Time-domain spectroscopy of molecular free-induction decay in the infrared

Ian Coddington,1,2 William C. Swann,1 and Nathan R. Newbury1,3
1National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305, USA
2ian@boulder.nist.gov
3 nnewbury@boulder.nist.gov

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Time-domain spectroscopy using dual, coherent frequency combs is used to measure free-induction decay from a molecular gas sample in the near-IR with a time-domain signal-to-noise ratio of $\sim 10^6$ over a $\sim 6$ ns window at 55 fs time resolution (corresponding to the 9 THz source bandwidth) and a frequency/timing accuracy set by the frequency combs. The free-induction decay exhibits the expected periodic pulses from the rephasing of the multiply excited rovibrational levels. This demonstration represents the first high-resolution, high-accuracy, broadband measurement of optical free-induction decay, to our knowledge.

A simplified schematic of the setup is shown in Fig. 1. The two comb sources are stabilized erbium-doped femtosecond fiber lasers with repetition rates $f_r$ $\sim 100$ MHz that differ by $\Delta f_r = 3.14$ kHz. With modest spectral broadening the combs cover an $\sim 9$ THz bandwidth centered at 1560 nm. Pulses from one comb excite the molecules, and the resulting transmitted signal is a train of unperturbed pulses, each followed by a much longer and weaker tail containing the FID signal. The asynchronous local oscillator (LO) pulse train acts to sample or down-mix the FID signal and a reference pulse that by-passed the sample. Deconvolution of the reference and signal yields the normalized sample response with an effective frequency resolution limited through apodization to about twice $f_r$. The nearly continuous measurement of the signal and reference allows for calibration of every interferogram, offering a high degree of immunity to drifts in the laser spectrum or other experimental parameters. Furthermore, with this time-multiplexed approach to normalization, both signal and reference share much of the same optical path and use a common detector, which suppresses ripple in phase or magnitude caused by inadvertent etalon reflections in the optical paths by $> 30$ dB.
While it would be possible to detect the entire 9 THz spectrum at once, the peak signal would exceed the dynamic range of the commercial balanced detector and 12 bit digitizer; therefore we use a tunable optical filter (coarse spectrometer) with 2 nm (250 GHz) bandwidth. This also limits the instantaneous signal bandwidth to below the effective Nyquist limit set by our choice of $f_r$ and $\Delta f_r$ [9–17]. The response is acquired as the filter is stepped across the spectrum, and finally the total signal is coherently stitched together over the full 9 THz from the baseline-corrected response at each setting. The LO comb is frequency shifted for filter settings that would otherwise yield a heterodyne signal at baseline or Nyquist. An inverse Fourier transform yields the full FID signal. In addition to mitigating the dynamic range limit, the use of a tuned filter flattens the optical spectrum and puts stringent limits on aliasing.

The LO pulse train scans or walks through the entire signal pulse period every $\Delta t_{\text{sc}}^{-1}$ ~ 320 $\mu$s to generate a single interferogram. Because of the dynamic range limitations of the detection, the SNR on one interferogram is poor and is improved through coherent signal averaging without excessive data storage by phase locking the two comb sources such that the LO and signal pulses always arrive at the beginning of each 320 $\mu$s interferogram with exactly the same pulse and carrier overlap [17]. Under these conditions, we simply add successive interferograms (and FID signals) either in firmware or software for up to ~3 s, limited by drifts in the relative optical paths. For averaging times beyond 3 s, averaged interferograms are phase corrected based on the centerburst [19] before co-adding [see Fig. 1(b)].

Figure 2(a) shows the measured FID decay from the C—H overtone stretch vibration in hydrogen cyanide (HCN). In effective time, the trace extends from ~2 ns before the incident pulse to ~4 ns after the pulse at a time resolution of 55 fs, yielding 110,000 data points. The noise background is the same before and after the pulse (as verified with an empty cell), and the SNR is $0.5 \times 10^6$. The corresponding frequency-domain noise varies but is $\sim 2.5 \times 10^{-4}$ in both phase (radians) and amplitude near the center [see Fig. 2(d)], with an additional small $5 \times 10^{-3}$ ripple due to residual comb phase noise. Because of downsampling and the coherent signal averaging, these low SNR levels are reached at an effective scan rate of 200 GHz/min in real time or 2700 s for the full 9 THz. The SNR scales as the square root of acquisition time, and much shorter acquisition times are easily realized with a corresponding loss of SNR.

The FID time-domain response is simply related to the complex linear susceptibility, $\chi(t)$, as the Fourier transform of $[1 + i4\pi^2 c^{-1} n L \chi(\nu)]$ over the 9 THz window, where $L$ is the cell length. For a set of rovibrational lines at frequencies $\nu_i$, line strength $S_{ij}$, Doppler FWHM $\Delta v_D$, and collisional FWHM $\Delta v_{Li}$, the time-domain response is

$$1 - \rho L \Delta \Sigma 2S_{ij} \cos(2\pi \nu_i t)e^{-\nu_i^2 \Delta v_D^2/(4 \ln 2)-\nu_i^2 \Delta v_{Li}^2},$$

where $\rho$ is the number density, $\theta(t)$ is the Heaviside step function, and $\Delta t$ the time resolution (~55 fs).

See Fig. 2(b) for a comparison of the data with this equation.

Because of the number of rotational levels, the FID structure is complicated, and it is convenient to use a sonogram to spread the information out over time and frequency as shown in Fig. 2(c). In this sonogram the vertical strip at $t=0$ is the incident signal pulse, and the trailing slowed light signal at later times is the FID. Because the rotation speeds are quantized, the molecules periodically rephase to generate additional pulses of coherently forward-scattered light called commensurate echoes [3]. These echoes are visible as vertical striations in the data and can yield information on molecular constants. For the $P$ branch (lower frequency) and the $R$ branch the occurrences occur with a period of $(2B''-2(B'-B'')J)^{-1}$ = 10.5 ps and $(4B''-2B''+2(B'-B'')J)^{-1}$ = 13.4 ps, re-
spectively, where $B''$ ($B'$) is the ground (excited) state rotational constant, and we assume an average $J$ value of 8 [19]. Depending on the spectral region, 140–170 rotational recurrences are visible out beyond 1.8 ns. Because of the $J$ dependence of rotational frequencies the recurrences slowly dephase, with broadband realigning again at intervals of $\frac{1}{B'' - B'} = 0.853$ ns for both branches.

While the SNR is significantly improved over [9], higher SNR is always desirable. The noise is roughly 80% detector noise and 20% shot noise; however, the real limit is set by the detector dynamic range. Employing the tunable filter to break up the spectrum reduces the peak signal and improves the overall SNR roughly as the square root of the number of filter positions. This dynamic range also could be increased through an improved detector, applying a differential chirp between the combs [11,13,18] or ignoring the saturating centerburst [2]. An even larger SNR increase would result from parallel acquisition incorporating multiple narrowband filters and a detector array [20].

The true promise of this approach clearly lies in achieving higher SNR and in moving to the mid-infrared [10,11], where molecular cross sections are larger. Finally, it is intriguing to consider combining such a comb system with synchronous pump–probe spectroscopy or nonlinear spectroscopic techniques such as 2D Fourier transform spectroscopy.

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References


