Chapter 5

Two-photon absolute frequency measurements

One desirable objective in atomic spectroscopy is the ability to obtain a global energy level picture of the atomic transitions. In fact, the stabilized comb has tremendous possibilities for mapping numerous transitions in a straightforward way. In this chapter, I will show that it is possible to obtain all of the allowed single- and two-photon transitions within the laser bandwidth by a quick scan of f_r (~ 26 Hz). This scanning method is efficient and eliminates the need for broadly tunable and absolutely referenced cw lasers. This is one of the main advantages of using a frequency comb directly for spectroscopy.

Previously, in Chapter 4, we scanned f_0 and kept f_r locked in order to characterize the primary contributions to systematic effects on both the line center and the linewidth. When these results are integrated into the the setup we have a system which can perform precision mesurements. In this chapter, I focus on some representative 5S-5D transitions for precision spectroscopy. Indeed, the measurement results approach the accuracy of those obtained in the best cw measurements to date.

Also, if we consider that we have locked the Ti:S comb to a commercial cesium clock and thus have generated an absolutely referenced set of optical frequencies, we can use these frequencies for identification of previously unmeasured transitions. As an example, we determine the previously unmeasured absolute frequency of the 5S-7S two-photon resonances. We thus demonstrate that prior knowledge of atomic transition frequencies is not essential for this technique to work, and indicate that it can be applied in a broad context.

5.1 Scanning f_r gives a full spectrum

In general, sweeping f_r has the advantage of yielding all the transitions within the laser bandwidth in only a ~ 26 Hz scan. This is due to the fact that the ratio of one-photon optical transition frequencies (participating in stepwise two-photon transitions) to f_r is $\sim 3.8 \times 10^6$, so that for a change in f_r of ~ 26 Hz the resonant enhancement is repeated by the next neighboring comb component.

However, the optical frequency for the two-photon transitions is ~ 770 THz, an f_r harmonic on the order of 7.7×10^6. Therefore, the two-photon resonance condition is satisfied every time f_r is changed by ~ 13 Hz, corresponding to a change in the comb frequency by $f_r\ /2$ for the mode orders around 3.85×10^6.

As an aside, I will discuss the two primary differences between scanning f_r and scanning f_0: (i) simply stated, f_r has the advantage of being multiplied by N, whereas f_0 does not and (ii) scanning f_r can easily tune over 100 MHz in the optical region, whereas scanning f_0 in the current configuration produces a 80 MHz sweep at the maximum. The trouble with scanning f_0 is that the beat can reside anywhere between 0 MHz and $f_r/2$ (there is of course a conjugate beat in the $f_r/2$ to f_r window) but, in order for us to lock f_0, we are restricted to the 7-47 MHz range. Thus, to obtain broader tunability in the current experimental configuration, we scan f_0 up to 47 MHz, then change the sign within the servo to acquire lock on the conjugate beat and finally, we proceed to scan this conjugate beat up to -47 MHz. This gives a total tuning of 80 MHz. (Note that we can adapt the current setup, for example by including acousto-optic modulators in the ν-to-2ν interferometer, to obtain continuous tuning without having to change the servo sign.)

Figure 5.1 presents the two-photon transition spectrum obtained by scanning

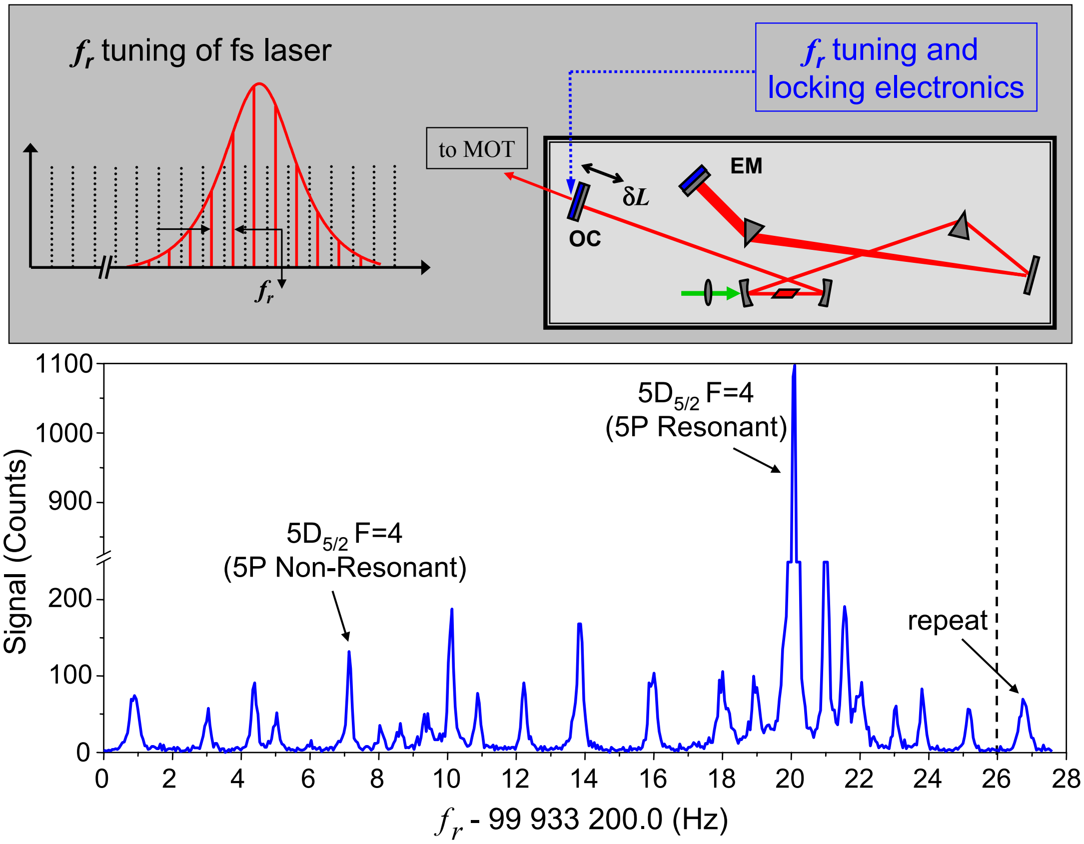

Figure 5.1: The top panel shows the experimental setup for scanning the laser repetition frequency f_r and the lower one presents the two-photon spectrum obtained from such a scan. All possible 5S-5D transitions are observed; this includes the non-resonant and resonantly enhanced transitions.

f_r for a fixed value of f_0. It shows the 14 transitions (there are 39 possible pathways for the case of linearly polarized light) that I identified for the $5S_{1/2} \rightarrow 5D_{3/2}$ and $5S_{1/2} \rightarrow 5D_{5/2}$ two-photon resonances. The data clearly show that the larger, one-photon resonantly enhanced peaks repeat after a change of f_r by ~ 26 Hz, as expected from the simple calculation above. As mentioned in section 4.2, for the resonantly enhanced peaks, the pair of comb modes that is actually tuned onto the 5S-5P and 5P-5D resonances makes the dominant contribution to the two-photon transition rate.

In Fig. 5.2, we also present the theoretical spectrum corresponding to the set of parameters used in the experiment. The two insets show signal magnitude on a logarithmic scale to enhance the visibility of the smaller peaks. The peak corresponding to non-resonant excitation of the $5S_{1/2}$ $(F = 2) \rightarrow 5P_{3/2}$ $(F'=3) \rightarrow 5D_{5/2}$ $(F''=4)$ transition, made possible by the collective action of many comb modes, is larger than that theoretically predicted because the comb spectral phase is not flat and the comb spectrum is not symmetric around the P state; thus, the destructive interference mentioned earlier in section 4.2 is reduced. Furthermore, as the detuning from the P state becomes greater than a few THz, the effect of phase mismatching between comb pairs over the spatial dimension of the MOT can be non-negligible.

There are a couple of interesting spectral features that we notice when looking at Fig. 5.2. The two resonance peaks observed in the experimental spectrum, which are not present in the theory model, are due to the $5S_{1/2} \rightarrow 7S_{1/2}$ two-photon transitions. Their observation prompted us to consider both their theoretical modeling and experimental investigation. However, it is more complicated to include these transitions in the model than to include the 5S-5D two-photon transitions, primarily because their frequency has never been measured before. In fact, this led us to actually experimentally measure their absolute frequencies, as presented in section 5.3. I had not initially intended to study them, though this shows again one of the powerful features of our direct frequency comb technique, the fact that we can observe all the transitions within the fs laser bandwidth.

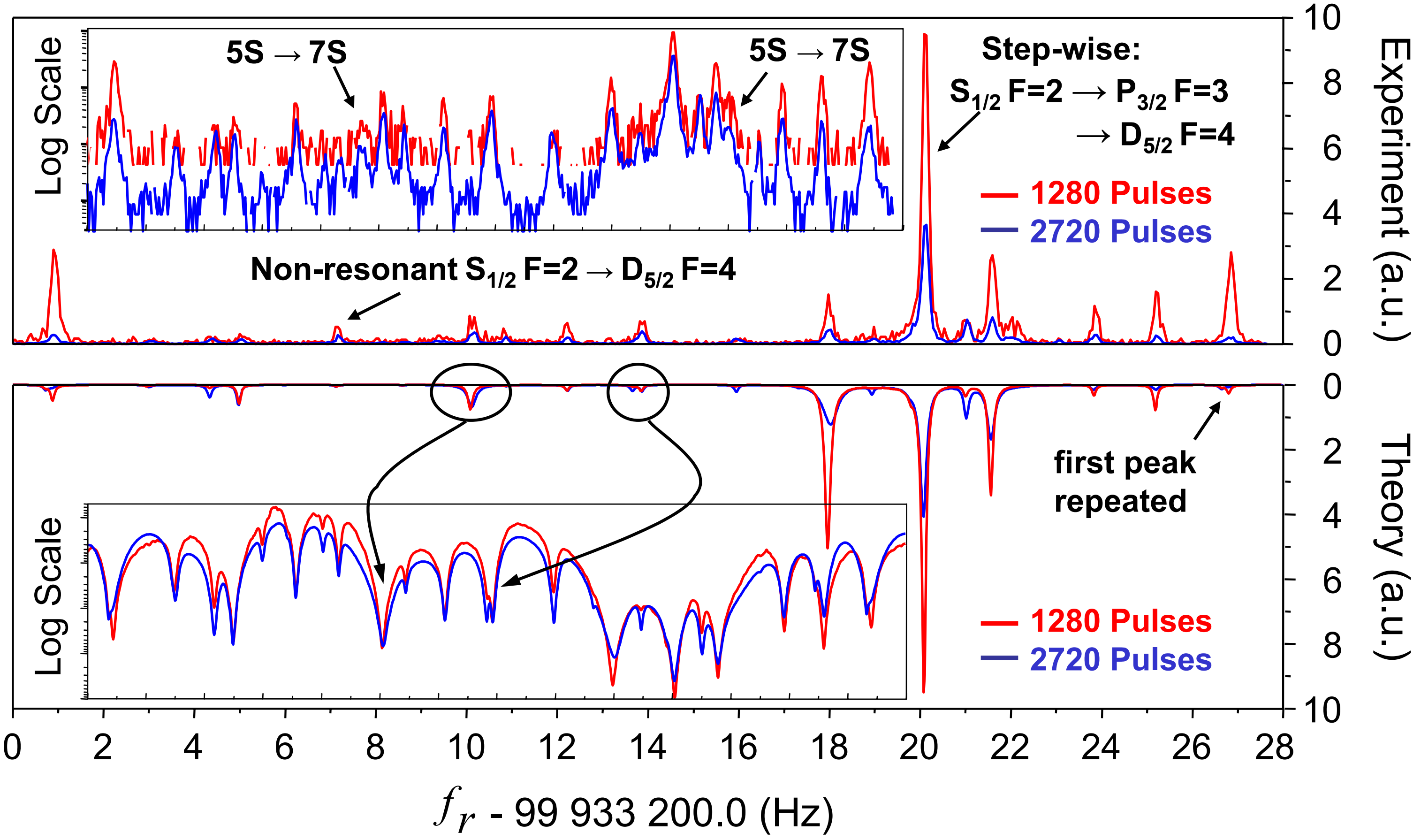

Figure 5.2: Experimental (top) and simulated (bottom) two-photon spectra obtained with a frequency scan of f_r. Shifting f_r by 26 Hz shifts the comb spectrum by 100 MHz, or f_r, approximately repeating the original comb structure. The changes in relative peak sizes from the spectrum obtained after 1280 pulses (in red) to that after 2720 pulses (in blue) illustrate population transfer dynamics by optical pumping as well as heating effects. Two resonances in the data due to the 5S → 7S transitions are not included in our model.

For this f_r scan, the initial ground-state population is in F=2. At longer times (blue curves), all the transitions starting on F=2 are decreasing in amplitude compared to shorter time scales (red curves) due to ground-state population redistribution and heating. Most of the F=1 peaks remain unchanged or become larger. Our density matrix simulation accounts for the time dependence of the shutter response and optical pumping dynamics, but does not include any heating effects. The signal size shown in Fig. 5.2 has been normalized against the square of the probe power. Not surprisingly, both theory and experiment reveal that the most dominant transition pathway is the closed $5S_{1/2}$ (F=2)→ $5P_{3/2}$ (F′=3) → $5D_{5/2}$ (F″=4) transition.

The relative size of the features in Fig. 5.2 after any fixed number of pulses reflects intermediate-state resonant enhancement as well as population transfer. Thus, the spectrum contains all of the fine and hyperfine structure pertinent to the 5D states.

5.2 Absolute frequency measurements

After accounting for the systematics discussed in Chapter 4, we have analyzed spectra similar to the ones shown in Fig. 5.2 to construct a table of absolute transition frequencies from 5S to 5D (see Table 5.1). We isolated the five two-photon transitions which start in F=2, and go through $5P_{3/2}$ F′=3, i.e. two-photon transitions which have the 5S-5P step as a closed transition. This closed first step may help with the optical pumping, giving better signal-to-noise ratios to determine their absolute frequency.

These representative transition frequencies are determined directly from the comb structure and are given in the table, along with comparisons to available published values [75]. The measurement accuracy is currently a few kHz to a few tens of kHz for the 5D states and on the order of 100 kHz for the 5P states, comparable to the highest resolution measurements made with cw lasers. All the measurement errors reported here are statistical errors (one standard deviation of the mean).

Measured transition	Measured frequency (kHz)	Literature value (kHz)
$5S_{1/2}$ F=2→ $5D_{5/2}$ F″=2	770 569 184 527.9 (49.3)	770 569 184 510.4 (16.0)
$5S_{1/2}$ F=2→ $5D_{5/2}$ F″=3	770 569 161 560.5 (11.1)	770 569 161 555.6 (16.0)
$5S_{1/2}$ F=2→ $5D_{5/2}$ F″=4	770 569 132 748.8 (16.8)	770 569 132 732.6 (16.0)
$5S_{1/2}$ F=2→ $5D_{3/2}$ F″=3	770 480 275 633.7 (12.7)	770 480 275 607.6 (10.0)
$5S_{1/2}$ F=2→ $5D_{3/2}$ F″=2	770 480 231 393.9 (38.1)	770 480 231 385.2 (10.0)
$5S_{1/2}$ F=2→ $7S_{1/2}$ F″=2	788 794 768 921.4 (44.5)	788 794 768 878.0 (40.0)
$5S_{1/2}$ F=1→ $7S_{1/2}$ F″=1	788 800 964 199.3 (121.9)	788 800 964 042.0 (40.0)

Table 5.1: ^{87}Rb level structure from direct frequency comb spectroscopy. All the values are obtained by extrapolating the line center to zero probing time and power. The first six transitions presented here are resonantly enhanced by the $5P_{3/2}$ F′=3 state and thus have a closed first step. The final seventh transition passes through the $5P_{3/2}$ F′=1 intermediate level.

We will now move on to discuss the measurement of the two extra resonances that appeared in the spectra shown in Fig. 5.2.

5.3 5S-7S absolute frequency measurements

After observing the two resonances, we reviewed the literature and discovered that in fact no one had measured these transitions with high precision. Without *a priori* information of the 7S energy levels, we have determined their absolute transition frequencies [76]. We have used the transition wavelength reported in the online NIST atomic database, which was of course covered by the fs laser spectrum, so we were able to determine the resonance frequencies. A single optical comb thus provides atomic structural information in the optical, terahertz, and radio-frequency spectral domains.

I will discuss in some detail now the 5S-7S two-photon frequency measurements. They were performed in a similar manner to the 5S-5D measurements, with the important change that we used a Pockels cell with a 8-ns rise time instead of the liquid crystal shutter ($\sim 30\ \mu$s response time). As a consequence, we did not have to account for the shutter turn-on when obtaining the final frequency values, which made it easier to extrapolate to zero power. The experiment cycle and general method remained the same, especially since the 7S levels also decay through the 6P levels, which means that we were able to use the same PMT. As seen from the general frequency diagram in section 4.2, the wavelengths for the second step of the resonantly enhanced 5S-7S transitions are 741 nm for transitions via $5P_{3/2}$ and 728 nm for transitions via $5P_{1/2}$. The energy degenerate two-photon transition is at 760 nm. This makes it more difficult to cover them in our spectrum, optimized for 778 nm. This fact is especially true about 728 nm wavelength. Shifting the spectrum to smaller wavelengths is definitely doable, the problem is having a sufficient signal-to-noise ratio for the f_0 beat to properly maintain phase-lock of the Ti:S. The degradation in the signal-to-noise ratio of the f_0 beat occurs because the microstructure fiber is optimized for its zero GVD point near 800 nm. Thus, I usually center the fs spectrum at 770 nm for these measurements and I try to use only transitions enhanced by a $5P_{3/2}$ intermediate level.

Shown in Fig. 5.3(a) is a typical $7S_{1/2}$ $F''=2$ Lorentzian lineshape, generated by stepping the offset frequency f_0 for a fixed value of the repetition rate f_r and recording the subsequent blue fluorescence corresponding to the 7S population. For each data point, to obtain a better signal-to-noise ratio, the 80 ns-binned counts arising from the fluorescence are integrated over 2.4 μs. Alternatively, this lineshape is retrieved by sweeping f_r with f_0 fixed at some convenient value.

Once the lineshape has been acquired, what remains is to identify the correct mode number N associated with each transition. If the optical frequency is already known to within $f_r/2$, this is a straightforward task. For the case of the 5S-7S two-photon transitions, where the resonance frequencies are not known *a priori* ($\nu_{opt} = (N_1 + N_2)f_r + 2f_0$), we scan the resonances for two different values of f_r and unambiguously deduce the sum of the two associated integers $(N_1 + N_2)$ [77, 78]. In our case, the two repetition rates used are separated by 600 kHz to eliminate possible uncertainties arising from estimations of the f_0 value corresponding to the peak of the resonance.

After identifying the comb numbers associated with the transition and reducing

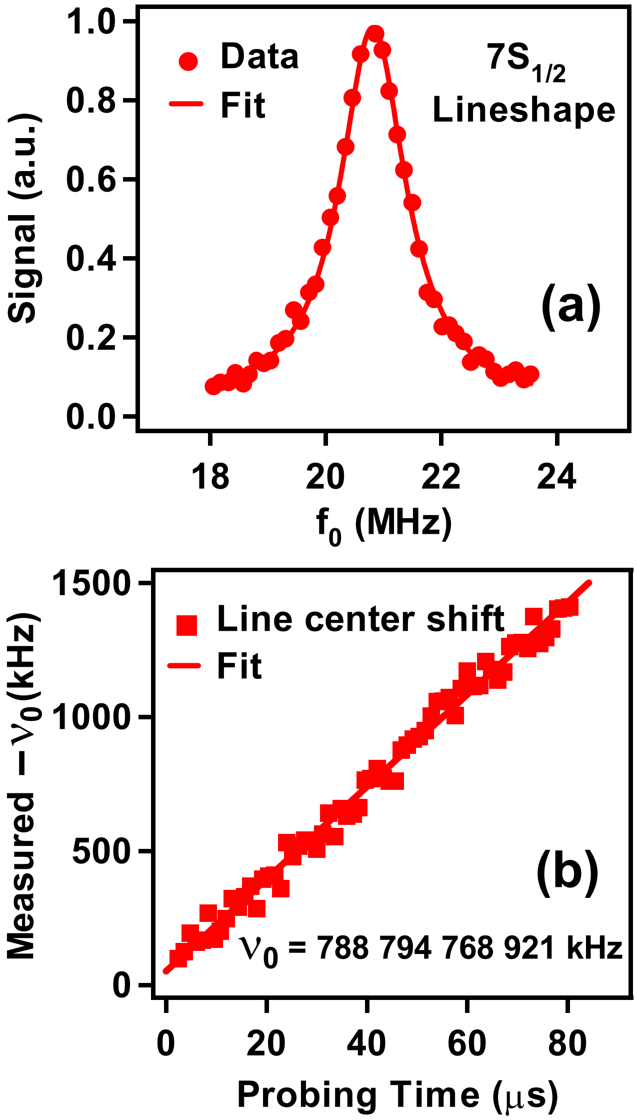

Figure 5.3: (a) Typical $5S_{1/2}$ F=2→ $7S_{1/2}$ F″=2 two-photon Lorentzian lineshape obtained from a scan of the offset frequency f_0 for a fixed value of the repetition rate f_r . For each data point, the 80 ns-binned counts arising from the fluorescence are integrated over 2.4 s. (b) Frequency shift of the transition line center vs. probing time resulting from the momentum transferred by the femtosecond laser to the cold ^{87}Rb atoms. Extrapolation to zero interrogation time gives absolute atomic transition frequencies, as well as roughly the natural linewidth, free of radiation pressure effects.

the systematic error arising from AC Stark shift (by probing on optimal resonance i.e., zero detuning for both the intermediate state and the final state), the remaining error from radiation pressure is suppressed by extrapolating to zero interrogation time, as shown in Fig. 5.3(b). We determine for the $5S_{1/2}$ F=2 → $7S_{1/2}$ F″=2 and the $5S_{1/2}$ F=1 → $7S_{1/2}$ F″=1 two-photon transitions in ^{87}Rb the absolute optical frequencies of 788 794 768 921(44) kHz and 788 800 964 199 (122) kHz, respectively (see Table 5.1). The excited state hyperfine interval of 639 404 (130) kHz agrees very well with a previous differential measurement performed with a picosecond pulsed laser [70]. The transition spectra reported in [70], as well as a continuous-wave (cw) laser-based scan [79], indicated that the F=2 → F″=2 and the F=1 → F″=1, i.e. ΔF=0 transitions, were the only allowed 5S-7S transitions in ^{87}Rb. However, we observe additional lines, as the resonant intermediate 5P state also enables the F=2 → F″=1 and F=1 → F″=2, i.e., ΔF=±1, two-photon transitions. Similar ΔF=±1 S-S transitions have been previously observed in Na in a two-step excitation experiment employing two tunable cw dye lasers, which enabled a direct measurement of the excited state hyperfine splitting [80].

We recently learned that conventional, cw laser-based measurements of the 5S-7S transitions in Rb were reported by Chui *et al.* [81]. Our measurements agree with their results, within one standard deviation of the mean for the reported values, as can be seen from Table 5.1. Thus, we have demonstrated that by using DFCS, the absolute value of the $5S_{1/2}$ → $7S_{1/2}$ two-photon transitions in ^{87}Rb is conclusively determined, with no *a priori* knowledge about their optical frequency.

In the next chapter I will discuss single-photon frequency measurements that we recently made. As described there, one indirect way to determine the absolute frequencies of the 5S-5P transition is to scan the 5P state by using a set of f_r and f_0 pairs that have a range of detunings from the 5P state and are all two-photon resonant. I will show that detailed dynamics of population transfer driven by a sequence of pulses have to be taken into account for the measurement of the 5P states via resonantly enhanced two-photon transitions.