Ramsey-comb spectroscopy: Theory and signal analysis

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We recently demonstrated that the spectroscopic accuracy and resolution of optical frequency combs can be obtained from a series of Ramsey-like measurements using only two amplified frequency comb pulses at variable delays. In this work we present a comprehensive analytical framework of this Ramsey-comb method in both time and frequency domains. It is shown that as opposed to traditional forms of spectroscopy, the signal analysis can be performed purely in the time domain, based on the temporal phases of the individual Ramsey signals. We give a detailed description of the robust fitting algorithm relying solely on this phase information and discuss special features such as an insensitivity to (transition-independent) spectral line-broadening mechanisms and constant phase shifts, e.g., due to the ac Stark effect from the excitation pulses themselves. The precision and resolution of the Ramsey-comb fitting method is assessed via numerical simulations, including cases of transition-dependent broadening mechanisms and phase shifts.

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I. INTRODUCTION

Optical frequency combs (FCs) based on mode-locked lasers have become an indispensable tool in many laboratories performing ultrahigh-precision frequency measurements [1–4]. Because of their ability to link optical frequencies with radio frequencies from atomic clocks, FCs enable precise calibration of narrow-band spectroscopy lasers, leading to frequency measurements with up to 17-digit accuracy [5,6]. Moreover, FCs themselves can be employed to perform direct FC spectroscopy [7–11]. Amplification of the pulsed output of FCs is very desirable, as it allows one to perform spectroscopy on weak (multiphoton) transitions and the deployment of nonlinear processes such as wavelength conversion to explore frequency ranges inaccessible to continuous-wave lasers. Full repetition rate amplifiers have been used to increase the pulse energy of, e.g., Ti:sapphire FC lasers [12] and Yb-fiber FCs [13]. Additionally, enhancement cavities can be employed to further increase the power level [14,15] and pulse energies at the 10–μJ level have recently been achieved with this method [16]. Producing higher-energy FC pulses remains very challenging because of average power limitations and dispersion in the enhancement cavities. One way to circumvent this problem is the phase-coherent amplification of (two) selected pulses derived from a FC oscillator. We demonstrated amplification of such pulse pairs to the mJ level, which allowed for efficient frequency conversion via high-harmonic generation in a gas jet and enabled precision spectroscopy in the extreme ultraviolet wavelength region at 51 nm [17]. However, with the experimental system in [17] only two consecutive FC pulses could be amplified. As a consequence, the Ramsey-type measurement could only record single isolated transitions and the accuracy was limited by phase shifts during the amplification and in the harmonic up-conversion. We therefore developed an alternative system, capable of producing amplified FC pulses at the mJ level with interpulse delays that can be changed over a wide range (in steps of the cavity round-trip time of the FC) without affecting the optical phase [18–20]. The system provides the possibility to record a series of Ramsey signals at different macrodelays. This enables Ramsey-comb spectroscopy [21], which is related to yet fundamentally different from traditional Ramsey or standard direct FC spectroscopy.

In this paper we present an analytical framework of the Ramsey-comb method and introduce fitting models for both the spectral and the temporal domain; the latter was used to obtain the high-accuracy frequency results in [21]. First we recall the principle of quantum-interference excitation with laser-pulse pairs in order to establish the basic concept for describing the multidelay Ramsey-like signals. This concept is then extended to multiple transitions and effects such as constant and time-dependent phase shifts as well as spectral line-broadening mechanisms are included. With the help of the developed framework, we then briefly introduce an approach to fit the spectrum as calculated from the Ramsey signals. Subsequently, we describe in detail the significantly more robust time-domain-fitting procedure, based on the combined fit of the individual Ramsey-signal phases. Finally, the performance of this phase-fitting procedure is evaluated on a range of simulated data series.

II. ANALYTICAL FRAMEWORK

A. Quantum-interference excitation with laser-pulse pairs

Ramsey-comb spectroscopy is based on Ramsey’s method of separated oscillating fields [22,23]. In the optical domain it is performed by looking at the quantum-mechanical interference of atomic amplitudes created by excitation with resonant laser pulses (see, e.g., [24,25]). Figure 1 shows a schematic visualization for an atomic system with an isolated transition. When a resonant laser pulse interacts with such a system, it creates a quantum-mechanical superposition of the lower and the upper state (with energies $E_L$ and $E_u$, respectively). While the initial phase of the atomic superposition is determined by the laser-pulse carrier, it subsequently evolves with an angular frequency of $2\pi f_k = (E_u - E_L)/\hbar$, where $\hbar$ is the reduced Planck constant. If after a certain delay time a second atomic superposition is created by another laser pulse, both

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superpositions will interfere depending on their relative phase, resulting in an enhanced or decreased net amplitude of the atomic excitation. The squared absolute value of the resulting amplitude is proportional to the upper-state population of the atom and forms the experimental signal in Ramsey-type measurements. Based on the definitions used in [23], we take the excitation field as square light pulses with an electric field according to $E(t) = E_{0} \cdot \text{rect}(t - t_{p})$, which acts as an external dipole perturbation to a two-level system. An analytical expression for the upper-state population $P$ after the second excitation pulse can be derived as [23,26]

$$P = \frac{4\Omega_{1}^{2}}{b^{2}} \sin^{2}(b t_{p}) \left[ \cos(b t_{p}) \cos\left(\frac{1}{2} \frac{\Delta \tau_{\text{free}}}{\Delta f} - \theta_{\text{ex}}\right) - \frac{\pi \Delta f}{b} \sin(b t_{p}) \sin\left(\frac{1}{2} \frac{\Delta \tau_{\text{free}}}{\Delta f} - \theta_{\text{ex}}\right) \right]^{2},$$

where $\tau_{p}$ is the duration of the square excitation pulses, $\tau_{\text{free}}$ is the duration of the field-free evolution in between the excitations, $\Delta f = f_{k} - f_{L}$ is the detuning between the transition and the laser carrier frequency, $\Omega_{R} = \mathbf{d} \cdot \mathbf{E}/\hbar$ is the so-called Rabi frequency (which in turn depends on the electric dipole operator $\mathbf{d}$), $b = \sqrt{\Omega_{R}^{2} + (\pi \Delta f)^{2}}$ is known as the Rabi flopping frequency, and $\theta_{\text{ex}}$ is a possible phase shift between the two excitation fields [27]. We now want to cast Eq. (1) in a form more convenient for describing Ramsey signals from laser-pulse excitation. In Ramsey’s original derivation $\tau_{\text{free}}$ denotes the time in between the two excitation zones, while for laser excitation typically the time interval (pulse delay) $\Delta t$ from the center of the first to the center of the second laser pulse is used, hence $\Delta t = \tau_{\text{free}} + \tau_{p}$ (see Fig. 2 for a visualization of $\tau_{\text{free}}, \tau_{p}$, and $\Delta t$). This substitution causes an additional phase term of $\tau_{p} \cdot \Delta f$. Furthermore, traditionally, the detuning $\Delta f$ is changed to obtain Ramsey signals. In contrast, for pulsed laser excitation typically the (effective) relative phase $\delta_{\text{ex}}$ of the excitation pulses is changed. This latter can be done, e.g., by varying the pulse delay $\Delta t$ via small adjustments of the laser repetition rate $\Delta f$ (while keeping the carrier-envelope phase offset fixed). This induces an effective phase change between the excitation zones according to $\delta_{\text{ex}} = -\Delta t / 2\pi f_{L}$ as visualized in Fig. 2. With the help of some basic trigonometric relations, we can now transform Eq. (1) into a compact form describing the optical Ramsey signal [at frequency $2\pi f_{k}$ (see Fig. 1)] as a function of the pulse-to-pulse delay time $\Delta t$ as

$$P = A[1 + \cos(2\pi f_{k} \Delta t + \theta)],$$

with the amplitude

$$A = \frac{2\Omega_{1}^{2}}{b^{2}} \sin^{2}(b \tau_{p}) \left[ \cos^{2}(b \tau_{p}) + \left(\frac{\pi \Delta f}{b} \sin^{2}(b \tau_{p})\right)^{2}\right].$$

For zero detuning between laser and transition frequency ($\Delta f = 0$) it can be seen that $\theta = 0$. For nonzero detuning and in the low-power regime ($\Omega_{R} \ll |\Delta f|$) one can approximate $b \approx \pi \Delta f$, which also leads to $\theta = 0$. For these cases, one obtains the well-known expression describing optical Ramsey fringes (see, e.g., [25])

$$P = A_{k}[1 + \cos(2\pi f_{k} \Delta t)] = \frac{A_{k}}{2} \cos^{2}(2\pi f_{k} \Delta t),$$

with

$$A_{k} := 2\sin^{2}(\Omega_{R} \tau_{p}) \cos^{2}(\Omega_{R} \tau_{p}).$$

However, $\Omega_{R} \ll |\Delta f|$ does not hold in general, in particular when a sizable excitation probability is involved. Therefore, we perform a Taylor expansion of $\theta$ around $\tau_{p} = 0$.

$$\theta = \frac{2\pi}{3} \Omega_{R}^{2} \Delta f \tau_{p}^{3} + O(\tau_{p}^{5}).$$

We can expect the maximum possible detuning to be of the order of the spectral bandwidth of the pulse $\sim 1/\tau_{p}$, thus from the leading term in the Taylor expansion we obtain

$$|\theta| \lesssim \frac{2\pi}{3} \Omega_{R}^{2} \tau_{p}^{3}.$$
resulting in a further suppression of the phase shift by the factor $|\tau_p/\Delta f|$ as compared to Eq. (8). Since $\theta$ scales with the intensity of the excitation pulses ($\alpha|\Omega_2|^2$), the influence of $\theta$ is in practice usually included in the ac Stark shift calibration of the coupling from additional, nonresonant levels. In fact, $\theta$ can be regarded as an ac Stark shift on the resonant transition due to the intensity of the excitation pulses ($|\Omega_2|^2$ domain signal. Here $S_f$ can be regarded as an ac Stark shift on the resonant transition due to a frequency-domain representation of the signal $S_f$ can then be derived via a convolution of the Fourier transformations of the two individual terms

$$S_f = S_{f,k} \star W_f.$$  

In the time domain, the window function $W_f$ consists of a series of rectangular envelopes $\text{rect}(x) = 1$ for $|x| < 1/2$ and 0 otherwise, which can be converted to the frequency-domain representation $W_f$ with the help of basic Fourier transformations

$$W_f = \sum_{n=1}^{N} \text{rect}\left( \frac{\Delta t - nT}{\delta t} \right),$$  

$$W_f = \delta t \sin(c(f \delta t)|\exp[-i(N + 1)\pi f T]\sin(N\pi f T)/\sin(\pi f T),$$  

with $\sin(x) = \sin(\pi x)/\pi x$. These window functions are combined with the part that depends on the transition frequency $f_k$, which in the case of a single resonance with a transition amplitude $A_k$ can be written as [see Eq. (2)]

$$S_{f,k} = A_k \cos(2\pi f_k \Delta t),$$  

$$S_{f,k} = A_k \delta (f - f_k) + \delta(f + f_k).$$  

Note that because in practice the constant offset of the measured Ramsey signals [see Eq. (2)] is typically removed by centering the signals around zero, we neglected it in Eq. (11b) and will continue so in the following derivations. In addition, we initially also refrain from including potential phase shifts between the excitation pulses such as $\theta$.

If we limit ourselves to positive frequencies [28] and define $S_{f,k}^+ := A_k \delta(f - f_k)$, we can rewrite the expression for the spectrum as a superposition of cosines of different harmonic orders

$$|S_f|^2 = |S_{f,k}^+ \star W_f|^2$$

$$= \left( \frac{A_k \delta t}{2} \right)^2 \sin^2[(f - f_k)\delta t]$$

$$\times \sum_{n=1}^{N} [2(N - n)\cos(2\pi T(f - f_k)) + 1],$$  

which resembles the spectra from FC pulse trains. However, note that in Ramsey-comb spectroscopy the temporal signal $S_f$ is comprised of individual Ramsey-like measurements of the upper-state population of the atom. In contrast, the frequency-domain signal in traditional, full repetition rate FC spectroscopy is based on the coherent superposition of the upper-state amplitudes, accumulated over many excitation pulses. This fundamental difference between these two techniques will become more apparent in the following section.
C. Extension to multiple transitions

Up to now we have considered only the case of a single resonant transition. When extended to \( M \) simultaneously excited transitions of amplitudes \( A_k \) and frequencies \( f_k \), Eqs. (11a) and (11b) become

\[
S_{f,k} = \sum_{k=1}^{M} A_k \cos(2\pi f_k \Delta t), \tag{13a}
\]

\[
S_{f,k} = \sum_{k=1}^{M} \frac{A_k}{2} \left[ \delta(f - f_k) + \delta(f + f_k) \right]. \tag{13b}
\]

This assumes that coherent effects can be neglected in the measurement of the excited populations (e.g., by suppressing quantum beats in fluorescence detection by averaging the signal over long times compared to the beating period or by ionization detection of the excited states).

The full expression for the spectral signal amplitude (restricted to positive frequencies) can then be written as

\[
S_f^+ = \sum_{k=1}^{M} A_k \sin\left[\left( f - f_k \delta t \right) \delta t \right] \frac{\sin\left[ N \pi T (f - f_k) \right]}{\sin\left[ \pi T (f - f_k) \right]} \times \exp[-i(N + 1)\pi T (f - f_k)]. \tag{14}
\]

Because of the transition-dependent phase terms, the spectrum [proportional to the absolute value squared of Eq. (14)] exhibits complex interferences. In order to see this more clearly, we limit ourselves to two transitions \( (M = 2) \), introduce the shorthand notation

\[ ss_{N,2}(f_k) := \frac{A_k \delta t}{2} \frac{\sin[N \pi T (f - f_k)]}{\sin[\pi T (f - f_k)]}, \tag{15} \]

and approximate

\[ \sin\left[ \left( f - f_k \delta t \right) \delta t \right] \approx 1 \tag{16} \]

for \( (f - f_k)\delta t \ll 1 \). We can then write the positive-frequency spectrum in the compact form of

\[ |S_f^+|^2 = ss_{N,1}^2 + ss_{N,2}^2 + 2 \cos[(N + 1)\pi T (f_2 - f_1)] ss_{N,1} ss_{N,2}. \tag{17} \]

Apart from the linear superposition term \( ss_{N,1}^2 + ss_{N,2}^2 \), which would also be seen in traditional FC spectroscopy, there is an additional interference term that depends on \( f_2 - f_1, N, \) and \( T \). It is these interferences that complicate the frequency-domain analysis as shown in Sec. III A.

D. Constant phase shifts

We will now discuss the so far neglected possibility of additional phase shifts between the Ramsey scans of different macrotransitions. At first we consider the case of a potential constant (transition-independent) phase shift \( \phi_c \). With the inclusion of \( \phi_c \), Eqs. (13a) and (13b) become

\[
S_{f,k} = \sum_{k=1}^{M} A_k \cos(2\pi f_k \Delta t + \phi_c), \tag{18a}
\]

\[
S_{f,k} = \sum_{k=1}^{M} \frac{A_k}{2} \left[ e^{i\phi_c} \delta(f - f_k) + e^{-i\phi_c} \delta(f + f_k) \right]. \tag{18b}
\]

It is apparent that in the time domain a constant phase shift simply causes a global shift of all Ramsey scans together. However, this common shift does not influence the frequency of the Ramsey fringes. This is even more obvious from the frequency-domain representation, where the constant phase shift only produces an additional phase factor. When the (positive-frequency) spectrum is calculated, this phase factor simply drops out, as visualized in Fig. 4(a).

The insensitivity to constant phase shifts fundamentally distinguishes Ramsey-comb spectroscopy from traditional Ramsey-type experiments, where phase shifts of all kinds can cause frequency errors. This feature was particularly important for the high-accuracy Ramsey-comb spectroscopy based on amplified FC pulses in [21]; because the differential phase shift during the amplification process was constant (independent of the delay time), it did not affect the measurement accuracy in a significant way. Furthermore, in Ramsey-comb spectroscopy also the well-known light shift due to the ac Stark effect from the excitation pulses themselves simply manifests itself as a constant phase shift of the Ramsey signal (as long as the energy of the excitation pulses is constant with respect to the delay time). Since in many practical cases, such as for the hyperfine transitions in cesium and rubidium measured in [21], this constant phase shift is common for the investigated transitions so that it simply drops out in the analysis. Note that the same holds for shifts based on quantum-mechanical interference from off-resonance states, which do not scale with the power of the excitation pulses and therefore cannot be determined in the traditional way by repeated measurements at different power levels [29].

E. Time-dependent phase shifts

Although Ramsey-comb spectroscopy is insensitive to common constant phase shifts as discussed previously, the observed frequencies are altered by phase shifts that depend on the delay time between the two excitation pulses. The most simple case comprises a phase shift that is linear in time and
can be described as \( \phi_\tau \) is a delay-independent constant
\[ \phi_i = \Delta\tau \frac{\phi_\tau}{T}. \] (19)

Setting \( \phi_i = 0 \) for simplicity, Eqs. (13a) and (13b) then become
\[
S_{i,k} = \sum_{k=1}^{M} A_k \cos(2\pi f_k \Delta t + \phi_i)
\]
\[
= \sum_{k=1}^{M} A_k \cos \left[ 2\pi \left( f_k + \frac{\phi_\tau}{2\pi T} \right) \Delta t \right]. \] (20a)
\[
S_{f,k} = \sum_{k=1}^{M} \left\{ \delta \left[ f - \left( f_k + \frac{\phi_\tau}{2\pi T} \right) \right] + \delta \left[ f + \left( f_k + \frac{\phi_\tau}{2\pi T} \right) \right] \right\}. \] (20b)

The result is an effective frequency shift of \( \frac{\phi_\tau}{2\pi T} \), which is schematically depicted in Fig. 4(b). For a correct interpretation of the Ramsey-comb frequency results it is therefore of vital importance to accurately characterize potential delay-dependent phase shifts. One candidate of such a phase shift typical for spectroscopy relying on FCs is the carrier-envelope phase slip between consecutive laser pulses, which is straightforwardly measured in a self-referencing \( f \rightarrow 2 f \) setup and stabilized via a feedback loop [1,2].

### F. Spectral line-broadening mechanisms

In practice, the spectral line shapes of the transitions will often be affected by various broadening mechanisms due to, e.g., the Doppler effect or a finite upper-state lifetime of the excited transitions. In the case of the latter, spontaneous emission causes the upper-state population induced by the first pulse to decay over time, so the achievable Ramsey-fringe contrast after the second excitation will decrease accordingly. Hence, in the time domain, this effect is incorporated into the model via a multiplication of the Ramsey signals with an exponential decay function \((\tau \text{ is the lifetime of the upper state})\)
\[ S_{i} \rightarrow S_{i} e^{-\Delta t/2\pi}. \] (21)

In the single-transition case, the corresponding spectral shape is obtained via a convolution with a Lorentz function with a linewidth of \( 1/2\pi \tau \),
\[ |S_{f}^+|^2 \rightarrow |S_{f}|^2 \ast \left[ \frac{4\tau}{1 + (4\pi f \tau)^2} \right]. \] (22)

As visualized in Fig. 4(c), this results in a broadening but not a shift of the spectral line positions. Similar to the inclusion of lifetime effects, other line-broadening mechanisms such as Doppler broadening or a finite laser linewidth can be incorporated via the appropriate multiplications and convolutions in the time and frequency domains.

However, for more than one simultaneously excited transition, the effect of the spectral broadening mechanisms has to be incorporated into the complex spectral amplitudes described by Eq. (14). It will therefore also affect the spectral interference terms [see Eq. (17)] and thus cause slight systematic shifts of the spectral line positions. Hence, in the multitransition frequency-domain analysis of Ramsey-comb spectroscopy, all line-shaping effects have to be carefully taken into account for a correct interpretation of the spectral data.

### III. FITTING OF THE RAMSEY-COMB SIGNALS

The main motivation for the development of the analytical Ramsey-comb model is to enable the fitting of the experimentally obtained signals so that the properties of the excited resonances can be extracted. In this section we will first briefly discuss the more intuitive frequency-domain-fitting approach. Afterward we will focus on an alternative fitting method used to analyze the experimental signals in [21], based purely in the time domain and found to be significantly more robust than the spectral fit approach.

#### A. Frequency-domain approach

For a single isolated transition, the spectral analysis is as straightforward as in traditional direct FC spectroscopy. However, for multiple transitions, the previously discussed interference terms [see Eq. (17)] complicate the spectral fitting procedure. In order to increase the robustness, an iterative approach can be applied. For that we split up the absolute squared value of Eq. (14),
\[ S_f := |S_f|^2 = \sum_{k=1}^{M} s_k^2, \] (23)
with
\[ s_k := \left( \frac{A_k \delta t}{2} \right) \sin(N\pi T(f - f_k)) \sin[N\pi T(f - f_k)] \sin[N\pi T(f - f_k)] \times \exp[-i(N + 1)\pi T(f - f_k)]. \] (24)

into a part without cross terms (note the different order of summing and taking the absolute value)
\[ S_f^0 := \sum_{k=1}^{M} |s_k|^2 \] (25)
and the cross term (interference term) itself
\[ S_f^I = S_f - S_f^0 = \sum_{k=1}^{M} \left( 1 - \delta_{kl} \right) s_k(s_k)_{c.c.}, \] (26)
where c.c. denotes the complex conjugate and the Kronecker delta is defined as \( \delta_{kl} = 1 \) for \( k = l \) and 0 otherwise. The iterative fitting procedure then consists of the following steps.

(i) Fit \( S_f^0 \) to the experimental spectrum, which is corrected for the interferences \( S_f^I \) based on the initial parameter guesses.

(ii) From the obtained fit results, (re)calculate \( S_f^I \).

(iii) Fit again the spectrum corrected for the most current \( S_f^I \) and continue with the second step until the fit has converged.

An example of this fitting approach is depicted in Fig. 5, based on simulated data from two transitions 40 MHz apart with an amplitude ratio of \( A_2/A_1 = 0.8 \), \( N = 25 \), and \( T = 8 \) ns [see Eq. (14)]. Given initial parameter guesses 500 kHz away from the modeled transition frequencies, the correct interference term \( S_f^I \) is obtained within \( \sim 100 \) iterations; the
final fit results match the modeled frequencies within 1–2 kHz. In general, however, experimental noise and the incorporation of line shapes as discussed in Sec. II F severely affect the convergence of the spectral fit approach. Furthermore, it is in practice very challenging to fully include all line-shape mechanisms because apart from Doppler and lifetime broadening, there are various other physical and experimental effects that contribute to the actual line shape. The obtained fitting results are therefore prone to (small) systematic deviations. Because of these issues, we developed an alternative fitting approach based purely in the time domain, which is described in detail in the following section.

B. Time-domain approach

In the time domain, the signal from multiple resonances consists of a complex beating pattern with a time-dependent amplitude, carrier, and phase. While it is possible to simultaneously fit all Ramsey scans on a global time axis using Eq. (9a), typically the fitting process is not very robust because of the periodicity of the fit function and the strong coupling between the different fit parameters. In addition, analogous to the frequency-domain approach described in the previous section, the inclusion of line-broadening effects further compromises the robustness of the fitting procedure. Therefore, we developed a fitting model based solely on the phases of the individual Ramsey fringes. This is possible because both the amplitudes and transition frequencies are fully encoded in the phase evolution of the complex beating pattern as visualized in Fig. 6; when multiple transitions are excited simultaneously, the phase of the Ramsey signals becomes a complex but characteristic function of the delay time. It is this phase trace that is sampled in Ramsey-comb spectroscopy and used for the frequency determination.

For analytical convenience, we introduce the complex quantity

\[ \tilde{S}_t := \sum_{k=1}^{M} A_k \exp[-i(2\pi f_k \Delta t + \phi_t)]. \]  

(27)

with the real part of \( \tilde{S}_t \) corresponding to \( S_{t,k} \) as defined in Eq. (18a). The argument (angle) of \( \tilde{S}_t \),

\[ \arg(\tilde{S}_t) = \Phi_{(A_1_{\text{ref}},A_{M,\text{ref}},f_{M,\phi_c,\text{ref}})}(\Delta t) - \phi_c, \]  

(28)

describes the phase of the Ramsey signals and contains both transition amplitudes and frequencies as parameters, as well as the common constant phase shift \( \phi_c \). While this phase shift no longer simply drops out as in the spectral domain approach, it is still decoupled from the transition frequencies.

Figure 7 visualizes how Eq. (28) is used to perform the time-domain fitting. At first, the phase of the signal carrier at different macrodelays is determined relative to a fixed reference frequency \( f_{\text{ref}} \) by fitting each individual Ramsey scan with

\[ g(\Delta t, \Delta \phi) = a \cos(2\pi f_{\text{ref}} \Delta t + \Delta \phi). \]  

(29)

While the exact value of \( f_{\text{ref}} \) is not important as it is only used for comparison, it is conveniently chosen close to the average signal carrier to facilitate straightforward fitting of the individual Ramsey signals. The obtained relative phases \( \Delta \phi_n \) \((n = 1,2,\ldots,N, \) where \( N \) is the number of measured Ramsey scans) can then be compared to

\[ \Phi_{\text{fit}} := \Phi_{(A_1_{\text{fit}},A_{M,\text{fit}},f_{M,\text{fit},\phi_c=0})}(\Delta t) - \phi_c - 2\pi f_{\text{ref}} \Delta t, \]  

(30)

as depicted schematically in Fig. 7(b). The minimization of \( |\Phi_{\text{fit}}(\Delta t) - \Delta \phi_n| \) for \( \Delta t = nT \) \((n = 1,\ldots,N) \) represents an \( N \)-dimensional \( \chi^2 \) problem. As long as the number of Ramsey scans is greater than or equal to the number of free parameters, numerical solutions can be obtained via
a standard least-squares-fitting algorithm. Note that, as in traditional direct FC spectroscopy, the frequencies can only be determined modulo the repetition rate \( f_{\text{rep}} \) of the FC oscillator [see Fig. 7(c)]. This ambiguity, however, can be solved either by previous knowledge or by comparing measurements with slightly different repetition rates.

C. Numerical simulations of the time-domain-fitting algorithm

In order to investigate the performance and precision of the developed fitting algorithm, the phase-fitting procedure was tested on a set of simulated Ramsey signals. The parameter space was kept comprehensible by limiting the simulations to two transitions (\( M = 2 \)) with frequencies \( f_1 = 800 \) THz and \( f_2 = f_1 + 40 \) MHz and amplitudes \( A_1 = 1 \) and \( A_2 = 0.8 \), unless stated otherwise.

Figure 8 shows an example phase trace that is obtained from \( N = 25 \) simulated Ramsey scans. Gaussian noise with a standard deviation of 0.1 was added to model experimental noise and a common upper-state lifetime of \( \tau = 40 \) ns was incorporated according to Eq. (21) as an example of a line-broadening mechanism.

As can be seen from Fig. 8, the reduction of signal amplitude due to the modeled lifetime leads to a less accurate determination of the Ramsey-signal phases for longer delay times. However, because the sensitivity of \( \Phi_{\text{fit}} \) to changes in signal amplitude or frequency increases with delay time, also the signal phases for longer delays still have a comparable influence on the fitting result. In order to show this, \( \Phi_{\text{fit}} \) was detuned from its best-fit result by changing \( f_1 \) by 500 kHz [the dashed line in Fig. 8(a)]. While for shorter delays the detuned phase function is still reasonably close to the obtained signal phases, it exhibits a more pronounced deviation for longer delay times.

Based on the parameter set shown in Fig. 8, a number of fits were performed for different sets of noise and randomly chosen
initial fit parameters: The initial values for the frequencies and amplitudes were varied with standard deviations of 200 kHz and 10% of their absolute values, respectively. In Fig. 9, the results for 300 of such fits are shown. Note that during the fitting process, the amplitude of the first transition was kept fixed since \( \Phi_\text{fit} \) is only sensitive to the ratio of the amplitudes. Also, the common constant phase \( \phi_c \) is not actually fitted, but in each fit iteration step the average offset between signal and fit phases is subtracted from the fit results. Figure 9 shows that not only the transition frequencies but also the amplitude ratio can be obtained very accurately, without any knowledge of the upper-state lifetime or a potential (transition-independent) constant phase shift. The achievable precision of the fitting (the standard deviation of the fit results, based on 300 data sets with different noise and starting parameters) depends on the modeled signal to noise ratio of the Ramsey signals and scales approximately linearly with the standard deviation of the applied Gaussian noise.

1. **Influence from neighboring transitions**

As the presented fitting algorithm acts purely in the time domain and is insensitive to common line-shape mechanisms, it is interesting to investigate the resolution of this method, i.e., how the algorithm performs for two transitions close in frequency. In particular, for the case of two very unequal transitions one typically expects a strong effect for the weaker transition. We therefore simulated sets of 25 Ramsey signals as described previously, but with a more unequal amplitude ratio of \( A_2/A_1 = 0.4 \) and various frequency spacings. As can be seen from Fig. 10, the fit precision gets worse when the two transitions are within about one linewidth (\( \approx 5 \text{ MHz} \)) of the transitions.

However, even when the two transitions are almost indistinguishable in the spectral domain, still the transition frequency results can be obtained without sizable systematic offsets.

2. **Transition-dependent phase shifts and spectral line-broadening mechanisms**

So far we have assumed that both line-broadening mechanisms and constant phase shifts affect all transitions exactly the same way. While this is a good approximation for many practical spectroscopic targets of Ramsey-comb spectroscopy, one can also extend the phase fit function \( \Phi_\text{fit} \) to incorporate these transition-dependent effects according to

\[
\Phi^\text{ext}_\text{fit} := \Phi^\text{ext}_{\{A_1(\Delta t),\ldots,A_M(\Delta t),f_1,\ldots,f_M,\phi_1,\ldots,\phi_M,\phi_c=0\}}(\Delta t)
\]

where \( \Phi^\text{ext} \) now relates to an extended version of Eq. (27):

\[
\hat{\Delta}_k := \sum_{k=1}^{M} A_k(\Delta t)\exp[-i(2\pi f_k \Delta t + \phi_k + \phi_c)].
\]

The \( \phi_k \) terms allow for additional transition-dependent phase shifts, whereas \( \phi_c \) still represents a transition-independent constant phase shift and is treated as before. Furthermore, the previously constant amplitudes \( A_k \) can now also have a dependence on delay time \( \Delta t \), which allows us to incorporate individual spectral line-broadening mechanisms.

To investigate individual phase shifts, again 300 data sets are produced analogously to the simulations that led to the results shown in Fig. 9, but this time incorporating a constant phase shift of 0.4 rad for the first transition and 0.7 rad for the second; the initial starting parameters for the individual phase shifts were varied with a standard deviation of 10%
of their absolute value. The results of the fitting series are shown in Fig. 11. It can be seen that, as compared to the results without a differential phase shift (Fig. 9), the errors for the transition frequencies have increased by about a factor of 2, but still no systematic deviation is introduced. In addition, also the value of the differential phase shift \( \Delta \phi_{21} = \phi_2 - \phi_1 \) is obtained from the analysis (the common phase shift of 0.4 rad is incorporated in \( \phi_1 \)). Note that apart from \( A_1 \), also \( \phi_1 \) was fixed during the fitting, as only the differential value is of significance.

Returning to common constant phase shifts (\( \phi_i = 0 \)), we now investigate the influence of delay-time-dependent amplitudes \( A_k(\Delta t) \). For the case that all transitions are affected the same way, we already discussed in Sec. II F the reduction of signal strength due to, e.g., natural decay of the upper state or the Doppler effect. Analogous to Eq. (21), we now incorporate individual lifetimes \( \tau_k \) in the form of delay-dependent amplitudes according to

\[
A_k(\Delta t) = A_k(0)e^{-\Delta t/\tau_k}.
\]

Again, the performance of \( \Phi_{tot}^{ext} \) is investigated by simulating 300 signal sets as before, but with a 10% increased lifetime for the second transition of \( \tau_2 = 44 \text{ ns} \); the initial starting parameters for the lifetimes \( \tau_k \) were varied with a standard deviation of 10%. From the results in Fig. 12 we see again that the errors increased, in contrast to the results shown in Fig. 9. Nevertheless, the inclusion of the lifetime does not induce sizable systematic shifts on the determination of the frequencies or the amplitude ratio.

IV. CONCLUSION

In this paper we presented a comprehensive framework describing the temporal and spectral representation of spectroscopic signals obtained by the Ramsey-comb method [21], which relies on the combination of optical Ramsey signals at variable macrodelays. Based on this framework, fitting algorithms in both time and frequency domains were developed. The spectral-domain approach was found to be severely compromised because of additional interference terms, which are not present in traditional comb spectroscopy. In the time domain, however, it was shown that the spectroscopic analysis can be performed solely based on the Ramsey-signal phases from different macrodelays. The performance of the fitting algorithm was investigated via numerical simulations, verifying that common line-broadening mechanisms and constant phase shifts, e.g., due to the ac Stark effect, do not affect the fitting outcome. Furthermore, the inclusion of also transition-dependent line-broadening mechanisms and constant phase shifts only affects the uncertainty of the fit results, but does not introduce sizable additional shifts.

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[28] While in general the leakage of the negative frequencies diminishes with scanning more individual Ramsey scans (longer $\delta t$), the influence of negative-frequency components can also be minimized by an appropriate choice of the individual scanning interval $\delta t$. In order to make the overall envelope from the negative-frequency components zero around the positive transition frequency, one has to ensure that $\sin(2\pi f_0\delta t) = 0 \iff \delta t = \frac{u}{2f_0}$, with $u$ being an integer. This translates into scanning a multiple of half-cycle Ramsey fringes at each macrodelay step.