$ and $s_{N,2}^2$ are the linear superposition states and the last term is a cross term. This additional term complicates the spectrum and the fitting procedure in the frequency domain [76]. Therefore the transition frequency is extracted from the signals in the time domain only.

2.5.2.3 Extracting the transition frequency

The transition frequency is extracted from a Ramsey-comb scan by performing a global fit of the phases of the individual fringes. This phase function encodes the information of the transition frequency f_k and the relative amplitude A_k of the transition (the line strength amplitude is only relevant if more than one transition is excited at the same time). In the time domain, the Ramsey signal can be described by the complex quantity

$$S_t = A_k \exp -i(2\pi f_k \Delta t + \Delta \phi_c), \qquad (2.91)$$

where $\Delta \phi_c$ is a constant phase shift. The phase evolution of this signal as function of time is given by

$$\arg(S_t) \coloneqq \Phi_{fit} = \Delta \phi(A_k, f_k, \Delta \phi_c) \Delta t.$$
(2.92)

The individual phases $\Delta \phi_n$ (where n = 1, 2, 3..., N) of the carrier at different macro-delays are obtained by first performing a cosine-fit with a fixed reference frequency f_{ref} , which is chosen close to the expected transition frequency. This fit function is given by

$$f(a, \Delta t, \Delta \phi_n) = a \cos(2\pi f_{ref} \Delta t + \Delta \phi_n).$$
(2.93)

The obtained phases are compared with $\Phi_{fit}(\Delta t)$ and a minimization of $|\Phi_{fit}(\Delta t) - \Delta \phi_n|$ is performed for $\Delta t = nT_{rep}$ to extract the transition



Figure 2.13 – The RCS signal and the corresponding phase evolution (shown relative compared to exciting a single transition as shown the first panel) for excitation of one, two and three atomic transitions. For a single transition the phase evolution is simply linear, which is taken as the reference and hence the flat line. For multiple transitions with unequal amplitude, a more complicated beating pattern is observed of which the phase evolution makes phase jumps of π .

frequency.

For a single frequency the phase evolution as a function of delay is simply linear, as is illustrated in the left column of Fig. 2.13, and the transition frequency can straightforwardly be extracted. When exciting several transitions simultaneously, the signal consists of several cosinecontributions and becomes more complex. However, the corresponding phase evolution still encodes the full information of the transition frequencies f_k and the corresponding relative amplitudes A_k . These can be extracted from a single Ramsey-comb measurement, as long as the number of Ramsey-scans is equal to or bigger than the number of free parameters and the interaction time is sufficiently long to observe the beating pattern. This was demonstrated in 2014 by J. Morgenweg *et al.* [73] by simultaneously exiting several hyperfine levels of the twophoton 5S - 7S transition in rubidium. In the work presented in this thesis only single transitions were excited and the fitting procedure was more straightforward. 2.5. Ramsey-comb spectroscopy in combination with high-harmonic generation

2.5.3 Combining Ramsey-comb spectroscopy and high-harmonic generation

In order to successfully combine the Ramsey-comb method with highharmonic generation for high-precision spectroscopy in the VUV and XUV spectral range, the influence from plasma formation on the phase of the up-converted pulses (Sec. 2.4.3) has to be characterized.

2.5.3.1 Delay-dependent phase shifts from plasma formation

The most obvious cause of phase shifts in the generated harmonic field is due to the acquired dipole phase of the electron in the continuum (Eq. 2.45). However, because the intensity and energy of the two excitation pulses is made as equal as possible, the induced dipole phase of the generated HHG light is also nearly equal for both pulses. In RCS the influence from this effect on the extracted transition frequency is further suppressed, because the potential phase shift is common mode for a constant pulse energy as a function of delay. Therefore, even with two unequal (but constant) pulses the effect is suppressed and does not induce a shift of the extracted transition frequency. Experimentally, the pulse energy is kept constant to a level of 0.1% as a function of pulse delay.

However, a more subtle effect arises from performing HHG with two pulses, as is illustrated in Fig. 2.14. The harmonics are generated by focusing the two amplified pulses in a gas sample. Here, up-conversion of the first Ramsey-comb pulse can cause a change in refractive index as seen by the second pulse. This effect is induced by two processes: the depletion of the neutral atom density (Eq. 2.61) and the generation of plasma (Eq. 2.60). The magnitude of the phase shift due to the two contributions can be expressed in terms of the ionized fraction (η) according to

$$\phi_{hhg} = \Delta k(\eta) L, \qquad (2.94)$$

where L is the interaction length. The ionized fraction is dependent on the driving intensity of the fundamental beam and is initially zero, therefore the phase shift experienced by the second pulse due to up-



Figure 2.14 – Visualization of the influence of HHG on RCS. The plasma formed during up-conversion of the first excitation pulse, shifts the phase of the second up-converted excitation pulse. The induced phase shift $\Delta \phi(t)$ is delay-dependent because the plasma moves out of the interaction region.

conversion of the first pulse can be approximates by

$$\Delta \phi = \phi_{hhg}(\eta) - \phi_{hhg}(0) \tag{2.95}$$

The induced phase shift as a function of η for seventh harmonic of 770 nm is shown in Fig. 2.15. The pressure in the interaction region is taken to be p = 10 mbar of argon and the interaction length (related to the Rayleigh length of the beam and the diameter of the nozzle) is L = 1 mm. The influence of the free electrons in the plasma, is clearly much bigger than the effect introduced by the depletion of the neutral atoms. The phase shift due to the plasma dispersion can be on the order of a few radians for a fully ionized gas sample, i.e. $\eta = 1$. Fortunately, typical values of η are in the range of a few percent in order to fulfill proper phase-matching conditions (Sec. 2.4.3.4). However, the influence from plasma formation can still lead to a significant shift of the phase as a function of delay. For the correct interpretation of the RCS signal, the time dependence of this additional phase shift has to be understood. This is determined by the evolution of the plasma and the gas in the interaction zone at time scales on the order of T_{rep} , i.e. in the range of tens of nanoseconds.

The dynamics of the neutral gas from a supersonic expansion is well understood. The time it takes for the neutral atom density to recover is determined the transit time of the atoms through the interaction region,

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Figure 2.15 – The calculated phase shift of the second HHG pulse at the seventh harmonic of 770 nm as a function of the ionized fraction η of argon atoms used for HHG. The induced shift from (a) the depletion of neutral atoms and (b) the generation of plasma (only taking the electrons into account). The calculations were performed with an interaction length of L = 1 mm and a pressure of p = 10 mbar. The contribution from free electrons is clearly dominating.

which is given by size of the interaction region and the speed of the atoms. The interaction region is given by the shape of the fundamental beam in the gas sample. Assuming that the fundamental beam is focused through the gas jet, the interaction region is cylindrically shaped. We are only interested in the preferred direction of motion (y) of the atoms, which is perpendicular to the propagation direction of the fundamental beam. For a focused Gaussian beam with waist w_0 , the dispersion as a function of position in the beam, can be written as

$$\Delta k_n(y) = \Delta k_{n,0} \exp\left[-\frac{2y^2}{(w_0/a)^2}\right],$$
(2.96)

where $\Delta k_{n,0}$ is the maximum dispersion in the center of the beam and a is a scaling factor which gives the size of the ionized region. For a supersonic expansion, the mean forward velocity of the gas v_{atom} can be calculated using a thermodynamic approach

$$v_{atom} = \sqrt{\frac{2k_BT}{m}} \frac{\gamma}{\gamma - 1},\tag{2.97}$$

where k_B is the Boltzmann constant, T is the temperature of the gas, m is the mass of the atom and $\gamma = c_p/c_v$. Substituting $y = v_{atom} \times t$ we can obtain a first-order estimate for the time-dependent dispersion from the depletion of neutral atoms

$$\Delta k(t) = \Delta k_n \exp\left[-\frac{2(v_{atom}t)^2}{(w_0/a)^2}\right].$$
(2.98)

For HHG in argon ($v_{atom} = 550 \text{ m/s}$) with an interaction region of 50 µm, the neutral atom density recovers after ~ 100 ns. Therefore the second Ramsey-comb pulse will experience a delay-dependent phase shift over the first 100 ns from up-conversion of the first pulse. Although this effect is relatively slow, the magnitude is small (Fig. 2.15(a)).

The dynamic behavior of the generated plasma on long time scales is not so straightforward to calculate, because it involves a large number of charged particles which interact strongly with each other and the laser field. Moreover, the electrons in the plasma can be accelerated to relativistic speeds in the direction of the light pulse due to radiation pressure [102]. The magnitude of the induced phase shift from the free electrons is much larger than the other contributions, but the dynamics is also much faster, on a fs and ps timescale.

Because the influence of the dynamic plasma on Ramsey-comb spectroscopy is not easy to calculate, the induced phase shift is measured by tracking the phase evolution of the Ramsey fringes as a function of delay. The phase evolution of the signal from a single transition is linear, as is illustrated in Fig. 2.13. A delay-dependent phase shift of the second excitation pulse from plasma formation during up-conversion leads to a deviation from this linear dependency. The measurement characterizing this effect is one of the key results of this thesis and an extensive description of it is given in Chapters 5 and 6.

2.5.3.2 The influence from phase noise after up-conversion

Another effect which has to be taken into account is the up-conversion of the phase-noise amplitude of the fundamental Ramsey-comb pulses. Although the phase noise of the Ti:sapphire frequency comb (Sec. 3.1.1) is typically low (between a few tens of mrad and 150 mrad, depending on the time scale) [103–105], excess phase noise is introduced in the parametric amplification process. This is mainly caused by intensity

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Figure 2.16 – The simulated contrast of the Ramsey fringes for different phase noise amplitude (1σ) in units of radians. The phase noise at the excitation wavelength has to stay well below π to observe Ramsey fringes.

fluctuations of the pump pulse and phase mismatch due to (local) wavefront errors (Sec. 2.3.2.1). The phase noise amplitude of the harmonic field scales linear with the harmonic order, due to the up-conversion of the frequency. These phase fluctuations directly translate to noise on the phase of the Ramsey fringes and therefore lead to a reduction of contrast. The contrast of a Ramsey fringe is defined as

$$contrast = \frac{\max(S_t) - \min(S_t)}{\max(S_t) + \min(S_t)},$$
(2.99)

where S_t is the obtained signal in the time domain from a single Ramsey scan. For a transition with an infinitely long upper state lifetime, the contrast as a function of phase noise is plotted in Fig 2.16. The contrast was obtained from simulated Ramsey excitation with pulses that have additional phase noise, which was assumed to be normally distributed. The simulations did not include any other broadening mechanisms or noise sources in this case. The contrast vanishes completely for a phase noise amplitude of π (1 σ of the normal distribution) at the excitation wavelength, e.g. for the seventh harmonic, only $\pi/7$ at the fundamental. This can be understood in a more intuitive way from the argument that the fringe varies over half of an optical cycle and completely washes out. Therefore the higher the harmonic that is used for experiments, the more stringent the demands for low phase noise in the fundamental frequency comb pulses. This is discussed further in Chapters 5 and 6.
CHAPTER 3

The experimental setup

This chapter gives an overview of the experimental setup and techniques which were used for the work described in this thesis. The first part gives a detailed overview of the laser setup, which was used to amplify a pair of frequency-comb pulses for Ramsey-comb spectroscopy. The second part describes the newly developed vacuum setup which was designed to combine Ramsey-comb spectroscopy with high-harmonic generation. The main purpose of this setup is to enable 1S - 2S spectroscopy in He⁺, but it was first tested on the $5p^6 \rightarrow 5p^58s\ ^2[3/2]_1$ transition in xenon (Chapters 5 and 6) for which it was slightly altered.

3.1 The Ramsey-comb laser setup

A schematic overview of the Ramsey-comb laser is shown in Fig. 3.1. The Ramsey-comb laser system provides two amplified frequency-comb laser pulses of a few mJ pulse energy. The peak intensity of these pulses is sufficient for efficient up-conversion to shorter wavelengths using nonlinear processes. The frequency-comb pulse pair is amplified in a noncollinear optical parametric chirped pulse amplifier (NOPCPA), which is seeded with the pulse train from a Ti:sapphire frequency-comb laser and pumped by a pair of high-energy pulses from a home-build pump laser system. A series of fast switching modulators are implemented in the pump laser to adjust the delay between the pulse pair in integer steps of the repetition time, and for feedback on the energy of the two pulses. Only the FC pulse pair which has temporal overlap with these



Figure 3.1 – A schematic overview of the RCS laser. Two pulses from a Ti:sapphire frequency-comb laser are selectively amplified in a non-collinear optical parametric chirped pulse amplifier (NOPCPA) to the mJ-level. The pulse delay ($\Delta t = \Delta N \times T_{rep}$) is selected by the settings of the pump laser. The phase stability of the RC pulses is measured in a separate setup based on spectral interferometry.

two pump pulses is selectively amplified in the NOPCPA for Ramseycomb spectroscopy. A separate setup is used to measure the phase shift induced in the amplifier. The individual components of this laser system are discussed in detail in the following sections.

3.1.1 The titanium:sapphire frequency comb

The experiment runs on a home-built titanium:sapphire (Ti:Sa) Kerrlens mode-locked frequency-comb laser with a central wavelength of 800 nm and a bandwidth of ~ 75 nm. A schematic overview of the laser is shown in Fig. 3.2. The Ti:Sa crystal is pumped with 5 W of continuous-wave light at 532 nm. An acousto-optic modulator (AOM) (IntraAction Corp. AFM 804A1) is used in de pump beam to control the pump intensity and stabilize the carrier-envelope phase shift $\Delta \phi_{ce}$ through the Kerr-effect in the Ti:Sa crystal. The pump beam is strongly focused in the crystal and propagates through a pair of curved mirrors (r = 50 mm). These chirped mirrors are anti-reflection coated for the pump wavelength and highly reflective around 800 nm. Combined with two folding chirped mirrors and the end mirror, they compensate for group velocity dispersion in the cavity over a large bandwidth. By



Figure 3.2 – A schematic overview of the Ti:sapphire (Ti:Sa) frequency-comb laser. The Ti:Sa crystal is pumped by 5W at 532 nm from a commercial laser (Verdi-V5/Finesse Pure). Passive mode-locking is achieved through the Kerrlens effect, and the generated pulses are coupled out by an 85% output coupler (OC). The f_{ceo} is coursely tuned with a set of wedges in the cavity and finetuned by modulation of the pump intensity (with an AOM). A translation stage (TS) and piezo-electric transducer (PZT) are used for coarse adjustment and active stabilization of the cavity length, and therefore f_{rep} . The f_{ceo} is measured with an f - 2f interferometer based on a photonic-crystal fiber (PCF) and a β -barium borate (BBO) crystal. Both f_{rep} and f_{ceo} are referenced to a commercial Cs-clock.

changing the dispersion properties of the mirror-set, the bandwidth and the central wavelength of the laser can be tuned. The total (round-trip) cavity length is 2.4 m and can be coarsely adjusted by changing the position of the end mirror, which is mounted on a translation stage. This enables operation at repetition frequencies ranging between 125.35 MHz and 127.40 MHz. Additionally, this same mirror is mounted on a piezoelectric transducer, which enables fast feedback on the cavity length. In order to compensate for thermal drifts, the temperature of the baseplate of the laser is actively stabilized through water cooling. As a result, the piezo is kept within range and the cavity can be locked for at least several hours. The pulses are coupled out through an 85 % reflective output coupler. The average output power of the laser is 450 mW at a repetition frequency of 126.6 MHz, which corresponds to a pulse energy of 3.6 nJ.

In order to actively stabilize the repetition frequency, the pulse train is measured with a fast photo-diode (Electro optics technology, EOT4000) and the signal is mixed with the output of a stable frequency generator (Agilent PSG-L E8241A) at 9.6 GHz (the 76th harmonic of f_{rep}). This scheme enables a tighter lock than at the fundamental due to the high locking frequency. The generator is referenced to a Cs atomic clock (Symmetricon CsIII 4310B) for absolute calibration of the frequency. In order to scan the repetition rate of the laser during the RCS experiments, the beat signal is offset by 28 MHz and mixed with the output of a digital frequency synthesizer (AD9912, Analog Devices). The resulting signal is used for active feedback on the piezo through a PID loop and enables scanning of f_{rep} at the level of a few µHz.

The carrier-envelope offset frequency $(f_{ceo} = f_{rep}(\Delta \phi_{ce}/2\pi))$ is measured with an f - 2f interferometer (see Fig. 3.2). For this purpose, 25% of the power is split-off at the exit of the laser and is sent through a photonic crystal fiber (PCF) of 16 cm length with a $2 \,\mu m$ core. In this manner the spectrum is broadened to span an octave. Interaction within a nonlinear crystal (a 3 mm thick BBO crystal in our case) then produces sum frequencies of the modes (at roughly the double frequency) at the frequencies $f_m = m f_{rep} + 2 f_{ceo}$. These modes are then made to interfere with the closest comb-modes from the original broadened spectrum. The beat spectrum is obtained by combining light from the newly generated frequencies and the original beam with a Michelson-interferometer and detecting the beat on an avalanche photo-diode (Analog Modules Inc. 712-A). The lowest beat frequency is equal to f_{ceo} , which is electronically isolated electronically with a low-pass filter. The interferometer is used to temporally overlap the original and 'doubled' pulses by compensating for the different group velocity in the PCF. The carrier-envelope offset frequency is obtained directly from the beat frequency and is mixed with the reference signal from the Cs atomic clock at 10 MHz for stabilization.

The carrier-envelope phase shift $\Delta \phi_{ce}$ is a result of a mismatch between group and phase velocity in the cavity (Sec. 2.1.1). Therefore, it can be changed by tuning the dispersion. Coarse adjustment is realized by inserting a pair of wedges in the cavity, of which one can be moved in



Figure 3.3 – The measured phase stability of the Ti:Sa frequency-comb laser using the Finesse Pure pump laser. The upper window shows the stabilized f_{ceo} frequency and the lower panel shows the phase difference between the reference signal from the commercial Cs clock (Symmetricon CsIII 4310B) and the f_{ceo} . During this measurement, the rms-phase stability was determined to be 115 mrad.

and out of the beam using a translation stage. Fast feedback to f_{ceo} is provided by modulating the intensity of the pump beam with the AOM. This leads to a change of the refractive index in the Ti:Sa crystal.

For the experiments described in Chapter 4, the pump light was delivered by a Verdi-V10 laser. For the experiments conducted in Chapters 5 and 6, the pump laser was replaced by a Finesse Pure with a maximum output of 8 W. In order to test the performance of this laser, the $\Delta \phi_{ce}$ stability was measured.

The phase-noise on the pulses emitted from the Ti:Sa laser is strongly dependent on the power stability of the pump laser. The phase stability was measured by comparing the phase of the detected beat signal, when it is locked, with that of the reference signal. The result is shown in the lower panel of Fig. 3.3, together with the observed beat note (upper panel). The time trace was acquired with an oscilloscope, which has a 1 GHz bandwidth (Tektronix, TDS 5104). The recorded time trace is 1 ms long and consists of 2.5×10^6 points. The obtained rms-phase stability (in-loop) from this measurement was 115 mrad, which is comparable to what was achieved with the Verdi-V10 laser [104]. However, the power stability of the Finesse pump laser relies heavily on the active feedback mechanisms inside the laser, which do not always work properly. This can give rise to unpredictable behavior, and occasionally leads to broadening of the beat note or the appearance of additional side bands, which degrade the performance of the system (and potentially of the Ramsey-comb spectroscopy measurement). However, during the RCS measurements the beat note is carefully monitored to avoid such unexpected degradation.

3.1.2 The pump laser system

The pump laser system for the NOPCPA outputs a pair of high-energy picosecond-pulses at 1064 nm. The system is based on a Nd:YVO₄ oscillator from which a pulse-pair is selected by a series of fast modulators. The pulses are then pre-amplified to slightly below 1 mJ in a high-gain three-stage bounce amplifier, also based on Nd:YVO₄. A set of Pockels cells is implemented to compensate for gain depletion and actively stabilize the seed pulses going into the high-energy post-amplifier based on Nd:YAG. In this section the individual parts of this laser system will be described in detail.

3.1.2.1 The Nd:YVO₄ laser

A schematic overview of the passively mode-locked Nd:YVO₄ oscillator is shown in Fig. 3.4. The crystal is pumped by 28.5 W of continuouswave light at 880 nm, which is produced by a fiber-coupled pump diode (JOLD-30-CPXF-1L). A one-to-one telescope is used to image the exit face of the fiber into the crystal.

The cavity consists of a telescope of two curved mirrors and an additional folding mirror, in between two flat end mirrors. One end mirror is



Figure 3.4 – The mode-locked Nd:YVO₄ oscillator. The crystal is pumped by 28.5 W at 880 nm produced by a fiber-coupled pump diode. The linear cavity is mode-locked using a SESAM (modulation depth of 1.2%) as the end mirror. The pulses are coupled out with a dichroic mirror and spectrally clipped. Two pulses are selected with a combination of an AOM and an EOM for high contrast and fast picking. The relative amplitude of the pulses is adjusted with the EOM to compensate for gain depletion in the subsequent amplification stages. HP = Half-wave plate, QP = Quarter-wave plate, PZT = piezo-electric transducer, TS = translation stage, FI = Faraday isolator.

a semiconductor saturable absorber mirror (SESAM; BATOP GmbH), which has a modulation depth of 1.2% and a relaxation time of 10 ps. It provides the mode-locking mechanism by introducing higher losses at lower intensity. The other end-mirror is the partially reflection-coated (90% reflectivity) end face of the crystal, which also acts as an output coupler. One of the curved mirrors is placed on a translation stage for coarse control of the repetition frequency of the laser and the flat folding mirror is mounted on a piezo-electric transducer for fast feedback on the cavity length. In order to compensate for long term drifts, the base-plate of the cavity is water cooled and active feedback is provided to the temperature to keep the piezo in range. Laser pulses are emitted at a repetition frequency of 126.6 MHz with an average output power of 5 W. The laser wavelength is centered around 1064 nm and has a bandwidth of 0.25 nm, which is much larger than the gain bandwidth of

Nd:YAG later used for amplification. Therefore, the spectrum is clipped to a bandwidth of 0.05 nm with an adjustable slit in the Fourier plane of a 4f-grating system. The position of this slit is adjusted to tune the central wavelength and achieve maximum amplification. Due to spectral clipping, the pulses are stretched to a length of 60 ps and the energy is reduced to 1 nJ.

Pulse picking of the required pulse pair is realized with a series of fast modulators. An acousto-optic modulator (AOM; Gooch and Housego T-M150-0.4) with a high extinction ratio ($>50 \, dB$) is used to select a train of a few hundred pulses. It has a relatively slow rise time, of 30 ns, which does not enable single-pulse-selection. Therefore, it is used in series with a fast fiber-coupled electro-optic modulator (EOM; Jenoptik AM 1060 HF) based on an integrated Mach-Zehnder interferometer to modulate the intensity. It has an extinction ratio of only 33 dB, but is fast enough to select single pulses. The EOM requires only 3V and can therefore be driven with a commercial delay generator (Stanford Research Systems DG645). The pulse selection is repeated at a rate of 28 Hz.

3.1.2.2 The Bounce amplifier

The selected pulse-pair is amplified in a high-gain three-stage Nd:YVO₄ bounce amplifier [106, 107]. A schematic overview of the amplifier is shown in Fig. 3.5. It consists of two crystals of which the front and end face, i.e. the sides where the amplified beam goes through, are cut at an angle of 5° to prevent lasing from back reflections. The crystals are pumped from the side by a quasi-continuous diode array at 880 nm. They have an anti-reflection coating for 880 nm at the pump surface and an anti-reflection coating for 1064 nm at the entrance and exit face. The pump pulse is 130 µs long and has a peak power of 170 W. The polarization of the pump light is set to be aligned with the c-axis of the crystal using a half-wave plate. A set of cylindrical lenses is used to match the pump beam profile with the crystal dimensions ($2 \times 4 \times 10 \times \text{mm}^3$ for the first crystal and $4 \times 6 \times 20 \times \text{mm}^3$ for the second crystal). The pulse length is limited by the fluorescence lifetime (90 µs for Nd:YVO₄) of the gain medium.

After the losses of the modulators, the remaining pulse energy for seed-

3.



Figure 3.5 – Schematic overview of the high-gain bounce amplifier. It consists of three amplification stages in two Nd:YVO₄ crystals, which are pumped by quasi-cw laser diodes (LD) at 880 nm. The seed beam is injected in a grazing incidence configuration to ensure a homogeneous beam profile after amplification. The amplifier is seeded with unequal pulses to compensate for gain depletion of the first pulse. Faraday isolators (FI) are placed in between each amplification stage to avoid damage and lasing from back-reflections. HP = Half-wave plate.

ing is 30 pJ. The seed pulses are focused into the crystals at a grazing incidence angle and undergo a total internal reflection. In this way, the seed beam experiences a homogeneous gain region through the crystal, even though it is asymmetrically pumped, resulting in a good beam quality after amplification [107]. The first crystal is used in double-pass and the second crystal is used in single pass. In between each amplification stage a Faraday optical isolator is placed to suppress any dangerous back-reflections, which can cause lasing due to the high gain in the crystal.

The first pulse takes out a significant amount of stored energy, which leads to a lower gain as seen by the second pulse. In order to compensate for this gain-depletion effect, the seed pulses are injected with unequal (1:3 ratio) pulse energy. This is realized by reducing the transmission of the first pulse through the EOM. In this way, both pulses are amplified to a pulse energy of 0.85 mJ at the output of the amplifier.

3.1.2.3 The post-amplifier

The pulses are further amplified in a high-energy post amplifier based on Nd:YAG, see Fig. 3.6. The amplifier module consists of a 14.6 cmlong Nd:YAG rod with a diameter of 6.4 mm. It is pumped from the side by five bars of quasi-continuous diodes, which are symmetrically distributed around the rod. The module is pumped during 300 μ s (fluorescence lifetime Nd:YAG is 230 μ s) with a combined peak power of 24 kW.

Similarly as in the bounce amplifier, the seed pulses are injected with unequal pulse energy to compensate for the gain depletion effect. This is realized with two fast switching Pockels cells (Lasermetrics 5046ER) in combination with an optical isolator. Additionally, the isolator protects the laser system from any back-reflections, which might cause lasing and damage in the bounce amplifier. The second Pockels cell is put to a fixed switching voltage for maximum transmission of the second pulse. By adjusting the switching voltage of the first Pockels cell, the amplitude of the corresponding pulse can be adjusted. The seeding ratio is typically 1:2, and active feedback can be applied to achieve equal pulse energy at the output of the amplifier.

When the amplifier is seeded with a Gaussian beam, the imprint of the five-fold symmetry of the pump diodes can be clearly seen in the amplified beam [92]. Therefore, the seed beam has a flat intensity profile and a 20% smaller diameter than the Nd:YAG rod. This so-called flat-top head beam is created by magnifying the seed beam to a diameter of 6 mm FWHM and selecting only the center part with a 3.5 mm diameter pinhole. This method causes diffraction from the hard edges of the pinhole, which is not optimal for amplification. Moreover, it can cause high-intensity hot-spots, which can easily exceed the damage threshold of the optical elements. Therefore, the plane where the pinhole is placed, is relay-imaged throughout the rest of the system.

The first image is created in the amplifier rod with a magnifying telescope, which increases the beam size to 4.9 mm. After the first amplification stage, the beam is back-reflected for a second amplification pass. The amplifier induces thermal depolarization, which is compensated in the second pass by rotating the polarization by 90° with a Faraday rotator in between the two passes. A telescope ensures that the beam is



Figure 3.6 – The high-energy post amplifier based on a Nd:YAG module. A 14.6 cm crystal rod with 6.4 mm diameter is pumped by 5 bars of quasicontinuous diodes. The relative amplitude of the two seed pulses are adjusted with two Pockels cells (*PC*) in combination with a Faraday Isolator (*FI*) to compensate for gain depletion effects. The intensity profile of the seed beam is converted into a flat top-hat using a 3.5 mm-pinhole (*PH*) to extract the maximum energy. The amplifier is used in double pass in between which the polarization is rotated by 90° with a Faraday rotator (*FR*) to compensate for thermal depolarization. The beam is subsequently relay-imaged throughout the system to avoid intensity hot spots from diffraction.

again imaged on the rod in the second pass. The amplified beam is coupled out with a thin-film polarizer that is placed after the amplification module. A pulse energy of 25 mJ is typically reached when the diodes are operating at 85.5 A.

3.1.3 Amplification of the frequency-comb pulse pair

The FC pulses are amplified in a non-collinear optical parametric chirped pulse amplifier (NOPCPA). The FC pulses emitted from the Ti:Sa laser which seed the NOPCPA have a pulse length of ~ 15 fs, while the pump pulses are 60 ps long. This mismatch in pulse length is not optimal for efficient amplification in the NOPCPA. Therefore, the FC pulses are stretched to ~ 10 ps by introducing group velocity dispersion (GVD) in



Figure 3.7 – The 4f-grating stretcher is used to apply group-velocity dispersion and for wavelength selection. The two gratings are set at $f - \Delta X$ from the lenses (with focal distance f) to induce group-velocity dispersion. For this purpose the gratings are placed on translation stages (*TS*). The slit is adjustable to select the bandwidth and mounted on a TS to select the central wavelength.

a 4f-grating stretcher [108]. In addition, the bandwidth of the pulses is reduced, and the central wavelength is tuned with an adjustable slit in the Fourier plane of the stretcher. This leads to more favorable spectral properties for the spectroscopy experiments later described in this thesis.

3.1.3.1 The 4f-grating stretcher

A schematic overview of the 4f-grating stretcher is shown in Fig. 3.7. The spectrum is dispersed (-1^{st} order) by a gold-coated plane ruled reflection grating with d = 1200 lines/mm (Richardson, 53-*-360R). The individual colors are focused by a lens (f = 100 mm) in the Fourier plane where a slit is placed for spectral clipping. A second lens and grating (again with d = 1200 lines/mm) are used to collimate the individual colors alongside each other, after which the beam is back-reflected with a slight vertical displacement to enable output coupling. The two lenses, both of focal length f, in between the two gratings form a one-to-one telescope, i.e. they are placed at 2f from each other, while group velocity dispersion (GVD) is introduced by displacing the gratings with respect to the lenses by ΔX from f. In this manner, the colors are again

spatially overlapped, but the pulses are stretched due to the added GVD. The amount of GVD $(\partial^2 \phi / \partial \omega^2)$ applied at an angular frequency ω in this configuration is given by [85]

$$\frac{\partial^2 \phi}{\partial \omega^2} = \frac{8\pi^2 c}{\omega^3 d^2} \frac{2\Delta X}{\cos^3 \theta},\tag{3.1}$$

where θ is the angle of diffraction with respect to the normal vector of the grating. The gratings are used at a diffraction angle of $\theta = 62^{\circ}$. The displacement, ΔX , of the gratings was adjusted depending on the bandwidth used for the different experiments, for optimum overlap with the pump pulse length.

3.1.3.2 The non-collinear optical parametric chirped pulse amplifier

A schematic picture of the NOPCPA is shown in Fig. 3.8 and is based on the design from [109]. The NOPCPA consists of three amplification stages based on β -BaB₂O₄ (BBO) crystals of 5 mm length. The pump pulses are provided by the home-built pump laser (Sec. 3.1.2), which emits pulses of 25 mJ at 1064 nm. A small fraction (a few percent) of the power is split off by a combination of a half-wave plate and a thinfilm polarizer. This part is used to pump the first two crystals, while the remainder of the power is used to pump the last crystal. In both arms, the flat-top head beam is imaged onto a BBO crystal for frequency doubling to $532 \,\mathrm{nm}$ with a maximum conversion efficiency of $\sim 60\%$. The resulting 532 nm beam is decreased to about 1 mm in the first two BBO crystals and $3.5 \,\mathrm{mm}$ in the third crystal to reach $\sim 2-3 \,\mathrm{GW}/\mathrm{cm}^2$ in all three amplifier crystals. The exact splitting ratio and therefore pump intensity in the different crystals is tweaked from day-to-day to achieve optimal operating conditions. This typically means that the first pass is not saturated and the seed pulses are amplified in the exponential gain regime, while the second and third pass are slightly saturated for a more stable output of the amplifier. The seed beam has a Gaussian profile with a slightly bigger diameter than the pump beam to reduce the influence of beam pointing instabilities. The total gain of the system is $\sim 10^8$ leading to typical pulse energies of 2-5 mJ depending on the amplified bandwidth (0.2-12 nm).



compensate for walk-off induced beam pointing instabilities (see text). The two seed pulses are amplified to 2-5 = half-wave plate, TFP = thin-film polarizer, SHG1/2 = second harmonic generation in BBO mJ/pulse depending on the bandwidth. R1 = -600 mm, R2 = -300 mm, R3 = -500 mm, R4 = -75 mm. HWP Figure 3.8 – A schematic overview of the non-colinear optical parametric amplifier. It is based on three amplifirst two OPA crystals indicate the optical axis, which is reversed in the second crystal with respect to the first to laser. The pump beam is imaged in each crystal to maintain the flat top-hat intensity profile. The arrow on the fication stages in BaB_2O_4 (BBO). The amplifier is pumped by two pulses at 532 nm from a home-built pump



Figure 3.9 – The measured propagation direction for the two RC pulses after implementing walk-off compensation in the first two passes of the NOPCPA. The beam profile was measured using a lens with f =100 mm. The observed walk-off angle was below 20 μ rad in both the vertical and horizontal direction, which is a 20-fold improvement with respect to the uncompensated configuration.

During the experiments described in Chapters 5 and 6, it became apparent that amplification in the NOPCPA is influenced by the effects of spatial walk-off between the interacting waves (Sec. 2.3.2.2). This led to an unequal wavefront tilt of the two amplified FC pulses, because the two pump pulses have a slightly different temporal profile due to gain depletion effects in the amplifiers of the pump laser system (Sec. 3.1.2) [92]. This led to a slight difference in beam pointing between the two amplified FC pulses due to pump-to-signal phase transfer in the amplifier. The induced difference in propagation direction reduces the interaction region of the Ramsey-comb spectroscopy experiments and therefore the achievable maximum pulse delay (because the atoms fly faster through the interaction zone). For this reason, this effect had to be compensated by rotating the crystal axis in the second pass with respect to the orientation in the first pass (Fig. 2.6). In this way the walk-off direction is reversed in the second pass and its influence on the amplified signal beam suppressed [97].

Because the induced walk-off is highly gain dependent, the biggest effect was observed from amplification in the first two passes. The induced walk-off effect is not exactly identical in the two passes and it can therefore not be perfectly compensated. Nonetheless, a significant suppression of this effect was observed in this way. The difference in propagation direction of the two pulses was measured by focusing the beam (f = 100 mm) through a pinhole, which was significantly smaller than the focus size. The pinhole was mounted on an XYZ-translation stage to scan it through the beam in two independent directions. The obtained transmission of the two pulses as a function of pinhole position in both the vertical and horizontal direction are shown in Fig. 3.9. After careful alignment of the NOPCPA, the remaining induced walk-off angle difference between the two amplified pulses is $\rho_{\rm hor} = 16 \pm 6 \,\mu {\rm rad}$ in the horizontal direction and $\rho_{\text{vert}} = 3 \pm 6 \,\mu\text{rad}$ in the vertical direction. This is a big improvement with respect to the previous situation (without compensation in the first two passes), where a difference of up to 0.5 mrad was observed. The remaining small difference in propagation direction is most likely caused by the uncompensated third pass. This is more difficult to compensate because it requires splitting this amplification stage into two parts to reverse the walk-off direction. In addition, a dichroic mirror should be used to remove the idler beam in between these two parts. This is geometrically very challenging to combine with the non-collinear amplification scheme.

3.1.4 Phase measurement setup

After amplification, the phase stability of the pulses is measured using a method based on spectral interferometry. A schematic overview of the setup is shown in Fig. 3.10.

A small fraction of the FC beam is split-off before the parametric amplifier and sent through a delay line which matches the path length of the amplified pulses in the NOPCPA. The original FC pulses are then separately stretched in a 4f-grating stretcher, which is similar as the one discussed in Sec. 3.1.3.1. The reason for this additional stretcher is that the parametric amplification process induces spectral broadening due to saturation effects. Therefore, the bandwidth of the reference pulses are matched to that of the amplified pulses by increasing the bandwidth of the second stretcher slightly. The amplified pulses are then spatially overlapped with the reference pulses in a single-mode fiber. The two sets of pulses are separated from the full pulse train of the FC laser with two Pockels cells, which are used in a double-pass configuration



Figure 3.10 – A schematic overview of the phase measurement setup. The phase is extracted using a spectral interference pattern. For this purpose the reference pulses pass through a stretcher (S2) after which they are spatially overlapped with the amplified pulses in a single mode fiber. Light from the full FC pulse train is suppressed using two Pockels cells (PC) in double pass. A third PC is used to project each interferogram separately on the CCD camera.

to achieve a contrast of $1:10^4$ after additional polarizing optics. This is necessary to sufficiently suppress background light on the camera. A third PC is used in combination with polarization optics to introduce a slight vertical offset between each set of pulses in a small delay line. In this manner, the interferogram of both amplified FC pulses can be projected individually on the CCD camera (IMI-TECH IMB-716-G). The spectral interferograms are obtained by combining a gold grating of 1200 lines/mm with a lens of f = 350 mm. The delay between the amplified and reference pulse can be adjusted with a translation stage in the delay line of the reference pulses to tune the period of the interference fringes. The geometrical phase, which arises from misalignments on the camera are calibrated by exchanging the projection on the camera with the timing of the third Pockels cell. The phase difference between the pulses is extracted from the interferograms using a Fourier-transform based method [109, 110].

3.1.5 Spatial filter and compressor

The amplified beam has a flat top-hat intensity profile, because the pump beam is partly imprinted on the amplified beam after the parametric amplification process. It is converted back into a Gaussian beam with a spatial filter, which consists of a telescope and a pinhole. The pinhole is mounted in a vacuum tube, which is at 10^{-2} mbar to avoid breakdown or other unwanted nonlinear processes, such as self-phase modulation in air. The amplified beam has a diameter of 1.2 mm and is loosely focused with a lens of focal length f = 500 mm. The entrance and exit windows of the vacuum tube are placed only a few centimeters from the lenses to keep the peak intensity as low as possible and avoid self-phase modulation in the windows. They are mounted at Brewster angle to reduce reflection losses and avoid direct back-reflections. The pinhole has a diameter of 500 µm and is placed in the focus of the first lens. It only transmits the TEM₀₀ mode, leading to an overall transmission efficiency of 70%.

The experiment described in Chapter 4 is done with up-converted pulses using frequency doubling and sum-frequency mixing in BBO. For these processes, a relatively moderate peak intensity is sufficient, while also a narrow bandwidth (0.2-0.3 nm) is required. Moreover, two-photon excitation based on beams from opposite sides is not sensitive to frequency chirp [111]. Therefore, the amplified chirped pulses are up-converted immediately after the spatial filter without compression, and directed towards the molecular beam machine for the experiments. Details on the rest of the setup are given in Chapter 4.

The experiments discussed in Chapters 5 and 6 rely on up-conversion using high-harmonic generation, which requires a peak intensity of 10^{14} W/cm². This strong-field regime can only be reached with ultra-short (fs-range) pulses and therefore the chirped amplified pulses are first recompressed before they are up-converted. This is done in a gratingbased pulse-compressor using highly efficient blazed transmission gratings (Lightsmyth, T-1850-800s). These have a groove spacing of d =1850 lines/mm and an efficiency of $\eta > 94\%$ over a 100 nm bandwidth. A schematic overview of the compressor is shown in Fig. 3.11. Group velocity dispersion (GVD) is introduced by adjusting the distance (L) between two parallel gratings. From geometrical considerations, it can



Figure 3.11 – The compressor is based on two high-efficiency blazed transmission gratings. The second grating is mounted on a translation stage (TS) to tune the group velocity dispersion and the whole setup is mounted on a rotation stage (RS) to rotate around the point of incidence of the laser beam and tune third-order dispersion. A vertical displacement is introduced between the forward and backward traveling beam using a periscope (PS) to enable output coupling.

be shown that the amount of second-order dispersion introduced at frequency ω in this configuration is [85]

$$\frac{\partial^2 \phi}{\partial \omega^2} = -\frac{8\pi^2 c}{\omega^3 d^2} \frac{L}{\left[1 - (\frac{\lambda}{d} - \sin\gamma)^2\right]^{3/2}}$$
(3.2)

where γ is the angle of incidence with respect to the normal vector of the grating. The amount of GVD can be tuned by moving the second grating, which is mounted on a translation stage. Additionally, third-order dispersion (TOD) can be minimized by tuning the angle of incidence of the beam. For this purpose, the whole compressor is built on a rotation stage.

The GVD and TOD introduced in the stretcher (Sec. 3.1.3.1) can be fully compensated in the compressor by optimizing the parameters γ and *L*. In order to determine the optimal values of these parameters, the GVD and TOD are calculated as a function of wavelength. The GVD of the stretcher and the compressor are given by Eq. 3.1 and Eq. 3.2, respectively and the TOD is calculated with the first derivative of these expressions to ω . The results (Fig. 3.12) show that GVD and TOD can



Figure 3.12 – The calculated curves for the second- (green curve) and thirdorder dispersion (red curve) of the amplified pulses after subsequently stretching and compressing. Full compensation of $k^{(2)}$ and $k^{(3)}$ can be achieved for a limited range around 770 nm, but a significant amount of fourth-order dispersion remains.

be fully compensated at the central wavelength of 770 nm for $\gamma = 29.4^{\circ}$ and $L = 3.69 \,\mathrm{mm}$. However, a significant amount of higher-order dispersion is still present, and proper compensation is only achieved within a rather limited bandwidth. In addition, the required angle of incidence reduces the diffraction efficiency of the gratings (which were designed to operate at $\gamma = 47.8^{\circ}$) significantly and can lead to a strong reduction of peak intensity. Therefore, it could be more beneficial to not fully compensate the TOD, but use the grating at a more favorable angle. In order to investigate this, the effect of TOD on the pulse shape and peak intensity were calculated. The obtained results are shown in Fig. 3.13. For a Gaussian pulse with a bandwidth of 8 nm, the Fourier limited pulse length is 109 fs (red curve). However, after spectral clipping in the stretcher, the pulse length increases significantly to 220 fs (blue curve). Fortunately, the pulse length does not increase further by adding TOD $(-1 \times 10^6 \text{ fs}^3 \text{ in the green curve})$ and the pulse shape is only altered a little bit. Due to the asymmetry of TOD, the wings of the pulse are slightly suppressed at the leading end of the pulse and slightly amplified at the trailing end. This additional effect might even be beneficial for



Figure 3.13 – The calculated Fourier-limited pulse shape for a 8 nm-wide Gaussian spectrum (red curve), a clipped spectrum (blue curve) and a clipped spectrum with additionally -1×10^6 fs³ TOD (green curve). The main reduction in peak power is caused by spectral clipping and not by the uncompensated higher-order dispersion.

HHG, as long as the TOD has the right sign leading to a suppression of pre-pulses. Therefore, the angle of the compressor was optimized on diffraction efficiency, rather then compensation of TOD.

The re-compressed beam is magnified to a diameter of 4 mm FWHM and is then sent to the vacuum setup in which the pulses are up-converted with high-harmonic generation in a gas jet and used for Ramsey-comb spectroscopy.

3.2 The spectroscopy setup

The main considerations in the design of the vacuum setup were made for future experiments in singly-ionized helium. In order to explain these considerations properly and describe the setup, some key features of this future experiment are first discussed. The slight alterations which were made to the setup for the experiments presented in Chapters 5 and 6 are discussed in detail in these chapters and in Appendix A.

3.2.1 1S - 2S spectroscopy in He⁺

Excitation of the 1S - 2S transition in He⁺ requires extreme ultraviolet (XUV) light. The energy difference between the 1S and 2S state is equivalent to $\sim 30 \,\mathrm{nm}$ and excitation requires two photons. On first sight, the most sensible excitation scheme is to use two photons at 60 nm from opposite directions to suppress Doppler effects. However, the excitation probability is extremely low for this scheme and it therefore requires a high-power XUV source [27, 112]. This is not easily realized and additional losses from the lack of proper optics at this wavelength complicates this configuration further. In order to enhance the excitation probability, we propose to use two unequal photons. The first is a high-energy photon at $32 \,\mathrm{nm}$, which spans most of the gap, and the second is a photon at the fundamental wavelength of 790 nm. This asymmetric scheme, in combination with the high available intensity at the fundamental wavelength, enhances the excitation probability significantly. For the relevant energy levels and a description of some initial tests of this excitation scheme in krypton, see Appendix B.

Although the excitation probability can be boosted in this way, additional complications arise from it. The unequal photon scheme does not allow for Doppler cancellation. This can be resolved by using the RCS technique in combination with excitation in an ion trap. By carefully matching the secular frequency of the ion in the trap with the mode spacing of the FC pulses, RCS is virtually Doppler free. This can be understood from the fact that the modes in the spectrum of the RCS signal (Sec. 2.5.2) coincide with the Doppler shift. The equivalent principle in the time-domain picture is that excitation of both pulses happens when the ion is at the same point in its oscillation, which leads to a common mode shift in RCS. This method requires a clean mode spectrum of the motion of the ion in the trap and a high secular frequency. For this reason excitation takes place perpendicular to the trap axis and the He⁺ ion will be decoupled from the Be⁺ ion, which is used for sympathetic cooling.

An additional complication arises from the recoil of the single-sided ex-



Figure 3.14 – A simplified overview of the He⁺ excitation scheme. (a) The He⁺ ion is trapped alongside a Be⁺ ion to achieve ground state (GS) cooling. (b) The He⁺ ion is decoupled from the Be⁺ ion for excitation of the 1S - 2S transition using RCS. (c) Successful excitation will lead to excitation to a higher motional state in the trap, which can be detected with a state-selective technique on the cooling transition of Be⁺.

citation scheme. However, this can be used to our advantage for stateselective detection purposes. In the case of a successful excitation, the ion is transferred to a higher motional state (called a 'coherent state') in the trap and it becomes 'hotter'. This can be observed by recombining the Be⁺ and the He⁺ ion and performing state-selective detection on the cooling transition of Be⁺. This adds the requirement that the He⁺ ion is initially cooled to the quantum-mechanical ground state of the trap, which is possible, but technically more challenging. A simplified illustration of the experimental scheme is shown in Fig. 3.14.

The following sections will discuss the apparatus which was designed to realize this experiment. The main focus is on the generation and refocussing of the excitation beam, but some considerations of ionization and cooling will also be discussed. In addition to the vacuum setup, a basis for the cooling-laser was constructed, which will be described in the final part of this chapter.

3.2.2 The HHG chamber

A schematic overview of the vacuum setup is shown in Fig. 3.15. The final design of the setup is shown in the form of a CAD-drawing in Fig. 3.16.



sympathetically cooled by Be⁺. 5S = 5-axes stage. will be created by non-resonant ionization of meta-stable He⁺ atoms and trapped in an rf-trap where they will be of the fundamental beam can be varied using an adjustable iris in the second vacuum chamber. The helium ions Figure 3.15 – The vacuum system for RCS in combination with HHG. High-harmonics are generated in a gas with one photon from the fundamental beam at 790 nm and one at the 25th harmonic at 32 nm. The intensity toroidal mirror pair (M1 and M2) at grazing incidence onto the He⁺ ion. The 1S - 2S transition will be excited jet of argon in the first cube. The harmonics co-propagate with the fundamental beam and are refocused with a



toroidal mirror on a manual 5-axes stage. (4) The chamber with the second toroidal mirror on a piezo driven 5-axes Figure 3.16 – A CAD-drawing of the vacuum setup, which spans approximately 3 m. (1) The chamber used for HHG in argon. (2) The chamber with an adjustable iris to tune the NIR intensity. (3) The chamber with the first (6) A source chamber, which is used to produce meta-stable helium atoms. (7) The chamber with an XUV camera stage. (5) The main chamber with the ion trap, which is placed in the focus of the excitation beam (XUV+NIR). to monitor the excitation beam and the HHG spectrum.

The XUV light is created using HHG in a gas jet of argon atoms, which is produced by a pulsed supersonic expansion from a piezo valve (5 bar backing pressure). The two amplified laser pulses are focused down to a $50 \,\mu\text{m}$ (FWHM) beam waist with a lens of $f = 250 \,\text{mm}$ to perform HHG. In this configuration, typical peak intensities of $\sim 1 \times 10^{14} \,\mathrm{W/\,cm^2}$ (assuming a pulse length of 200 fs) are reached, which is sufficient for HHG in argon $(I_p = 15.76 \,\mathrm{eV})$. The piezo value is mounted on a stack of translation stages, which enables movement in all three dimensions. Phase matching of harmonics from only the short quantum path is achieved by aligning the valve along the propagation direction of the beam and minimizing the divergence of the XUV beam (see Sec. 2.4.1). In practice, this means that the jet is typically located slightly after the focus of the laser. The harmonic beam co-propagates with the fundamental beam, which is convenient for our excitation scheme of 1XUV+1NIR. However, in order to stay well below the regime of multi-photon ionization, the energy of the fundamental NIR beam has to be reduced significantly. The estimated required pulse energy is $\sim 100 \,\mu$ J. This is achieved by converting the intensity of the fundamental beam to a donut-shape with a pinhole, which is placed at 2f before the focusing lens. An image of this beam is created in the second vacuum chamber holding an adjustable pinhole, which can be used to block (a part of) the fundamental beam and fully transmit the harmonic beam.

3.2.3 Refocusing the XUV beam

In the experiment, a single He⁺ ion will be trapped alongside a single Be⁺ ion, for sympathetic cooling to the ground state. It is crucial to have good control over the alignment of the excitation beam, because additional charge patches can be created by hitting the electrodes of the trap with the beam which leads to excess micromotion. Both the high-energy XUV photons from the up-converted beam and the high-intensity beam at the fundamental wavelength can create free electrons and charge-up the electrodes. Moreover, the Be⁺ ion might ionize further when it is hit by either one of these beams, after which the time consuming process of reloading is required. Because of these issues, and the need to focus the beam to drive the 1S - 2S two-photon transition, the excitation beam is refocused onto the He⁺ ion with a pair of graz-

ing incidence toroidal mirrors. These form a one-to-one telescope which images the HHG interaction region onto the He⁺ ion. The mirrors are identical and have an effective focal length of 250 mm at an angle of incidence (AOI) of 7.5° (R1 = -3830.7 mm and R2 = -65.3 mm) [113]. Coma and other aberrations are only fully compensated when the AOI at both mirrors is equal and therefore the beam quality in the interaction zone is extremely sensitive to the alignment. In order to align the mirrors in vacuum, they are mounted on vacuum-compatible stages with five adjustable axes. The first stage is controlled manually via a 5axes stage (Newport 9082-V-M) with mechanical vacuum feedthroughs while the second stage is UHV compatible and controlled by pico-motors (Newport 8081M-UHV) for fine adjustment. Retractable silver mirrors are mounted a few centimeters behind each toroidal mirror to reflect the NIR beam out of the vacuum for alignment purposes. This is crucial for the initial alignment of the mirrors and for monitoring of the beam quality from day to day using a simple webcam. An example of an image from the NIR beam after the second toroidal mirror is shown in Fig. 3.17(a). A FWHM beam waist of $50 \,\mu\text{m}$ at the fundamental wavelength was achieved, which is consistent with a one-to-one image and therefore no significant additional abberations were observed.

In order to make sure that the XUV beam is also properly aligned, it can be monitored at the end of the setup with an XUV sensitive CCD camera (Andor Newton SY, DY940P). An example of an image is shown in Fig. 3.17(b). This camera is also sensitive to light from the much more powerful fundamental beam. Therefore the intensity of the fundamental beam has to be suppressed by a factor of at least 10^6 (assuming an upconversion efficiency of below 10^{-6}). Two 200 nm-thick aluminum filters (Luxel) are used for this purpose, of which one is mounted at an angle of 45° to reflect the high-power NIR out of the vacuum setup and avoid back-reflections onto the ion trap. In addition, this enables monitoring of the NIR beam during the experiment.

The recorded beam (Fig. 3.17(b)) has a FWHM diameter of $500 \,\mu\text{m}$, which is in agreement with the expected size at this position. The stripe which appears in the vertical direction above the beam, is caused by an artifact from the read-out procedure of the CCD and can be avoided by implementing a mechanical shutter in the fundamental beam. One can also recognize a faint diamond shape around the XUV beam, which is



Figure 3.17 – The recorded images of the refocused (a) fundamental beam in the focal plane and (b) the XUV beam in the far field.

caused by the adjustable pinhole in the second vacuum chamber. The image plane of the pinhole almost exactly coincides with the position of the camera, which explains the sharp feature.

In addition, a transmission grating can be inserted in the XUV beam a few centimeters before the XUV camera to enable a measurement of the spectrum of the generated harmonics. Although this spectrum is very coarse and not absolutely calibrated, it does enable monitoring of the relative intensity of the individual harmonic orders.

3.2.4 The ion trap and ionization procedure

The atoms will be ionized using non-resonant multi-photon ionization with a high power picosecond-pulse at 355 nm. Starting from the ground state of helium, this requires seven photons due to its high ionization potential. Therefore, the helium atoms will be first brought into the meta-stable $2^{3}S_{1}$ state using a pulsed source with a hot filament and an anode mounted in the front of the valve [114]. This state lives for over 8000 s and lies 20 eV above the ground state and it therefore reduces the amount of required photons to two. The meta-stable atoms will be produced in a vacuum chamber, which is mounted at a 23° angle in the vertical direction. In this way the atoms are directed towards the turbomolecular pump underneath the main chamber and the gas is pumped away quicker. In addition, a fast piezo valve will be used to produce the atomic beam, which emits gas pulses of only $30 \ \mu s$ so that a relatively low gas load is reached while a high pulse density is retained.

The main chamber has 13 ports, of which at least eight are used for optical access. This will enable ground state cooling and ionization along the trap axis. The beryllium atoms can be created from either an oven in the chamber or an ablation target below the trap and will also be non-resonantly ionized in this case with three photons at 355 nm.

Creation of charge patches is a serious concern. Not only because of the excitation beam, as discussed in Sec. 3.2.3, but also because all other wavelengths used in this experiment lie exclusively in the UV spectral range. The ionization laser pulse is at 355 nm and the cooling transition in Be^+ is at 313 nm. Additionally, the internal energy of the meta-stable helium atoms is sufficient to also free electrons from metal surfaces. Therefore, the ion trap will be surrounded by pinholes in all directions of the beams to shield it from scattered photons/atoms. A re-entrant window mounted on the top flange of the main chamber will enable imaging of the Be^+ ion with a high numerical aperture of 0.5. For the experiments described in Chapters 5 and 6, the setup was slightly altered. The source chamber was used to generate a pulsed xenon beam,

and was then placed in the horizontal plane to simplify the alignment. The excited atoms (using RCS) were state-selectively ionized in the center of the interaction chamber. A time-of-flight mass spectrometer was attached to the top flange of this chamber, to isotope-selectively detect xenon ions. Details on the excitation and detection geometry are given in Appendix A.

3.2.5 Vacuum requirements

The demands on the vacuum level in the main chamber are very high, because it determines the lifetime of the ions in the trap. In order to reach a vacuum of $\leq 10^{-10}$ mbar in the ion trap chamber, multiple vacuum pinholes are placed in between the HHG chamber and the spectroscopy interaction zone. By differential pumping, a pressure drop of 6 orders of magnitude is expected.

The first chamber is pumped with a turbo-molecular pump (TMP) (Pfeiffer, TMH 521) with a pumping speed of 500 l/s. The jet is directed towards the pump, but due to the high gas load in the HHG chamber the

average pressure is still at the level of 10^{-4} mbar during operation. The second and third vacuum chamber are pumped (together) by another 500 l/s TMP (Pfeiffer, TMU 521), and a vacuum pinhole (diameter of $1.5 \,\mathrm{cm}$) is placed in between the first and second chamber. This leads to a pressure drop of a factor 100 and therefore a pressure of 10^{-6} mbar in the second and third vacuum chamber. After this the beam propagates through a long tube (70 cm) with a relatively small diameter (38 mm inner diameter) which already leads to a significant reduction of gas load on the fourth chamber. In addition, a small pinhole ($\sim 100 \,\mu m$) will be placed in the focus of the laser beam, which will be used to both spatially filter the excitation beam and to improve the differential pumping further. With a mild bake-out of the fourth chamber and a TMP of 300 l/s (Pfeiffer Vacuum, HiPace300), a pressure of 10^{-9} mbar is then expected. The main chamber is also pumped by a 300 l/s TMP and a 5 mm pinhole is placed in between the connection to the other chambers to improve the differential pumping. In addition, the main chamber will be baked to a high temperature beforehand to reduce the load from hydrogen in the steel as much as possible. The load from the source chamber is reduced by using a skimmer (3 mm) in the atomic beam. In this manner a pressure of $< 10^{-10}$ mbar is expected to be achieved in the main chamber, which leads to a lifetime of at least several hours for the ions in the trap. For the experiments in Chapters 5 and 6, only a moderate vacuum of 10^{-7} mbar was required, which was easily achieved.

3.2.6 UV generation for laser cooling of Be⁺

In addition to the vacuum setup, also the basis for the cooling laser for Be^+ was constructed. Excitation of the cooling transition requires light at 313 nm, which is created using a design similar to that of [115, 116]. A schematic overview of the setup is shown in Fig. 3.18.

The starting point of the system is a set of fiber-based lasers in the nearinfrared spectral range. The first is a commercial ultra-stable erbiumdoped fiber laser at 1542 nm (Menlo Systems GmbH, ORS1500). The cavity is made from ultra-low expansion glass and the linewidth is specified to be < 2 Hz. A part of the output (~ 6 mW) of this laser is split-off and coupled into a 30 m-long single mode fiber. This fiber transports the light to a commercial fiber-based amplifier (NKT Photonics, Koheras



Figure 3.18 – Schematic overview of the cooling-laser system. The setup is based on two amplified fiber lasers, which are combined in a PPLN crystal (PPLN1) to generate the sum-frequency at 626 nm. Subsequently, this light is frequency doubled in an enhancement cavity based on LBO. In addition, the output of the amplified ultra-stable light is frequency doubled in a second PPLN crystal (PPLN2). This serves as a reference and enables monitoring of the Ti:Sa frequency-comb mode linewidth. HW = half-wave plate, DM= dichroic mirror, EOM = electro-optic modulator, PZT = piezo-electric transducer.

Boostik HPA), which can amplify the light to a maximum of 10 W. The fiber link is not stabilized and therefore the linewidth at the output of the amplifier is expected to be broadened to at least a few hundred Hz. The second laser source is extracted from a commercial ytterbium-doped fiber laser system (NKT photonics, Koheras Basic) at 1054 nm with a specified linewidth of 20 kHz and an output power of 10 mW. It is also amplified in a similar fiber amplifier to a maximum power of 5 W. The output beams of these two amplifiers are combined with a dichroic mirror and focussed through a 4-cm-long periodically poled lithium niobate (PPLN) crystal (Covesion MSFG626-0.5-40), where the sum-frequency at 626 nm is generated. The crystal consists of five channels with an aperture of 0.5 mm. In each channel the crystal orientation is reversed with a certain period to achieve quasi-phase matching, see e.g. [117,118].

The required poling period can be coarsely adjusted by selecting a different channel. Fine-tuning of the optimal phase-matching conditions is achieved by tuning the temperature. For this reason, the crystal is placed in an oven of which the temperature is stabilized to 0.01°C. The efficiency of the sum-frequency generation (SFG) stage is defined

$$\eta_{SFG} = \frac{P_{SFG}}{P_{f1} \times P_{f2} \times L},\tag{3.3}$$

where P_{SFG} is the power generated at the sum-frequency, L is the crystal length and P_{f1} and P_{f2} are the power at the two fundamental frequencies f1 and f2, respectively. The efficiency, which was achieved with this setup was $\eta_{SFG} = 1.8 \ \% W^{-1} \,\mathrm{cm}^{-1}$, which is slightly below what was reported in [115, 116]. This is possibly caused by the less than optimal matching of beam sizes of the two fundamental beams. However, without pushing the amplifiers to their maximum capacity, sufficient power levels at 626 nm were reached to perform the future experiments. At typical operating conditions, both amplifiers were set to emit 5 W of infrared light, which led to the production of 2 W at the sum-frequency. The generated light at 626 nm is subsequently frequency doubled in a lithium triborate (LBO) crystal to generate the required 313 nm light. For this stage, an enhancement cavity is used with a finesse of ~ 200 . The choice for LBO was made because it has a significantly lower walkoff angle than beta-barium borate (BBO), which is typically used for this purpose, and therefore produces light with a better beam quality. The cavity has a bow-tie geometry with two curved mirrors that focus the beam in the crystal, which was cut at the Brewster angle to reduce reflection losses. In addition, an anti-reflection coating was applied to both the entrance and exit surface of the crystal and the crystal was heated to 45°C to protect it from surface degradation due to hygroscopic effects. The input coupler (1.2% transmission) is matched with the intra-cavity losses to achieve proper impedance matching. The other flat mirror is mounted on a piezo-electric transducer to provide feedback to the cavity length. The locking signal is produced with a Pound-Drever-Hall (PDH) scheme. For this purpose, an electro-optical modulator (EOM) was placed in the 626 nm beam to generate side bands at 23.5 MHz from the carrier.

as



Figure 3.19 – The generated 313 nm second harmonic output power (blue points) as a function of light that was coupled into the cavity at 626 nm and the corresponding conversion efficiency (red points). The linear fit (blue line) indicates the saturated regime where the conversion losses are significant and the conversion efficiency approaches a constant value of 30% (red dotted line).

The generated UV power as a function of input power is shown in Fig. 3.19 together with the corresponding SHG efficiency. At low incident power, the intra-cavity losses are low and the circulating power in the cavity increases linearly. This leads to a quadratic increase of the generated second-harmonic power. At higher fundamental power the conversion increases and the losses become more significant, leading to only a linear increase of UV power. In this regime, a constant conversion efficiency of slightly below 30% was observed. The maximum achieved output power at the second-harmonic is 450 mW. Note that the amplifiers were not yet pushed to their maximum output and therefore more power could still be extracted if necessary.

Another important parameter for future experiments in He⁺ is the stability of the generated light, because the readout of the experiment relies on it. For this purpose, the output was monitored over a period of 100 minutes. The result is shown in Fig. 3.20. The observed RMS stability of the harmonic beam was 1.3 %. There are some clear power drops visible, indicating that the cavity was shortly out of lock. Drifts on



Figure 3.20 – Stability measurement of the output power of the cavity over a time span of 100 minutes. The observed RMS stability was 1.3 %.

timescales of a few seconds can be actively compensated with an additional acousto-optic modulator.

The achieved stability and output power is a good basis for laser cooling of Be⁺. However, a lot of work is still required to produce a cold trapped Be⁺ ion. The ion first needs to be cooled down to the Doppler limit of ~ 1 mK using a Doppler cooling scheme, after which it needs to be cooled down further to the quantum mechanical ground state of the trap using a Raman-scheme. For this purpose a variety of acoustoand electro-optic modulators will be added to the setup to generate the required frequencies. Then the different beams will be transported through several UV-compatible single-mode fibers [119] to the trap, to decouple the alignment of the laser system and the ion trap.

In addition to the cooling-laser system, a fraction of the amplified ultrastable laser at 1542 nm is split-off and frequency doubled to 771 nm using a second 2-cm-long PPLN crystal (see Fig. 3.18). This light can be used to optically lock the Ti:sapphire frequency comb (Sec. 3.1.1) to achieve narrower FC modes (a few hundred Hz). In this way the noise on the repetition rate, induced by mechanical vibration and electronic noise on the cavity, can be reduced and much longer coherence times (> 500 ns) can be reached in RCS with the Ti:Sa based setup.

The generated frequency-doubled light was so far only used to measure
the linewidth of the FC laser by making a heterodyne beat. After vibration isolation and optimization of the repetition-rate lock, a linewidth of 150 kHz (FWHM) was observed. However, the current feedback does not allow for a direct optical lock with the ultra-stable laser, because the mechanism is not fast enough. In the future, this should be possible with a newly developed high-current piezo driver and a low-noise, high bandwidth PID-controller.



Deep-UV frequency metrology of H_2 for tests of molecular quantum theory

Abstract

Molecular hydrogen and its isotopic and ionic species are benchmark systems for testing quantum chemical theory. Advances in molecular energy structure calculations enable experimental verification of quantum electrodynamics and potentially a determination of the proton charge radius from H₂ spectroscopy. We have measured the ground state energy in ortho-H₂ relative to the first electronically excited state by Ramsey-comb laser spectroscopy on the $EF^1\Sigma_g^+$ - $X^1\Sigma_g^+(0,0)$ Q1 transition. The resulting transition frequency of 2 971 234 992 965(73) kHz is two orders of magnitude more accurate than previous measurements. This paves the way for a considerably improved determination of the dissociation energy (D_0) for fundamental tests with molecular hydrogen.

This chapter is based on: Deep-UV Frequency Metrology of H_2 for Tests of Molecular Quantum Theory, R.K. Altmann, L.S. Dreissen, E.J. Salumbides, W. Ubachs, K.S.E. Eikema Physical Review Letters **120**, 043204 (2018)

4.1 Introduction

The fully quantized version of electrodynamics (QED) constitutes an important part of the standard model and is arguably the best tested theory in physics, based (among other experiments) on spectroscopic measurements of atomic hydrogen [56, 120, 121]. The molecular counterpart, H₂, has served as the model system for molecular quantum theory dating back to 1927 when Heitler and London first explained the existence of a bound state between two hydrogen atoms [122]. Although the increased complexity of the electronic structure and the additional vibrational and rotational degrees of freedom impose serious theoretical and experimental challenges, it also provides additional opportunities to explore new physics. Measurements of various level energies [31, 32, 123–126] are in excellent agreement with the most recent theoretical predictions [127–129]. Comparisons between the experimental results and theory provide constraints on possible physics beyond the standard model, such as hypothetical fifth forces and extra dimensions [34–36, 130]. In particular the dissociation energy of molecular hydrogen $D_0(H_2)$ serves as an important benchmark number for molecular quantum physics, and it has stimulated improvements by seven orders of magnitude in its experimental and theoretical determinations over nearly a century [131]. On the theoretical side a number of refined calculations have been performed to verify and improve the initial results [132]. The Born-Oppenheimer potential of H_2 was calculated to 10^{-15} precision [133], the adiabatic correction was improved by three orders of magnitude to $3 \times 10^{-7} \,\mathrm{cm}^{-1}$ [128], non-adiabatic corrections of rovibrational levels were calculated to $10^{-7} \,\mathrm{cm}^{-1}$ precision [129], the $m\alpha^6$ QED corrections were explicitly calculated [28], and methods to solve the Schrödinger equation were improved [134]. This heroic program led to a value of $D_0(H_2) = 36118.0691(6) \text{ cm}^{-1}$, which is more accurate but consistent with the initial value [132]. Moreover, recent breakthroughs in calculating molecular structure and QED now indicate that it will become feasible to determine the proton-charge radius from a sufficiently accurate determination of $D_0(H_2)$ [28, 134]. This is particularly interesting in view of the proton-charge radius puzzle [8, 21, 135–137].

To obtain an experimental value of D_0 , it can be related to the ion-



Figure 4.1 – Simplified energy level diagram of H₂. Interesting numbers in view of testing molecular-QED are e.g. the dissociation energy (D_0) and the fundamental ground tone (FGT). For this purpose we measured the deep-ultraviolet two-photon Q1 line, as indicated on the left.

ization energy $E_I(H_2)$ via a thermodynamic cycle involving the well known atomic ionization energy $E_I(H)$ and also well known dissociation energy of the ion $D_0(H_2^+)$ [31]. The value $E_I(H_2)$ can in turn be determined experimentally by measuring two frequency intervals (EF - Xand $54p1_1 - EF$) by laser spectroscopy, and as a third step, extrapolation of the np-Rydberg series measured with millimeter wave excitation [38]. In Fig. 4.1 the energy intervals and their relations are shown to obtain a new value for $D_0(H_2)$) by measuring $E_I(H_2)$ (see also [131]).

Previous experimental values for D_0 [31] were found to be in good agreement at a level of 0.0004 cm⁻¹ (12 MHz) with molecular quantum calculations [132]. Agreement was also obtained for D₂ [123], and both results featured thereupon in interpretations in terms of constraints on fifth forces [36] and extra dimensions [35] for typical intra-molecular distances at the 1 Å scale.

In this chapter we report on a determination of the $EF^1\Sigma_a^+ - X^1\Sigma_a^+(0,0)$

Q1 transition in H₂ (as discussed before, an essential ingredient for determining $D_0(H_2)$) with a nearly two orders of magnitude improved accuracy compared to previous measurements [37,138]. We employ Ramseycomb two-photon spectroscopy [73,77] in the ultraviolet at 201.80 nm, achieving a fractional uncertainty of 2.5×10^{-11} .

4.2 Method

Our experimental approach is based on Ramsey-comb spectroscopy [73, 77], combining Ramsey's method of separated oscillatory fields [74] with frequency-comb lasers [9,10]. This method utilizes interference between two excitation contributions in an atom or molecule induced by two time-delayed coherent laser pulses. It leads to a variation of the excited state population ($|c_e|^2$) as a function of pulse delay (t) and pulse phase difference ($\Delta \phi$) according to:

$$|c_e(t,\Delta\phi)|^2 \propto \cos\left(2\pi f_{tr}t + \Delta\phi\right) \tag{4.1}$$

The transition frequency (f_{tr}) can be determined from this signal, provided that t and $\Delta \phi$ are known with sufficient precision [71,72]. Frequency-comb lasers are therefore a convenient source of light pulses as their repetitive pulsed output (with spacing T_{rep}) and controlled phase slip between successive pulses (the carrier-envelope phase slip $\Delta \phi_{ce}$) can be referenced with high accuracy to an atomic clock.

To increase the pulse energy of frequency combs for nonlinear frequency up-conversion, amplification and enhancement resonators have been employed to increase the pulse energy to the μ J level at full repetition rate [52,83,139,140]. In contrast, our method relies on the amplification of only two pulses, enabling orders of magnitude higher pulse energy (>mJ). By choosing pulse pairs with a delay of multiples of T_{rep} , and scanning the pulse delay on a much smaller scale using adjustments of T_{rep} via the comb laser, a series of Ramsey signals starting at time delays $t = T_0 = \Delta N T_{rep}$ is obtained. Here ΔN is an integer, denoting the delay expressed in the number of comb laser pulses. Combining a series of Ramsey signals for different ΔN constitutes a Ramsey-comb measurement [77]. The transition frequency is obtained from it by analyzing only the relative phase evolution between the Ramsey signals [73]. As



Figure 4.2 – Schematic overview of the experimental setup. Amplified comb pulse pairs are frequency up-converted in sequential doubling (SHG) and mixing (SFG) stages in BBO. Between each stage a special waveplate $(\lambda_1 \text{ and } \lambda_2)$ rotates the polarization to maintain type-I phase matching. The generated 201.80 nm beam is split equally by a metallic beamsplitter (BS) where they recombine again after one roundtrip to form a Sagnac interferometer (SI). The molecular beam is formed from a pulsed supersonic expansion and is collimated by a skimmer and subsequent slit aperture.

a consequence, the measurement becomes insensitive to any phase shift that is independent of ΔN . This includes a possible constant phase shift caused by amplification and nonlinear up-conversion of the frequencycomb pulses, and also phase shifts induced in the atom by the laser-atom interaction (the ac-Stark shift), provided that the pulse energy is constant as a function of ΔN . The accuracy of the method is mainly limited by the maximum time delay that one can experimentally achieve and the accuracy of how constant $\Delta \phi$ is as a function of ΔN .

4.3 Experimental setup

The starting point of the experimental setup is a Kerr-lens mode-locked Ti:sapphire frequency-comb laser, operating at a repetition time of $T_{rep} =$

7.9 ns ($f_{rep} = 1/T_{rep} = 126$ MHz). Both T_{rep} and $\Delta \phi_{ce}$ are actively stabilized and referenced to a cesium atomic clock (Symmetricon CsIII 4310B) to provide an absolute time and frequency calibration. The comb laser pulses are chirped by 2.5×10^6 fs² of second-order dispersion in a 4f-grating based stretcher for chirped-pulse amplification. In addition, an adjustable slit placed in the Fourier plane of the stretcher selects only 0.2 - 0.3 nm bandwidth of the frequency-comb spectrum centered around 807.18 nm, resulting in pulses of approximately 10 - 15 ps duration and an energy of 40 pJ. The small bandwidth is chosen to only excite the Q1 line in H_2 , and avoid excitation of the nearby Q0 and Q2 lines, which are at respectively 806.73 nm and 808.09 nm in terms of the fundamental frequency-comb wavelength (see Fig. 4.1). Only two comb pulses are selectively amplified (at a repetition rate of 28 Hz) in a noncollinear optical parametric chirped-pulse amplifier (NOPCPA) to a pulse energy of 2.4 mJ (for details see [92, 107, 141]). The amplified pulses are up-converted to the fourth harmonic by frequency doubling and two stages of sum-frequency mixing to produce $62 \,\mu J$ of $201.80 \,nm$ radiation, see Fig. 4.2.

The two-photon transition is excited with counter-propagating pulses to suppress the first-order Doppler shift. In both arms a quarter wave plate is used to convert linear to circular polarization. Together with the strong chirp on the pulses [66, 67], this suppresses unwanted (Doppler shifted) excitation from a single side by a factor of ten. The intersection point of the ultraviolet pulses is crossed at right angles with a beam of hydrogen molecules generated from a collimated pulsed supersonic expansion. A pulse at 355 nm provides state-selective ionization, and the created H_2^+ ions are extracted through a 25 cm time-of-flight drift tube and detected with a combination of an electron multiplier (ETP AF880) and a boxcar integrator (Stanford Research SR250).

4.4 Phase stability measurement

The well-defined phase relation of the original frequency-comb pulses can be distorted by the amplification process, and any delay-dependent component ($\delta\phi_{res}$) will lead to a frequency shift proportional to $\delta\phi_{res}/\Delta NT_{rep}$ [92]. We verify the phase of the amplified pulses using spec-



Figure 4.3 – Measurements of the relative phase shift between the first and second excitation pulse in the infrared as a function of delay time between the pulses. Measurements for various bandwidths from 3 nm down to 0.4 nm (two sets) were performed (indicated by the different markers and colors). No systematic effects as a function of bandwidth are observed.

tral interferometry with the unamplified comb laser pulses [73,77]. The optimum bandwidth of the laser pulses (0.2 - 0.3 nm) for H₂ excitation reduces the number of spectral fringes in the phase measurement, hampering its accuracy. Therefore we measured the phase effects for bandwidths ranging from 3 nm down to 0.4 nm, as shown in Fig. 4.3. The calculated frequency shifts for these measurements are between -26 kHz and 42 kHz, all with an uncertainty of 40 kHz, and do not show any significant trend. Therefore we take the value of 14(40) kHz at $\Delta \lambda = 0.4 \text{ nm}$ to be representative, as it is closest to the 0.2 - 0.3 nm bandwidth used for the excitation.

4.5 Results

In Fig. 4.4 an example of a Ramsey-comb measurement is shown where the pulse delay is varied up to a maximum time delay of 380 ns, corresponding to a separation of $\Delta N = 48$ pulses. At each ΔN the repetition time is scanned over a range of 600 as to observe \sim 1.5 period of the Ramsey signal. The uncertainty of the data points is based on the fluctuations of the ion signal averaged over 500 laser shots. The reduction of the signal and modulation contrast as a function of delay is caused by effects such as the laser linewidth, Doppler broadening, transit time, and the lifetime of the excited state ($\approx 200 \text{ ns}$ [142]). A typical Ramseycomb measurement consist of sets of three or four Ramsey-scans over a maximum time delay between 181 and 221 ns, which is chosen for optimal signal-to-noise and speed of measurement to minimize the influence of drifts. To avoid a systematic effect on the frequency determination we always skip $\Delta N = 1$, to bypass any transient effects, and the measurements were performed in random order (within a ΔN), spread out over many days. One Ramsey-comb measurement typically has a statistical uncertainty of 45 kHz (for details on the signal analysis procedure see Sec. 2.5.2.3 and [73]). However, the observed transition frequencies fluctuated more than expected based on the 1σ uncertainty of a single measurement. Because no statistically significant correlation could be found with any of the experimental parameters, the uncertainty of each measurement was increased by a Birge factor [143,144] of 1.9 to correctly account for the true statistical uncertainty.

4.5.1 Doppler shift

Concerning systematic effects besides phase shifts discussed before, the Doppler effect is one of the more prominent. The speed of hydrogen molecules from a supersonic expansion at 311 K is 2530 m/s, and therefore the first- and second-order Doppler shift have to be carefully considered. The excitation geometry strongly suppresses the first-order Doppler shift, but a residual first-order Doppler shift can still be present due to an asymmetry in the spectrum, a chirp induced first-order Doppler shift [56] or a residual angle between the two counter-propagating beams. As a first step to minimize these effects the counter-



Figure 4.4 – Example of a Ramsey-comb measurement with a step size of $\Delta N = 5$, where each Ramsey scan starts at $T_0 = \Delta N T_{rep}$. The signal is shown as blue data points and the fit (red line) is based on Eq. (4.1).

propagating beams are aligned as parallel as possible by observing a dark fringe at the output port of the Sagnac interferometer (see Fig. 4.2). Any residual Doppler effect after this procedure (on the order of $\pm 200 \,\mathrm{kHz}$) is detected by changing the velocity of the molecular beam. To this end the nozzle is cooled to 97 K by liquid nitrogen, leading to a most probable velocity of 1420 m/s. The Doppler-free transition frequency can then be determined by extrapolating the measured transition frequencies at both temperatures to zero velocity (taking a $\pm 10\%$ velocity uncertainty into account). In this procedure the second-order Doppler shift correction of 107 and 33 kHz for 2530 and 1420 m/s was taken into account. In total seven sets of measurements were obtained to determine the Doppler-free transition frequency, each consisting of 20 or more Ramsey-comb measurements at both temperatures (and therefore velocity). All measurements are in agreement with each other within the statistical uncertainty, leading to a weighted average of all measurements (before other corrections) of 2971234992948(60) kHz.



Figure 4.5 – Light shift measurements (see text). Each point is the ac-Stark shift at $62 \,\mu J$ per pulse, based on an extrapolation to zero energy from measurements performed at $18 \,\mu J$ and $62 \,\mu J$ per pulse. The different colors indicate measurements taken on different days and each data point consist of at least four Ramsey-comb measurements.

4.5.2 ac-Stark shift

Although the Ramsey-comb method is to first order insensitive to effects proportional to the pulse energy (such as the ac-Stark effect or phase shifts in the up-conversion) a residual light shift might still be present. We test this by measuring the transition frequency at pulse energies of 18 μ J and 62 μ J (the energy at which all other measurements where performed, within 5%). Extrapolation to zero intensity then gives the shift at 62 μ J pulse energy. In total 91 determinations of this kind are taken into account, each consisting of at least four Ramsey-comb measurements (Fig. 4.5). The resulting light shift correction is 3(13) kHz, showing that the Ramsey-comb method is for all practical purposes ac-Stark shift free.

4.5.3 dc-Stark shift

A dc-Stark shift is avoided by ramping-up the ion-extraction fields after the ionization pulse. The uncertainty for any residual electric field during the excitation is ± 0.17 V/cm. By comparing with measurements at a static electric field of 8.33 V/cm we determined a possible frequency shift of 0(2) kHz due to dc electric fields.

4.5.4 Zeeman shift

To avoid a possible Zeeman-shift the magnetic field is measured and minimized with additional coils to a precision of 0.2 G. A possible shift due to a residual magnetic field was determined by comparing with measurements at a magnetic field strength of 6 G in directions parallel and orthogonal to the polarization of the excitation pulses. No Zeemanshift was detected, leading to an uncertainty due to this effect of 2 kHz. It should be considered that for ortho-hydrogen the total nuclear spin I = 1, which leads to hyperfine structure in the Q1 line. The splitting in the ground state is too small ($\leq 500 \text{ kHz}$) to be observed [145], and in the excited state even unknown. Therefore the presented value is a weighted average of the hyperfine components of the Q1 line. The Q0 transition from the true ground state in para-hydrogen does not have hyperfine structure, but is three times weaker for unpolarized hydrogen. For this reason Q1 was measured in previous experiments, and therefore also in the current one.

4.6 Conclusions

Taking all effects into account results in a transition frequency of 2971 234 992 965(73) kHz for the $EF^1\Sigma_g^+ \cdot X^1\Sigma_g^+(0,0)$ Q1 transition in ortho-H₂ (see Table 4.1). The relative uncertainty of this result is 2.5×10^{-11} , and is in agreement with the previous measurement [37], but two orders of magnitude more accurate (see Table 4.2). The new two-photon transition frequency of the Q1 line of ortho-hydrogen can be used to obtain an improved value for the (rotationless) dissociation energy $D_0(H_2)$ of para-hydrogen, using the procedure shown in Table 4.2 [31]. The result is consistent with previous experimental determinations and theory (Table 4.2). However, in a recent study a complete calculation of the relativistic corrections was targeted to reach a full-fledged molecular quantum calculation [29]. In [132] the relativistic correction was partially based on an older study [146]. The new refined calculation surprisingly produces a disagreement of 50 MHz (0.0017 cm⁻¹)

Table 4.1 – Contributions (in kHz) to the measurement of the Q1 transition frequency in H_2 . The light induced effects include the ac-Stark shift and nonlinear effects.

	Value or correction	(1σ)
Doppler-free transition frequency	$2\ 971\ 234\ 992\ 948$	(60)
Light induced effects	3	(13)
dc-Stark shift	0	(2)
Zeeman-shift	0	(2)
Amplifier phase shift	14	(40)
Total	$2\ 971\ 234\ 992\ 965$	(73)

with the previous and current experimental values, equal to 2.4σ (see Table 4.2). However, as the authors state, this disagreement is to be considered preliminary since relativistic nuclear recoil corrections have not yet been reliably calculated. Our result now shows that possible deviations are not due to measurements of the EF - X interval, given its new highly accurate value.

The full potential of our measurement can only be reached if the energy separation between $X^+ - EF$ is improved to a level comparable with 70 kHz or better, to bring down the uncertainty of D_0 (H₂). This will enable to put further constraints on the strength of fifth forces [34] and on the compactification sizes of extra dimensions [35]. Moreover, given the ≈ 200 ns lifetime of the excited state it seems feasible to ultimately reach 10 kHz accuracy on the Q0 transition (instead of Q1 to eliminate the influence of hyperfine structure). A theoretical and experimental comparison at this level would enable a determination of the proton-charge radius with an accuracy of 1%, therewith resolving the proton-charge radius puzzle. Furthermore, another benchmark test of molecular quantum theory, the determination of the fundamental ground tone splitting (see Fig. 4.1), can be considerably improved now with a measurement of the $EF^1\Sigma_a^+$. $X^1\Sigma_a^+(0,1)$ Q0 transition.

\mathbf{H}_2	sn	
ra-]	vio	
pa	pre	
and	the	
\mathbf{I}_2	$^{\mathrm{th}}$	
Io-F	wi	
srth	red	
of c	npa	
ial	con	
ent	are	
pot	rk	
on	ΜO	
zati	his	
zinc	in t	
ie ie	ed	
f tŀ	ain	
n o	obt	
atio	ues	
inŝ	val	
ern	he	
det	н Ц	
the	sted	ues.
or t	trac	val
ls f	eх	cal
rva	2 IS	reti
inte	Ъ-Н	leoi
Sy	para	it tl
ner	of]	ates
ıt e	D_0	le lá
var	ch	l th
tele	whi	anc
н 	Ш	ion
1.2	frc	nat.
le	n^{-1}	rmi
ab	l CĽ	etei
F	п.	Ū.

$Transition^a$	Previous	results	This result	Theory	Deviation
(1) $EF \leftarrow X$	$99\ 109.731\ 39(18)$	37	$99 \ 109.731 \ 204 \ 9(24)$		$0.000\ 19(18)$
(2) $54p1_1 \leftarrow EF$	$25\ 209.997\ 56(29)$	31			
$(3) \ X^+ \leftarrow 54p1_1$	$37.509\ 013(10)$	38			
$(4)E_{\rm I}^{\rm ortho} = (1) + (2) + (3)$	$124\ 357.237\ 96(34)$		$124\ 357.237\ 78(29)$		$0.000\ 19(45)$
(5) X(0,1) - X(0,0)	$118.486\ 84(10)$	[147]			
(6) $X^+(0,1) - X^+(0,0)$	$58.233\ 675\ 1(1)\ [1_4$	48 - 150			
(7) $E_{\rm I}^{\rm para} = (4) + (5) - (6)$	$124\ 417.491\ 13(36)$		$124\ 417.490\ 94(31)$		$0.000\ 19(47)$
(8) $D_0(H_2^+)$	$21\ 379.350\ 232(49)$	[31]			
(9) $E_I(H)$	$109\ 678.771\ 742\ 6(10)$	[31]			
$D_0 = (7) + (8) - (9)$	$36\ 118.069\ 62(37)$	[31]	$36\ 118.069\ 45(31)$	$36\ 118.069\ 5(10)\ [132]$	$0.000\ 1(10)$
				36118.0691(6) [28]	-0.0004(7)
				36118.0678(6) [29]	-0.0017(7)

^aThe table was adjusted with respect to the published version in [78] to correct for the errors it contained and elaborate on the procedure which is used to determine D_0 .

CHAPTER 5

High-precision Ramsey-comb spectroscopy based on high-harmonic generation

Abstract

High-harmonic generation (HHG) is widely used for up-conversion of amplified (near) infrared ultrafast laser pulses to short wavelengths. We demonstrate that Ramsey-comb spectroscopy, based on two such pulses derived from a frequency-comb laser, enables us to observe phase effects in this process with a few mrad precision. As a result, we could perform the most accurate spectroscopic measurement based on light from HHG, illustrated with a determination of the $5p^6 \rightarrow 5p^58s\ ^2[3/2]_1$ transition at 110 nm in 132 Xe. We improve its relative accuracy 10⁴ times to a value of 2.3×10^{-10} . This is 3.6 times better than shown before involving HHG, and promising to enable 1S - 2S spectroscopy of He⁺ for fundamental tests.

This chapter is based on: *High-Precision Ramsey-Comb Spectroscopy Based on High-Harmonic Generation*, L.S. Dreissen, C.F. Roth, E.L. Gründeman, J.J. Krauth, M. Favier, and K.S.E. Eikema, *Phys. Rev. Lett.* **123**, 143001 (2019)

5.1 Introduction

High-precision spectroscopy in calculable atomic and molecular systems is at the heart of the most precise tests of bound-state quantum electrodynamics (QED) and searches for new physics beyond the Standard Model [7,79,130,151–153]. Instrumental in this development was the invention of the optical frequency comb (FC) [9,10] which enables precise optical frequency measurements referenced to an atomic clock. However, uncertainties in finite nuclear-size effects are hampering further progress [154]. Instead, spectroscopy has been used to measure the proton size in atomic and muonic hydrogen, but with partly conflicting results [20, 21, 23, 24, 135–137]. High-precision spectroscopy of the 1S - 2S transition in He⁺ would provide new possibilities for fundamental tests as the uncertainty there is less dominated by nuclear size effects [27]. Combined with muonic He^+ spectroscopy [25, 26] one can extract e.g. the alpha particle radius or the Rydberg constant. A major experimental challenge arises from the requirement of extreme ultraviolet (XUV) light at 60 nm (or shorter), to excite the transition. A similar challenge exists for spectroscopy of highly-charged ions [152], or the Thorium nuclear clock transition near 150 nm in the vacuum ultraviolet (VUV) [155, 156]. At those wavelengths a relative accuracy of 0.1 ppm has been achieved with Fourier-transform spectroscopy techniques [157], and 0.03 ppm with low harmonics from nanosecond pulsed lasers [46]. A higher accuracy can be reached with light from high-harmonic generation (HHG), induced by focusing ultra-fast high-energy laser pulses in a noble gas at intensities of $\sim 10^{14} \,\mathrm{W/\,cm^2}$. The process can be understood using the three-step model [80,81], involving tunnel-ionization and recollision of an electron. This highly coherent process leads to the generation of a series of odd harmonics, which are tightly linked to the fundamental wave [52, 53, 140, 158, 159]. In combination with frequencycomb lasers, it has been used to achieve a spectroscopic accuracy of about 1 ppb at VUV and XUV wavelengths [72,83].

To improve on this we recently developed the Ramsey-comb spectroscopy (RCS) method [73,76], based on pairs of powerful amplified FC pulses in a Ramsey-type [74] excitation scheme. Using only two pulses can compromise the accuracy provided by the FC laser [72], but the differential nature of RCS leads to the recovery of this accuracy [73] and also to a

strong suppression of the influence of the ac-Stark (light) shift. Other advantages of RCS compared to spectroscopy using cavity-based FC up-conversion [52, 53, 140] include easy tunability, simple up-conversion in a gas jet (no resonator required), a high excitation probability and a nearly 100% detection efficiency. RCS has been demonstrated successfully at wavelengths ranging from the near-infrared (NIR) [73], to the deep-ultraviolet, using low-order nonlinear up-conversion in crystals [77, 78].

Extending RCS to shorter wavelengths with HHG is not trivial because a dynamic plasma is produced in HHG. This can lead to a reduced HHG yield and a time-dependent influence on the phase (and phase-matching) of the generated harmonics [82,100,160], and therefore errors in the extracted transition frequency. Plasma effects in HHG have been investigated at picosecond-timescales, showing a nearly instantaneous response based on electron dynamics [161,162], but not at longer timescales relevant for precision spectroscopy.

In this chapter we show that the phase evolution of an atomic excitation obtained from RCS can be used to investigate the phase influence of plasma formation in HHG. We can monitor this on a nanosecond timescale and with mrad phase sensitivity. The results obtained at 110 nm (the seventh harmonic of 770 nm) show that most of the phase effects are caused by free electrons in the plasma and therefore strongly decrease within a few nanoseconds. Under the right conditions, the effects can be made negligibly small, enabling spectroscopy with unprecedented accuracy using radiation from HHG. This is demonstrated with a measurement of the $5p^6 \rightarrow 5p^58s \ ^2[3/2]_1$ transition in xenon with a relative accuracy of 2.3×10^{-10} .

5.2 Method

Ramsey-comb spectroscopy [73, 76] requires phase and time-controlled laser pulses. The output of a FC laser [9, 10] is the ideal source for this as both the repetition time T_{rep} and carrier-envelope phase evolution $\Delta \phi_{ce}$ of the pulses can be referenced to an atomic clock. For two pulses that are resonant with a two-level system at a transition frequency f_{tr} , each excitation pulse can be thought to induce a superposition of the ground and excited state. These contributions interfere depending on the phase evolution $2\pi f_{tr}\Delta t$ of the superposition state (where Δt is the pulse delay) and the phase difference $\Delta \phi$ between the two laser pulses (which includes $\Delta \phi_{ce}$). The excited state population after the second laser pulse can be written as $|c_e(\Delta t, \Delta \phi)|^2 \propto \cos(2\pi f_{tr}\Delta t + \Delta \phi)$. When a scan of T_{rep} is made on a femtosecond or attosecond timescale, the effect of the phase evolution on $|c_e|^2$ can be observed in the form of a Ramsey fringe. A series of these fringes can be obtained at different multiples of the repetition time $(\Delta N \times T_{rep})$ by selecting different pairs of pulses. The transition frequency is then extracted from the phase difference between these Ramsey fringes [76], which leads to a cancellation of any induced, but constant, phase shift. This includes the optical phase shift between the two pulses (e.g. from amplification), but also the ac-Stark light shift of the energy levels for a constant pulse energy [78].

5.3 Experimental setup

The starting point of the laser system is a mode-locked Ti:sapphire FC laser ($T_{rep} = 7.9$ ns) which is referenced to a Cs atomic clock (Symmetricon CsIII 4310B). The pulses are spectrally filtered within a 4f-grating stretcher to a bandwidth of 8-10 nm centered around 770 nm to avoid excitation of neighboring transitions.

A Non-collinear Optical Parametric Chirped Pulse Amplifier (NOPCPA), based on 3 Beta-Barium Borate (BBO) crystals, is used to selectively amplify two of the FC pulses. The delay between these pulses is an integer multiple of T_{rep} and depends on the settings of a home-built doublepulse pump laser at 532 nm [92,107]. A typical energy of 2 mJ/pulse is reached after recompression to a ~220 fs pulse length. HHG is performed (see Fig. 5.1) by focusing (f = 25 cm) the beam (4 mm FWHM diameter) in an argon gas jet. A central beam block of 1 mm diameter is used to convert the intensity profile of the fundamental beam to a donut-like shape before HHG. This enables efficient separation of the fundamental and harmonic beam with an adjustable iris after HHG, because the harmonics travel on axis and with a much lower divergence than the fundamental beam. A LiF plate blocks harmonics with $\lambda < 105$ nm,



incidence. Xenon atoms from a pulsed source are excited at 90° angle to reduce the first-order Doppler effect. An Figure 5.1 – Schematic of the HHG-RCS setup. A pair of pulses from a Ti:Sa FC laser is selectively amplified at jet (shown 90° rotated). The seventh harmonic is refocused using a pair of toroidal mirrors (M1 and M2) at grazing ionization pulse at 1064 nm is delayed by 2 ns with respect to the last excitation pulse and selectively ionizes the different multiples of the repetition time $(\Delta N \times T_{rep})$ in a NOPCPA. They are up-converted using HHG in an argon excited atoms. After pulsed field extraction, the ions are detected with an ETP AF880 electron multiplier (EM)at the end of a 47 cm long time-of-flight (TOF) drift tube. G = grating (3600 lines/mm).

while the seventh harmonic at 110 nm is transmitted with an efficiency of 40%. The beam is subsequently refocused using a pair of grazingincidence gold-coated toroidal mirrors, acting as a 1:1 telescope. The refocused VUV beam is crossed at 90° with a pulsed supersonic beam of xenon (backing pressure 500 mbar, pulse length $\approx 40 \,\mu$ s). Excited atoms are detected by state selective ionization with a 3 mJ pulse at 1064 nm, and the resulting ions are recorded isotope-selectively with a time-offlight mass separator. Despite previous reports of Xe cluster formation in supersonic expansions [163, 164], no evidence for it was found in our experiment, even after many tests with different skimmers and valves. A more extensive overview of the excitation and detection configuration is given in Appendix A.

5.4 Results

A typical RCS scan of ¹³²Xe with $\Delta N = 1-4$ is shown in Fig. 5.2. Most measurements were done with only a pair of Ramsey fringes (e.g. $\Delta N =$ 2 and $\Delta N = 4$), taking just 6.6 minutes, to minimize the influence of possible drifts. For the same reason, the data points were recorded in random order and sorted according to pulse delay afterwards, instead of a sequential scan as was done in previous RCS experiments.

The contrast of the Ramsey fringes $(80 - 90\% \text{ for } \Delta N = 1)$ decreases notably as a function of ΔN . This is partly caused by the limited upperstate lifetime of $\approx 22 \text{ ns}$ [165], Doppler effects, and a 50 - 70 mrad rms phase noise of the amplified FC pulses. However, the decay of contrast was dominated by the limited transit time of the xenon atoms through the focused VUV beam. Therefore astigmatism was introduced to increase the interaction time from 16 ns (focus diameter 15 µm) to 32 ns (30 µm) at the expense of a maximum local wavefront tilt of ≈ 1.5 mrad. This was inferred from the fundamental beam profile in the focal plane. The combination of HHG with the refocusing optics revealed a subtle but interesting effect originating from the NOPCPA. An intensity (and alignment) dependent spatial walk-off induced effect led to a slight difference in beam pointing (<0.5 mrad) between the two amplified pulses (for more detail see Sec. 2.3.2.2). This reduced the overlap between the two refocused VUV pulses and further limited the interaction time



Figure 5.2 – Typical Ramsey-comb scan of the $5p^6 \rightarrow 5p^58s\ ^2[3/2]_1$ transition at 110 nm in 132 Xe. ΔN refers to the inter-pulse delay in multiples of $T_{rep} = 7.9$ ns of the FC and T_0 indicates the initial delay. The individual data points are obtained by averaging over 700 laser shots, which leads to a measurement time of 3.3 min/fringe. The fringes are fitted with a fixed frequency to determine their phase.

with the atoms. It also led to a strong, initially unexplained, day-to-day variation of Ramsey signal contrast. After implementation of a walk-off compensating configuration [97] in the first two passes of the amplifier (Sec. 3.1.3.2), the beam pointing difference was reduced to below 20 μ rad (see Fig. 3.9). This was a crucial step to be able to combine HHG with RCS. In previous RCS experiments with low harmonics in crystals [73,77,78], the walk-off induced beam pointing difference had little effect and went unnoticed because mm-size, collimated beams could be used.

5.4.1 Plasma induced phase effects

With the aforementioned improvements, the influence of the generated plasma in the HHG process on the phase of the VUV light could be measured. For this we investigated the phase dependence of the Ramsey fringes on different conditions in the HHG process.

In Fig. 5.3(a) the phase at $\Delta N = 1,3$ and 4 relative to $\Delta N = 2$ as a function of the driving intensity is shown. This intensity was deter-



Figure 5.3 – The influence of plasma-induced effects from HHG on the phase and the intensity of the second VUV pulse. (a) The phase difference between $\Delta N = 2$ (reference) and $\Delta N = 1, 3$ and 4 as a function of driving intensity. The data is fitted with $\phi \propto I^7$ and the shaded area indicates the 1σ uncertainty. The dashed line shows the intensity I_0 at normal operation and the inset shows a zoom-in at this value. (b) The intensity of the second VUV pulse as a function of delay for different driving intensities. (c) The harmonic yield of the two pulses and their sum as a function of driving intensity. The lines connecting the data points are splines to guide the eye.

mined from the measured pulse energy, beam waist and pulse length (using frequency-resolved optical gating). We have chosen the phase at $\Delta N = 2$ as a reference, because the dynamics changes markedly at this delay (15.8 ns) and the signal quality was better than for the larger delays. The observed phase shift as a function of the intensity shows a

near-exact seventh-order dependence (see fitted curves in Fig. 5.3(a)). At $\Delta N = 1$, a maximum phase shift of 1 rad is observed. This is reduced by an order of magnitude at larger pulse delays, from which we conclude that the phase shift, especially at $\Delta N = 1$, is dominated by the influence of fast moving free electrons (leaving the interaction zone on a ps to few ns time scale). As the atoms and ions move much slower, their contribution is seen mostly at later times.

This difference in dynamics between slow atoms (ions), and fast electrons is also illustrated in Fig. 5.3(b), which shows the relative intensity of the second VUV pulse as a function of delay. The yield is significantly reduced up to 70% for high driving intensity because up-conversion of the first pulse leads to a significant depletion of neutral atoms. Note that this also leads to a reduction in contrast of the Ramsey fringes due to the imbalance between the two excitation contributions, and therefore a larger uncertainty on the phase (Fig. 5.3(a)). The intensity of the second VUV pulse revives to a similar level as the first in 50 – 100 ns, depending on the driving intensity. This is in agreement with the expected transit time of argon atoms ($v \approx 500 \text{ m/s}$) through the focus (50 µm) and it is much slower than the observed electron dynamics.

5.4.2 Determination of the absolute transition frequency

These results show that RCS can be combined successfully with HHG for precision measurements at short wavelengths. To demonstrate this, we made an absolute calibration of the probed transition. Most of the observed phase effects occur at short pulse delays, and therefore only Ramsey fringes from $\Delta N = 2$ or higher were used to determine the transition frequency. In addition, the driving intensity was moderated to $I_0 = 0.78 \times 10^{14}$ W/cm² (the dashed line in Fig. 5.3(a) and (b)). The remaining shift in this case is -2(5) mrad between $\Delta N = 2$ and $\Delta N = 3$ and -7(9) mrad between $\Delta N = 2$ and $\Delta N = 4$ (inset in Fig. 5.3(a)). This corresponds to a shift of -32(91) kHz and -67(86) kHz, respectively, of the extracted transition frequency and is consistent with zero within the uncertainty. Only a small penalty of 15-20% of the maximum VUV yield (the sum of pulse 1 and 2) is paid by reducing the fundamental intensity (Fig. 5.3(c)). The influence of the adiabatic HHG phase shift [81], which depends on the driving NIR intensity, is suppressed in RCS, similar to ac-Stark shift. It is estimated to be below a few mrad (< 30 kHz) in the VUV for an energy stability of < 0.2% in the NIR. The phase stability of the fundamental pulses is measured using spectral interferometry (see Sec. 3.1.4) [92] and found to be constant well within 1 mrad at 770 nm (a detailed description of this measurement is given in Chapter 6). The corresponding frequency uncertainty is 140 kHz in the VUV.

5.4.2.1 Determination of the comb-mode

The RCS signal is repetitive and leads to a frequency ambiguity of multiples of $f_{rep} = 1/T_{rep}$ (Sec. 2.5.2) [72]. Therefore the measurements have been repeated with three slightly different values of T_{rep} to obtain a single transition frequency with 99.2% confidence over a 4σ range of the former measurements [84].

5.4.2.2 Doppler shift

After the identification of the transition frequency, several systematic effects were investigated. The largest one was the Doppler effect, which was quantified and reduced by comparing the transition frequency obtained from pure xenon (velocity of 285(30) m/s) with that from a 3:1 Ar:Xe mixture (480(30) m/s). The angle between the atomic and the VUV beam was adjusted to minimize the observed frequency difference to a few MHz, after which the Doppler-free transition frequency was determined by extrapolation to zero velocity. In total, 300 measurements have been performed and the result is shown in Fig. 5.4. Besides the Doppler effect, RCS is also affected by the recoil shift due to the absorption of a single photon [166]. This is accounted for by applying a correction of 125 kHz.



Figure 5.4 – The Doppler-free transition frequency of the $5p^6 \rightarrow 5p^58s^{2}[3/2]_1$ transition in ¹³²Xe at 110 nm. Each data point is based on 10 measurements at two different speeds of xenon. The blue shaded area indicates the 1σ uncertainty.

5.4.2.3 Evaluation of additional systematic effects

The RCS method strongly suppresses the influence of ac-Stark shifts [77, 78]. Measurements at different intensity levels were done to check for a residual effect, leading to an uncertainty of 20 kHz from the NIR light (estimated at $1 \times 10^{11} \text{ W/ cm}^2$) and 85 kHz from the VUV intensity (estimated at $5 \times 10^7 \text{ W/ cm}^2$). A detailed account of these measurements are given in Chapter 6. The DC-Stark shift and Zeeman shift were reduced by exciting in a field-compensated environment. An additional uncertainty of 20 kHz and 52 kHz, respectively, is taken into account for the possible influence of residual stray fields.

The final result of the $5p^6 \rightarrow 5p^5 8s \ ^2[3/2]_1$ transition frequency in 132 Xe has a total accuracy of 630 kHz and the value, together with the corrections and error budget is listed in Table 5.1.

5.5 Conclusion

To conclude, we demonstrated the first RCS measurement in combination with HHG. It enables extending RCS to much shorter wavelengths than what is possible with nonlinear crystals [77, 78]. However, HHG

	Value or correction	(1σ)
Doppler-free transition frequency	$2\ 726\ 086\ 012\ 596$	$(600)^1$
Light induced effects	0	(87)
DC-Stark shift	0	(20)
Zeeman-shift	0	(52)
Amplifier phase shift	0	(140)
Recoil shift	-125	(10^{-7})
Total	$2\ 726\ 086\ 012\ 471$	(630)

Table 5.1 – Contributions (in kHz) to the measurement of the $5p^6 \rightarrow 5p^58s \ ^2[3/2]_1$ transition frequency in 132 Xe.

¹ Including the uncertainty of ≈ 90 kHz due to the residual HHG phase shift (see text) and the correction for the second-order Doppler shift of 1.2 kHz for pure Xe and 3.5 kHz for the mixture.

is also known to introduce detrimental phase shifts from plasma formation. These effects have been investigated with RCS using xenon atoms as a phase detector, leading to mrad-level sensitivity. We are able to discriminate between two effects which originate from different aspects of plasma formation. The intensity of the generated light is predominantly influenced by the depletion of neutral atoms. This effect persists for relatively long pulse delays (50 - 100 ns), because it depends on the dynamics of neutral atoms in a gas jet. On the other hand, the phase of the generated light is mainly affected by the dispersion from the generated free electrons. As these electrons move faster than the atoms, a significant reduction of this effect is already observed at 16 ns, which enables RCS on the $5p^6 \rightarrow 5p^58s \ {}^2[3/2]_1$ transition in xenon at 110 nm with a sub-MHz accuracy.

The obtained transition frequency is in good agreement with the previous determination [84], but improves upon it by a factor 10^4 . With this measurement an unprecedented fractional uncertainty of 2.3×10^{-10} is achieved using light obtained with HHG.

The HHG process contributes remarkably little to the error budget of the frequency determination (Table 5.1). The only reason that previous RCS experiments [73, 77, 78] without HHG reached a higher accuracy was the longer pulse delay that could be applied in those cases. The short maximum transit time of 32 ns (and therefore pulse delay) in the current experiment is caused by the tight focus of the harmonic beam, because the setup has been designed for 1S-2S spectroscopy of a single trapped He⁺ ion. This limited the accuracy for xenon as the influence of most systematic errors reduce proportionally to the pulse delay. Fortunately, future targets, such as He⁺, can be trapped and observed for much longer times. Then pulse delays in the microsecond range can be used, with the added benefit that HHG phase effects are then effectively zero, even at high levels of ionization. This makes RCS very promising for precision measurements with (sub)kHz-level accuracy at VUV and XUV wavelengths.

CHAPTER 6

Demonstration of Ramsey-comb precision spectroscopy in xenon at VUV wavelengths produced with HHG

Abstract

The remarkable progress in the field of laser spectroscopy induced by the invention of the frequency-comb laser has enabled many new high-precision tests of fundamental theory and searches for new physics. Extending frequency-comb based spectroscopy techniques to the vacuum and extreme ultraviolet spectral range would enable frequency measurements of transitions in e.g. heavier hydrogen-like systems and open up new possibilities for tests of quantum electrodynamics and measurements of fundamental constants. The two main approaches, full-repetition rate up-conversion in a resonator, and two-pulse amplification and up-conversion for the Ramsey-comb technique, rely on high-harmonic generation (HHG), which is known to induce spurious phase shifts from plasma formation. After our initial report [167], in this article we give a detailed account of how the Ramsey-comb spectroscopy technique is used to probe the dynamics of this plasma with high

This chapter is based on: Demonstration of Ramsey-Comb Precision Spectroscopy in Xenon at Vacuum Ultraviolet Wavelengths Produced with High-Harmonic Generation, L.S. Dreissen, C.F. Roth, E.L. Gründeman, J.J. Krauth, M. Favier, and K.S.E. Eikema, Submitted

precision, and enables accurate spectroscopy in the vacuum ultraviolet. It is based on recording Ramsey fringes that track the phase evolution of a superposition state in xenon atoms excited by two up-converted frequency-comb laser pulses. In this manner, phase shifts of up to 1 rad induced by the HHG process could be observed at nanosecond timescales with mrad-level accuracy at 110 nm. We also show that such phase shifts can be reduced to a negligible level of a few mrad. As a result we were able to measure the $5p^6 \rightarrow 5p^5 8s^{-2} [3/2]_1$ transition in ¹³²Xe at 110 nm (the seventh harmonic of 770 nm) with sub-MHz accuracy, leading to a value of 2726086012471(630) kHz. This value is 10^4 times more precise than the previous determination and the relative accuracy of 2.3×10^{-10} is 3.6 times better than the previous best spectroscopic measurement using high-harmonic generation. Additionally, the isotope shifts between 132 Xe and two other isotopes $(^{134}$ Xe and 136 Xe) were determined with an accuracy of 420 kHz. The method can be readily extended to achieve kHz-level accuracy by increasing the pulse delay, e.g. to measure the 1S - 2Stransition in He⁺. Therefore, the Ramsey-comb method shows great promise for high-precision spectroscopy of targets requiring vacuum ultraviolet and extreme ultraviolet wavelengths.

6.1 Introduction

Precision spectroscopy in calculable systems enables tests of fundamental theory and searches for physics beyond the standard model. Recent experimental advances have led to unprecedented accuracy and the most stringent test of bound-state quantum electrodynamics theory (QED) [7,79,130,151–153]. Further improvements are hampered by the uncertainty of experimental parameters such as the nuclear charge radius, which influences the energy structure through finite nuclear size effects. This problem can be inverted to extract improved values for these parameters using spectroscopic measurements in combination with accurate theoretical calculations. In 2010, this instigated the so-called *proton radius puzzle* [20], where the inferred proton radius from spectroscopy on muonic hydrogen was 4% smaller than that obtained from electronic hydrogen spectroscopy [7,22], which was equal to a 4.4σ discrepancy [20–22, 135–137]. However, three out of four recent measurements have now confirmed the smaller (muonic) proton radius [8,23,24], including the most recent result from electron-proton scattering [168]. This makes new targets with a bigger nuclear-size induced frequency shift, such as the He^+ ion, particularly interesting [169], as similar comparisons with muonic He^+ can be made [25, 26]. Especially because the QED contributions are much larger in He⁺ than in hydrogen as a result of the higher-order scaling with the nuclear charge Z of these terms. Therefore, in combination with the expected improved determination of the alpha radius from muonic He^+ [25, 26], this can lead to a more stringent test of QED. With further theoretical improvements, also a value of the Rydberg constant can be determined from He⁺ spectroscopy, which is effectively independent from hydrogen spectroscopy (because the required alpha particle charge radius, determined from muonic He⁺ spectroscopy, only weakly depends on the Rydberg constant). The obvious challenge for a measurement of the 1S - 2S transition in He⁺ arises from the short excitation wavelength, which lies in the extreme ultraviolet spectral range [27].

Spectroscopic measurements at these short wavelengths can be realized by using e.g. radiation from a large synchrotron facility to perform Fourier-transform spectroscopy at wavelengths down to 40 nm [157, 170]. In this manner, relative accuracies of 1×10^{-7} have been demonstrated [171]. However, a higher accuracy can be reached with laser spectroscopy in combination with nonlinear up-conversion. For example, amplified and up-converted nanosecond pulses have been used to reach a relative accuracy of 0.9×10^{-8} at 58 nm [46]. This approach is based on traditional frequency-scanning spectroscopy, but uncertainties due to frequency-chirp induced by the amplification process and the relatively broad bandwidth of the excitation pulses ultimately limit this approach. A much higher spectroscopic accuracy can be reached with pulses from a frequency-comb (FC) laser [9, 10].

The pulses emitted by a FC laser have a typical pulse energy of a few nJ, which is insufficient for up-conversion to the vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) spectral range using high-harmonic generation. Therefore the peak intensity of these pulses has to be increased to reach this part of the spectrum. One approach is based on intracavity HHG to up-convert the full frequency-comb pulse train to the XUV spectral range [52, 53]. In 2005 this technique was first demonstrated and in 2012, Cingöz *et al.* have shown that they could perform

spectroscopy in argon at 82 nm with 3 MHz accuracy (0.8 ppb) using such an XUV-comb [83].

Alternatively, a single pair of FC pulses can be amplified to the mJ-level using chirped-pulse amplification followed by subsequent up-conversion using HHG in a single pass. In 2010 Kandula *et al.* demonstrated this technique and performed a Ramsey-type experiment in neutral helium atoms where they achieved an accuracy of 6 MHz at 51 nm (1 ppb) [72]. This accuracy was limited by detrimental phase shifts arising from amplification and up-conversion.

We use a modified version of the latter spectroscopy method, called the Ramsey-comb spectroscopy (RCS) technique [73], that bypasses these limitations. It is based on multiple recordings with pairs of up-converted FC pulses to obtain a *series* of Ramsey fringes from which the transition frequency can be extracted by comparing the relative phase. As a result, common mode phase shifts arising from e.g. amplification and upconversion, but also the ac-Stark shift, are suppressed strongly [76,78]. The technique combines the high precision from a FC laser with the advantages of pulse amplification, leading to e.g. easy tunability, simple up-conversion in a gas jet (no resonators required), high excitation probability and a nearly 100% detection efficiency, because the detection can be carefully timed (e.g. using a state-selective ionization pulse). The method has been demonstrated to work very well over a broad spectral range (from NIR to DUV) [73, 77, 78]. We recently showed that RCS can be combined with HHG to extend the method to the VUV and XUV spectral range [167]. The extension of RCS with HHG was so far hampered by the unknown detrimental phase shifts which arise from ionization during up-conversion [160, 172, 173]. The influence from plasma formation has been previously investigated only on short timescales, ranging from a few hundred femto-seconds to a few picoseconds [161, 162], but not on timescales relevant to RCS (i.e. at tens to hundreds of nanoseconds).

In this chapter we give a detailed account of how the RCS method can be used to provide insights into plasma-induced phase shifts arising from HHG by tracking the atomic phase evolution of excited atoms (xenon) with mrad-scale precision. Moreover, we show how this results in highprecision spectroscopy with light from HHG in the vacuum ultraviolet on the $5p^6 \rightarrow 5p^58s[3/2]_1$ transition in xenon at 110 nm.

6.2 Experimental methods and techniques

In the original Ramsey spectroscopy scheme, molecules or atoms are excited by two separated phase-locked oscillatory fields in the radiofrequency (RF) domain [74]. The Ramsey-comb spectroscopy (RCS) technique [73] also uses two interaction pulses, separated in time instead of space and in the optical domain, based on pairs of phase-locked laser pulses from a frequency-comb laser.

6.2.1 The Ramsey-comb spectroscopy technique

A two-level system with transition frequency f_{tr} can be brought in a superposition of the ground and the excited state by a resonant laser pulse. Excitation with two phase-locked pulses leads to interference between two such contributions. The interference pattern can be probed by observing the excited state population (e.g. through detection of fluorescence, or more efficiently, by photo-ionization). The phase evolution of the interfering contributions depends on the delay (Δt) and the phase difference ($\Delta \phi$) between the pulses, leading to an oscillating upper state population ($|c_e(\Delta t, \Delta \phi)|^2$), which is described by

$$|c_e(\Delta t, \Delta \phi)|^2 \propto \cos\left(2\pi f_{tr} \Delta t + \Delta \phi\right). \tag{6.1}$$

A FC laser is a very suitable source for this excitation scheme, because it provides accurate control over the pulse delay through the pulse repetition time (T_{rep}) and the relative phase through the carrier-envelope phase slip $(\Delta\phi_{ce})$. One can adjust either one of these parameters to obtain a Ramsey fringe, but experimentally it is more convenient to adjust the delay $\Delta t = T_{rep} + \delta t$. The range over which the delay is scanned, is related to the transition frequency and is typically on the order of a few hundred attoseconds.

The amplification process induces a phase shift of up to 300 mrad on the excitation pulses $(\Delta \phi_{opt})$, which is added to the carrier-envelope offset phase $\Delta \phi = \Delta \phi_{ce} + \Delta \phi_{opt}$. This contribution is typically hard to determine with high accuracy. However, it is possible to construct an amplifier based on parametric amplification that can keep the phase shift between the two amplified pulses constant at the mrad-level as a function of delay. Therefore in RCS one records a series of Ramsey fringes



Figure 6.1 – A series of Ramsey fringes from two broadband resonant FC pulses is recorded at different multiples of the repetition time $(\Delta N \times T_{rep})$. Each individual fringe is obtained by changing the delay by δt , which is on an attosecond timescale. The transition frequency is extracted from the relative phases of the fringes, suppressing the influence of common mode phase shifts of the Ramsey fringes on the extracted transition frequency.

at different pulse delays separated by an integer times the repetition time $(\Delta N \times T_{rep})$, as illustrated in Fig. 6.1. The transition frequency is obtained by comparing the relative phase of these fringes, leading to a suppression of common mode shifts. A constant phase shift between the amplified FC pulses manifests itself as a global phase shift of the fringes and does not influence the extracted transition frequency. This argument also holds for other common mode effects, such as the ac-Stark shift [76,78]. Additionally, the accuracy of the measurement improves proportionally with the inter-pulse delay, as the frequency that fits the measured phase evolution as a function of the delay time becomes more sensitive for longer delays.

The transition frequency extracted in RCS is affected by both the firstorder Doppler shift and the recoil shift from the absorption of a single photon during excitation. Cadoret *et al.* have shown that the phase Φ of the superposition of ground and excited state after a free evolution
time Δt in a Ramsey interferometer can be written as [166]

$$\Phi = \omega \Delta t + \Delta \phi + \left(\frac{\mathbf{v}_e + \mathbf{v}_g}{2}\right) \cdot \left(\mathbf{v}_e - \mathbf{v}_g\right) \frac{m \Delta t}{\hbar}, \tag{6.2}$$

where ω is the excitation frequency, \mathbf{v}_g and \mathbf{v}_e are the velocities of the atoms in the ground and excited state, respectively, and m is the mass of the atom. The recoil velocity after excitation is given by $\mathbf{v}_e - \mathbf{v}_g = \hbar \mathbf{k}/m$. Substituting this into Eq. 6.2 and taking only the velocity component along the propagation direction z of the excitation laser into account, one obtains

$$\Phi = \omega \Delta T + \Delta \phi + (v_{e,z} + v_{g,z}) \frac{\omega \Delta t}{2c}, \qquad (6.3)$$

where c is the speed of light. The last term in Eq. 6.3 is a combination of Doppler and recoil shift, which can be viewed as a generalized Doppler shift [174]. It also means that in Ramsey-comb spectroscopy the recoil frequency shift has to be taken into account for one-photon excitation. Note that in two-photon spectroscopy in a counter-propagating configuration $(k_1 = -k_2)$ [77, 78], the recoil shift is canceled and does not influence the extracted transition frequency.

6.2.2 Combining RCS with HHG

Higher-order harmonic generation uses the nonlinear response of a gas to coherently up-convert frequencies from the infrared or visible spectral range to the vacuum ultraviolet or extreme ultraviolet spectral range. An intuitive picture of HHG is given at a single-atom level by the semi-classical three-step recollision model (Sec. 2.4.1.1) [80] (a quantum-mechanical description is given by the Lewenstein model, see Sec. 2.4.2 [81]).

The principle is based on focusing a powerful short laser pulse in a medium (typically a gas jet, or a gas filled capillary) to reach an intensity of approximately 10^{14} W/cm². At these intensities, the electric field of the laser pulse can significantly perturb the Coulomb potential of the least bound electrons, and for a high enough field this enables the electron to tunnel out into the continuum. After ionization, the electron gains energy as it is accelerated in the strong electric field of the laser. It can return to the parent ion because the field of the fundamental laser changes sign after half a period of the optical wave. When

it returns it can recombine, leading to the emission of a high-energy photon. The recollision probability is highest near every zero-crossing of the electric field and the process is therefore tightly linked in time to the fundamental wave, leading to a high degree of coherence. This has been demonstrated in several experiments involving interference of HHG beams, see e.g. [158,159]. For a symmetric medium, such as a simple gas jet, only odd harmonics of the fundamental optical carrier frequency are produced. The efficiency of the HHG process is often very low (typically 10^{-6} in a simple gas jet) and most electrons might not recombine but instead become permanently ionized. Over time a significant fraction of the medium can become ionized and a plasma can be formed. In order to combine RCS with HHG, the effect of this plasma formation on the phase of the up-converted FC pulses has to be carefully considered.

In RCS common mode effects are significantly suppressed and therefore the plasma build-up during each pulse does not influence the extracted frequency. If the pulses do not influence each other, the plasma-induced shift is equal for both up-converted FC pulses. However, the second pulse can experience a phase shift due to a change in the refractive index of the HHG medium because of the plasma formed during the first pulse. This shift is dependent on the inter-pulse delay because the ions and electrons leave the interaction region, and partly recombine. It therefore leads to a delay-dependent phase shift, and as a result, a shift of the extracted transition frequency. This is illustrated in the zoom-in of Fig. 6.3. There are three contributions to the change of the refractive index: the free electrons, the generated ions and the depletion of neutral atom density [82, 100]. The influence from the free electrons in the plasma is dominant over the contribution from the atom depletion and the ions (see Sec. 2.4.3.4). The latter is usually neglected, because the energy levels scale up for higher charge states, leading to a refractive index close to unity. The different contributions will be discussed in more detail in Sec. 6.4.2.

Another effect, which has to be considered when combining HHG with RCS, is the influence of phase noise. In HHG the amplitude of the phase noise originating from the frequency comb and the amplification process is multiplied-up by the harmonic order, and can therefore lead to a significant reduction of contrast of the Ramsey fringes. The phase noise amplitude should remain well below π at the excitation wave-

length to retain enough contrast (> 20%) for a RCS measurement (see also Sec. 2.5.3.2).

6.3 Experimental setup

The RCS setup is based on selective amplification of a FC pulse pair using parametric chirped pulse amplification. The re-compressed amplified pulses have a sufficiently high peak-intensity to create high-harmonics in a simple single-pass gas jet. After up-conversion, the pulse pair is refocused in an atomic xenon beam to excite the $5p^6 \rightarrow 5p^58s[3/2]_1$ transition at 110 nm. The excited atoms are state-selectively ionized and detected using a time-of-flight mass spectrometer. In this section, the individual components of the system are described in detail.

6.3.1 The Ramsey-comb laser system

An overview of the laser setup is shown in Fig. 6.2. The starting point is a Kerr-lens mode-locked titanium:sapphire frequency-comb laser with an average output power of 450 mW and a repetition frequency of f_{rep} = 126.6 MHz. The spectrum of the laser is centered around 800 nm and has a bandwidth of ~75 nm. The repetition frequency and the carrierenvelope offset frequency (f_{ceo}) are stabilized using a commercial cesium atomic clock (Symmetricon CsIII 4310B). This enables accurate control over the repetition time $T_{rep} = 1/f_{rep}$ and the carrier-envelope phase slip $\Delta \phi_{ce} = 2\pi f_{ceo}/f_{rep}$.

The FC pulses are stretched and spectrally clipped in a 4f-grating stretcher to improve the temporal overlap of the FC pulses with the pump pulses in the parametric amplifier. The stretcher introduces a group velocity dispersion (GVD) of 1.5×10^6 fs² and an adjustable slit in the Fourier plane of the stretcher selects a spectrum with a bandwidth of typically 8 nm that is centered around 770 nm. The combination of stretching and spectral clipping leads to a pulse length of ~10 ps.

A three stage non-collinear optical parametric chirped pulse amplifier (NOPCPA) based on three beta-barium borate (BBO) crystals is then used to amplify the FC pulses. It is pumped by a home-built laser system providing a pulse pair at 532 nm with an energy of 17 mJ/pulse and a pulse length (full-width at half maximum) of 60 ps [92, 106]. The



Figure 6.2 – Pulse pairs with a delay of $\Delta N \times T_{rep}$ from a Ti:sapphire frequency-comb laser are stretched (S1) and selectively amplified in a noncollinear optical parametric chirped pulse amplifier (NOPCPA). The pulse pair is selected by adjusting the settings of the pump laser. A typical energy of $3 \,\mathrm{mJ/pulse}$ is reached of which the main part is compressed in a grating compressor (C) and up-converted using high-harmonic generation. A small fraction of the amplified beam is used to measure the phase difference between the pulses in the setup shown in the lower panel. For this purpose a second stretcher (S2) is used to stretch the reference FC pulses after which they are spatially overlapped with the amplified pulses in a single mode fiber. The pulse pairs are separated from the full FC pulse train using two Pockels cells (PC)in double pass. A third PC is used to introduce a slight vertical displacement for the first or the second pulse pair in order to project them separately on the CCD camera. By introducing a small time delay (typically < 1 ps) between the amplified and reference pulses, a spectral interferogram is recorded using a spectrometer based on a grating and a CCD camera from which the phase difference between the amplified pulses is obtained.

inter-pulse delay between the pump pulses can be adjusted by an integer number ΔN of the repetition time (T_{rep}) with a set of modulators [92], leading to selective amplification of the corresponding FC pulse pair. A typical energy of 3 mJ/pulse is reached in this manner.

The amplified pulses are re-compressed to a pulse length of 220 fs (fullwidth at half maximum) using a grating compressor, based on transmission gratings (Lightsmyth T-1850-800s). One of the gratings in the compressor is mounted on a translation stage so that the amount of induced GVD can be adjusted. The whole compressor is build on a rotation stage to tune the angle of incidence and compensate for thirdorder dispersion. However, the hard edges used for wavelength selection in the stretcher leads to a sinc-like pulse shape and therefore to preand after-pulses of a few percent with respect to the main peak. The remaining pulse energy after re-compression is typically 2 mJ/pulse.

6.3.2 The phase-measurement setup

The phase difference between the amplified FC pulses is measured in a separate setup, shown in the lower panel of Fig. 6.2, which is based on spectral interference. For this purpose a small fraction of the amplified beam is split-off before the compressor and spatially overlapped with the original unamplified FC pulse in a single-mode fiber. Saturation effects lead to a slightly wider spectrum of the amplified pulses, therefore the reference pulses pass through a separate 4f-grating stretcher. It introduces the same amount of GVD as the first, but the selected bandwidth is slightly wider. Moreover, nonlinear effects in the fiber are avoided as well by using stretched pulses. Each amplified pulse and its corresponding reference pulse is selected out of the full FC pulse train with two Pockels cells (PC), which are used in double pass (with a combined contrast of $1:10^4$) to reduce background light. A third PC is used in combination with polarization optics to introduce a slight vertical offset between each set of pulses in a small delay line. In this manner the interference pattern of the two sets of pulses can be projected above each other on a CCD camera (IMI-TECH IMB-716-G) so that both spectral interference patterns can be observed simultaneously. An example of the observed interferograms is shown in the lower panel of Fig. 6.2. The spectrometer consists of a gold grating of 1200 lines/mm (Richardson, 53-*-360R) in combination with a 350 mm lens, which projects the spectrum on the camera. The period of the interference pattern can be adjusted by changing the delay between the original FC pulse and the amplified pulse in the delay line of the reference arm. The geometrical phase difference arising from slight misalignments of the two interference patterns on the camera is calibrated by exchanging the projection of the two pulses using the third PC. The phase difference between the pulses is extracted from the interferograms using a Fourier transform-based method [109, 110].

6.3.3 The spectroscopy setup

A schematic overview of the vacuum setup is shown in Fig. 6.3. Highharmonics are created in a gas jet of argon atoms in the first vacuum chamber. The jet is created by a supersonic expansion from a homebuilt piezo valve, which operates at a backing pressure of 5 bar. Before HHG, the center part of the amplified beam is cut-out with a 1-mmdiameter beam block at a distance of 2f before the focusing lens (with a focal distance f = 250 mm). This leads to a donut-shaped intensity profile of the beam which is then imaged in the second vacuum chamber to separate the harmonic light from the fundamental light with an adjustable iris. The generated harmonics propagate on axis with a much lower divergence than the fundamental. Therefore, the iris transmits the harmonic beam, while it blocks the ring of fundamental light around it. A peak intensity of up to 1.3×10^{14} W/cm² is reached in the interaction region below the nozzle of the valve. The position of the valve can be adjusted in three orthogonal directions to optimize the harmonic yield. In particular, the alignment in the direction of propagation is important for reaching proper phase-matching conditions of the HHG process (Sec 2.4.3.4). This is achieved by adjusting the valve position such that the divergence of the harmonic beam is minimized, which typically leads to a focus position just in front of the jet.

Due to the low ionization potential of xenon, direct one-photon ionization is allowed with harmonics of order q > 7. Therefore, a 1-mm-thick lithium fluoride window is placed in the beam, which only transmits light at $\lambda > 105$ nm. An absolute transmission efficiency of 40 % was measured for the seventh harmonic at 110 nm.



only transmits light $\lambda > 105 \,\mathrm{nm}$. The VUV beam is refocused using a toroidal mirror pair (M1 and M2) and overlapped with a pulsed xenon beam at an angle of 90°. An ionization pulse at 1064 nm is delayed by 2 ns with An XUV camera and a monochromator (G is a grating of 3600 lines/mm) are used for diagnostic purposes. The Figure 6.3 – The NIR beam is focused to generate harmonics in argon. A combination of a beam block and an adjustable iris is used to separate the harmonics from the fundamental beam while a LiF plate acts as a filter and respect to the second VUV pulse and selectively ionizes the excited atoms. The ions are extracted with a pulsed zoom-in shows that the plasma generated by the first pulse, leads to a delay dependent phase shift of the second electric field and detected through a time-of-flight (TOF) drift tube by an ETP AF880 electron multiplier (EM). VUV pulse because the ionized region moves out of the interaction zone.

A toroidal mirror pair operating at a grazing angle of 7.5° is used to refocus the harmonic beam in the interaction region. It forms a oneto-one telescope with an effective focal length of 250 mm. Coma and other aberrations are fully compensated at equal angle of incidence, but for a slight angular deviation the beam quality in the spectroscopy region is significantly perturbed. A retractable silver mirror is placed a few centimeters behind the second toroidal mirror to monitor changes in day-to-day alignment and ensure a proper quality of the refocused fundamental beam. The harmonic beam itself can be detected in the far field (400 mm from the focal plane) with an XUV sensitive CCD camera (Andor Newton SY, DY940P).

The xenon atoms are excited at a 90° -angle in a pulsed atomic beam to reduce influences from the first-order Doppler effect. The gas pulse is created from a home-built piezo valve with a 0.3 mm nozzle opening, operating at 0.5 bar backing pressure. The formation of clusters from the gas expansion, as reported in previous studies [163, 164], was thoroughly investigated by changing the parameters of the expansion (backing pressure, pulse timing, pulse length) and by changing skimmers and valve types (solenoid and piezo based with different valve openings from 0.15 mm to 0.8 mm), but no evidence for the production or influence of clusters was found in the Ramsey signals or time-of-flight (TOF) mass spectrometer data. After these tests we based the atomic beam geometry for the measurements on two skimmers to reduce Doppler broadening. The first skimmer is placed at a distance of 200 mm from the valve and has a circular aperture with a diameter of 8 mm. This relatively large opening was chosen to reduce possible effects of skimmer clogging. The second one is an adjustable slit skimmer set to a width of 1 mm. It is made from 0.150 mm thick stainless steel foil and bent into a slit skimmer pointing towards the source. The slit is orientated perpendicular to the atomic and VUV beam. It is placed at a distance of 460 mm from the value, leading to a maximum atomic beam divergence of < 1.5 mrad.

The excited xenon atoms are selectively ionized by a 3 mJ, 60 ps ionization pulse at 1064 nm, which is delayed by 2 ns with respect to the second excitation pulse. This pulse is derived from the second pump laser pulse, and therefore automatically shifts with the different pulse delays which are selected for the RC measurement. The ionization beam is focused in the vertical direction with a cylindrical lens to match the shape of the interaction region and to reach the saturation intensity of the ionization step. The ions are extracted through a 40 cm long TOF drift tube, separating the different isotopes temporally. They are measured by a fast electron-multiplier (ETP ion detect, AF880) and the signal from the selected isotope is obtained with a boxcar integrator (Stanford Research). The whole experiment is repeated at a rate of 28.2 Hz.

6.4 Results

A typical Ramsey-comb scan is shown in Fig. 6.4. The lower panel shows four Ramsey fringes at $\Delta N = 1 - 4$. Each Ramsey measurement was obtained by scanning the inter-pulse delay over a range of 475 as. The phase difference between the two FC pulses drifts on the order of 10 mrad at a ten minute timescale, due to subtle changes (mostly related to temperature) in the amplifier system. Therefore the measurement time was set to be only 3.3 minutes/fringe at the expense of signal-to-noise ratio, and only pairs of Ramsey fringes were used ($\Delta N = 2$ and $\Delta N = 4$). Additionally the data points were recorded in random order, as shown in the upper panel of Fig. 6.4, reducing the influence of drifts further by a factor of ~4.

6.4.1 The Ramsey fringe contrast

The contrast of the fringes clearly decays as a function of delay (ΔN) . This has several causes: the finite upper state lifetime (22 ns [165]), Doppler broadening, phase noise on the amplified and up-converted pulses, and the short transit time of the xenon atoms through the refocused excitation beam. The latter was the dominant cause for a relatively fast decay of the Ramsey fringe contrast in this experiment. The 1:1 toroidal telescope refocuses the HHG beam to a spot similar in size as at the HHG source, which is $\leq 50 \,\mu\text{m}$ for the fundamental beam and typically a few times smaller in the VUV. This configuration was chosen in preparation for 1S - 2S excitation in He⁺ (requiring refocusing), but was not ideal for the current Xe experiment. Therefore the toroidal mirrors were deliberately slightly misaligned (with respect to



Figure 6.4 – A typical Ramsey-comb scan at $\Delta N=$ 1-4. The upper panel shows the signal as a function of measurement number, where the different markers show the data points corresponding to a specific ΔN . In the lower panel, the data is sorted according to pulse delay, leading to clear Ramsey fringes. The signal was obtained by scanning the pulse delay over 475 as, while a 7.9 ns delay is introduced between each Ramsey measurement by changing the pulse pair.

perfect one-to-one imaging configuration) to introduce a small amount of astigmatism, which increases the transit time at the expense of a local wavefront tilt. As a result, the maximum pulse delay was increased from 16 ns (diameter of ~15 µm) to 32 ns (~30 µm). The purple data points in Fig. 6.5 show the measured Ramsey signal contrast at different inter-pulse delays ($\Delta N = 1 - 4$) after increasing the interaction region. In order to gain more insight into the influence of the individual contributions that affect the Ramsey fringe contrast, the Ramsey-comb signal was simulated and a comparison with the data was made. The simulations were performed with an upper state lifetime of 22 ns [165] and the maximum achievable contrast based on this value is shown with the orange curve in Fig. 6.5. Other parameters that were fixed based on prior knowledge were the maximum atomic beam divergence of 1.5 mrad (black curve) and the wavefront tilt of 1.25 mrad (blue curve) based on the introduced astigmatism in the VUV beam. The latter two were estimated from the geometrical configuration. The remaining two parameters, namely the size of the interaction region and the phase noise were fitted to match the decay and the offset of the measured contrast. The phase noise manifests itself as an overall reduction of the Ramsev fringe contrast, while the limited transit time affects the decay of the curve. The purple line shows the best match with the experiment and led to a $26 \,\mu\text{m}$ VUV beam size at full width half maximum and a $400 \,\text{mrad}$ phase noise amplitude at the seventh harmonic. This indicates that the phase noise amplitude of the amplified NIR pulses is 57 mrad, taking the linear scaling with the harmonic order into account. This result agrees well with the extracted value from direct phase measurements at the fundamental frequency, which will be discussed in Sec. 6.4.3. Even though the beam size was increased by almost a factor of two, the loss of contrast is still dominated by the short transit time of the atoms (green curve).

Due to the high sensitivity to the transit time of the atoms in this experiment, it became apparent that the two amplified pulses initially had a slightly different propagation direction. This was caused by an intensity dependent spatial walk-off effect in the parametric amplifier.

The two pump pulses of the NOPCPA have a slightly different intensity profile as a result of saturation effects in the amplifiers of the pump laser [92]. This leads to a different walk-off induced propagation angle for the two amplified FC pulses caused by pump-to-signal phase transfer. This problem was solved by implementing a walk-off compensating configuration for the first two passes [97], which is based on the reversal of the walk-off direction between the first two crystals by rotating one of the crystals around the proper axis. In this manner the beam pointing difference was reduced from ~ 0.5 mrad (depending on the day-to-day alignment) to 20 µrad. Note that previous RCS measurements [77, 78] were not affected by this because they used large collimated beams in combination with *low* harmonic generation.



Figure 6.5 – The measured Ramsey fringe contrast as a function of pulse delay (purple points) and the best fit (purple curve). The individual curves that show the influence on the contrast are obtained by assuming an upper state lifetime of 22 ns (orange curve), a wavefront tilt ot 1.25 mrad (blue curve), an atomic beam divergence of 1.5 mrad (black curve) and an effective interaction region of 26 μ m (green curve). The curves clearly show that for this experiment the dominant contrast-reduction effect was caused by the short transit time of the atoms through the interaction region. The fit also includes an additional phase noise amplitude of 400 mrad at the seventh harmonic.

6.4.2 Plasma-induced effects

The influence from plasma formation on the HHG process was investigated by varying the driving intensity with a half-wave plate and a thin-film polarizer. As illustrated in Fig. 6.6, the depletion of the neutral atoms after up-conversion of the first pulse influences the VUV yield of the second pulse. Fig. 6.6(a) shows the individual VUV pulses at the seventh harmonic for five different driving intensities. Up to 0.7×10^{14} W/cm², the yield of both VUV pulses benefit from a higher driving intensity, but a further increase leads to the stagnation and eventually a decrease of the yield of the second pulse. At the highest driving intensity $(1.3 \times 10^{14} \text{W/cm}^2)$ the second VUV pulse is almost completely suppressed. Note that in this regime, the phase matching condition, which depends on the dispersion, is also significantly influenced. As a result also the total VUV yield, i.e. the sum of the two pulses, stagnates as is shown in Fig. 6.6(b). Above $0.9 \times 10^{14} \text{W/cm}^2$ there is no significant improvement of the total yield.

A revival of the second VUV pulse occurs for larger inter-pulse delays, as shown in Fig. 6.6(c), because the plasma leaves the interaction region and the gas sample refreshes. The typically observed timescale on which this revival occurs, depends on the size of the interaction region and therefore the driving intensity. The reason for this is that a higher driving intensity leads to a bigger volume where the intensity is high enough for tunnel ionization and therefore HHG. It then also takes longer for all the ions to leave the interaction zone. Recovery times of 50-100 ns were observed as is shown in Fig. 6.6(c), which matches well with what is expected for a focus diameter in the HHG zone of about 50 μ m and the estimated velocity of the argon atoms from a supersonic expansion (v = 550 m/s).

The plasma-induced phase shift of the second VUV pulse was extracted from the phase evolution of the Ramsey fringes as a function of the driving intensity. The absolute phase of the VUV Ramsey fringes drifts over longer timescales (typically a few mrad per minute), therefore only the relative phase between the fringes was used so that this effect did not appreciably influence the measurements. The phase at $\Delta N = 2$ was chosen as a reference, because a remarkable change in the dynamics was observed after this delay (16 ns), but also because the signal-to-noise is better than at longer delays and subtle shifts could be measured more accurately.

Fig. 6.7 shows the measured phase shift between $\Delta N = 1, 3, 4$ and $\Delta N = 2$ as a function of the driving intensity. Based on the curve at $\Delta N = 1$, there is a nearly exact seventh-order dependence of the phase on the intensity ($\Delta \phi \propto I^7$), which is therefore used to fit all the data.

At the shortest delay ($\Delta N = 1$), phase shifts as large as 1 rad are observed at the highest driving intensity. This shift is significantly reduced for larger inter-pulse delays, indicating that there are much faster dy-



Figure 6.6 – (a) The recorded VUV yield of the two individual pulses at the seventh harmonic for different driving intensities. Initially both pulses increase as a function of driving intensity, but above $0.9 \times 10^{14} \text{ W/ cm}^2$ the yield of the second pulse stagnates and eventually decreases due to the depletion of the neutral atom density. (b) The amplitude of the individual VUV pulses and sum of the two. The lines connecting the data points are splines to guide the eye. (c) The extracted amplitude of the second VUV pulse as a function of inter-pulse delay for different driving intensities. The lines are fits to the data assuming the fundamental pulses have a Gaussian beam profile. A revival of the second pulse occurs on a timescale of 50-100 ns.

namics involved in this process than what is expected from the dynamics of ions and atoms (Fig. 6.6(c)). Therefore we conclude that the phase effects are predominantly caused by free electrons in the plasma, which can leave the interaction zone much faster than the atoms and ions (on a ps timescale instead of ns timescale). This is in agreement with the expected dominant contribution to the change in refractive index due to plasma formation [82, 100]. Note that the errorbars increase for higher driving intensity because the two excitation pulses (Fig. 6.6(a)) and therefore the excitation contributions become unequal, which directly leads to a lower contrast of the Ramsey fringes.

By moderating the driving intensity to $I_0 = 0.78 \times 10^{14} \text{ W/ cm}^2$ (indicated by the dotted vertical line in Fig. 6.6(c)) and skipping $\Delta N = 1$, the observed shift is reduced to -2(5) mrad between $\Delta N = 2$ and $\Delta N = 3$, and -7(9) mrad between $\Delta N = 2$ and $\Delta N = 4$. The corresponding frequency shift for this transition of -32(91) kHz and -67(86) kHz, respectively, is consistent with zero within the uncertainty. Fig. 6.6(b) shows that this moderation of the intensity to I_0 leads to a reduction of 15% of the total VUV yield and therefore only a slight reduction of the total signal level.

The spectrum of the generated harmonics at the different values of the driving intensity was measured with the monochromator at the end of the vacuum system (Fig. 6.3). The spectra are acquired with only a single pulse and do not represent the total yield of the double-pulse configuration. Fig. 6.8 shows four spectra obtained at different driving intensities. The harmonics of orders between q = 5 (154 nm) and q = 15(51 nm) are clearly observed. The high-frequency end of the spectrum is limited by the poor reflectivity of the aluminum grating that was used (model 33009FL01-510H from Newport) at a relatively small angle of incidence ($< 45^{\circ}$). The geometry of the monochromator prevents the low-frequency end of the spectrum to be observed, therefore the third harmonic is missing. The measured amplitudes of the harmonic orders were corrected for the wavelength dependent sensitivity of the electron multiplier (gray curve in Fig. 6.8). However, the diffraction efficiency (-1^{st} order) of the grating is unknown, because the grating is only specified down to 130 nm. Therefore the curves in Fig. 6.8 only give an indication of the spectral intensity of the different harmonic orders. Nevertheless two conclusions can be drawn from the observed spectra.



Figure 6.7 – The observed phase shift at $\Delta N = 1,3$ and 4 relative to the reference phase at $\Delta N = 2$ as a function of driving intensity. The data is fitted with $\Delta \phi \propto I^7$ and the shaded area represents the 1σ uncertainty interval. The zoom-in shows the residual shift at normal operating conditions ($I_0 = 0.78 \times 10^{14}$).

The first is that the highest harmonics are produced even at the lowest driving intensity, indicating that the regime of tunnel ionization is reached in the HHG process at those levels of intensity. Secondly, there is an increase of about a factor of 4 in harmonic yield for wavelengths below 80 nm at higher intensities. For future experiments (like 1S - 2SHe⁺ excitation) where the pulses will be more than 100 ns apart, one can fully use this improved HHG yield because in that case there is no influence of atom depletion or related phase shifts on the second pulse. It is not clear why there is a (reproducible) sudden change in power scaling behavior for the 11^{th} and 13^{th} harmonic. It could in part be induced by changing phase matching conditions (optimized for the seventh harmonic) due to ionization and perhaps subtle pulse shape changes (induced by the optics used to vary the intensity).



Figure 6.8 – The obtained harmonics spectrum between order q = 5 (154 nm) and q = 15 (51 nm) for four different values of the driving intensity. The individual points are the measured intensities at the indicated (by the number below the points) harmonic order. The curves are corrected for the sensitivity of the Electron Multiplier (EM) consisting of BeO (gray curve), but not for the unknown wavelength-dependent efficiency of the grating, so it only gives an indication of the harmonic yield. Generation of the highest harmonics q > 7 indicate that the region of tunneling ionization is reached, even for low driving intensity. The different power scaling behavior of the 11^{th} and 13^{th} harmonic is reproducible, but not fully understood.

6.4.3 Calibration of the absolute transition frequency

The measured plasma-induced phase shifts indicate that high-precision spectroscopy is possible, even for RCS with relatively small pulse delays. To demonstrate this and show the full potential of RCS in combination with HHG, the absolute transition frequency has been determined. Due to the periodicity of the signal in Ramsey-comb spectroscopy, the extracted transition frequency is only known modulo the effective mode spacing $(f_{rep}/\Delta N)$. Therefore, the repetition frequency was varied over a range of 1.6% in three steps to determine the actual transition frequency. A few of the possible values for the transition frequency are shown in Fig. 6.9 relative to the previous determination from Yoshino *et al.* [84]. The upper panel shows the extracted frequencies at five different values of the mode spacing. The results obtained from the combination of $\Delta N = 2$ and $\Delta N = 4$ yields the best statistical accuracy but reduces the effective mode spacing to $f_{rep}/2$, which leads to twice as many possible transition frequencies. Therefore, half of the possibilities were excluded by also performing measurements at $\Delta N = 2$ and $\Delta N = 3$. The combination leads to only a single coincidence point of the transition frequency within a 4σ range of the previous determination [84].

The probability that the obtained transition frequency is at the given coincidence point is calculated by constructing Gaussian distributions from the extracted transition frequencies (μ_n) and the corresponding uncertainties (σ_n) according to

$$P_n(f) = \frac{1}{\sigma_n \sqrt{2\pi}} e^{-\frac{(f-\mu_n)^2}{2\sigma_n^2}}.$$
 (6.4)

The distributions obtained with different mode spacing are multiplied to obtain the probability (P_C) that the transition frequency is at a certain coincidence point, which is shown in the lower panel of Fig. 6.9. In this manner, the obtained coincidence point was determined with 99.2% confidence.

After identification of the proper transition frequency ('mode'), the absolute transition frequency was determined by evaluating a series of systematic effects. The main systematic effect is caused by the firstorder Doppler shift. This was calibrated by comparing the transition frequency obtained from a beam of pure xenon with that obtained from a mixture of argon and xenon in a ratio of 3 to 1. The mixture accelerates the xenon atoms, which unfortunately also reduces the transit time so that only a maximum pulse delay of $\Delta N = 3$ could be used in this case.

In the TOF mass spectrometer geometry, two deflection plates were included in the direction of propagation of the atoms to compensate for the forward velocity and to steer the ions onto the detector. The observed signal level as a function of deflection voltage was compared to simulated trajectories (and resulting signal) using COMSOL to calibrate the forward velocity. From this we established a speed of 285(30) m/s



Figure 6.9 – The upper panel shows the extracted possible transition frequency with respect to the previous value [84] at 5 different effective mode spacings, which are indicated in the upper-right corner. The lower panel shows the probability of the coincidence point at the possible frequencies. The coincidence point with the highest probability (normalized to 1) is indicating the true transition frequency, and was determined with 99.2% confidence.

for pure xenon, and 480(30) m/s for xenon in the mixture.

The atomic beam was first coarsely aligned to be perpendicular to the excitation beam by minimizing the observed frequency shift to the level of a few MHz. The Doppler-free transition frequency was then obtained by extrapolating the residual shift to zero velocity after correction for the HHG shift and the second-order Doppler shift (1.2 kHz for pure xenon and 3 kHz for the mixture). In total more than 300 measurements were recorded over a period of 17 days from which the final result was obtained, which is shown in Fig. 6.10.

As was discussed in Sec. 6.2.1, the recoil from absorption of a single photon affects the extracted transition frequency. Therefore, a correction of 125 kHz was applied in the evaluation of the final result.

Although the ac-Stark shift is known to be significantly suppressed in the RCS method [76, 77], we have investigated the presence of possible residual shifts. Both the VUV pulses and the residual light from the fundamental beam can induce a shift of the energy levels in the atom.



Figure 6.10 – The obtained Doppler-free transition frequency. Each data point shows the extracted transition frequency from 10 measurements with pure xenon and 10 measurements in the 3:1 Ar:Xe mixture. The shaded area shows the 1σ uncertainty interval.

To determine the magnitude of the effect, the induced phase shift of a single Ramsey fringe was measured as a function of intensity.

The influence of the residual NIR light was measured by slightly opening the iris (in the second vacuum chamber) that normally blocks as much of the NIR beam as possible. For normal operating conditions the NIR intensity in the interaction region was estimated to be $1 \times 10^{11} \,\mathrm{W/\,cm^2}$. The measured phase shift as function of NIR intensity for $\Delta N = 2$ and $\Delta N = 3$ is shown in Fig. 6.11(a) and (b), respectively, and the solid line shows a linear fit to the data of which the 1σ uncertainty interval is indicated by the shaded area. A significant intensity-induced phase shift of 1.65 rad was observed by increasing the intensity by a factor of 4.6. However, the differential nature of RCS leads to a strong suppression of the influence of this effect on the extracted transition frequency. This is shown Fig. 6.11(c), where the difference between the induced shift at $\Delta N = 2$ and $\Delta N = 3$ is plotted. The fit shows that the dependency of the phase on the intensity is practically equal (within the statistical uncertainty) for both pulse delays (a small difference is seen because the measurements were performed sequentially instead of simultaneously and without random scanning, which leads to a small residual



Figure 6.11 – The observed phase shift of the Ramsey fringe in the VUV as a function of NIR intensity in the interaction region for (a) $\Delta N = 2$, (b) $\Delta N = 3$ and (c) their difference. The solid line represents a linear fit of the data and the shaded area indicates the 1σ uncertainty interval. A maximum shift of 1.65 rad was observed by increasing the intensity in the interaction region by a factor of 4.6. However, the fitted slopes of the curves at $\Delta N = 2$ and $\Delta N = 3$ are almost equal, with a small residual difference, as is shown in (c), due to drifts of the setup as the measurements where performed sequentially (see text).

phase drift). Therefore the effect is common mode and barely affects the extracted transition frequency. Given that the NIR pulses are actively kept constant to the level of 0.2%, the ac-Stark effect is suppressed by a factor of 500, leading to a frequency shift of less than 20 kHz.

A similar procedure was performed to calibrate the ac-Stark shift induced by the VUV pulses. Here the intensity was decreased by a factor of 3 with respect to normal operating conditions (estimated at $5 \times 10^7 \,\mathrm{W/\,cm^2}$). To this end the gas pressure in the HHG interaction zone was lowered by reducing the drive voltage on the piezo valve. A phase shift of 0.7 rad was observed, which, in combination with the measured stability of the VUV intensity (about ten times worse than that of the NIR), results in a frequency uncertainty of 85 kHz.

The dc-Stark effect was suppressed by using a pulsed electric field to extract the xenon ions. A possible residual shift from stray electric fields was estimated by deliberately increasing the field in the interaction zone to 29 V/cm. The observed frequency shift of 2.5(1.0) MHz, gives rise to a shift of < 20 kHz assuming an estimated maximum stray field of $< \pm 0.25$ V/cm.

A similar procedure was performed to calibrate the Zeeman shift. A set of six coils was used to reduce the magnetic field in the interaction zone to below 0.1 Gauss. Based on measurements at 3 Gauss (in different directions), we determined the uncertainty from stray magnetic fields to be below $52 \,\text{kHz}$.

Finally, the phase stability of the amplified FC pulses was measured using the setup described in Sec. 6.3.2. The absolute phase shift introduced in the amplification process is typically on the order of a few hundred mrad. The observed phase noise amplitude was 40-70 mrad, depending on the exact operating conditions in the NOPCPA. This is in agreement with the estimation made, based on the contrast of the Ramsey fringes, as was discussed in Sec. 6.4.2. The origin of the phase noise was traced back to the amplification process itself [90]. A clear correlation was observed between the output power of the amplified FC beam and the phase stability of the pulses, indicating that local wavefront fluctuations (and therefore phase mismatch) give rise to added phase noise, rather than effects such as self and cross phase modulation [90, 92].

The stability of the phase as a function of pulse delay was measured as well, as this can have an influence on the extracted transition fre-



Figure 6.12 – The optical phase shift of the fundamental beam at 770 nm as a function of the pulse delay. The data points are obtained by averaging over 15 measurements, each with a statistical uncertainty of 1.5-2.5 mrad. This number of averages is equivalent to a typical measurement day. The resulting average phase stability is considerably better than 1 mrad.

quency. A set of 15 measurements, each with a statistical uncertainty of 1.5-2.5 mrad, were averaged to obtain the phase stability over a typical measurement day. The result is shown in Fig. 6.12. The phase difference remains constant well within 1 mrad as a function of the delay, which conservatively leads to an uncertainty of 140 kHz on the transition frequency in the VUV.

The final result, and all the contributions to the error budget, are shown in Tab. 6.1. The transition frequency of the $5p^6 \rightarrow 5p^58s^{-2}[3/2]_1$ transition in ¹³²Xe was determined to be 2726 086 012 471(630) kHz, which improves upon the previous determination by a factor of 10^4 [84]. The achieved relative accuracy of 2.3×10^{-10} is a factor of 3.6 better than the previous best spectroscopic measurement using HHG [83].

6.4.4 Isotope shift measurement

Xenon has seven observable stable isotopes, as shown in Fig. 6.13. Two of them have a nuclear spin and therefore hyperfine structure, namely ¹²⁹Xe and ¹³¹Xe. This leads to excitation of several transitions simultaneously and therefore a beating of the corresponding Ramsey signals.

	Value or correction	(1σ)
Doppler-free transition frequency	$2\ 726\ 086\ 012\ 596$	$(600)^1$
Light induced effects	0	(87)
dc-Stark shift	0	(20)
Zeeman-shift	0	(52)
Amplifier phase shift	0	(140)
Recoil shift	-125	(10^{-7})
Total	$2\ 726\ 086\ 012\ 471$	(630)

Table 6.1 – Contributions (in kHz) to the measurement of the $5p^6 \rightarrow 5p^58s \ ^2[3/2]_1$ transition frequency in 132 Xe.

¹ Including the uncertainty of $\approx 90 \text{ kHz}$ due to the residual HHG phase shift (see text) and the correction for the second-order Doppler shift of 1.2 kHz for pure Xe and 3.5 kHz for the mixture.

In principle RCS can be used to obtain all the transition frequencies and the relative amplitudes of these contributions if the phase evolution can be measured over a sufficiently long delay, see Sec. 2.5.2.2 and [73, 76], but due to the short transit time of the xenon atoms this could not be realized, and therefore only the even isotopes were considered.

Of the remaining five even isotopes, three provided enough signal to perform accurate measurements. Therefore the isotope shift of the $5p^6 \rightarrow 5p^58s \ ^2[3/2]_1$ transition for both 134 Xe and 136 Xe relative to isotope 132 Xe was determined.

As shown in Fig. 6.13, the signal from the different isotopes can be resolved easily and acquired separately using two Boxcar integrators. In this manner, most systematic shifts are common-mode for both isotopes and the isotope shift $f_X - f_{132}$ can straightforwardly be extracted. Note that each isotope clearly shows a double-peak structure, which only became apparent because of the high resolution of the mass-spectrometer (about 5 ns). The origin of this structure was investigated thoroughly by exchanging e.g. the valve and the skimmers, but no conclusive reason for this observation was found. However, the most probable cause of the multi-peak structure is the existence of different velocity classes. Therefore, only the signal coming from the first peak was acquired for each isotope with the Boxcar integrators.



Figure 6.13 – A typical time-of-flight (TOF) trace of xenon isotopes (using only one 110 nm pulse to avoid isotope-dependent interference effects). The relative amplitude shows the natural abundance of the isotopes. All stable isotopes, except for ¹²⁴Xe and ¹²⁶Xe, are clearly observed and resolved. Due to the high resolution of the TOF mass spectrometer, a double-peak structure was observed for all isotopes of which the origin could not be determined with certainty. It is most likely caused by different velocity classes in the atomic beam. To record Ramsey signals, only the first peak of each isotope was recorded with a Boxcar integrator in the experiment.

The ambiguity of the determined frequency shift due to the effective mode spacing is again removed by varying the repetition frequency of the laser, similar as discussed in Sec. 6.4.3. This results in a single coincidence point for each isotope shift frequency, which were both determined with >95% confidence. The isotope shifts have been obtained from more than 50 measurements for each isotope, which were taken over a period of 8 days. The final result of the extracted shift for both isotopes is shown in Fig. 6.14. The isotope shift was determined to be $-164\,910(420)\,\text{kHz}$ and $-509\,750(425)\,\text{kHz}$ for ^{134}Xe and ^{136}Xe , respectively, relative to ^{132}Xe .



Figure 6.14 – The measured isotope shift of the $5p^6 \rightarrow 5p^5 8s\ {}^2[3/2]_1$ transition for 134 Xe (upper panel) and 136 Xe (lower panel), with respect to 132 Xe. Each point is obtained from eight simultaneous measurements of 132 Xe and one of the other isotopes. The shaded area represents the 1σ uncertainty interval of the mean of the values.

6.5 Conclusion and Outlook

We have given a detailed account of the first demonstration of Ramseycomb spectroscopy in combination with HHG. A key aspect of this work is the time-dependent plasma-induced phase effects from HHG. These were investigated by exciting xenon atoms to a superposition state with two up-converted phase-locked laser pulses, while varying the conditions in the HHG process. The phase effects derived from the Ramsey-comb signal could be tracked with mrad-level accuracy and on nanosecond timescales. It shows that the effects from ionization of the HHG medium (argon) on the phase is dominated at short timescales (of a few ns) by the influence of free electrons, leading to phase shifts of up to 1 rad at 8 ns pulse delay. However, we found that this effect can easily be reduced to a negligible level by increasing the pulse delay to at least 16 ns and moderating the driving intensity. This enabled us to measure the absolute transition frequency of the $5p^6 \rightarrow 5p^58s^{-2}[3/2]_1$ transition in 132 Xe with RCS at 110 nm with sub-MHz accuracy.

The final result of the transition frequency is $2726\,086\,012\,471(630)$ kHz, which is in agreement with the previous determination [84], but improves upon the accuracy by a factor of 10^4 . The achieved relative accuracy of 2.3×10^{-10} is unprecedented using HHG for up-conversion and improves upon the previous best measurement by a factor of 3.6 [83].

This demonstration shows the potential of RCS in the VUV and XUV spectral range. Combining the accurate pulse control that the FC laser offers with the advantages of high-power amplified pulses results in straightforward single-pass up-conversion, a high excitation probability due to the high pulse energy, easy wavelength tunability, and enables detection methods, such as state-selective ionization, that can be made nearly background free and with high efficiency.

The achieved accuracy of the presented experiment is almost completely limited by the short transit time of the xenon atoms through the excitation beam, because the setup was in fact designed for 1S-2S excitation in He⁺ with a refocused XUV beam. The interaction time can therefore be increased by using a collimated excitation beam, which would immediately give rise to a higher accuracy as the largest contributions in the error budget scale down with increasing pulse delay. Alternatively, the transit time can be increased by using a trapped atom (ion) such as He⁺, which has the added benefit that Doppler effects can be reduced significantly. Therefore, this method shows great promise for 1S - 2Sspectroscopy of singly-ionized helium. The much higher harmonic order required for He^+ excitation (effectively the 26^{th} in a scheme combining 32 nm with 790 nm, see Sec. 3.2.1) [169] sets a more stringent limit on the allowed phase noise of the amplified FC pulses. However, the current system can produce pulse pairs with a relative phase noise of about 50 mrad rms, which would still lead to Ramsey fringes with contrast of 35%. Both the FC and parametric amplifier can be improved to reduce phase noise further, leading to higher contrast. Moreover,

the upper-state lifetime of the 2S state is 1.9 ms, so that, compared to the present experiment, a much larger pulse separation can be applied. Therefore there are good prospects for RCS to reach kHz-level accuracy in the VUV and XUV spectral range. This is of great interest for new high-precision tests of quantum electrodynamics theory, determination of fundamental constants such as the Rydberg constant or the alpha particle radius, and searches for physics beyond the standard model.

CHAPTER 7

Outlook

One of the main motivations for the work presented in this thesis was to perform high-precision spectroscopy of molecular hydrogen for more stringent tests of molecular quantum theory. In Chapter 4 a new result of the X - EF transition frequency was presented which improved upon the previous value by two orders of magnitude by performing Ramseycomb spectroscopy at deep ultraviolet wavelengths. This value has recently been used in combination with a series of other measurements in H₂ to obtain the most accurate value of the dissociation energy so far D_0 [79], which is in excellent agreement with the most recent theoretical value [30]. The second main goal was to combine RCS with high-harmonic generation (HHG) for high-precision spectroscopy of the 1S - 2S transition in singly-ionized helium. For this purpose, a new vacuum setup was build-up and tested on the $5p^6 \rightarrow 5p^58s^{-2}[3/2]_1$ transition at 110 nm in xenon. The results presented in Chapters 5 and 6 show that the RCS method has enabled accurate characterization of the influence of plasma formation during up-conversion, which led to the most accurate spectroscopic measurement so far using a HHG source. This is a great step towards the first ever 1S - 2S excitation in He⁺ and shows that a high accuracy is achievable using the RCS method.

The first part of this chapter gives a brief overview of potential technical improvements that can be made for a more accurate determination of the X - EF transition frequency in H₂. The second part gives a short overview of the status of the He⁺ experiment and an outlook on the potential conclusions which can be drawn from it.

7.1 Improvements on the X - EF transition in H_2

The frequency determination of the $EF^1\Sigma_g^+ - X^1\Sigma_g^+(0,0)$ Q1 can be improved further, as it was not limited by the natural line width. The main source of uncertainty was caused by the limited interaction time with the H₂ molecules. This led to a maximum pulse delay of 380 ns, which is 'only' twice the upper-state lifetime. The two main limitations to the maximum pulse delay were a result of the repetition rate noise of the Ti:Sa frequency-comb (FC) laser and the transit time of the hydrogen molecules through the excitation beam. The first problem can be solved by using a more stable FC laser. For this purpose (and in preparation of 1S - 2S spectroscopy in He⁺) an ultra-low noise (ULN) FC laser (Menlo Systems, FC1500-250-ULN) was acquired. Most of the preparations have been made to incorporate it in the rest of the Ramseycomb laser system (Sec. 3.1). This will reduce the comb mode linewidth from 150 kHz to <1 kHz, which is more than sufficient for this transition (upper state lifetime is ~200 ns).

A longer transit time of the molecules can possibly be reached by increasing the size of the excitation beam. However, the two-photon signal scales quadratically with the intensity and therefore, the pulse energy should also be improved. This is possible by implementing a second amplifier module in the post-amplifier (Sec. 3.1.2.3), which increase the power of the pump pulses in the parametric amplifier (Sec. 3.1.3.2) and as a result also the output power of the amplified FC pulses. This is not a trivial improvement as it requires a serious rebuild of a large part of the laser system.

Alternatively, the hydrogen beam could be slowed down by a combination of liquid nitrogen cooling and mixing with a heavier gas such as neon. The problem is that the current valve cannot produce a dense beam at low temperatures. However, through a collaboration between our group and the group of F. Merkt from the ETH Zurich, we have acquired a new piezo valve which was specifically designed to produce a high-density beam of molecular hydrogen. The valve can be cooled down to liquid nitrogen temperature and reheated to room temperature in quick succession, which would improve the Doppler calibration. In addition, the molecular beam line is being upgraded by implementing an additional and bigger skimmer at a larger distance. These two implementations improve the density of the hydrogen beam such that it either compensates for the loss of signal from the magnification of the VUV beam or enables measurements in a gas mixture to further slow down H₂ and improve the transit time and the Doppler shift calibration. By increasing the maximum pulse delay, also the influence on the frequency determination of the phase noise and residual shifts of the amplified pulses will be smaller (since this scales inversely proportional with pulse delay). This was the second largest uncertainty in the error budget of the measurement described in Chapter 4. In addition, the experimental setup for the phase calibration can be improved by using a more efficient transmission grating.

These adjustments could potentially lead to a further reduction of the uncertainty to the level of 10 kHz, at which the dissociation becomes sensitive to the proton charge radius at the percent level. This is sufficient to discriminate between the two discrepant values obtained from electronic and muonic hydrogen and possibly contribute to a solution of the proton radius puzzle [20]. Additionally, the same transition in parahydrogen can be measured, which does not have hyperfine structure and therefore enables a direct determination of the dissociation energy D_0 from the 'true' ground state.

A downside of determining the dissociation energy is that it always requires a combination of transitions, that are measured in different research groups. A direct test of theory in H₂ can be performed in our group from a determination of the fundamental ground tone (the vibrational splitting between the v = 0 and v = 1 state) [32]. This can be achieved by combining two measurements from different ground vibrational states, to a common excited state. Only about 10% of the population can be transferred to the v = 1 state using a discharge and therefore this measurement would also greatly benefit from the proposed improvements to the molecular beam.

7.2 Outlook on spectroscopy of the 1S - 2Stransition in He⁺

In preparation of the first ever measurement of the 1S - 2S transition frequency in He⁺, the vacuum system was already built-up and partly tested. In addition, the cooling laser has been built and has shown to performing well. However, the actual 1S - 2S excitation still requires a lot of other technical development.

For the experimental realization of this measurement, the helium ion has to be created, trapped and cooled. The first step is straightforward and most components are available. Helium atoms will be ionized from the meta-stable 2 ${}^{3}S_{1}$ state as discussed in Sec. 3.2.4. For this purpose, a pulsed meta-stable helium source has been developed and initial tests have been performed. A scheme of non-resonant ionization at 355 nm will be used for ionization. For this purpose a high-power laser pulse at 1064 nm is extracted from the pump laser system (Sec. 3.1.2) and up-converted using third-harmonic generation. The same laser will be used for three-photon ionization of beryllium, which will be extracted from an oven or an ablation target.

Trapping of the He⁺ and Be⁺ ions requires more technical development. The experiment requires a high degree of control over the motion of the ion, which is very challenging in combination with the high power (X)UV laser pulses. The (X)UV can lead to the creation of charge patches which will alter the trap potential and lead to excess micro-motion. Therefore a large effort is currently being made to design the trap such that it is shielded as much as possible from stray light, while still retaining optical access. In addition, a design is made to create the required laser frequencies for Doppler and ground state cooling. For the actual trap development, a collaboration has been started with T. Mehlstäubler and P. O. Schmidt from PTB in Braunschweig. They have shown to have the lowest heating rate ever achieved in a rf-trap [175], which is very beneficial for this experiment.

Although the results presented in Chapters 5 and 6 show great promise for the experiment in He⁺, the harmonic order was quite a bit lower than what is required for 1S-2S excitation and some additional aspects have to be considered when using light at effectively the 26th harmonic. The linear scaling of the phase noise amplitude with the harmonic order sets much more stringent limits on the phase noise of the fundamental FC pulses. From the estimated combined (FC and amplifier) phase noise of 50 mrad at the fundamental wavelength, a maximum Ramsey-fringe contrast of $\sim 35\%$ is expected for He⁺. This is sufficient to observe a Ramsey fringe, but not comfortable from an experimental point of view. Any additional broadening effect might completely wash out the Ramsey fringes and therefore a reduction of phase noise is desirable. The main source of phase noise originates from the parametric amplifier. Therefore, a new Ramsey-comb setup, based on the ULN frequency-comb laser, is being developed. The gain medium in the parametric amplifier will be changed to reduce the sensitivity to wavefront deviations and decrease the induced phase noise amplitude.

Because of the long upper-state lifetime, the maximum pulse delay in the experiment is determined by the technical limit set by the laser. The lifetime of the gain media in the pump laser system is 90 µs for Nd:YVO₄ and 330 µs for Nd:YAG. Therefore, the gain significantly reduces for a pulse delay which is a sizable fraction of the lifetime. This can be partly compensated, but for the initial experiments, a maximum pulse delay of 10 µs is assumed. This corresponds to a mode spacing of 100 kHz from which the transition frequency can be determined with an accuracy of ~1 kHz.

This level accuracy is much higher than what is reported from theory. The uncertainty on the calculated transition frequency is currently 300 kHz, which is fully dominated by the uncertainty of the nuclear charge radius extracted from scattering experiments [176]. The second largest contribution comes from the uncertainty in two-loop QED effects, which has recently been calculated with an impressive accuracy of 41 kHz [177–179]. With the (near) future improvements on the determination of the alpha-particle radius from spectroscopy of muonic He⁺, the uncertainty of the finite nuclear size effect is expected to reduced to the level of 60 kHz, which is then limited by the uncertainty of nuclear polarizability contributions [26]. This enables a test of QED theory at the level of 1 ppm, due to the large contribution of the Lamb-shift difference on the 1S - 2S interval in He⁺. Alternatively, an independent value for the nuclear charge radius can be obtained from this measurement and with further theoretical improvements, the Rydberg constant can be extracted independently from hydrogen spectroscopy. In addition, the 1S-2S transition frequency in ³He⁺ can be determined. This would allow for an accurate determination of the nuclear charge radius difference between the two isotopes, which is currently also under debate [15, 180, 181]. However, due to the hyperfine structure of ³He⁺,

and possibly a redesign of the main vacuum chamber.

this requires a much higher degree of control over stray magnetic fields

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Excitation and detection geometry of the xenon experiment

The measurements presented in Chapters 5 and 6 demonstrate the first RCS measurement in combination with HHG on the $5p^6 \rightarrow 5p^58s\ ^2[3/2]_1$ transition at 110 nm in 132 Xe. The experiments were conducted to test these techniques and the presented setup described in Sec. 3.2. This section contains some additional details on the experimental configuration and the alterations that were made of the setup to make the experiments work. An overview of the excitation configuration is shown in Fig. A.1. The individual elements of this configuration will be discussed in more detail in the following sections.

A.1 The pulsed atomic beam

The atomic beam was generated from a pulsed supersonic expansion of xenon atoms. A piezo valve with a nozzle diameter of $300 \,\mu\text{m}$ was used to create short gas pulses ($30 \,\mu\text{s}$) in vacuum. This led to a low gas load on the vacuum and enabled the use of a large skimmer in between the source and interaction chamber to avoid effects of skimmer clogging. The valve was mounted on a stack of translation stages to align it to the skimmer in two orthogonal directions. The backing pressure was deliberately kept low, because of previous reports of cluster formation

A. Excitation and detection geometry of the Xenon experiment



Figure A.1 – The excitation geometry of the xenon experiment. A pulsed atomic beam is created with a piezo valve and two subsequent skimmers (S1 and S2). The atoms are excited by a linearly polarized (y direction) focused VUV beam under a 90° angle and state-selectively ionized with a 1064 nm pulse. The ionization beam is focused only in the y direction using a cylindrical lens. Three sets of coils are used to compensate for the earth magnetic field.

in xenon [163, 164]. However, several tests with different pressures, nozzle diameter, skimmers and even a different valve (solenoid based) have not led to any evidence of such an effect in our experiment. The average pressure while operating the valve was 8×10^{-6} mbar in the source chamber and 1.8×10^{-7} mbar in the interaction chamber.

A skimmer with a circular aperture of 8 mm diameter was used at a distance of 200 mm, which is well below the mean free path of the xenon atoms. A second adjustable slit-skimmer was used at a distance of 460 mm from the valve to collimate the beam. It was made in house from 0.1 mm stainless steal foil. It consists of two separate parts, which were folded at an angle ($\sim 60^{\circ}$) to avoid excess collisions from direct back reflections of atoms. The two parts were mounted on a set of translation stages to both adjust the width and the position of the skimmer. For the experiments in Chapters 5 and 6 a width of 1 mm was used, which geometrically limits the maximum divergence of the beam to 1.4 mrad.

A.2 Excitation and ionization geometry

An overview of the excitation geometry is shown in Fig. A.1. The atoms were excited with two VUV pulses at a distance of 560 mm from the front face of the valve. The excitation beam is focused and intersects the atomic beam at an angle of 90°. Therefore the interaction zone has the form of a cylinder, of which the diameter is given by the refocused XUV beam (typically $15 - 30 \,\mu\text{m}$ at FWHM) and the length is determined by the slit width. The excitation beam is linearly polarized in the vertical (y) direction and the earth magnetic field is compensated with three sets of coils.

After excitation, the atoms are state-selectively ionized with a highpower 1064 nm, 60 ps laser pulse, which is delayed by 2 ns with respect to the second excitation pulse. The pulse is intense enough to create electrons from any metal surface. Therefore it is incident at 45° with respect to the atomic beam and cleanly pass through the vacuum chamber. The ionization beam profile is matched to the interaction geometry as good as possible. For this purpose the beam is focussed only in the vertical direction with a cylindrical lens. The lens is mounted on a translation stage, which enables motion in the vertical direction and simplifies the alignment with the interaction zone. The ions are extracted using a time-of-flight mass separator.

A.3 The time-of-flight mass separator

The time-of-flight (TOF) mass separator, which was designed for the experiments in Chapters 5 and 6, is shown in Fig. A.3. It consists of three round plates of 90 mm diameter, which are separated by 17 mm. In continuous-mode operation, the bottom plate is at 300 V, the middle plate is on 250 V and the top plate is grounded. The ions are created between the bottom and middle plate and accelerated upwards by the electric field towards a fast electron-multiplier detector (ETP ion detect, AF880). In pulsed operation the two bottom plates are initially both at 300 V so that there is no field between the plates, and then after excitation, the second plate is switched to 250 V in a few hundred nanoseconds. A drift tube of 46 cm is used to create sufficient separation of the dif-



Figure A.2 – A typical time-of-flight mass spectrum of xenon. Each individual isotope is clearly resolved. A zoom-in of the three isotopes of which the transition frequency was determined is shown in the lower right corner. The double peak structure is caused by a second velocity class in the atomic beam of which the origin could not be determined.

ferent xenon isotopes and the voltage ratio was chosen such that these are nicely focused in time at the detector position. The middle and top plate have a grid in the center, which transmit the ions and retains a nicely homogeneous electric field in the interaction region. A set of deflection plates were placed at a distance of 40 mm from the top extraction plate to compensate for the forward velocity of the xenon atoms. Due to geometrical constraints, the detector could not be placed exactly above the excitation zone, but was slightly displaced (13 mm off-axis). The ions were steered onto the detector, by optimizing the signal as a function of the deflection voltage. The whole system is attached directly to the top flange of the main vacuum chamber (Sec. 3.2) with threaded rods. The plates are isolated from the rods with ceramic spacers, which are shielded with stainless steel caps to avoid charging-up effects. The electron-multiplier detector operates at $-3 \, \text{kV}$ and a grounded grid is placed at 20 mm from the detector to reduce the electric field in the drift region.

A typical example of a xenon mass spectrum is shown in Fig. A.2. The time-of-flight of the xenon atoms is $\sim 30 \,\mu s$. The isotopes are clearly resolved and the time resolution is $\sim 5 \,\mathrm{ns}$. A zoom-in of the TOF spectrum of the three isotopes which were used in experiments described in Chapter 6 is shown in the lower right corner. It is clearly visible that the signal of each individual isotope shows a double peak structure. A thorough investigation of this effect did not lead to a determination of its origin. The only conclusion which could be drawn is that two peaks seem to come from two different velocity classes in the atomic beam, but no parameter of the expansion had a significant influence on the observed structure. Therefore, the first (and highest) peak was selected in the data acquisition system (using Boxcar integrators) to avoid potential issues with additional Doppler shifts and broadenings.

A. Excitation and detection geometry of the Xenon experiment



Appendix \mathbb{B}

Unequal-photon excitation scheme in krypton

Excitation of the 1S - 2S transition in He⁺ will be done with two unequal photons as is shown in Fig. B.1. One photon at the 25^{th} harmonic (32 nm) and one at the fundamental wavelength (790 nm). This scheme enhances the excitation rate significantly with respect to the more conventional 2×60 nm photon scheme. This has two reasons, namely that the detuning from the 2P state is much smaller at 32 nm than at 60 nm and that the excitation rate scales linearly with the intensity of the fundamental beam, which is much higher than at any harmonic.

Some initial test of this scheme was performed using the two-photon $4p^6 \rightarrow 4p^55p[1/2]_0$ transition in krypton. The transition is excited with one photon from the seventh harmonic at 121.5 nm and one photon from the fundamental beam at 850 nm as illustrated in Fig. B.1. An intermediate state, which is slightly detuned from the single VUV photon was used to enhance the excitation rate. The transition from the ground state to this $4p^55s[3/2]_1$ state is dipole allowed and it therefore couples strongly to the VUV photon. The excited Kr atoms were state-selectively ionized with a 355 nm photon. The NIR intensity is tuned to be well below the regime of multi-photon ionization. The initial excitation rate was below the detection limit, but by tuning the central wavelength closer to resonance of the intermediate state, the excitation probability was enhanced significantly (> 500 limited by the sensitivity of the detection method). Also, a strong intensity dependence of the NIR light was observed as expected. However, due to the relatively



Figure B.1 – Simplified energy level diagram in He⁺ and krypton. An unequal two-photon excitation scheme of the 1S - 2S transition in He⁺ and the $4p^6 \rightarrow 4p^55p[1/2]_0$ transition in krypton. The high density of states in krypton led to a large ac-Stark shift and unknown decay channels. These limitations will not be relevant for the He⁺ experiment because the gross energy structure is much wider spaced.

high density of states in krypton, Ramsey fringes could not be observed. There was a clear additional decay channel from the excited state, which was ionized by an additional NIR photon and therefore the coherence was lost. In addition, the situation in Kr is less convenient than in and He⁺, because the NIR beam strongly couples to other states from the excited $4p^55p[1/2]_0$ state. This leads to large ac-Stark shifts and therefore possible additional phase noise on the Ramsey fringes due to intensity fluctuations. This test system was therefore not suitable for a Ramsey-comb experiment, but nonetheless provided some useful insights into the excitation scheme.

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List of Publications

The chapters in this thesis are based on the following publications:

- Chapter 4: R.K. Altmann, L.S. Dreissen, E.J. Salumbides, W. Ubachs, and K.S.E. Eikema, "Deep-Ultraviolet Frequency Metrology of H₂ for Tests of Molecular Quantum Theory", *Phys. Rev. Lett.* **120**, 043204 (2018).
- Chapter 5: L.S. Dreissen, C.F. Roth, E.L. Gründeman, J.J. Krauth, M. Favier, and K.S.E. Eikema, "High-Precision Ramsey-Comb Spectroscopy Based on High-Harmonic Generation", *Phys. Rev. Lett.* 123, 143001 (2019).
- Chapter 6: L.S. Dreissen, C.F. Roth, E.L. Gründeman, J.J. Krauth, M. Favier, and K.S.E. Eikema, "Demonstration of Ramsey-Comb Precision Spectroscopy in Xenon at Vacuum Ultraviolet Wavelengths Produced with High-Harmonic Generation", Submitted.

The author also contributed to the following publications:

 R.K. Altmann, S. Galtier, L.S. Dreissen, and K.S.E. Eikema, "High-Precision Ramsey-comb Spectroscopy at Deep Ultraviolet Wavelengths", *Phys. Rev. Lett.* **117**, 173201 (2016).

- (ii) S. Galtier, R.K. Altmann, L.S. Dreissen, and K.S.E. Eikema, "High-Accuracy Deep-UV Ramsey-Comb Spectroscopy in Krypton", *Appl. Phys. B* 123, 16 (2017).
- (iii) L.S. Dreissen, H.F. Schouten, W. Ubachs, S.B. Raghunathan, and T.D. Visser, "Active Two-Dimensional Steering of Radiation from a Nanoaperture", *Nano Lett.* 18, 7207-7210 (2018).
Summary

The energy structure of simple atomic systems, in particular the hydrogen atom, has been studied for more than a century. The theoretical description of the energy levels of a hydrogen atom was first given by Niels Bohr, who stated that the electron in the atom can only occupy discrete energy levels, which later led to the formulation of quantum mechanics. The experimental investigations of transitions between these energy levels is called spectroscopy. Such transitions can be enabled by light, if the energy of the photons (related to the wavelength or frequency) of the light matches exactly with the energy between the two states. Therefore the field of spectroscopy has improved tremendously with the invention of the laser, as it has a high spectral purity. With increasing spectroscopic accuracy, substructure in the energy levels of the atom were revealed. These additional features led to the development of more extensive theoretical models, for example by including relativistic effects, and eventually to the formulation of the theory of quantum electrodynamics (QED). This theory describes the interaction of light and matter and the influence of the creation and annihilation of virtual particles on the energy structure of the atom. The ongoing comparison between more accurate measurements and improved calculations has tested this theory with extremely high precision and it has passed every time. The invention of the frequency-comb laser (referenced to an atomic clock) has been instrumental in this process because it provides an accurate absolute frequency calibration for the spectroscopy laser. As a result, the 1S - 2S transition frequency in atomic hydrogen has been determined with a dazzling 15-digit precision. The theoretical prediction of the transition frequency also relies on several fundamental quantities, such as the proton charge radius or the Rydberg constant, which can only be extracted from measurements. In some cases the accuracy of theoretical energy level predictions is limited by the accuracy of those fundamental quantities, and this hampers further tests of

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fundamental theory. In hydrogen it is the case with the proton charge radius and therefore the accuracy of the value was improved with spectroscopy on a more exotic atom: *muonic* hydrogen. The extracted value from this measurement was ten times more accurate but also 4% off from the generally accepted value, corresponding to a 5.6σ deviation. This conundrum is known as the proton radius puzzle, which is being investigated by performing more accurate measurements in atomic hydrogen, but also in other species as this might provide new insights.

The work presented in this thesis is focused on precision spectroscopy of singly-ionized helium and *molecular* hydrogen. As the first target is hydrogen-like its energy level structure can be calculated with a similar high level of precision. Because QED terms scale with higher-orders of the atom number (Z) they are bigger in He⁺. Moreover, a similar comparison as in hydrogen can be made with measurements which have been performed in muonic He⁺. The second target, the hydrogen molecule, is a benchmark system for tests of molecular quantum theory, as its ground state energy (relative to the dissociation or ionization energy) has been calculated with an impressive level of accuracy. The additional degrees of freedom, such as rotation an vibration, enrich the energy level structure and therefore enable extra possibilities to investigate potential extensions of the standard model, including hypothetical fifth forces on the angstrom length scale. The experimental challenge arises from the short excitation wavelength that these species require. Excitation to the first electronically excited state in H_2 requires 202 nm. which is deep in the ultraviolet part of the spectrum. The 1S - 2Stransition in He⁺ requires an even shorter wavelength of 60 nm or lower. This is in the extreme ultraviolet spectral range, which is absorbed by most materials including air. At these wavelengths, no (known) laser materials exist and therefore generation of this light for precision spectroscopy relies (mostly) on nonlinear processes for up-conversion of the frequency. For these processes, a high peak-intensity is required and therefore pulsed lasers are generally used for this purpose. The broad bandwidth of a pulsed laser typically limits the spectroscopic precision. However, the repetitive nature of a frequency-comb laser enables a much higher level of accuracy. We employ the Ramsey-comb spectroscopy technique, based on two amplified frequency-comb pulses, to combine the required peak-intensity with high spectroscopic precision. It was developed in our lab and has shown to perform well in the near-infrared and deep-ultraviolet wavelengths using low-harmonic generation in nonlinear crystals. The technique can readily be used for high-precision spectroscopy of the X - EF transition in H₂ by fourth-harmonic generation of 808 nm. One of the main goals of this work was to also extend this method with high-harmonic generation for 1S - 2S spectroscopy in He⁺.

As mentioned before, Ramsey-comb spectroscopy relies on a Ramseytype excitation with two amplified (and up-converted) frequency-comb pulses. In Ramsey spectroscopy, excitation with two consecutive pulses leads to interference between two created superpositions of the ground and the excited state. For two phase-locked pulses, the final excited state population is determined by the delay and the phase difference between the pulses. Scanning either one of these parameters leads to an oscillation of the excited state population, known as a Ramsey fringe, from which the transition frequency can be determined. The pulses emitted by a frequency-comb laser are ideal for Ramsey spectroscopy, as they have a fixed (and known) inter-pulse delay and a well-defined phase relation. However, a significant (and typically unknown) phase shift is induced by amplifying a pair of these pulses for efficient up-conversion, which leads to a shift of the extracted transition frequency. In order to circumvent this problem, a series of Ramsev fringes is recorded at intervals that are an integer multiple of the repetition time of the laser, while only the differential phase of the fringes is used to determine the transition frequency. This leads to a significant suppression of any constant phase shift (and also the ac-Stark shift). The extension of this technique with high-harmonic generation is not trivial, as the up-conversion process itself can lead to a phase shift which is delay-dependent. A more extensive description of this technique and other physical concepts are given in Chapter 2. It starts from some basic aspects of pulses and pulse trains, and is followed by a description of the key properties of the frequency-comb laser and nonlinear processes in both the perturbative and in the strong-field regime. After this, the method of Ramsey-comb spectroscopy is explained and the expected consequences from combining this technique with high-harmonic generation is discussed.

The experimental implementation of the Ramsey-comb technique is described in the first part of Chapter 3. The setup is based on a Ti:sapphire frequency-comb laser with an emission spectrum centered around 800 nm. The modes of this laser are is referenced to a commercial cesium-atomic clock. Two pulses emitted by the frequency-comb laser are selectively amplified in an optical parametric amplifier (also based on non-linear frequency conversion) to achieve peak-intensities of $\sim 10^{14} \,\mathrm{W/\,cm^2}$, which is sufficient for high-harmonic generation. The amplifier is pumped by two pulses from a home-built pump laser, of which a specific pair of pump pulses, and therefore also a pair of amplified frequency-comb pulses, can be selected. The amplified frequency-comb pulse pair is up-converted and used for Ramsey-comb spectroscopy.

For the experiments described in Chapter 4, the fourth harmonic was generated in non-linear crystals to excite the two-photon X - EF transition in H₂. A molecular beam was created from a liquid-nitrogen cooled value and the molecules were excited in a counter-propagating geometry to reduce Doppler effects. The obtained transition frequency of 2 971 234 992 965(73) kHz presents a hundred-fold improvement of the accuracy over the previous determination and has contributed to the most accurate determination of the dissociation energy of H₂.

The experiments described in Chapters 5 and 6 were performed in preparation of 1S - 2S spectroscopy in He⁺. For this purpose a new 3 m-long vacuum setup was designed and built-up. The main considerations for the design are given in the second part of Chapter 3. The setup consists of seven vacuum chambers, in which high-harmonics are created and refocused in a spectroscopy chamber using a toroidal mirror pair. In the future, an ion trap will be placed in the center of this chamber, where a single He^+ ion will be trapped alongside a single Be^+ ion for sympathetic cooling purposes. The setup was tested by performing Ramsey-comb spectroscopy on the $5p^6 \rightarrow 5p^5 8s^{-2}[3/2]_1$ transition in xenon at 110 nm (the seventh harmonic of 770 nm). Here, the xenon atoms were excited in an atomic beam at 90° angle to reduce the first-order Doppler shift. The main results of this experiment are given in Chapter 5. They show that the phase shifts from up-conversion with high-harmonic generation are significant on short timescales (up to 1 rad at 8 ns), but disappear almost completely when increasing the pulse delay. Therefore the absolute transition frequency could be calibrated with sub-MHz accuracy, which is unprecedented for spectroscopy with light from a high-harmonic generation source. The obtained transition frequency of 2726 086 012 471(630) kHz has a relative accuracy of 2.3×10^{-10} and improves upon the previous determination by a factor 10^4 . A more extensive description of the experiment in xenon and the obtained results is given in Chapter 6.

The results from Chapters 5 and 6 show great promise for future measurements of the 1S - 2S transition in He⁺, as the interaction time will then be much longer (because of the long upper state lifetime of 1.9 ms and the fact that the ion can be trapped for a long time) leading to a much higher accuracy. Chapter 7 gives a brief overview of the status of the He⁺ experiment, and an outlook on future improvements to the system to reach a higher spectroscopic accuracy in H₂. These future experiments will enable ppm-level tests of QED in the case of He⁺ and searches for physics beyond the standard model.

Samenvatting

De energiestructuur van eenvoudige atomaire systemen, in het bijzonder van het waterstofatoom, wordt al ruim een eeuw bestudeerd. De theoretische beschrijving van de energieniveaus in atomair waterstof werd als eerst beschreven door Niels Bohr. Hij poneerde dat het elektron in het atoom enkel discrete energieniveaus kon bezetten, wat later heeft geleid tot de formulering van de kwantummechanica. De experimentele observatie van een overgang tussen verschillende energieniveaus met behulp van licht heet spectroscopie. Zulke overgangen kunnen tot stand worden gebracht wanneer de fotonenergie van het licht (gerelateerd aan de golflengte of de frequentie) precies overeenkomt met het energieverschil tussen de twee niveaus. Het veld van spectroscopie heeft een snelle ontwikkeling doorgemaakt met de komst van de laser, omdat deze licht met hoge spectrale zuiverheid mogelijk maakt. Door de verbeterde spectroscopische nauwkeurigheid werden substructuren in de energiespectrum onthuld. Deze extra karakteristieken leidde tot meer uitgebreide theoretische modellen, waarbij bijvoorbeeld relativistische effecten meegenomen werden, en uiteindelijk tot de formulering van de kwantumelektrodynamica of QED (quantum electrodynamics). Deze laatste theorie beschrijft de wisselwerking van licht met materie, en de invloed van de creatie en annihilatie van virtuele deeltjes op de energieniveaus in een atoom. QED is rigoureus getest door voortdurend de vergelijking te maken tussen steeds nauwkeurigere metingen en verbeterde berekeningen van de energieniveaus in atomen en moleculen. De ontwikkeling van de frequentiekamlaser (FK-laser) is cruciaal geweest in dit proces, omdat het een absolute frequentiekalibratie verschaft. Met behulp van deze FKlaser is de 1S - 2S overgangsenergie (die evenredig is met de frequentie) in atomair waterstof gemeten met een indrukwekkende nauwkeurigheid van 15 cijfers. De theoretische bepaling van deze overgangsfrequentie is afhankelijk van een aantal fundamentele constanten, zoals de Rydberg constante en de effectieve ladingstraal van de proton, welke enkel experimenteel kunnen worden bepaald. In sommige gevallen wordt de nauwkeurigheid van de berekende overgangsfrequentie gelimiteerd door de onzekerheid van een dergelijke fundamentele grootheid en niet door het theoretische model zelf, wat verdere toetsing van de theorie belemmert. In waterstof is dit het geval met de protonstraal (r_p) en daarom is de waarde hiervan verbeterd door middel van spectroscopie aan een meer exotisch atoom: muonisch waterstof. Het muon is ~ 200 keer zwaarder dan het elektron, waardoor het zich gemiddeld gezien dichter bij de atoomkern bevindt en dus gevoeliger is voor de invloed van de kern. De resulterende verkregen waarde voor r_p was daardoor tien keer nauwkeuriger dan de tot dan toe algemeen geaccepteerde waarde, maar week hier ook 4% vanaf, wat overeenkomt met een verschil van 5.6 σ . Dit raadsel is sindsdien bekend als de *protonstraalpuzzel* en wordt onderzocht met continu nauwkeurigere metingen in atomair waterstof, maar ook met behulp van andere systemen omdat deze wellicht kunnen leiden tot nieuwe inzichten.

Het werk waarop dit proefschrift berust, is gericht op hoge-precisie spectroscopie in enkelvoudig geïoniseerd helium (He⁺) en *moleculair* waterstof (H_2) . Het eerste systeem heeft maar één enkel elektron, d.w.z. het is atomir waterstof-achtig, en de energiestructuur kan daarom met een hoge precisie worden berekend. De interessante QED-termen schalen met hogere-ordes van het atoomgetal (Z) en omdat He⁺ een zwaarder atoom is, zijn deze dus groter in dit systeem. Hierdoor zou potentieel de validiteit van QED met een hogere precisie getest kunnen worden. Bovendien kan er een vergelijking gemaakt worden met metingen die zijn uitgevoerd in muonisch He⁺, wat een vergelijkbare situatie opleverd als in atomair waterstof en dus potentieel kan leiden tot nieuwe inzichten in de protonstraalpuzzel. Het tweede systeem, moleculair waterstof, is een ijksysteem voor moleculaire kwantumtheorie, omdat de ionizatie- en dissociatienergie berekend kan worden met een zeer hoge nauwkeurigheid. H_2 bestaat uit twee gebonden waterstof atomen die ten opzichte van elkaar kunnen vibreren en roteren. Deze bijkomende vrijheidsgraden in moleculen verrijken de energiestructuur en geven daarom extra mogelijkheden tot het onderzoeken van potentiële uitbreidingen van het standaardmodel, waaronder een hypothetische fundamentele vijfde kracht op een angstrom lengteschaal. In beide systemen is de grote uitdaging de korte golflengtes die nodig zijn om de energiestructuur te kunnen onderzoeken. Excitatie van de eerste elektronisch aangeslagen toestand in H_2 vereist licht bij een golflengte van 202 nm, wat ook wel diep-ultraviolet genoemd wordt. Excitatie van de 1S-2S overgang in He⁺ heeft zelfs een nog kortere golflengte nodig, namelijk ≤ 60 nm. Dit ligt in het extreemultraviolette deel van het spectrum en wordt geabsorbeerd door meeste materialen, inclusief lucht. Voor het genereren van dit soort licht bestaan geen (bekende) laser materialen en precisie spectroscopie bij deze golflengtes is (voornamelijk) gebaseerd op niet-lineaire processen voor frequentieconversie. Deze processen berusten op de niet-lineaire respons van elektronen in een materiaal en vereisen daarom hoge piekintensiteiten. Zulke piekintensiteiten kunnen veelal bereikt worden met gepulsde lasers omdat de energie dan in een korte tijd geconcentreerd wordt. Echter, omdat deze pulsen zijn opgebouwd uit een groot aantal frequenties. limiteert de brede bandbreedte doorgaans de nauwkeurigheid van het experiment. Het repetitieve karakter van de frequentiekamlaser maakt een hogere nauwkeurigheid mogelijk. Wij gebruiken de Ramsey-kam spectroscopie techniek, gebaseerd op twee versterkte frequentiekam laserpulsen om het hoge benodigde piekintensiteit te combineren met hoge precisie. De Ramsey-kam techniek is ontwikkeld in ons lab en succesvol gedemonstreerd in het nabije infrarood en het diepe ultraviolet, waarbij het licht in het laatstgenoemde experiment gegenereerd is met behulp van lage-harmonische generatie in niet-lineaire kristallen. De techniek kan dus direct worden toegepast voor hoge-precisie spectroscopie van de eerste elektronische overgang (X - EF) in H₂ door middel van vierdeharmonische generatie van 808 nm. Excitatie van de 1S-2S overgang in He⁺ is aanzienlijk moeilijker omdat hiervoor de Ramsey-kam techniek gecombineerd moet worden met hoge-harmonische generatie.

Zoals al eerder aangegeven berust Ramsey-kam spectroscopie op een Ramsey-achtige excitatie met twee versterkte (en op-geconverteerde) frequentiekampulsen. In Ramsey-spectroscopie leidt excitatie met twee achtereenvolgende pulsen tot interferentie tussen de twee gecreëerde superposities van de grond- en de aangeslagen toestand. Voor twee fasecoherente pulsen is de resulterende populatieverdeling afhankelijk van het tijds- en faseverschil tussen de twee pulsen. Door één van deze twee parameters te scannen kan een oscillatie van de populatie in de aangeslagen toestand geobserveerd worden. Deze oscillatie staat bekend als een Ramsey-oscillatie en kan gebruikt worden om de overgangsfrequentie

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tussen de twee toestanden te bepalen. De pulsen die worden uitgezonden door een frequentiekamlaser zijn ideaal voor Ramsey-spectroscopie, omdat ze op een nauwkeurig bekend tijdsverschil worden uitgezonden en een goed gedefinieerde faserelatie tot elkaar hebben. Desalniettemin induceert het versterkingsproces een significante (en meestal onbekende) faseverschuiving, wat leidt tot een systematische verschuiving van het excitatiepatroon en daarmee de daaruit bepaalde overgangsfrequentie. Om dit probleem te vermijden wordt er een *serie* van Ramsey-oscillaties gemeten op een vast tijdsinterval van elkaar welke gelijk is aan een geheel aantal keer de repetitietijd van de laser. Hierdoor kan de overgangsfrequentie worden bepaald uit alleen het fase*verschil* tussen de gemeten oscillaties, wat leidt tot een significante onderdrukking van alle effecten die een *constante* faseverschuiving tussen de pulsen veroorzaken (en ook de ac-Stark verschuiving).

De uitbreiding van Ramsey-kam spectroscopie met hoge-harmonische generatie is niet triviaal omdat dit proces kan leiden tot een *tijdsafhankelijke* faseverschuiving van de excitatiepulsen. Zoals uitgebreid in Hoofdstuk 2 beschreven staat, berust hoge-harmonische generatie op ionisatie van atomen en het versnellen van het vrijgekomen elektron in het elektrisch veld van de laser. Tijdens de recombinatie van zo een elektron en het ion komt een extreem-ultraviolet foton vrij. Deze laatste stap is echter niet heel waarschijnlijk en daarom wordt er tijdens hoge-harmonische generatie een dynamisch plasma gecreëerd, wat invloed heeft op de fase van de gegenereerde extreem-ultraviolet excitatiepulsen. De resulterende onbekende en tijdsafhankelijke faseverschuiving leidt tot een systematische verschuiving van de verkregen overgangsfrequentie. Daarom is het noodzakelijk om deze effecten zeer zorgvuldig te karakteriseren, voordat Ramsey-kam spectroscopie succesvol verenigd kan worden met hoge-harmonische generatie.

Een meer uitgebreide beschrijving van de bovengenoemde technieken en andere fysische concepten zijn gegeven in Hoofdstuk 2. Het is opgebouwd vanuit een introductie van lichtpulsen en pulstreinen, gevolgd door een uitleg van de belangrijkste eigenschappen van de frequentiekamlaser en niet-lineaire optische processen in zowel het perturbatieveals in het sterke-veld-regime. Hierna wordt de methode van Ramsey-kam spectroscopie uitgelegd en de verwachtte consequenties van de combinatie van deze techniek met hoge-harmonische generatie beschreven. De experimentele realisatie van de Ramsey-kam techniek is beschreven in het eerste gedeelte van Hoofdstuk 3. De opstelling is gebaseerd op een Ti:saffier frequentiekamlaser met een centrale emissiegolflengte rond 800 nm en die gekalibreerd is aan een commerciële Cesium-klok. Twee frequentiekampulsen worden selectief versterkt in een optische parametrische versterker (ook gebaseerd op niet-lineaire frequentieconversie) om piekintensiteiten van ~ 10^{14} W/ cm² te behalen, wat voldoende is voor hoge-harmonische generatie. De versterker wordt van energie voorzien ('gepompt') door twee pulsen die worden gegenereerd door een huisgemaakte pomplaser, waarvan het specifieke pomp-pulspaar, en dus ook het versterkte frequentiekampulspaar, kan worden aangepast. De versterkte frequentiekampulsen worden op-geconverteerd en gebruikt voor Ramsey-kam spectroscopie.

Voor de experimenten die beschreven zijn in Hoofdstuk 4, is de vierdeharmonische gegenereerd in niet-lineaire kristallen voor excitatie van de twee-foton X - EF overgang in H₂. Een moleculaire bundel werd gecreëerd vanuit een met vloeibaar stikstof gekoelde klep en de moleculen werden geëxciteerd met tegenovergesteld propagerende laserbundels om de Doppler effecten te verkleinen. De verkregen overgangsfrequentie van 2 971 234 992 965(73) kHz is honderd keer nauwkeuriger ten opzichte van de vorige meting en heeft mede geleid tot de meest nauwkeurige bepaling van de dissociatie-energie in H₂.

De experimenten die staan beschreven in de Hoofdstukken 5 en 6 zijn uitgevoerd ter voorbereiding van 1S-2S spectroscopie in He⁺. Voor dit doeleinde is een nieuwe 3 m-lange vacuüm opstelling ontworpen en opgebouwd. De voornaamste overwegingen voor het ontwerp staan beschreven in het tweede gedeelte van Hoofdstuk 3. De opstelling bestaat uit zeven vacuümkamers voor het genereren en herfocusseren van een hogeharmonische bundel in een spectroscopiekamer met behulp van twee toroidale spiegels. In de toekomstige experimenten zal hier een enkel He⁺ ion gevangen worden naast een enkel Be⁺ ion voor sympathetische koelingsdoeleinden. Deze opstelling is getest door Ramsey-kam spectroscopie aan de $5p^6 \rightarrow 5p^58s\ ^2[3/2]_1$ overgang in xenon bij 110 nm (de zevende harmonische van 770 nm) te verrichten. Hierbij zijn de xenon atomen geëxciteerd in een atoombundel onder een hoek van 90° om de eerste-orde Dopplerverschuiving te verkleinen. De voornaamste resultaten van dit experiment zijn beschreven in Hoofdstuk 5. Ze laten zien dat

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de faseverschuivingen, geïnduceerd door het hoge-harmonische proces, significant zijn op korte tijdsschaal (tot 1 rad bij 8 ns), maar dat deze vrijwel helemaal verdwijnen op grotere tijdsschalen. Hierdoor kon de overgangsfrequentie bepaald worden met sub-MHz nauwkeurigheid, wat nog nooit eerder bereikt was met licht afkomstig van hoge-harmonische generatie. De verkregen overgangsfrequentie van $2.726\,086\,012\,471(630)\,\text{kHz}$ heeft een relatieve nauwkeurigheid van 2.3×10^{-10} , wat de vorige meting verbetert met een factor 10^4 . Een uitgebreide beschrijving van het experiment in xenon wordt gegeven in Hoofdstuk 6.

De resultaten uit de Hoofdstukken 5 en 6 zijn zeer veelbelovend voor toekomstige metingen van de 1S - 2S overgang in He⁺, omdat de interactietijd dan veel langer zal zijn (door de lange 1.9 ms levensduur van de aangeslagen toestand en het feit dat het ion gevangen kan worden voor lange tijd) wat leidt tot een veel hogere nauwkeurigheid. Hoofdstuk 7 geeft een kort overzicht van de status van dit experiment, en een vooruitzicht van toekomstige verbeteringen aan het systeem voor een hogere spectroscopische nauwkeurigheid in H₂. Deze experimenten zullen de mogelijkheid geven tot ppm-niveau toetsingen van QED in het geval van He⁺ en nieuwe zoektochten naar mogelijke uitbreidingen van het standaardmodel.

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