Summary

The field of spectroscopy is concerned with the precise measurement of transition frequencies in a wide variety of e.g. atomic and molecular systems. Such frequency measurements are the most accurate measurements possible, and they give detailed insight into the structure of matter as well as into the interaction between matter and radiation. As such, it is hardly astonishing that they have been a driving force behind many advancements of the physical description of nature. And although the precision of measuring frequencies has progressed from the crude solar-oriented measurements of ancient times to modern atomic clock measurements of an astonishing 1-part-in-10-quadrillion accuracy, this is by no means the limit. Even currently available technology still allows for large improvements in accuracy, although the experiments in that direction are very complicated.

An important role in the emergence of modern frequency metrology experiments has been and still is being played by the laser, because such a device can be made to emit a very well-defined frequency. When stabilized, this narrow-band light can be used as a very pure source to probe the transition frequencies of e.g. atoms. Still, the laser frequency must be calibrated using a stable reference frequency, such as an atomic clock. Today's primary frequency standard is the cesium atomic clock, which produces a frequency of 9.2 GHz, in the radio frequency (RF) domain. This poses quite a problem, as the optical frequencies that are produced by lasers are some 100 000 times larger. For that reason, linking optical frequencies to the RF standard has always been a very difficult and inefficient endeavor, especially since these experiments could be used for only one frequency.

The invention of the frequency comb laser in 1999 caused a revolutionary simplification of these experiments. Such a laser does not emit continuous light, but produces very short pulses, lasting only about a millionth of a billionth of a second (10 fs). In contrast to single-mode lasers, the frequency spectrum of comb lasers consists of a large number of simultaneously oscillating modes which have a very regular spacing equal to the repetition frequency of the laser pulses, f_{rep}. This comb structure of modes can be stabilized when both the spacing of the teeth, f_{rep}, and the offset of the entire comb are carefully controlled. This second parameter is related to the pulse-to-pulse difference in the phase shift between the carrier wave and the envelope of the pulses, hence the name carrier-envelope offset frequency (f_{ceo}). As both these parameters are RF frequencies, they can be locked easily to a reference oscillator. The frequency comb then acts much like a ruler, to which unknown frequencies can be compared and thus measured. With this technique, the accuracy of a radio-frequency atomic clock could be transferred to the optical domain, simplifying absolute frequency measurements enormously.

Several important lines of research stand to gain from these developments. Theories of the structure of matter, like quantum-electrodynamics (QED), can be tested to unprecedented levels of accuracy, provided the precision of the experimental methods is comparable to that of theoretical calculations. As the latter are most accurate for the ground-state transitions in simple atoms and ions, such as hydrogen, helium and hydrogen-like ions, performing experiments on these transitions is especially attractive. However, these transitions invariably lie in the vacuum ultraviolet (VUV) or the extreme ultraviolet (XUV) wavelength regions, which are extremely arduous to cover using conventional laser technology.

The development of modern clock devices is similarly linked to progress in ultra-precise spectroscopy. Higher precision can be obtained by using a higher clock frequency: a clock that ticks faster, divides time in smaller chunks. Great experimental effort is expended in order to replace today's microwave atomic clocks with clocks that run on optical frequencies. Undoubtedly these will in turn be supplanted by clocks operating on UV, VUV or even XUV frequencies in the future.

Performing high-resolution laser spectroscopy at the high frequencies demanded in these and other applications is not an easy task. Narrow-band lasers at XUV or VUV wavelengths are almost impossible to construct, so the traditional methods of laser spectroscopy, with or without a frequency comb to calibrate the narrow-band laser, are not viable. The work presented in this dissertation, therefore, provides a new method to extend the high accuracy of a frequency comb laser to higher frequencies.

This method, of which the theoretical, conceptual and experimental details are presented in chapters 2–4, is based on two ideas. The first is to use the pulsed output of a frequency comb to excite the studied system (e.g. the atom) directly. The excitation contribution of consecutive phase-locked pulses will interfere, and by changing the phase difference between the pulses, the excitation can be modulated. From this modulation signal, the transition frequency can be determined. This approach is closely related to Ramsey's method of separated oscillatory fields, which is routinely used for atomic clocks in the microwave region.

The other cornerstone of the method described in this thesis is the up-conversion of the comb pulses to the required wavelength range using frequency mixing in crystals or gases. If the phase coherence of the comb pulses survives this frequency-conversion process, the pulses can be used to perform direct frequency comb spectroscopy in the VUV or even XUV. Because such frequency-conversion processes are usually quite inefficient, it is necessary to amplify the comb pulses before up-conversion. Again, the phase coherence of the pulses must not be compromised by this amplification process.

Careful control of the two parameters of a frequency comb laser is required for such an experiment to work, and in chapter 5 detailed studies are presented on the carrier-envelope phase (ϕ_{ce}) dynamics of our comb laser system. Real-time measurements were performed on the influence of the feedback loops, the nonlinear interaction in the micro-structured fiber employed in the ϕ_{ce} detection system, the pump laser and environmental influences. The most important findings were that the effects of fiber nonlinearities are too small to be detected in our experiments, and that the use of a single-mode pump laser dramatically improves the stability of phase control compared to the use of a multi-mode pump laser.

The feasibility of the proposed method of direct frequency comb spectroscopy at high frequencies is demonstrated in chapter 6, where an experiment is described on a deep-UV transition in krypton at 2×212.5 nm. Short trains of comb pulses were amplified in a multi-pass non-saturating Ti:sapphire amplifier, and after two stages of frequency doubling in BBO crystals, the resulting deep-UV pulses were sent through a beam of krypton atoms, while any ions produced were detected. Careful measurement of the phase changes introduced by the amplifier ensured that the pulse-to-pulse phase difference was known. Changing the repetition rate of the frequency comb resulted in high-contrast modulation of the ion production, demonstrating that the deep-UV comb pulses retain the required phase coherence throughout the amplification and frequency-conversion processes. By recording modulation signals for different isotopes, the isotope shifts could be determined with a precision of a few hundred kHz. An

absolute frequency measurement could be performed by combining measurements at three sufficiently different repetition rates. In this way, the transition frequency could be determined with a precision of 3.5 MHz, which is an order of magnitude more accurate than earlier measurements using nanosecond-pulsed lasers.

Since this experiment used only frequency doubling in crystals, a new experiment was set up in order to test our method using harmonic generation in a gas. The interactions in gaseous media are much more likely to cause detrimental phase distortions than those occurring in crystals. Chapter 7 describes an experiment on the 125 nm transition in xenon, which is excited using amplified comb pulses which have been frequency doubled in a crystal and subsequently frequency tripled in a gas cell. Again high-quality interference signals were recorded. Extensive investigation of the effects of gas pressure and driving laser intensity have been performed using oxygen and acetylene for a medium. The xenon atoms were used as high-resolution phase detectors. No significant correlation was found between the harmonic-generation parameters and the recorded phases, from which the conclusion was drawn that direct frequency comb spectroscopy in the VUV using harmonic generation in a gas is indeed possible.

In this experiment, it was also demonstrated that an increase in resolution is possible not only by increasing the number of pulses, but also by increasing the delay between just two pulses. The latter method is preferred in our experiments, as measurements of the amplifier-induced phase shifts could only be performed on pulse pairs; apart from that, it is generally easier to amplify just two pulses.

The experiments of chapters 6 and 7 are complicated by the multi-pass amplifier used, which makes it necessary to track the phase changes it induces. A different amplification approach is presented in chapter 8. This approach concerns the use of a non-collinear optical parametric chirped-pulse amplifier (NOPCPA), which uses the instantaneous parametric interaction in a BBO crystal to transfer power from an intense pump laser beam to the frequency comb laser seed beam. As the interaction preserves the phase of the seed pulses, high-power phase-controlled frequency comb pulses can be produced.

To this end, a Nd:YAG pump laser system was built capable of delivering 160 mJ, 532 nm pulses at a 30 Hz repetition rate, which were synchronized to the frequency comb. This system was used to pump a three-stage NOPCPA system. Due to the high damage threshold of BBO, modest stretching could be applied to the seed pulses, leading to a very compact and stable setup. Adaptive pulse shaping was employed to fine-tune the dispersion compensation of the stretcher-compressor combination, yielding a compressed pulse duration of 7.5 fs. The complete NOPCPA system delivered 15.5 mJ pulses after compression, corresponding to 2 TW. Pulse contrast measurements showed a

2×10^{-8} pre-pulse contrast between the main pulse and the fluorescence background. An amplifier system like this is very useful in research on, for example, extreme-nonlinear optics, but can be put to very good use as well in direct frequency comb spectroscopy. To demonstrate this, the NOPCPA system described here will be employed in such experiments on helium in the near future.