Frequency modulation spectroscopy at 1.3 μm using InGaAsP lasers: a prototype field instrument for atmospheric chemistry research

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Two-tone frequency modulation spectroscopy has been used in conjunction with InGaAsP lasers in the 1.3-μm region to monitor weak water vapor absorptions in a long path White cell. Detection electronics that reduce the effect of Johnson noise are described. The system was capable of detecting optical densities corresponding to $<1.7 \times 10^{-6}$ in a 1-Hz bandwidth. Factors limiting the difference between observed and shot noise limited performance for these types of laser and condition are discussed. *Key words:* Frequency modulation spectroscopy, tunable diode lasers.

I. Introduction

Progress in understanding the chemistry of the atmosphere has frequently come about as the result of the identification and accurate field measurement of trace gas phase components of air. The instrumentation requirements for such studies are stringent. Mixing ratios of important compounds of perhaps a few parts per 10^{12} by volume (PPTV) must be discerned against a complex background of often similar species, leading to the main instrumentation requirements of specificity and sensitivity. Also, because it is often desirable to measure from fast moving aircraft platforms, a further requirement of high measurement speed is necessary if adequate spatial resolution is to be achieved. Absorption spectroscopy using tunable diode lasers is a satisfactory method for such studies[1] and is inherently very specific because of the high spectral resolution of the lasers. The best reported detection limits using Pb-salt mid-IR lasers in field conditions are of the order of 20-pptv NO_2,[2,3] equivalent to an optical density of $\sim 10^{-5}$ in a 200-m multiple reflection (White) cell. The measurement bandwidth was ~0.1 Hz and a separately recorded background (zero gas) spectrum had to be subtracted from the ambient air spectra to reach these detection limits.[3]

Some of the noise sources in diode laser absorption spectroscopy are associated with the laser itself: for example, the so-called laser excess noise which has significant power at the wavelength modulation frequencies (a few kilohertz) used in most field instruments up to the present. Very high frequency modulation (FM) spectroscopy as a technique sensitive to small absorptions was first introduced in 1980 by Bjorklund.[4] The technique is based on the principle of modulating a laser carrier (ν_c) with a radio frequency (ν_m) at which the laser has intrinsically low amplitude (laser excess) noise (ν_m is typically of the order of hundreds of megahertz). The effect of this RF modulation[5] is to produce two sidebands at the optical frequencies ($\nu_c \pm \nu_m$). For a visible (dye) laser this may be achieved using an external electrooptic phase modulator (EOM). In the mid- and near-IR, however, Lenth[6,7] was the first to demonstrate that the FM effect could be accomplished more directly by modulating the injection current to a diode laser. The technique has attracted much attention, and Gehrtz and co-workers demonstrated the applicability of the technique to Pb-salt diodes, thus allowing coverage of virtually the entire mid-IR region.[8]

In the last few years, a further, more convenient, development of the method has been realized. Modulating a laser simultaneously at two rf frequencies [two-tone frequency modulation spectroscopy (TTFMS)] was first proposed by Janik *et al.*[9] Here, two closely spaced RF frequencies $\nu_m \pm \frac{1}{2}\Omega$ (with ν_m typically of the order of 500 MHz and Ω typically 1–5 MHz) modulate the laser carrier frequency, but detection is accomplished by monitoring the beat signal at frequency Ω. This technique retains the advantage associated with normal, or single-tone FMS with diode lasers, that is, the laser is modulated at frequencies where it has little $1/f$ amplitude fluctuation, but the method removes the requirement for extremely fast detectors, since the response speed of the detector need only be of the order of a few megahertz rather than hundreds of megahertz or even 1 GHz. Cooper and co-workers[10–14] introduced this technique for the mid-IR region, where it is particularly advantageous since the high bandwidth detectors available for the mid-IR usually have minute active areas, are extremely damage sensitive, and are often prohibitively expensive. Using Pb-salt laser diodes manufactured for the 5–10-μm mid-IR region, Cooper *et al.*[10–14] have shown that optical densities as small as $\sim 2 \times 10^{-7}$ may be detected in a 2.4-Hz bandwidth. These values mean that the minimum detectable optical signal approaches that limit set by the Poisson nature of the photon distribution, i.e. the so-called quantum or shot noise limit.

Because of these advances in measurement technology, it has become possible to work in spectral regions where the line strengths of various gaseous species might otherwise be considered too weak to be of use. We have chosen to investigate the possibility of using TTFMS in the near-IR with InGaAsP lasers, which emit near 1.3 μm. To date, TTFMS has been used with 1.3-μm lasers by Stanton and Silver[15] to measure lines in the HCl second overtone band, as well as by Carlisle and Cooper[16,17] in experiments to reduce the effects of RAM and etalon fringes by using a dual beam balanced homodyne detection technique. Although the absorption cross sections in the near-IR are typically smaller than those found in the mid-IR, there are distinct advantages to working in the near-IR. First, both the lasing and detecting diodes have been extensively used by the communications industry, so that much effort has been invested in developing reliable diodes of high power and high modulation bandwidth. Second, there are typically fewer absorptions in the near-IR than in the mid-IR or visible, making it easier to find an interference-free absorption line with which to work. Third, since the Doppler widths are larger near 1.3 μm than in the mid-IR, higher measurement pressures may be used without pressure broadening becoming important. This partially offsets the problem of weaker line strengths in the near-IR, since the higher operating pressures effectively allow more absorbing molecules into the optical path when making tropospheric measurements. Finally, in terms of practicality, both the 1.3-μm lasers and the detectors are inexpensive and may be operated at or near room temperature, thereby avoiding the need for cryogenic cooling. This is especially important for the construction of a rugged, practical, inexpensive instrument for field monitoring. We have constructed a prototype of such an instrument using a multiple pass White cell and report here the measured detection limits as well as the factors preventing quantum limited performance. In addition, we have made a direct comparison of the detection limits achievable using TTFMS with those obtainable using conventional lock-in wavelength modulation techniques.[18]

II. Experimental

Figure 1 displays a schematic diagram of our system. The two-tone technique has been discussed in sufficient detail by Cooper *et al.*[10–14] so we focus here on only the distinguishing properties of our electronics and those features pertinent to the 1.3-μm lasers. Because the Doppler broadening is large for small molecules at these wavelengths ($\delta\nu_D = 660$ MHz for H_2O at $T = 300$ K and 1.3 μm), it is necessary to use a commensurately large RF modulation frequency ν_m. Directional coupling voltage standing wave ratio (VSWR) experiments for our laser diode and housing package showed that the impedance had an oscillatory behavior, with reflectance minima spaced approximately every 75 MHz. One such minimum was located near 465 MHz, near the maximum frequency of our RF generator. The RF modulation frequencies finally used, therefore, were 461.00 ± 1.50 MHz, i.e., $\nu_m = 461$ MHz and $\frac{1}{2}\Omega = 1.50$ MHz, with the signal detected at 3.00 MHz.

The laser used was an SFH 4300 InGaAsP diode from Siemens Corp. having room temperature emission at 7852 cm^{-1}. The two-tone RF modulation was bandpass filtered and coupled via a T-piece to a DC offset and 200-Hz ramp current provided by a modified Spectra-Physics SP 5820 LCM current supply, and the composite current was fed via a high frequency coupling into the vacuum housing holding the diode. Contact inside the housing was accomplished with shielded 50-Ω BNC cable brought as close to the diode cathode lead as possible; a gold clip contact fixed the cathode lead. The length of exposed contact was thus only a few millimeters. This is important since this lead dominates the mount impedance at higher frequencies. The diode was mounted on a copper block which was temperature stabilized using a PT-100 sensing element and a feedback circuit to drive a Peltier heating/cooling device. The temperature could thus be controlled with an accuracy of better than 0.001 K in the 265–313 K range.

The emitted light was collected by a gold first surface $f/2$ off-axis paraboloid (OAP) and focused into the White cell using a second OAP. The 1.5-m base path White cell was a double corner cube type,[19] and the path length used in these experiments was 132 m. Light exiting the White cell was collected by a third OAP and focused onto a high speed 13 PD-100 photodiode detector from Telecom Corp. The 13 PD-100 is an InGaAs PIN photodiode having a photosensitive diameter of 100 μm, a calculated D^* value of 1.8×10^{11} cm Hz$^{1/2}$ W^{-1}, and a rise time of ≤ 1 ns. (Note that the D^* for 77K HgCdTe detectors operating in the mid-IR is typically of the order of 2.5×10^{10} cm Hz$^{1/2}$ W^{-1} because of the higher background radiation in the mid-IR.) All transmissive optical elements were positioned at an angle to minimize étalons, and the windows on the laser housing and the White cell were of the wedge type to avoid internal etalons.

The detector diode output was dropped across a 125-kΩ resistor and impedance matched to 50 Ω with a Harris HA-5127 ultralow noise operational amplifier. The RF signal was then 10-MHz low pass filtered and

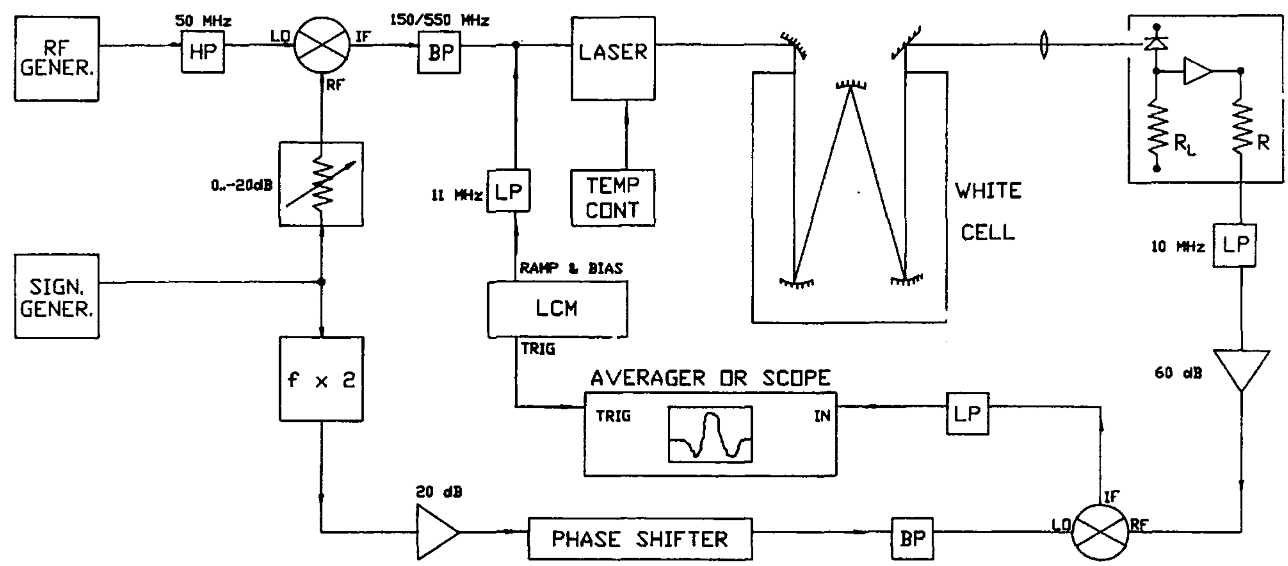

Fig. 1. Block diagram of the TTFMS spectrometer using InGaAsP lasers: *BP*, bandpass filter; *LP*, low pass filter; and *HP*, high pass filter.

amplified 60 dB by a SAT-500 broadband amplifier from SAT Electronics. The SAT-500 is nominally rated from 5 to 500 MHz but proved to have 60-dB linear amplification down to ~1.9 MHz. As expected, it introduced less noise than a series of three (low noise) 20-dB amplifiers. The amplified signal was demodulated with a Mini-Circuits ZFM-3 Level 7 Mixer, and care was taken to avoid saturation near the 1-dB compression point, which lay at approximately −5 dBm. The mixer IF output was low pass filtered at 1 kHz (3-dB point) and input to an oscilloscope for real time adjustment or to an EG&G 4203 signal averager for spectra collection. The displayed TTFMS spectra represent 1000 averages for a Δf_{eff} = 1-Hz effective bandwidth. We note that, except for the noise measurements, the reported spectra have not had backgrounds subtracted, but represent either real time data, or data obtained after a few seconds averaging.

To make as direct a comparison as possible between TTFMS and wavelength modulation spectroscopy (WMS), the same laser, detector, and optical arrangement were used with a wave function generator and a lock-in amplifier to record a conventional 2*f* WMS spectrum.[20] The modulation frequency was 17.5 kHz. The 1-ms minimum time constant on the lock-in amplifier allowed a maximum scan rate of 50 Hz. Thus, 160 scans were averaged so that the effective measurement bandwidth was 1 Hz, as in the FM experiment.

III. Results

The aim of this study was to investigate the detection limit for TTFMS using InGaAsP lasers and to compare this with the shot noise limit and with detection limits obtained using conventional modulation techniques. A further aim was to consider the design of a field spectrometer capable of measuring small concentrations of trace gases. The emphasis in our work, therefore, is not on extremely fast measurements (e.g., $\Delta f > 1$ kHz) but on low detection limits for a field instrument. As has been pointed out,[5,14] achieving quantum limited detection in a narrow bandwidth requires considerably more effort than for broad bandwidth measurements. Extrapolation from broad bandwidth measurements is in general not possible due to the differing Δf dependencies of the noise sources.[14]

To test the detection limit of our system, we chose to observe a water vapor absorption line strong enough to allow direct measurement of its optical density with ~1-Torr H_2O in the White cell, and then to reduce the pressure to produce signals near the detection limit. It has been empirically demonstrated[12] that the TTFMS signal is linear in gas concentration over several orders of magnitude. Figure 2(a) displays the two-tone signal obtained from a water vapor absorption near 7830 cm^{-1} with an optical density of 4.2×10^{-3}. The signal in Fig. 2(a) was obtained in a 1-Hz effective bandwidth by averaging a 5-ms scan 1000 times (1-kHz low pass). It should be pointed out that with such a strong signal, the spectrum may be easily observed and optimized in real time on an oscilloscope.

In Fig. 2(b), the signal corresponds to an optical density of 6.5×10^{-5} and has a peak-to-peak signal-to-noise ratio (SNR) of ~28. Because the signal in TTFMS is an rms value, while the noise is measured peak to peak,[14] the SNR value is divided by 3 (as a conservative estimate) to yield an rms signal-to-noise ratio of ~84. This corresponds to a detection limit of 7.7×10^{-7} for SNR unity. This noise figure is well above the detection electronics noise (*vide infra*). However, closer inspection of Fig. 2(b) reveals a shoulder to the right of the absorption line which we observed to be part of a reproducible background. This background could arise either from a long pitch étalon or from RAM (residual amplitude modulation), an effect which exists because laser diodes vary not only their wavelength but also their output power as the injection current is varied. However, we observed

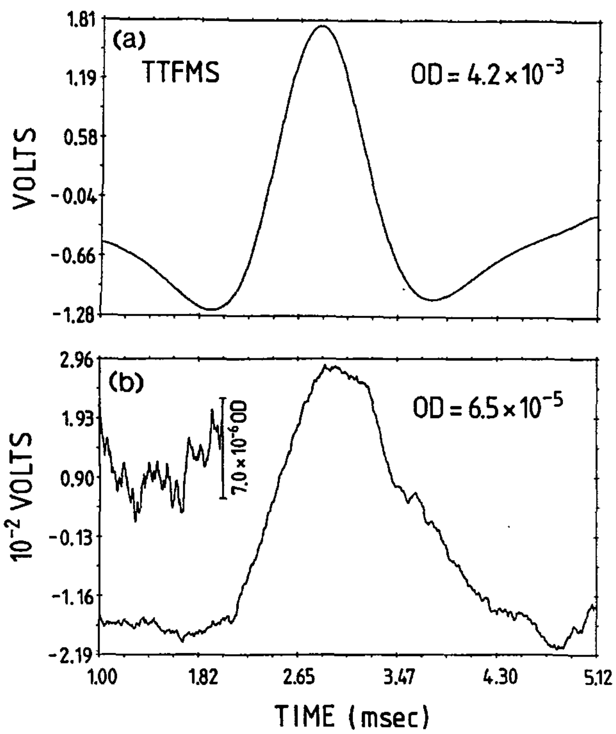

Fig. 2. (a) TTFMS signal from an H_2O absorption band near 7830 cm^{-1} having an optical density of 4.2×10^{-3}. (b) TTFMS signal from the same band with the pressure reduced to correspond to an optical density of 6.5×10^{-5}. The inset displays the difference between two successive spectra on the same abscissa; the vertical bar corresponds to an OD of 7×10^{-6}.

that, over a wider scan range, the background structure displayed no periodicity and the structure depended on the choice of laser temperature and current for constant output wavelength. We therefore conclude that the background in this case was related to RAM, not etalons.

The size of the main background feature in Fig. 2(b) is approximately half of that of the signal, i.e., $\sim 3 \times 10^{-5}$ OD. It is often the presence of such a background, and its reproducibility which governs the detection limit that may be achieved in practice.[21] To investigate the background reproducibility, a second spectrum was recorded directly after that shown in Fig. 2(b), and the two digitally subtracted. The difference spectrum in a region away from the signal peak is displayed in the inset. The region under the absorption feature was somewhat distorted due to a small change in the water pressure ($\sim$1.9 mTorr) between the two spectra. The difference spectrum has a peak-to-peak amplitude corresponding to an OD of $\sim 7.0 \times 10^{-6}$. This is equivalent to an rms noise in each individual spectrum ($\sim 3\sqrt{2}$ times smaller) of $\sim 1.6 \times 10^{-6}$-OD units. We believe this is then a realistic estimate of the detection limit for a 1-Hz bandwidth measurement made without long extrapolations from either large signals or broad measurement bandwidths and furthermore recorded with a White cell and the associated optics necessary for a field instrument capable of measuring low concentrations of trace gases in the atmosphere.

The $2f$ WMS spectrum was calibrated in the same way as for the TTFMS experiment, using the same H_2O absorption band, and the H_2O pressure reduced until a small signal remained. We averaged 160 scans using a 1-ms time constant ($\Delta f_{eff} = 1$ Hz) to obtain the signal in Fig. 3 which corresponds to an optical density of 9.0×10^{-4}. Note, however, the background (laser structure) present as a sloping baseline and that it has an amplitude comparable to the absorption, more than an order of magnitude larger than the background in the TTFMS spectra. A difference between two successive spectra was recorded as before, and the resulting noise/background instability is plotted in the inset. The peak-to-peak excursion of this difference spectrum is 4.5×10^{-5} OD, corresponding to an rms fluctuation of 1.1×10^{-5} OD in each spectrum, approximately an order of magnitude poorer than the TTFMS result.

IV. Discussion

Cooper and Warren[13] developed a detailed expression for the minimum detectable signal in TTFMS that takes into account not only the shot noise, but also the detector Johnson noise and the residual amplitude modulation (RAM), which has been characterized in terms of an amplitude modulation index M. Cooper and Warren determined that the maximum signals for TTFMS are obtained when the frequency modulation index β is ≈ 1.15. In our experiments the frequency

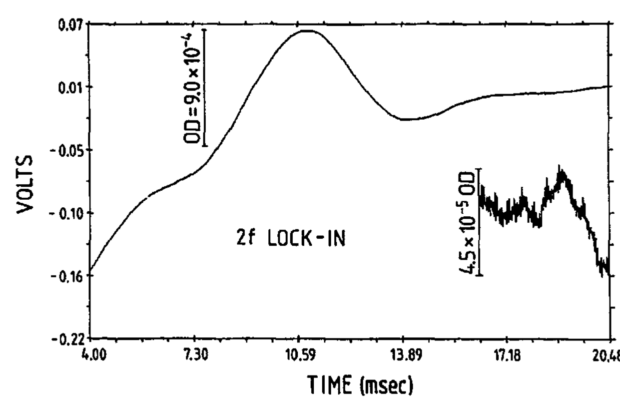

Fig. 3. A $2f$ lock-in signal from an H_2O absorption corresponding to an optical density of 9.0×10^{-4}. The inset displays the difference between two successive spectra on the same abscissa; the vertical bar corresponds to an OD of 4.5×10^{-5}.

modulation index β was estimated by observing the decrease in the line center intensity of an absorption band as the rf modulation was applied,[10] and an optimum TTFMS signal-to-noise ratio was found for $\beta \approx 0.8$. However, for $\beta = 1.15$,

$$\Delta\delta_{\min} \approx 2.1\left[\frac{1}{\mathrm{CNR_o}} + \frac{M^4\sigma^2}{\langle P_o\rangle^2}\right]^{1/2}, \tag{1}$$

where the carrier-to-noise ratio (CNR) is defined as

$$\mathrm{CNR_o} = \frac{2I_S^2}{I_{SN}^2\left(1+\frac{M^2}{2}\right)^2 + I_{JN}^2} = \frac{\left(\frac{\eta e}{h\nu}\right)^2 2\langle P_o\rangle^2}{2e\Delta f\left[\left(\frac{\eta e}{h\nu}\right)\langle P_o\rangle\left(1+\frac{M^2}{2}\right)^2 + \frac{2kT_N}{eR_{IP}}\right]}, \tag{2}$$

where $\langle P_o\rangle$ is the optical power, $\eta e/h\nu_c$ is the detector responsivity, and σ is the variance in laser power. The first term in the denominator of Eq. (2) is the shot noise arising from the interaction of the detecting element with the impinging photon flux. The second term in the denominator, $4kT_N\Delta f/R_{IP}$, represents the detector Johnson (thermal) noise[22] for a detection electronic input impedance R_{IP} and effective operating temperature T_N.[13] The photodiode also has a nonzero shunt resistance R_{shunt}, but this is small compared to R_{IP}.

If a measurement is to be shot noise limited, inspection of the two terms in the denominator of Eq. (2) suggests increasing the laser power $\langle P_o\rangle$ such that the shot noise dominates the Johnson noise. For example, if it were desired to make the shot noise equal to or larger than the thermal noise ($I_{SN}^2 = I_{JN}^2$), using a 50-Ω detection system and the present experimental conditions of $S_D = (\eta e/h\nu) = 0.8$ A/W, T = 298 K, and $M \approx 0$, a power of $\langle P_o\rangle \sim 1.3$ mW would be required at the detector. This is not practicable with diode lasers and multiple reflection cells. A second way of reducing the effect of the Johnson noise would be simply to increase R_{IP} such that the thermal noise term becomes negligible relative to the shot noise. Although this is not directly possible since most RF components have a fixed input impedance of 50 Ω, we achieved the same effect indirectly by first dropping the photocurrent across a high impedance load resistor $R_L = 125$ kΩ and using a low noise buffer to impedance match the resulting voltage to the $R = 50$-Ω impedance of our amplification system (see Fig. 1). A modified sensitivity analysis using Cooper's mean-square current noise is thus possible, but the signal and noise currents must now be considered *after* they have been impedance matched to 50 Ω, i.e., at the output of the box depicted in Fig. 1. For example, at the load resistor R_L there arises a Johnson noise voltage $V_{JN} = \sqrt{4kT\Delta f R_L}$; after this has been impedance matched to the system impedance R the square current Johnson noise is

$$I_{JN}^2 = \frac{V_{JN}^2}{R^2} = \frac{R_L}{R^2}(4kT\Delta f). \tag{3}$$

Similar considerations for the square current signal and square current shot noise,[23] after they have been impedance matched to the detection system impedance R, yield $I_S^2 = (R_L/R)^2 S_D^2\langle P_o\rangle^2$ and $I_{SN}^2 = [2e(\eta e/h\nu)\langle P_o\rangle\Delta f](R_L/R)^2$, respectively. On substituting these into Eq. (2) we have a modified $\mathrm{CNR_o}$ of

$$\mathrm{CNR_o} = \frac{\left[\frac{R_L}{R}\left(\frac{\eta e}{h\nu}\right)\right]^2 2\langle P_o\rangle^2}{2e\Delta f\left[\left(\frac{R_L}{R}\right)^2\left(\frac{\eta e}{h\nu}\right)\langle P_o\rangle\left(1+\frac{M^2}{2}\right)^2 + 2\frac{kT_N R_L}{eR^2}\right]}. \tag{4}$$

On first inspection Eq. (4) appears similar to Eq. (2), being multiplied in both numerator and denominator by $(R_L/R)^2$. However, in Eq. (2) the R_{IP} was fixed as the (usually 50-Ω) input impedance of the amplification electronics, whereas in the present case R_L denotes an actual load resistor whose value can be freely chosen. Herein lies the advantage of the buffer system: the signal and shot noise vary as R_L^2, while the Johnson (thermal) noise varies as R_L, and R_L can be made arbitrarily large. The expression (R_L/R) thus represents the factor by which the impedance buffer has decreased the required laser power such that $I_{SN} > I_{JN}$. With $R_L = 125$ kΩ, $R = 50$ Ω, and the other parameters as above, the power required such that $I_{SN}^2 = I_{JN}^2$ decreases from 1.3 mW to 0.51 μW, a more feasible value for diode lasers.

Thus far we have ignored the noise sources introduced by the (HA-5127) impedance buffer chip, but these must also be compared with the thermal and shot noises. Expressed in terms of currents, there are three purely electronic noise sources on the *input* side of the buffer: the current input noise I_{CN}, the voltage input noise V_{IN}/R_L, and the Johnson noise

$$\sqrt{\frac{4kT\Delta f}{R_L}},$$

where R_L is again the drop load resistor; that is,

$$\mathrm{Noise_{Elec}} = I_{CN}^2 + \frac{4kT\Delta f}{R_L} + \frac{V_{IN}^2}{R_L^2}. \tag{5}$$

As both Eqs. (4) and (5) suggest, R_L was chosen to be as large as possible, limited only by the consideration that the buffer not exceed its maximum output current. Using the $R_L = 125$-kΩ load resistor and a 1-Hz measurement bandwidth, we may then calculate the laser power at which the shot noise will be equal to the sum of the Johnson noise plus the buffer amplifier noises. Referring to the manufacturer's data for the HA-5127 low noise amplifier this yields the value $\langle P_o\rangle = 1.2$ μW. The laser power used in these experiments was $\langle P_o\rangle = 40$ μW.

To ensure that the detection system performed according to expectations, Fourier spectra of the noise sources were recorded. Figure 4, obtained using a Tektronix 2710 spectrum analyzer, shows successive contributions above the spectrum analyzer baseline floor (trace *A*) to the noise in our spectrometer. Trace *B* was acquired with the photodiode dark current dropped over $R_L = 125$ kΩ and buffered to 50 Ω; the spectrum therefore includes the Johnson noise, the

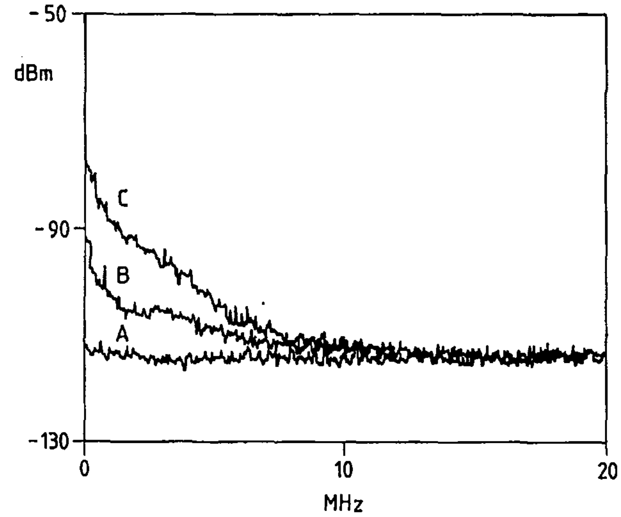

Fig. 4. Spectrum analyzer output of noise sources contributing to the TTFMS signal: *A*, spectrum analyzer baseline; *B*, with input from photodiode dropped over 125 kΩ and impedance matched to 50 Ω (i.e., detection system dark current); *C*, same as *B* but with 23 μW of laser power (no modulation) at the diode.

buffer noise, as well as the photodiode dark current and background noise, and has an ~$1/f$ or pink frequency spectrum. Trace *C* was acquired with 23 μW of unmodulated laser power focused on the diode, and the difference between traces *B* and *C* therefore represents the laser excess noise level above the detection electronic noise. It can be seen that at 3 MHz the laser excess noise is ~9 dB greater than the dark current, buffer noise, and Johnson noise. It would also appear that lower overall noise levels could be obtained by choosing an Ω closer to the buffer cutoff frequency of 10 MHz. Nevertheless, better SNRs were obtained with Ω = 3 MHz. We believe that the relatively narrow width of the VSWR (i.e., of the impedance match) minimum near 461 MHz is responsible for this effect. The VSWR minimum is not necessarily symmetrical about ν_m, and for higher Ω more asymmetry in the sideband pairs and therefore more RAM may be introduced. Better impedance matching should in principle allow use of a higher two-tone frequency Ω.

Substituting our experimental values of $\Delta f = 1$ Hz, $\eta = 0.76$, $R_L = 125$ kΩ, and $R = 50$ Ω into Eqs. (1) and (4) with $M \approx 0$ we find the theoretical detection limit for $\langle P_o \rangle = 40$ μW of $\Delta\delta = 1.50 \times 10^{-7}$. We compare our observed TTFMS detection limit (including both random noise and background instability) of 1.65×10^{-6} and see that it is 1 order of magnitude away from the theoretical limit, while the $2f$ WMS value of 1.1×10^{-5} is a further order of magnitude poorer. The best values achieved to date for bandwidths between 1 and 10 Hz are approximately a factor of 5 from the shot noise limit.[12,24] It should be noted here that measurements of the output mode structure of our laser using a monochromator showed that only about one third of the power lay in the mode giving rise to the absorption. This effectively raises the theoretical detection limit by ~$\sqrt{3}$ since the other modes contribute nothing to the signal but do contribute to the shot noise. However, we note that the thrust of this work is toward determining realistic detection limits for a field system, and multimode behavior in these lasers is common.

Our signal-to-noise ratio was empirically optimized and β was estimated to be ~0.8, so use of Eq. (2) or Eq. (4) is not strictly valid; however, the detection limit shows only a shallow minimum[11] in β, so only a small error is anticipated. Recently, other workers[24] (using GaAlAs lasers emitting near 800 nm) have also reported optimum SNR for β values less than unity and have pointed out that M is proportional to β for small β, and, in the presence of RAM, the noise includes a term dependent on M^4. Subsequent analysis has shown[25] that the minimum detectable signal Δδ as a function of modulation index β has an implicit dependence on the amplitude modulation index M. As a result, the $\beta = 1.1$ value that maximizes the TTFMS signal is not necessarily the value at which Δδ will be minimized. The minimum in Δδ (i.e., the best SNR) also depends on the ratio $r = M/\beta$, a ratio which is relatively constant for a given laser diode.

To achieve the detection limits cited here, considerable efforts were made to avoid étalons. As has been pointed out by Werle *et al.*,[26] the reduced optical power and the étalons associated with multiple reflection cells present a challenge to realizing low detection limits. Nevertheless, we have demonstrated that applied TTFMS techniques using a long path cell are an order of magnitude more sensitive both in terms of noise and background than $2f$ lock-in techniques. The TTFMS result is also 1–2 orders of magnitude better than values reported elsewhere for $2f$ with the InGaAsP lasers, although reflections from the cleaved end of the fiber pigtail may have limited the detection sensitivity in those experiments.[18]

V. Summary

At the present state of development, the detection level is within 1 order of magnitude of the theoretical shot noise limit. For both Pb-salt[12] and GaAlAs[24] laser diode systems, 1-Hz bandwidth detection limits using TTFMS that are approximately a factor of 5 above the theoretical quantum limit have been achieved. In both the Cooper *et al.*[10–14] and Wang *et al.*[24] work, the final obstacle to quantum limited detection has been attributed to laser excess noise. In the present studies, however, both laser excess noise and RAM make contributions to the noise at levels corresponding to optical densities of ~10^{-6}. Nevertheless, a detection limit of 1.65×10^{-6} has been achieved in a 1-Hz bandwidth. We estimate that detection limits for a field instrument based on InGaAsP lasers and a multireflection cell of the order of 1×10^{-6} for a 1-Hz bandwidth are possible, without having to purge the White cell to obtain a background spectrum. This further suggests the possibility of measuring in an open White cell at atmospheric pressures.

We have not investigated single-tone vs two-tone FMS. TTFMS, however, is easier to implement, more economical, and appears to have at least as sensitive detection limits as STFMS, and therefore is our method of choice for a field-oriented spectrometer. The present work has demonstrated an improvement in detection limit of 1–2 orders of magnitude over conventional techniques using InGaAsP lasers. This, combined with the lack of interference in the near-infrared, the relatively low cost of the components, and the ability to measure at or near atmospheric pressure, make a near-IR TTFMS spectrometer look very promising.

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