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Time-Resolved, NIR Two-Tone Frequency Modulation Spectroscopy for Quantitative Measurement of HO_2 Radical in Fuel Oxidation Reactions

Haifeng Huang, Chris Carlen, Brandon Rotavera and Craig A. Taatjes

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Time-Resolved, NIR Two-Tone Frequency Modulation Spectroscopy for Quantitative Measurement of HO_2 Radical in Fuel Oxidation Reactions

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Abstract

Time-resolved two-tone frequency modulation (TTFM) absorption spectroscopy has been used to measure, *in situ* and quantitatively, hydroperoxy (HO_2) radical in fuel oxidation reactions at the first overtone transitions ($2\nu_1$) of HO_2 near 1509nm. Typical HO_2 detection limit is on the order of 10^{11} molecule cm^{-3}, which corresponds to a relative absorption of 10^{-5}. TTFM method successfully removes low frequency thermal lensing noise in measured HO_2 kinetic time traces, which is a general noise source in fuel oxidation absorption experiments. Compared with previous works, we have upgraded the TTFM experiment with a NIR distributed feedback (DFB) diode laser, a fiber-coupled broadband phase modulator, and a two-channel wave generator, which have improve the performance of our experiment substantially.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. The authors thank Howard Johnsen, Kendrew Au, Erxiong Huang, Brian Patterson and Paul Fugazzi for great technical help.

CONTENTS

FIGURES

1. Introduction

Frequency modulation (FM) absorption spectroscopy [1, 2], also called wavelength modulation (WM) spectroscopy for low modulation frequency, has been a commonly used sensitive detection method for decades. In this method, the absorption signal is first modulated at a frequency out of the major part of the noise spectrum of a detection system (mainly laser amplitude noise), and then recovered by demodulation. Compared with direct absorption method, which measures the absorption signal near DC, FM method reaches much higher sensitivity by shifting the detection from DC to a high enough frequency having much lower noise density in a noise spectrum. With careful design, FM method can reach quantum noise limit [3]. In FM method, a fast detector with bandwidth matching modulation frequency (typically hundreds of MHz) is needed. When the probed absorption linewidth gets broader and broader at high temperature or pressure, such a fast detector can be not so easy to find [4]. One clever way of solving this difficulty is two-tone frequency modulation (TTFM) method [5], in which the probe laser is modulated with two frequencies: both frequencies are on the order of several hundreds of MHz but their difference is about several MHz, and the absorption signal is demodulated at the difference frequency. Therefore, a detector bandwidth of several MHz will be fast enough. With both modulation frequencies on the order of several hundreds of MHz, which are comparable with the linewidth of a typical absorption line, TTFM method inherits the differential detection feature of single frequency FM method [4, 5].

Previously, the laser chemistry lab of Combustion Research Facility used NIR TTFM method [6] to probe HO_2 radical in fuel oxidation reactions in order to remove strong thermal lensing noise caused by the reactions [7]. The phase modulator used was resonance enhanced electro-optic modulator (EOM) (New Focus, model 4423), which has a modulation coefficient about 0.1rad/V and narrow frequency coupling range (several MHz). Although the input RF power can be reduced by a factor of 10 with resonance enhancement, it is hard to realize high modulation index with this type of phase modulator because of maximum RF power limit. We have also measured HO_2 by differential direct absorption spectroscopy [8], which is able to remove most of thermal lensing noise by subtracting on-peak data trace by a second off-peak background

data trace. However, residual low frequency noise still exists and has a significant effect on HO_2 kinetic time traces, limiting the measurement time window to less than 10ms. In this report, we have upgraded our HO_2 experiment with a distributed feedback (DFB) diode laser, a fiber coupled broadband phase modulator, and a two-channel function generator. This upgrade has improved the performance of the experiment substantially. For example, the fiber coupled broadband phase modulator has a substantially lower half-wave voltage V_π than a normal EOM crystal, making large modulation index ($\beta \sim 1$) possible.

The HO_2 absorption transitions used in our experiment are the first overtone transitions of OH stretch ($2v_1$ band) at 1509nm [9, 10, 11]. Methanol (CH_3OH) oxidation system is a perfect reference system for HO_2 [6, 8]. Under typical fuel oxidation conditions, it has near unity conversion efficiency from initial radical (Cl atom) to HO_2 through reactions:

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \qquad (R1)$$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O \qquad (R2)$$

Because the coproduct of HO_2 in (R2) reaction is CH_2O, this reaction system is a quantitative standard for both HO_2 and CH_2O.

2. Details of Experimental Setup

Figure 1 is the schematic diagram of our TTFM setup. The details about the reactor and flow control can be found in previous publications from this group [6, 8, 12]. In this report, we mainly focus on the details of optical configuration of TTFM. Figure 2 is a picture of the TTFM part.

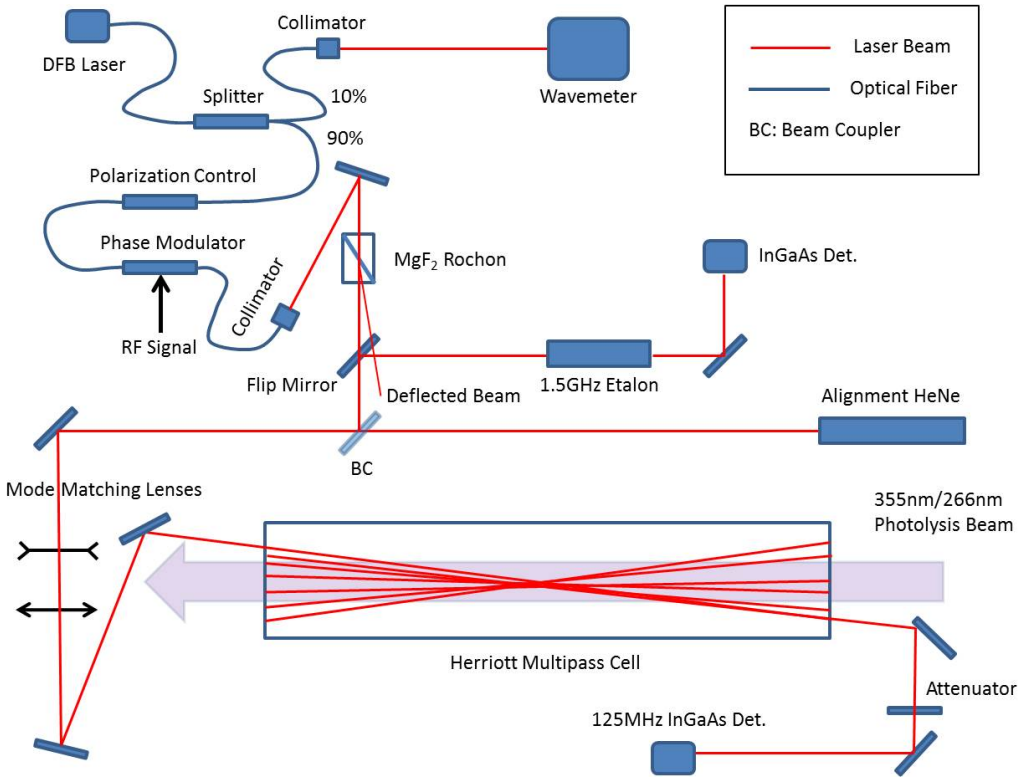

Figure 1. Schematic diagram of the TTFM setup

We have replaced previous cw external cavity diode laser (ECDL) with a DFB semiconductor diode laser at 1509nm (NTT Electronics, NLK1S5GAAA) (Figure 3). The laser wavelength can be tuned accurately by temperature and current tuning, with tuning rates of 0.1nm/K and about 0.005nm/mA respectively. Figure 4 is a picture of temperature (Thorlabs, TED200C) and current (Thorlabs, LDC200C) controllers. The linewidth of the laser is about 1MHz at short time scale (~1ms), much narrower than Doppler broadened HO_2 absorption lines. The stable laser temperature range is from about 0 to 40 degree-C, giving a tuning range of 4nm. With laser

temperature stabilized, the safe current range is from 10mA to 150mA. At 100mA current, the output power is more than 25mW, much more than the experiment needed. The total tuning range of the laser can cover several strong HO_2 lines, e.g. the strong line at 6625.784cm^{-1}. Because the output coupling of the diode laser is not through a polarization maintained (PM) fiber, the output light is normally slightly elliptically polarized.

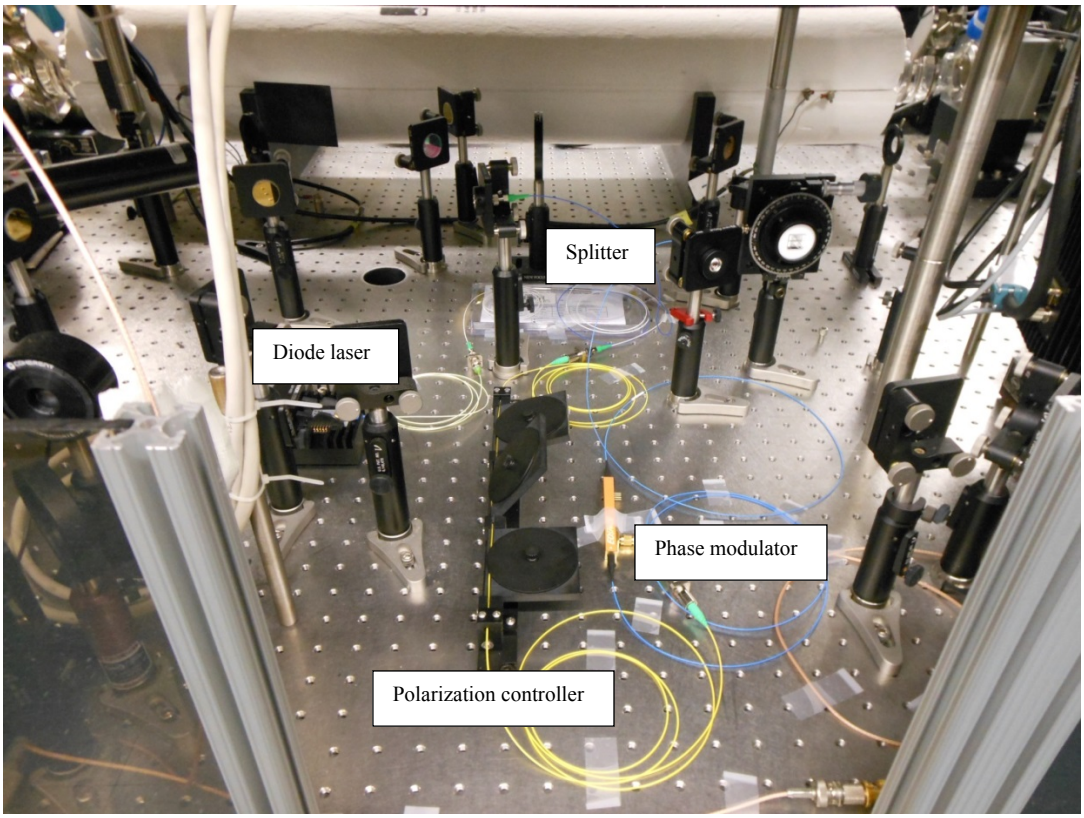

Figure 2. Picture of the setup

One 10/90 fiber coupler (Thorlabs, PMC1550-90B-APC - 1x2 PM) is used to split the laser output into two beams. The 10% beam is coupled to a wavemeter (Burleigh, WA-1500) for wavelength monitoring, and the 90% beam is connected to the input fiber of a polarization controller (Thorlabs, FPC562), which controls the laser polarization through three effective waveplates formed by three fiber coils: one λ/4 waveplate, one λ/2 waveplate and another λ/4 waveplate. The optical fiber of this polarization controller is not PM.

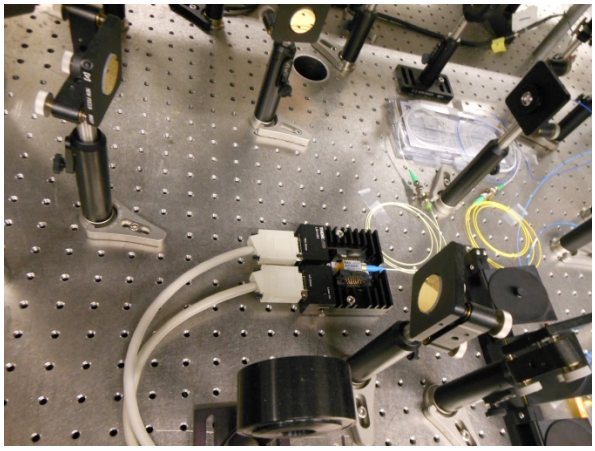

Figure 3. Picture of DFB diode laser

After the polarization control, the laser is coupled into a phase modulator (EOSpace, PM-0K5-10-PFA-PFA-1509) through a short piece of PM fiber. The phase modulator has the optimum modulation efficiency (equivalently lowest V_π) when the laser polarization is aligned with the TM mode of the waveguide of the modulator (parallel with the optical table in Figure 2). In reality, the laser output of the polarization controller is not perfectly linearly polarized. Therefore, some light is coupled into the TE mode in the modulator, in which the light has much lower modulation efficiency (equivalently much larger V_π). In order to fully utilize the high modulation efficiency of the TM mode, we have put one MgF_2 Rochon polarizer after the phase modulator output with the polarizer aligned with the TM mode in the modulator (parallel with the optical table) (Figure 2). After the Rochon polarizer, the laser beam is divided into two beams. Only the one of correct polarization is coupled into the reactor to probe HO_2 radical and the other one of wrong polarization (perpendicular to the optical table) is deflected, as shown in Figure 1. One can quickly examine the laser polarization by checking the relative intensity between these two beams by an IR sensor.

In order to measure the half-wave voltage V_π of the phase modulator, a flip mirror is used to direct the modulated light to one NIR etalon (Thorlabs, SA200), which has a free spectral range (FSR) of 1.5GHz and a resolution of 10MHz. For this measurement, the phase modulator was driven by pure sine waves with power from 0.88dBm (amplitude 0.35V) to 20.9dBm (amplitude

3.5V) (with 50ohm load). By using the NIR etalon, the measured intensities of different order sidebands (mainly ±1 and ±2 order) increase and that of the carrier frequency decreases when the amplitude of modulation sine wave increases. However, the sum of the intensities of all frequency components (sidebands + carrier) is almost a constant, a result of energy conservation. The intensity ratio between the first order sidebands (±1) and that of the carrier is used to calculate the modulation index β, because this ratio is equal to $(J_1(\beta)/J_0(\beta))^2$, with J the Bessel function of the first kind. Figure 5 shows a linear dependence between the modulation amplitude and modulation index β, giving a half-wave voltage V_π of 9.6V. However, the datasheet of the phase modulator gives a V_π of 4.3V. The reason of this discrepancy is not known. The frequencies of sine waves used in this measurement are 230MHz, 300MHz and 500MHz.

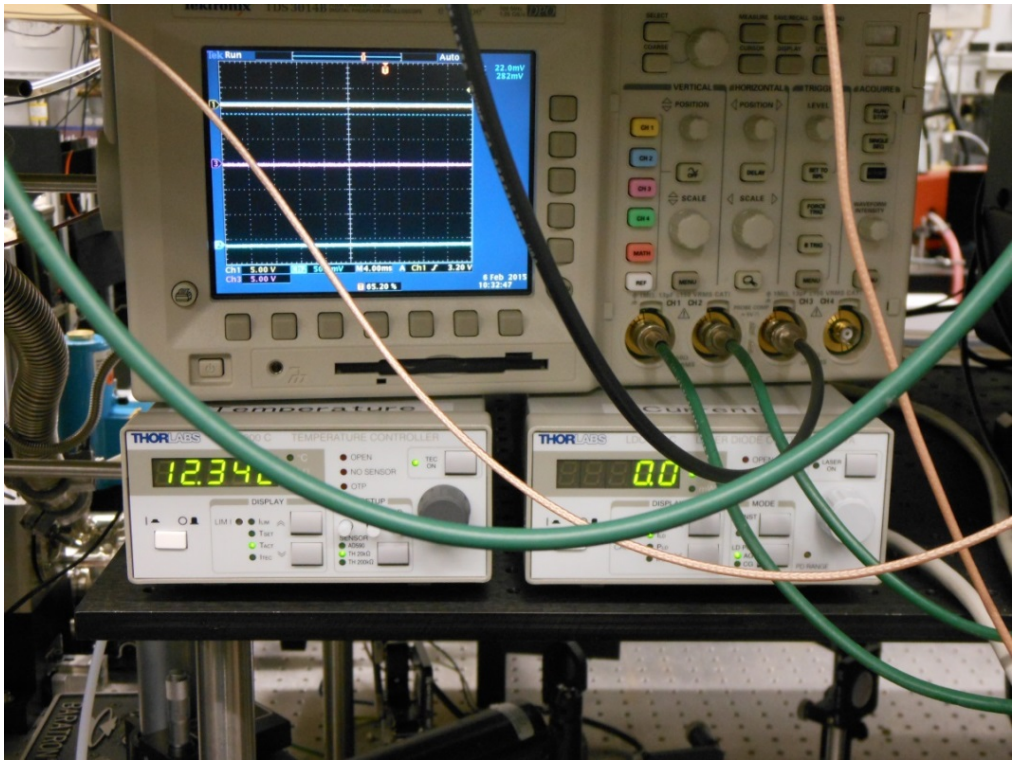

Figure 4. Temperature (left) and current (right) controllers of the laser

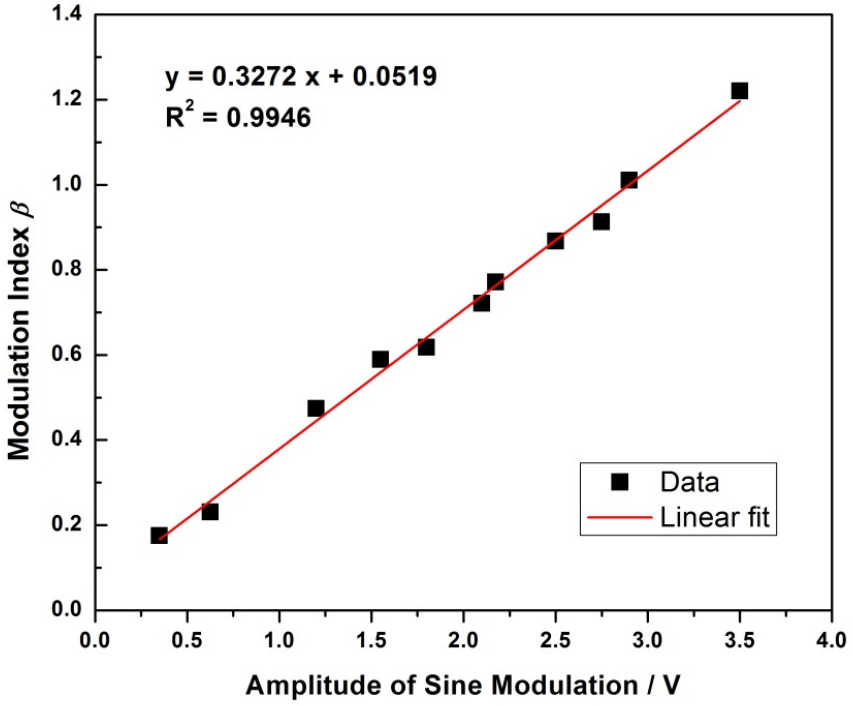

Figure 5. Linear relationship between pure sine modulation amplitude and modulation index β, which gives a half-wave voltage V_π of π/0.3272 = 9.6V for the phase modulator.

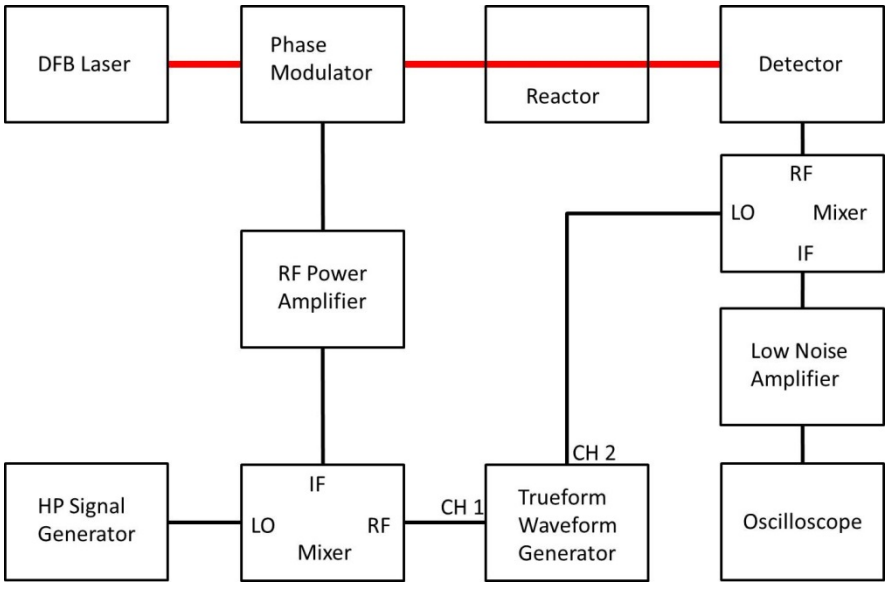

Figure 6. Block diagram of TTFM setup

Figure 6 is the block diagram of our TTFM setup. An HP signal generator (HP8847A) is used to generate a sine wave of 500MHz – 800MHz with 7dBm power (5mW), which is connected to the LO end of a mixer (Mini Circuits, ZFM-2-S+) (see Figure 7). The RF input signal is a sine wave of 4MHz from the channel one of a waveform generator (Agilent, Trueform 33500B) (see Figure 8). The IF output signal of the mixer is then connected to the input of a RF power amplifier (Pasternack, PE15A4017) and the output of the amplifier is used to drive the phase modulator.

The IF end output waveform of an ideal mixer is the direct product of RF and LO inputs. Typical two-tone frequency modulation waveform is shown in Figure 9, showing slight asymmetry. Considering the well-known trigonometric identities, ideal TTFM waveform is a direct sum of two sine waves of the same amplitude, and the amplitude of TTFM waveform is twice of the amplitude of the two pure sine waves. For example, in Figure 9, the waveform can be approximated to the sum of two sine waves: one at frequency 496MHz and the other at 504MHz. If we take the average of the amplitudes of two slightly asymmetric lobes as the amplitude of the TTFM waveform, which is about 1.4V, then the amplitude of each sine component is about 0.7V, half of 1.4V. With previously measured V_π, this calculated amplitude will be used to calculate the modulation index β for each sine component in our TTFM experiment.

After the modulated probe laser passes the reactor, a fast InGaAs detector (New Focus, model 1811, bandwidth DC - 125MHz) is used to record the signal, which contains both DC and different heterodyne frequencies from phase modulation (see next section for more details). The detector output is connected to the RF input of the second mixer (Mini Circuits, ZFM-2) directly (Figures 6 and 7). To avoid saturation and too small signal, the detector output voltage should be in the range from 1.5V to 2.0V when measured by a digital voltmeter. The LO input signal of the second mixer is provided by the second channel of Trueform wave generator, a sine wave of 8MHz and 400mV peak-to-peak amplitude. The reason why the absorption signal is demodulated at the difference frequency of the two modulation frequencies (two tones), will

be explained in detail in next section. We think that using a two-channel Trueform wave generator is a significant progress in performing TTFM experiments. Agilent Trueform wave generators have excellent stability of frequency (ppm level of settings in a yearlong time period), and very low phase noise for both channels. With a Trueform wave generator, both the amplitudes and initial phases of the modulation and demodulation sine waves can be adjusted independently and accurately. This is especially convenient for adjusting the phase of demodulation sine wave to recover the absorption signal, as with a lock-in amplifier. Previously, this phase adjustment was done by either changing the length of the cable carrying demodulation sine wave [1], or fine adjusting one of the two modulation frequencies (4MHz in our experiment), which is actually equivalent to cable length changing. Using the Trueform box avoids using a frequency doubler (e.g. Mini Circuits MK-3) which often distorts the demodulation sine wave. The demodulated absorption signal (IF end output of the second mixer) is send to one of the two channels of a low noise differential amplifier (Stanford Research Systems (SRS), SR560), which has a low-pass 1MHz bandwidth. This gives a time resolution of about 1μs. The gain of the amplifier is set to 500 or 1000. The signal is averaged by several hundreds of laser shots and saved by an oscilloscope.

Figure 7. Two mixers

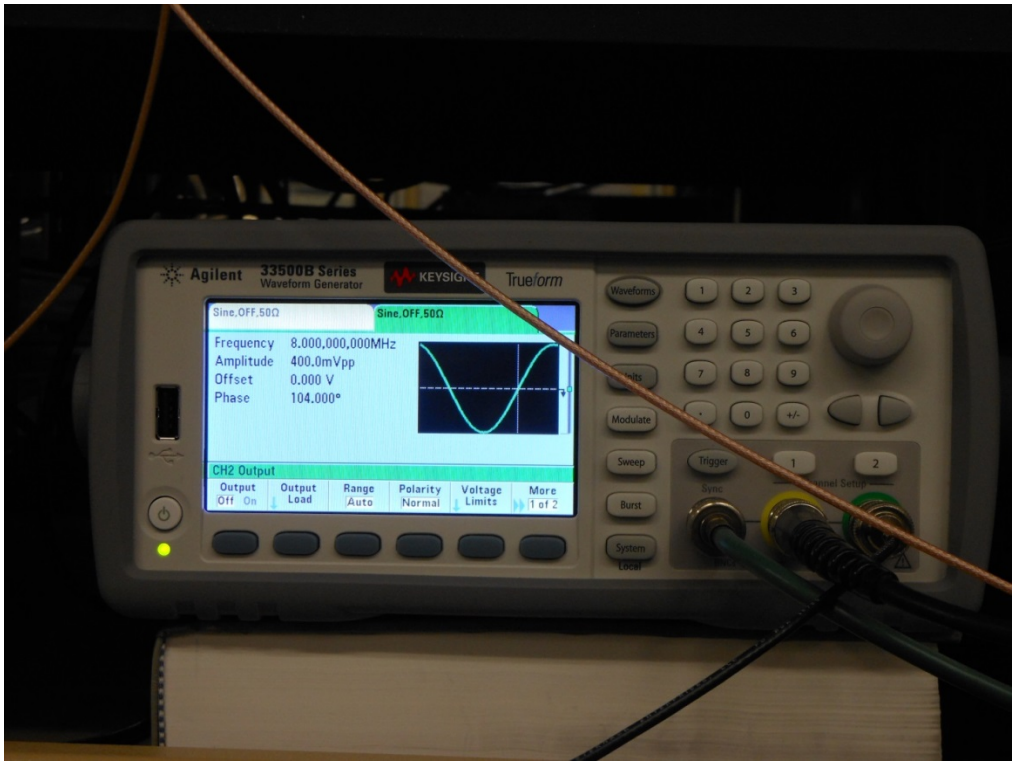

Figure 8. Agilent Trueform 33500B two-channel waveform generator

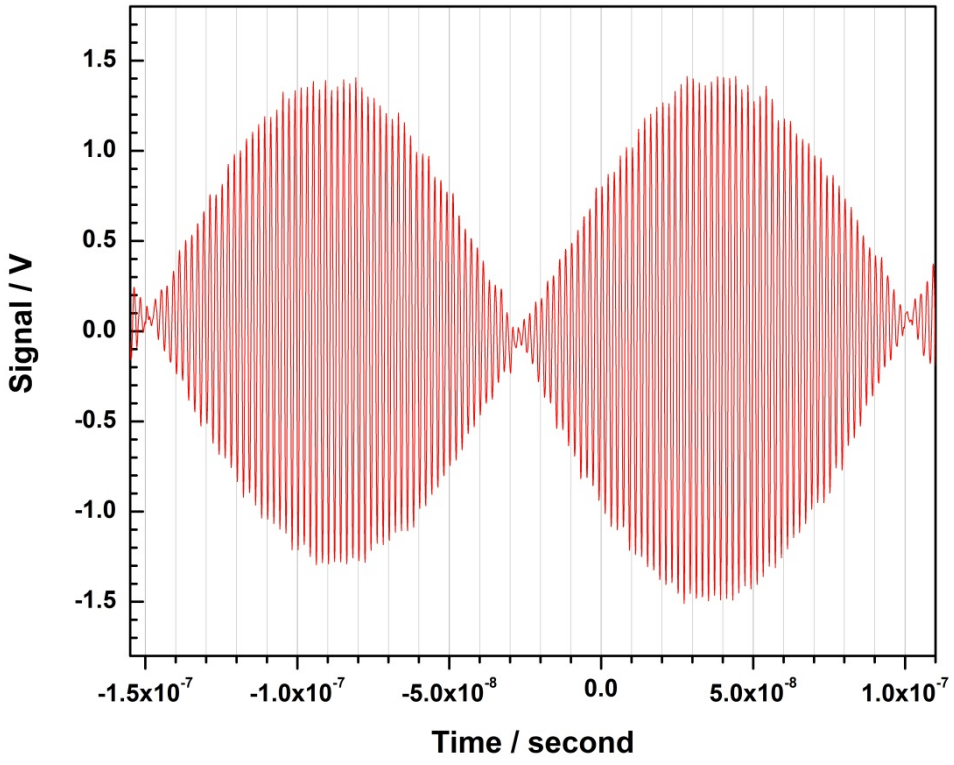

Figure 9. Typical modulation waveform (after amplification) in our TTFM experiment, which is generated with 7dBm 500MHz sine wave as LO input and 4MHz 200mV peak-to-peak sine wave as RF input. The waveform shape is close to the product of the two sine waves but contains slight asymmetry, which is possibly caused by the non-ideal mixer.

3. Two-Tone Frequency Modulation (TTFM) Spectroscopy for HO_2 Measurement

In this section, the principles of TTFM method will be discussed in details, especially for the case of high modulation index (β ~ 1). Following the clear physical picture presented in the first TTFM article written by Janik et al. [13], we will discuss how the measured absorption signal amplitude changes with modulation index.

A single sine wave phase modulation to a laser field will generate multiple sidebands (or frequency components). This can be described with the following equation.

$$E_m(t) = E_0 e^{i\omega_0 t} \sum_{n=-\infty}^{\infty} J_n(\beta_1) e^{in\omega_1 t}$$

In this equation, E_m(t) is the laser field after modulation, E_0 is the incident laser initial field amplitude, ω_0 is the incident laser angular frequency (or carrier frequency), ω_1 is the angular frequency of phase modulation, β_1 is the modulation index, *n* is an integer, and $J_n(\beta_1)$ is Bessel function. From the above equation, one can see the generated sideband frequencies are separated equally by ω_1 (in this report, we do not distinguish frequency from angular frequency purposely at some places). In TTFM, there are two frequencies of phase modulation (Figure 9). Simultaneous phase modulation at two frequencies is equivalent to performing successive modulations at each frequency [13].

$$E_m(t) = E_0 e^{i\omega_0 t} \sum_{n=-\infty}^{\infty} J_n(\beta_1) e^{in\omega_1 t} \sum_{p=-\infty}^{\infty} J_p(\beta_2) e^{ip\omega_2 t}$$

In the equation, ω_2 is the second modulation angular frequency, with β_2 the modulation index and *p* an integer. In our case, we assume $\beta_1 = \beta_2 = \beta$. If β is less than 1.5, we can truncate the two sums in the above equation to the second order sidebands, i.e. the integer *n* and *p* are equal to 0, ±1, and ±2 only. This approximation is reasonable because $J_3(1.5) = 0.06$ is small when compared with $J_0(1.5) = 0.51$, $J_1(1.5) = 0.56$ and $J_2(1.5) = 0.23$. In TTFM method, ω_1 and ω_2 are defined as following:

$$\omega_1 = \omega_m + \frac{\Omega}{2}; \omega_2 = \omega_m - \frac{\Omega}{2}$$

The difference between ω_1 and ω_2 is equal to Ω. In our TTFM experiment, ω_m is in the range of 500MHz – 800MHz, depending on the linewidth of HO_2 line at different temperatures, and Ω is 8MHz.

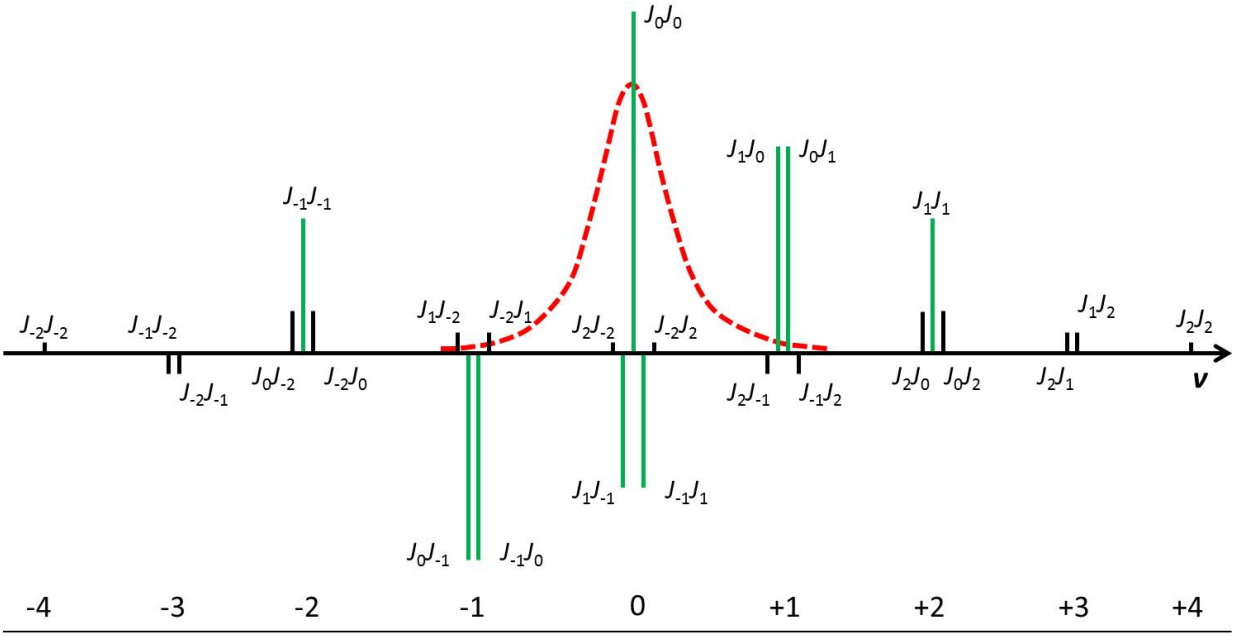

Figure 10. Spectrum of probe laser after two-tone phase modulation and approximated to the second order sidebands. Each vertical line corresponds to one frequency component, and its amplitude is labeled by a product of two Bessel functions, e.g. the amplitude of the carrier frequency is $J_0(\beta)J_0(\beta)$. The vertical lines pointing downwards have a phase difference of π from those pointing upwards. The red dashed curve means a separated absorption line of HO_2. The green vertical lines are the probe laser spectrum if it is approximated to the first order sidebands. The spectrum contains multiple clusters of sidebands separated by ω_m. In each cluster, sidebands are separated equally by angular frequency Ω. The integers below the spectrum are order indices of sidebands if the laser is modulated at angular frequency ω_m only. The separations between different frequency components in a cluster are not on scale because Ω is much less than ω_m.

Figure 10 is the spectrum of the probe laser after two-tone phase modulation for the case of β = 1.12 and approximated to the second order sidebands. There are multiple clusters of sidebands separated by ω_m in the spectrum. In each cluster, sidebands are separated evenly by Ω. Therefore, the heterodyne beat frequency between two successive frequency components will be either Ω or a frequency near ω_m, and the later heterodyne signal will be suppressed by detector bandwidth (125MHz) down to very low level. This is why the absorption signal is

demodulated at Ω instead of $\Omega/2$, and hence a detector with bandwidth slightly larger than Ω will be fast enough for TTFM experiments. The red dashed curve in Figure 10 represents an isolated HO_2 absorption line. With the above spectrum, one can easily write down the heterodyne signal at frequency Ω the detector measures, if the attenuation and phase shift to the light field caused by HO_2 absorption for each sideband cluster is known. Here we assume the attenuation and phase shift are the same for each component in the same cluster considering $\Omega << \omega_m$ [5, 13]. Starting with Figure 10, if the field attenuation and phase shift for the sideband cluster *j* (*j* = 0, ±1, ±2, ±3) are exp(-δ_j) and exp(-$i\varphi_j$) respectively, we can write down the equation of absorption signal in TTFM method.

$$I(\text{at } \Omega) = \frac{c}{8\pi}|E_0|^2\{2J_1(\beta)J_2(\beta)J_2(\beta)J_1(\beta)e^{-2\delta_{-3}} + 2J_1(\beta)J_2(\beta)J_2(\beta)J_1(\beta)e^{-2\delta_3} + 4J_0(\beta)J_2(\beta)J_1(\beta)J_1(\beta)e^{-2\delta_{-2}} + 4J_0(\beta)J_2(\beta)J_1(\beta)J_1(\beta)e^{-2\delta_2} - 4J_0(\beta)J_2(\beta)J_1(\beta)J_1(\beta)e^{-2\delta_{-1}} + 2J_0(\beta)J_0(\beta)J_1(\beta)J_1(\beta)e^{-2\delta_{-1}} - 4J_0(\beta)J_2(\beta)J_1(\beta)J_1(\beta)e^{-2\delta_1} + 2J_0(\beta)J_0(\beta)J_1(\beta)J_1(\beta)e^{-2\delta_1} - 4J_1(\beta)J_2(\beta)J_1(\beta)J_1(\beta)e^{-2\delta_0} - 4J_0(\beta)J_0(\beta)J_1(\beta)J_1(\beta)e^{-2\delta_0}\}\cos\Omega t$$

The above equation is the in-phase detector signal at frequency Ω, and independent with all the phase shifts. In the equation, *c* is the speed of light and E_0 is the initial amplitude of the probe laser. If there are no absorbents in the reactor or the frequency components do not reach any absorption lines, the heterodyne signal at frequency Ω will be zero. Ideally, TTFM method is a background free method. TTFM method measures the differential absorption among different orders of sideband clusters [5, 13]. When the absorption line gets broader and is larger than ω_m, the signal will decrease.

Figure 11 is typical HO_2 absorption signal in room temperature methanol oxidation measured by TTFM method at 6625.784cm^{-1}. When methanol was turned off, the HO_2 absorption signal disappeared completely. The peak S/N of the black trace is about 100 (1σ standard). The peak signal corresponds to [HO_2] ~ 10^{13} cm^{-3} and hence the HO_2 detection limit at room temperature is on the order of 10^{11} cm^{-3}. With a typical absorption length on the order of 10m and

absorption cross section of 10^{-19} cm^2, the minimum detectable absorbance of HO_2 in our experiment is on the order of 10^{-5}.

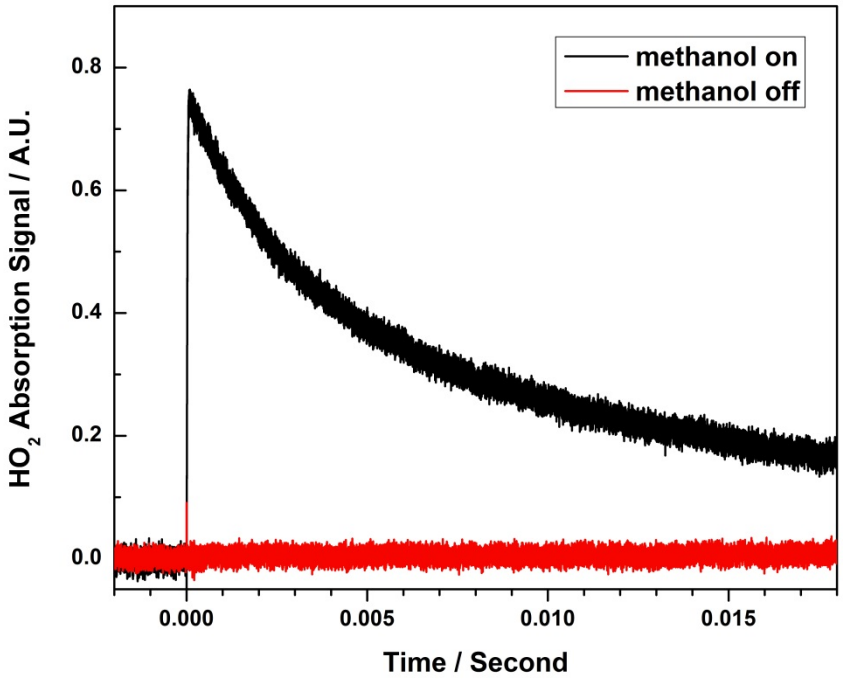

Figure 11. Time traces of HO_2 absorption in methanol oxidation measured by TTFM with a modulation index about 0.9, which contain almost zero low frequency noise in a time window of 20ms.

It has been pointed out by Cooper and Warren [13] that for an isolated absorption line (no interference lines in the range of $\pm 3\omega_m$ from the peak (Figure 10)), and if ω_m is substantially larger than the width of the absorption line, the optimum signal in TTFM will be realized with $\beta \approx 1.15$ when the probe laser is tuned to the peak of the absorption line. Figure 12 is a plot of TTFM signal amplitude versus modulation index β, containing both experimental data and model predictions. The red curve, calculated by using the equation of TTFM signal above, is the demodulated absorption signal versus β by assuming 0.001 absorbance ($\exp(-2\delta_0) = 0.001$ and all other δ_j is zero). The signal peaks at $\beta = 1.12$ and has been normalized to the peak value. This value is slightly different from $\beta \approx 1.15$ in Cooper and Warren's paper [13], which is because they have included contributions of higher order sidebands in their numerical calculations. The

black curve is calculated with a model approximated to the first order of sidebands (using only green vertical lines in Figure 10) assuming the same absorbance, and has been also normalized to the peak value of the red curve. This black curve peaks at β = 1.08, at which $J_0(\beta)J_1(\beta)$ reaches maximum. The black curve overlaps with the red curve very well for β < 0.8 and deviates from the red curve near the peak. The dotted green line is the model prediction for β << 1.0, with which $J_0(\beta) \approx 1$ and $J_{\pm1}(\beta) \approx \pm \beta/2$. The green dotted line predicts a β^2 dependence of the signal, which diverges for large β. The blue dots in Figure 12 are experimental data. Each dot corresponds to the peak amplitude of an averaged HO_2 time trace similar to the black one in Figure 11. The data have been normalized to the highest peak amplitude value in all measurements. The modulation index in the experiment is determined by the measured V_π = 9.6V and the amplitude of each modulation wave (see the discussion on Figure 9 in last section). The data agree with the red curve very well. In this measurement, HO_2 radical was probed at 6625.661cm^{-1}. For this absorption line, the nearest HO_2 absorption line is 3.7GHz away, which is more than 3 × v_m = 1.5GHz with $v_m = \omega_m/2\pi$ = 500MHz. The Doppler linewidth is 432MHz at room temperature. Figure 13 is a section of HO_2 spectrum near 1509nm from literature [10].

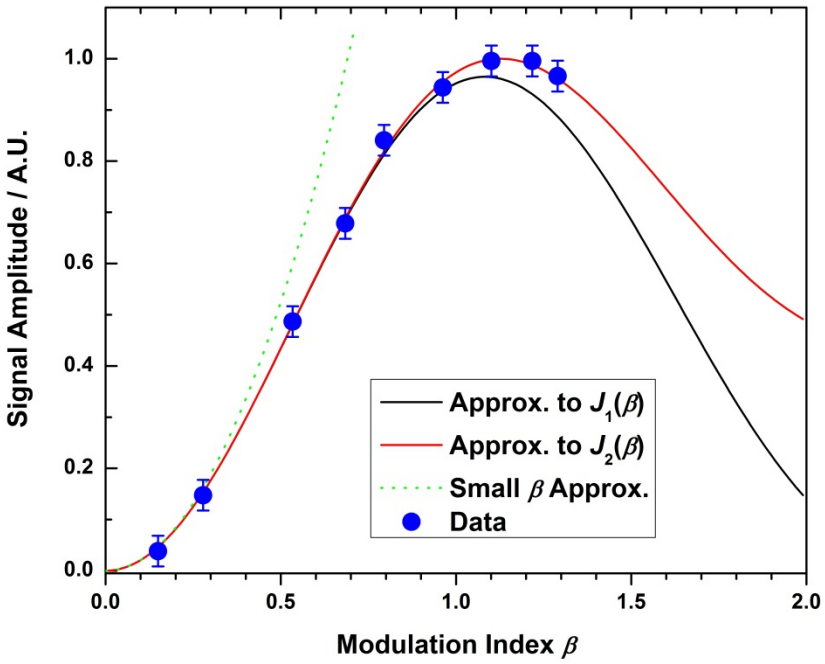

Figure 12. TTFM signal versus modulation index β. The error bars are of 2σ standard.

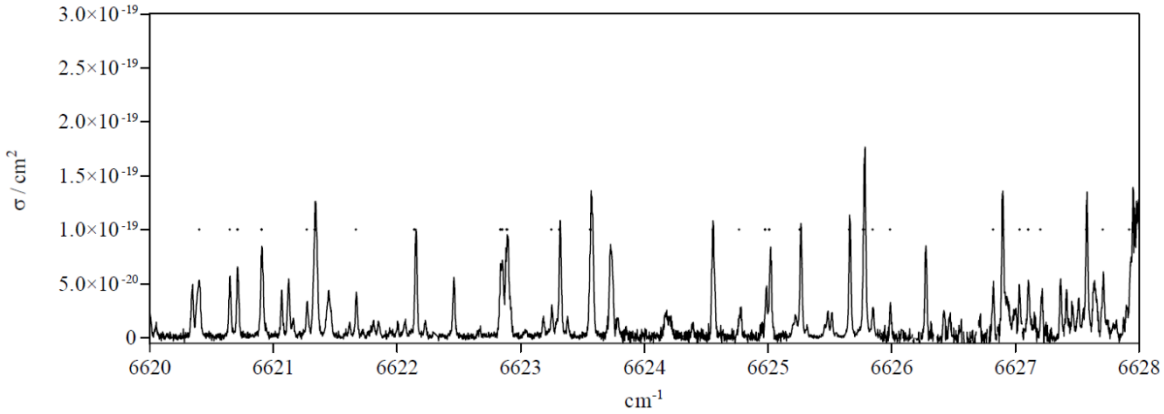

Figure 13. A section of HO_2 spectrum of $2\nu_1$ band [10]

5. Discussions

Ideal phase modulation will not generate any amplitude modulation. However, real phase modulation will always add residual amplitude modulation (RAM) to the modulated laser beam [13]. With a fast oscilloscope, we have recorded time traces of detector signal at 5GS/s after the phase modulated laser beam passed an empty reactor. Figure 14 is the FFT power spectrum of a recorded detector time trace. The spectrum show peaks below 20MHz, at 496MHz, 500MHz and 504MHz, and at other frequencies. Figure 15 is the DC – 40MHz section of the spectrum in Figure 14. Three major peaks can be seen: 4MHz, 8MHz, and 16MHz. This nonzero 8MHz peak with zero HO_2 absorption is caused by RAM in the phase modulation process, which changes the subtle balance among the phase modulation sidebands in Figure 10.

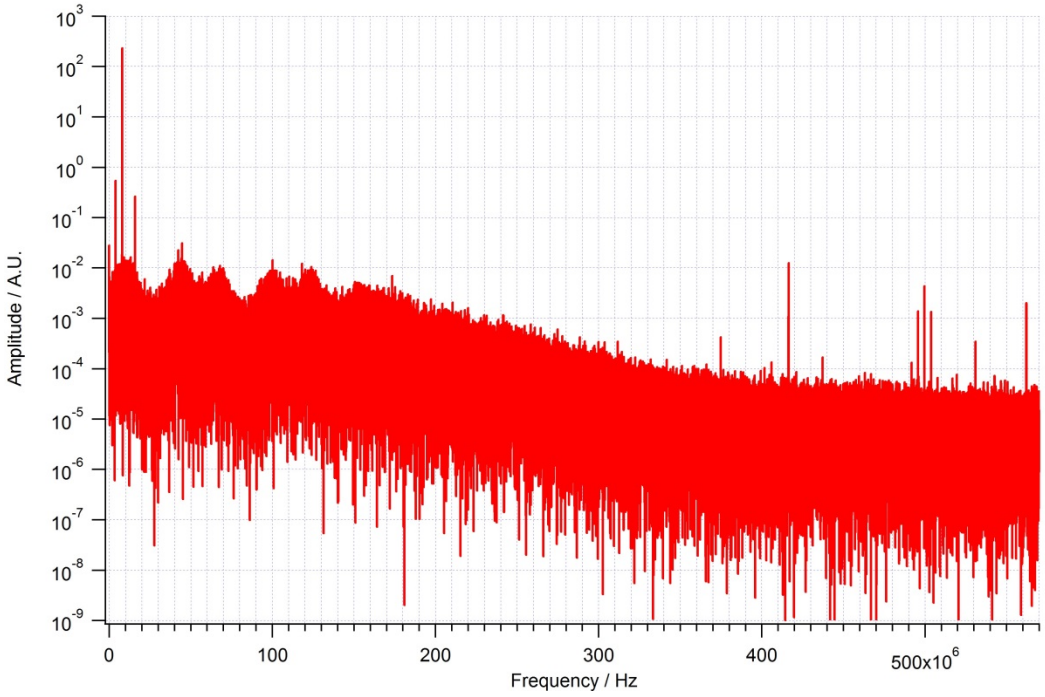

Figure 14. FFT power spectrum of a detector output time trace recorded at 5GS/s sample rate and AC coupling to remove the large DC component

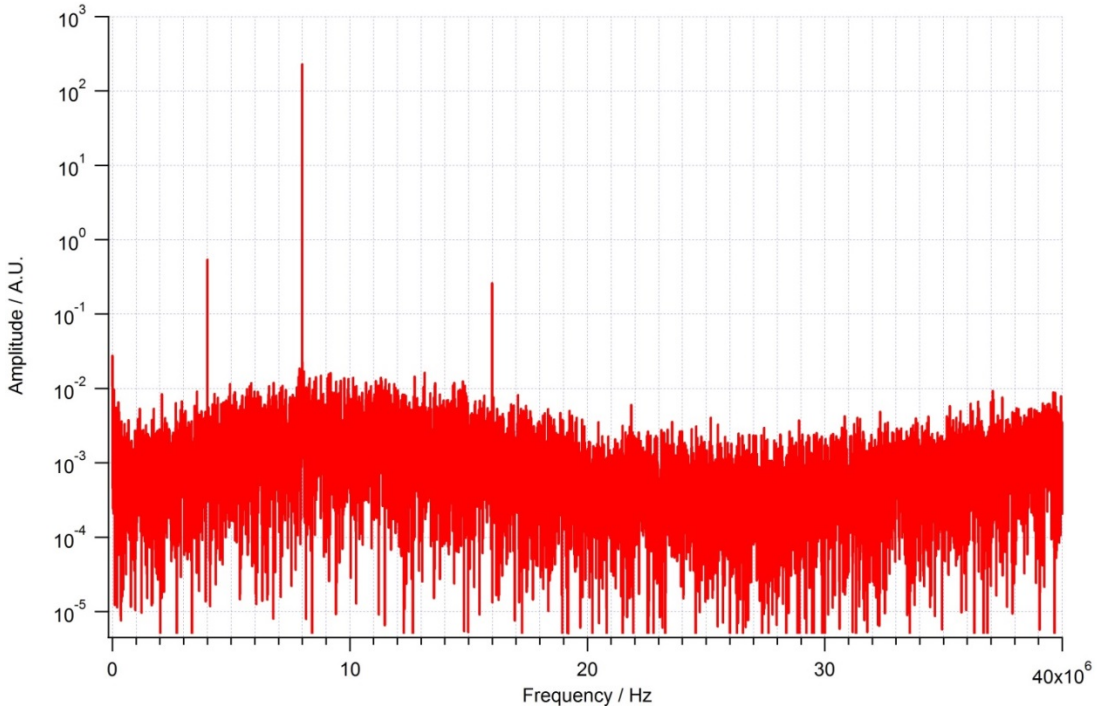

Figure 15. DC – 40MHz section of the FFT power spectrum in Figure 14, showing a strong peak at 8MHz

Cooper and Warren [13] have discussed the effect of RAM in TTFM method comprehensively. The change of sideband balance by RAM will cause a DC offset in the demodulated signal, but will not affect measurements of the time dependent HO_2 absorption. Figure 11 clearly shows this important point. Furthermore, the agreement between the data and the model prediction (red curve) in Figure 12 demonstrates that RAM effect and phase modulation are separable in modelling the data. In our experiment, the DC offset caused by RAM is compensated by applying a quiet DC voltage to the other input of the differential amplifier (SRS, SR560).

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