

Ramsey-comb spectroscopy with intense ultrashort laser pulses

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Optical frequency combs based on mode-locked lasers have revolutionized the field of metrology and precision spectroscopy by providing precisely calibrated optical frequencies and coherent pulse trains^{1,2}. Amplification of the pulsed output from these lasers is very desirable, as nonlinear processes can then be used to cover a much wider range of transitions and wavelengths for ultra-high precision, direct frequency comb spectroscopy^{3,4}. Therefore full repetition rate laser amplifiers^{5,6} and enhancement resonators^{7,8} have been employed to produce up to microjoule-level pulse energies⁹. Here we present a spectroscopic method to obtain frequency comb accuracy and resolution by using only two frequency comb pulses amplified to the millijoule pulse energy level, orders of magnitude more energetic than what has previously been possible. The new properties of this approach, such as cancellation of optical light-shift effects, are demonstrated on weak two-photon transitions in atomic rubidium and caesium, thereby improving the frequency accuracy by up to thirty times.

As an alternative to full repetition rate amplification and cavity enhancement of frequency combs, direct amplification of selected frequency comb pulses allows for much higher pulse energies and wavelength tunability. By amplifying two frequency comb pulses and subsequent harmonic upconversion, precision spectroscopy in the extreme ultra-violet near 51 nm has been demonstrated¹⁰. However, in ref. 10 the frequency comb resolution was sacrificed because only two consecutive frequency comb pulses could be amplified, and phase shift effects during the amplification process compromised the frequency comb accuracy. To realize both frequency comb resolution and accuracy in conjunction with mJ-pulse energies, we developed the method of Ramsey-comb spectroscopy. This method is based on a series of excitations with two selectively amplified frequency comb laser pulses, which can be varied in delay over a wide range without affecting the optical phase. The result is a form of spectroscopy that is related to, yet fundamentally different from, normal frequency comb spectroscopy, as we will discuss in the following.

Traditionally, excitation of atoms or molecules with two short and phase-coherent laser pulses is known as Ramsey spectroscopy^{11,12}. The pulses induce two excitation contributions that interfere, depending on the delay time (Δt) and a possible additional phase shift between the pulses ($\Delta\phi$, for example from a pulse-amplification process). For a two-level atom with transition frequency f_i , the excited state population will exhibit an oscillatory behaviour when Δt is changed, proportional to $1 + \cos(2\pi f_i \Delta t + \Delta\phi)$ (Fig. 1a and Supplementary Fig. 1). If this signal is measured over a few oscillation periods as a function of Δt (a Ramsey-scan), then the transition frequency can be determined very precisely, provided that Δt and $\Delta\phi$ are known. A larger Δt

leads to a more accurate determination of the transition frequency f_i . However, Ramsey spectroscopy based on a single scan can only measure one isolated transition at a time, and is sensitive to errors in $\Delta\phi$ (ref. 10).

Instead, in Ramsey-comb spectroscopy a series of individual Ramsey-scans are performed using coherently-amplified pulse pairs derived from a frequency comb laser. The coarse delay of the pulse pairs can be changed in steps of the frequency comb repetition time T , while fine tuning for a Ramsey-scan is achieved by small adjustments of T itself. As a result, we obtain a 'comb' of Ramsey signals, with three fundamental properties.

First, the frequency comb provides a precisely calibrated absolute time axis and phase control over a wide range of pulse delays ($>$ microseconds), enabling very precise frequency determination.

Second, if a constant phase shift $\Delta\phi$ affects the Ramsey signals, then it can be identified as a common effect in all the signals recorded at different time delays. It therefore drops out of the analysis and the full frequency comb accuracy is recovered. Note that this includes light-induced phase shifts due to AC-Stark and similar effects¹³, which often lead to frequency errors in (frequency comb) spectroscopy.

Third, by probing the excited state population over longer periods, multiple transitions can be measured simultaneously by observing a beating between the individual cosine contributions from each resonance at frequency f_i with transition strength A_i . The multi-transition signal will be proportional to:

$$S = \sum_i A_i [1 + \cos(2\pi f_i \Delta t + \Delta\phi)] \quad (1)$$

As an example, the expected upper state population signal for three transitions as a function of the inter-pulse delay is schematically depicted in Fig. 1b. It can be seen that analogous to the superposition of sound waves from slightly detuned tuning forks, the excitation signal exhibits a characteristic beating pattern. The excitation oscillations are related to those observed in traditional Fourier transform spectroscopy¹⁴, or similar methods with pulsed lasers based on physical optical delay lines^{15,16}. However, in Ramsey-comb spectroscopy the frequency comb source provides an absolute time axis for the pulse delay Δt , and this for timescales many orders of magnitude larger than any physical delay line can provide. Moreover, the individually acquired Ramsey-scans result in accurate information on the phase of the complex delay-dependent signal, as visualized by the colour-gradient of the signal trace in Fig. 1b. This phase information is robust against fluctuations of signal strength and encodes both the transition frequencies and strengths. The underlying resonances can therefore be obtained very accurately from a straightforward fit of the phase

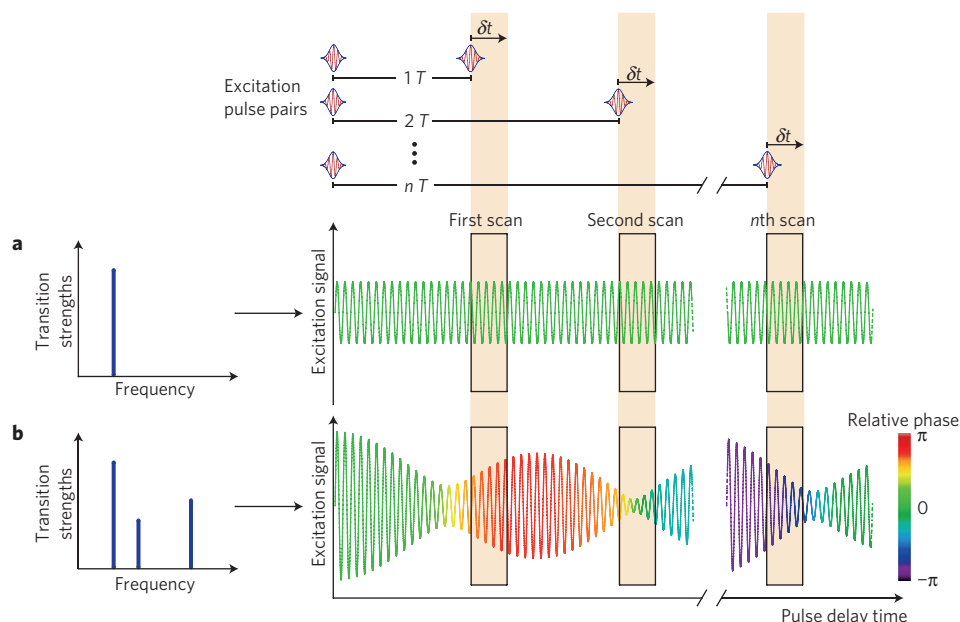


Figure 1 | The principle of Ramsey-comb spectroscopy. An atomic system is excited with two coherent laser pulses at a widely tunable and accurate delay, provided by a frequency comb. The laser pulses sample the excited population signal by a short Ramsey-scan over δt at macro-delays that are an integer (n) multiple of the comb repetition time T . From these scans the transition frequencies and strengths can be reconstructed with high precision. **a**, In the case of only one resonance, the excitation signal undergoes a single cosine modulation of constant amplitude, known as Ramsey fringes. **b**, If multiple transitions are excited simultaneously, the resulting signal will exhibit a complex amplitude and phase pattern. The phase evolution is visualized in colour relative to the single transition in **a**.

according to formula (1), without complications introduced by line shapes in the frequency domain (more details on the fitting procedure can be found in the Supplementary Information).

The frequency domain spectrum can also be calculated from the Ramsey-scans by a discrete Fourier transform over all measured delay zones. These spectra are subtly different from normal frequency comb spectroscopy, but enable straightforward identification of the transitions, and provide good starting values for the phase fit performed on Ramsey signals in the time domain (see Supplementary Information).

Experimentally, we obtain Ramsey-comb pulse pairs from a fully referenced Ti:sapphire frequency comb laser, operating near 760 nm with a repetition rate of $f_{\text{rep}} \approx 128$ MHz. Two pulses from this comb laser are parametrically amplified by more than a million times up to 5 mJ. The parametric amplifier supports broadband operation¹⁷, but for this experiment only a 5 nm wide part of the spectrum is selected. The pulse delay of the amplified frequency comb pulses is determined by the pump laser, as visualized in Fig. 2. Only the frequency comb pulses overlapping temporally with the high-energy pump pulses are amplified in the parametric amplifier. We verified that there is no delay-dependent phase shift introduced in the amplification process within an accuracy of $<1/1,000$ th of an optical cycle, based on spectral interferometry with the original frequency comb pulses¹⁸.

To demonstrate the capabilities of Ramsey-comb spectroscopy, the amplified frequency comb pulse pairs are used to perform non-resonant two-photon spectroscopy in an atomic vapour cell (Fig. 2). Although the investigated transitions are very weak, no focusing of the laser beam (which has a diameter of 3–6 mm depending on experimental conditions) is required because of the high pulse energy. At every macro-delay step n , the inter-pulse delay is scanned in steps of a few hundred attoseconds by small changes of the repetition rate of the frequency comb oscillator. This results in Ramsey-scans consisting of a few oscillations of the fluorescence signal, which is recorded with a photo-multiplier. Further experimental details can be found in the Methods.

A typical measurement for rubidium and caesium is shown in Fig. 3a; the signals are corrected for a constant background in the vertical direction. The change in Ramsey-signal amplitude between the macro-delay steps ($T = 7.8$ ns) is a direct result of the beating of the individual fluorescence signals from simultaneously excited transitions. Because these contrast changes appear on a nanosecond timescale, there is only a negligible effect on the signal amplitude within one Ramsey-scan of ~ 3 fs length. For longer delays (higher n), there is a further, general reduction in contrast due to the residual Doppler effect and spontaneous decay of the excited states. In the case of, for example, rubidium this limits the useable delay to about 345 ns ($n = 44$) owing to the upper state lifetime of 88 ns (ref. 19). Note that the experimental system can produce pulse pairs with significantly longer delays well into the microsecond range, which enables much higher accuracy measurements given sufficiently narrow transitions (longer lifetimes); the increasing timing jitter of the frequency comb seed oscillator for longer delays can be efficiently suppressed by directly locking the oscillator to a stable Hz-level reference laser²⁰.

Regarding the 5S–7S transition in ⁸⁵Rb we arrive at the transition frequency before hyperfine splitting ('centre of gravity frequencies', f_{cog}) and hyperfine A constants of $f_{\text{cog}} = 788,796,960,604(5)$ kHz and $A_{7S} = 94,684(2)$ kHz (based on 28 datasets). For the same transition in ⁸⁷Rb we find $f_{\text{cog}} = 788,797,092,129(7)$ kHz and $A_{7S} = 319,762(6)$ kHz. The uncertainties are a combination of statistical and systematic errors (see Supplementary Information for more details). Because of small laser power drifts up to a few per cent during the measurements, the AC-Stark (light) shift effect was not perfectly cancelled. However, still an effective ~ 50 times suppression was accomplished, leading to only small residual AC-Stark shift corrections of a few kHz.

The measurements presented here are in good agreement with previous experiments^{21,22}, and also of the same accuracy as the best determination recently obtained with full repetition rate comb excitation, employing strong focusing of the n -level laser pulses and coherent control²². This confirms that Ramsey-comb

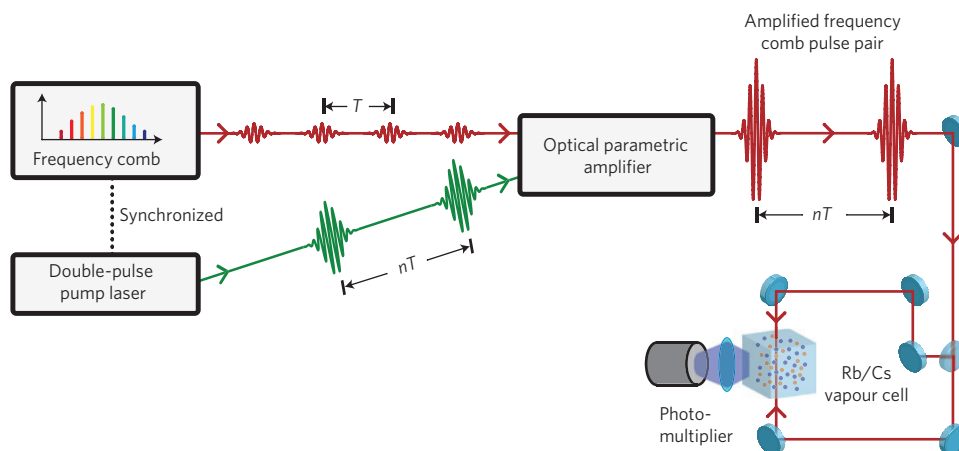


Figure 2 | Schematic of the experimental set-up. A high-energy pump-pulse pair selectively amplifies two pulses from a frequency comb laser pulse train. The macro-delay between the pump pulses, and hence the amplified frequency comb pulses, can be changed in steps of the cavity round-trip time $T = 7.8$ ns (where n is an integer number). The amplified pulse pairs are then split into counter-propagating copies to perform Doppler-reduced two-photon spectroscopy in a cell containing a mixture of atomic rubidium and caesium vapour. The signal is detected by monitoring the fluorescence decay of the excited atoms with a photo-multiplier tube.

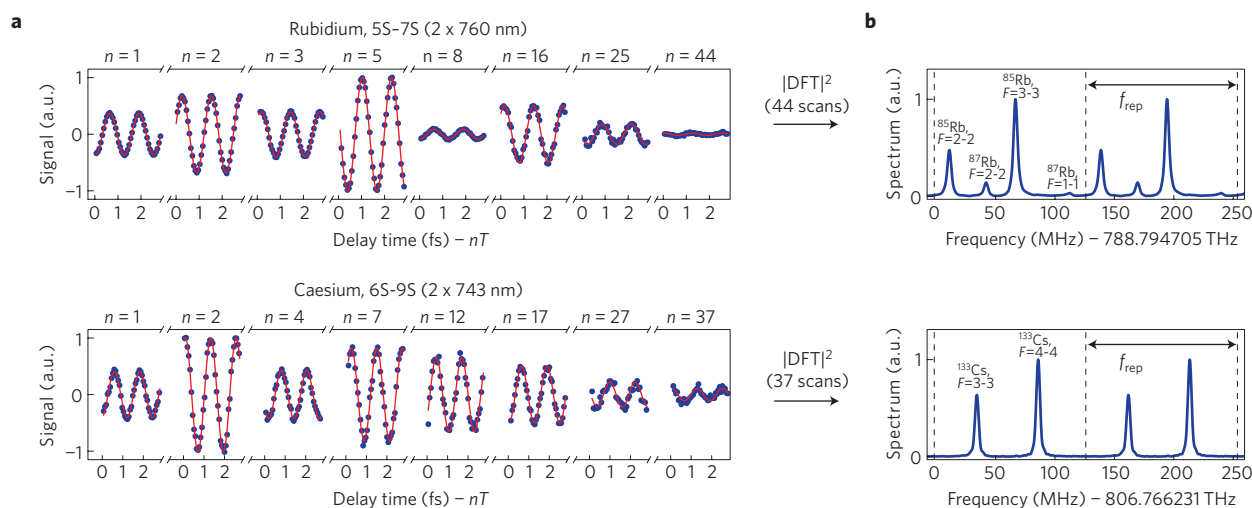


Figure 3 | Experimental demonstration of Ramsey-comb spectroscopy. **a**, Upper part: selection of the measured Ramsey-comb signal of the two-photon 5S-7S transition in atomic ^{85}Rb and ^{87}Rb , at macro-delays of nT ($T = 7.837,146$ ns). Lower part: similar for the 6S-9S transition in ^{133}Cs . For each delay step n , the inter-pulse delay Δt was fine-tuned over a range of $\delta t \approx 3$ fs to record a few oscillations of the signal beating pattern, such that $\Delta t = nT + \delta t$. The solid line represents a sinusoidal fit. **b**, Calculated spectrum based on the discrete Fourier transform (DFT) of the time domain signal from a total of 44 (rubidium) and 37 (caesium) Ramsey-scans. The spectral patterns repeat with a period of ~ 128 MHz ($=1/T$) and are used only for identification of the transitions (see text).

spectroscopy can be at least as accurate as full repetition rate frequency comb spectroscopy, but at many orders of magnitude higher pulse energy.

The advantage of high pulse energies becomes apparent when Ramsey-comb spectroscopy is applied on much weaker transitions, such as the investigated 6S-9S transition in ^{133}Cs . As shown in Fig. 3, a strong signal is obtained without any need for resonant enhancement by an intermediate level. From the analysis we find $f_{\text{cog}} = 806,761,363,429(7)$ kHz and $A_{9S} = 109,999(3)$ kHz, which is thirty times more accurate than the best previous measurement on this transition²³, which was based on frequency comb spectroscopy. The Ramsey-comb method therefore outperforms traditional forms of continuous wave or frequency comb laser spectroscopy on transitions that are too weak to be easily excited with unamplified frequency comb pulses.

Based on parametric amplification, Ramsey-comb spectroscopy combines high frequency precision with wide wavelength coverage

at mJ-level pulse energies. Because of the high peak energy, the frequency range of this method can straightforwardly and efficiently be extended via nonlinear crystals to the ultraviolet, or with high-harmonic generation in a gas jet to the extreme ultraviolet²⁴ (taking $T > 100$ ns to avoid phase shifts from ionization in the gas jet). Therefore there are many interesting targets for the Ramsey-comb method, such as the 1S-2S two-photon transition in He^+ to provide new information on the proton-size puzzle^{25,26}, or the two-photon X-EF transition in molecular hydrogen to put tighter constraints on speculative fifth forces beyond the Standard Model²⁷.

Methods

The frequency comb laser providing the seed pulses for the parametric amplifier is a home-built, Kerr-lens mode-locked Ti:sapphire oscillator. Both its repetition rate and carrier-to-envelope phase are locked to an atomic Rb-clock controlled by the Global Positioning system (fractional accuracy better than 2×10^{-12} for averaging times larger than 100 s). The oscillator emits pulses of 6 nJ energy, at a repetition time of 7.8 ns, and with a spectral bandwidth of ~ 40 nm centred at

760 nm. Before amplification, the pulses are stretched to 10 ps, by the combined effect of clipping the spectrum to about 5 nm around the desired wavelength and the application of $\sim 690,000 \text{ fs}^2$ of group delay dispersion. The stretched frequency comb pulses are selectively amplified in an optical parametric amplifier to the mJ-level by a high-energy 532 nm pump-pulse pair. The pump pulses originate from a separate, passively mode-locked Nd:YVO₄ oscillator, which is electronically synchronized to the Ti:sapphire frequency comb oscillator at the same $f_{\text{rep}} \approx 128 \text{ MHz}$. Using programmable pulse-pickers, two pulses are selected from the pump oscillator pulse train. These pulses are amplified to 40 mJ with an ultra-high gain Nd:YVO₄ pre-amplifier system^{28,29} and a Nd:YAG post amplifier, and subsequently frequency-doubled to 24 mJ at 532 nm. The parametric amplifier then produces amplified frequency comb pulse pairs up to an energy of 5 mJ at a repetition frequency of 28 Hz, which therefore determines the repetition rate of the total experiment. During the amplification process, both pump pulses travel exactly along the same optical path, assuring that their wavefronts are equal on a sub-milliradian level. This is essential because the parametric amplification is a highly nonlinear process and the amplified signal phase is very sensitive to differences in wavefronts¹⁸.

The Doppler-reduced two-photon spectroscopy is performed in a cell containing a mixture of rubidium and caesium vapour, heated to $\sim 50^\circ\text{C}$. Because of the relatively broad excitation spectrum, the Doppler effect is not suppressed completely²². Background signals originating from single-sided excitation are strongly suppressed because of the chirp of the amplified frequency comb pulses³⁰, combined with the use of quarter-wave plates to generate circular polarized light. The signal is proportional to the number of excited atoms as a function of inter-pulse delay, and is recorded by monitoring the fluorescence decay (420–459 nm) to the ground state after the second excitation pulse.

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Author contributions

K.S.E.E. conceived the concept of using multiple-delay, amplified frequency comb pulse pairs for precision spectroscopy. J.M. developed the laser system, performed the measurements and the data analysis; I.B. set up the spectroscopy part of the experiment. J.M. developed the theoretical framework of Ramsey-comb spectroscopy and wrote the paper together with K.S.E.E., who also supervised the project.

Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to K.S.E.E.

Competing financial interests

The authors declare no competing financial interests.