Appl. Phys. B 56, 118–122 (1993)

Applied Physics B Photophysics and Laser Chemistry

Frequency- and Wavelength-Modulation Spectroscopies: Comparison of Experimental Methods Using an AlGaAs Diode Laser

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Received 10 July 1992/Accepted 5 October 1992

Abstract. Low-wavelength modulation (1 kHz), high-wavelength modulation (100 MHz) and two-tone frequency modulation (390 ± 5 MHz) spectroscopies are systematically compared by measuring the minimum detectable absorption achieved using an AlGaAs diode laser tuned on a third-overtone methane transition at 886 nm. From the S/N behavior has been extrapolated a minimum relative absorption (1 Hz of bandwidth) of $4.5(1) \times 10^{-7}$ for the LMW, $9.7(3) \times 10^{-8}$ for the HWM and $6.4(2) \times 10^{-8}$ for the TTFM. In the LWM case the detection-limit value is represented by the laser amplitude $1/f$ excess noise, while for the high-frequency detection techniques this contribution is negligible with respect to other noise sources. These detection limits well agree with the calculated "quantum limited" values based on measured laser power, modulation index, noise figure of the electronic components, and other parameters of the apparatus.

PACS: 07.65.–b

In recent years the characteristics of semiconductor diode lasers in the visible nearinfrared have been improved essentially because of their commercial applications. However, due to their good spectral purity and low noise amplitude fluctuation, these lasers now represent attractive sources for inexpensive, room-temperature spectroscopic probing of a variety of molecular gases. Different applications are possible with this sources in the field of the high-resolution spectroscopy and high-sensitivity detection, as real time, non contact, pollution measurements. At present, GaAlAs lasers are available in the range 750–900 nm, InGaP lasers operate in the 630–690 nm range, while InGaAsP lasers are available in the range 1300–1500 nm. The frequency tuning of these lasers can be easily performed by means of temperature and injection current variations.

Semiconductor diode lasers offer a few advantages with respect to the lead salt diodes emitting in the infrared. First of all, semiconductor lasers operating at room temperature represent a more reliable system with respect to the cryogenic cooling system required for the Pb-salt diode lasers. Although molecular transitions in the nearinfrared are weaker than the fundamental ones in the infrared, remote sensing of atmospheric species could be more useful in the first region with respect to the latter one because of the reduced opacity of the atmosphere.

In view of high-sensitivity measurements, in the last years, different techniques have been developed. Wavelength-modulation spectroscopy was first used by Tang et al. [1–3] in conjunction with cw dye lasers as a sensitive method of derivative spectroscopy with a large tuning range. Wavelength modulation was extended to AlGaAs diode lasers by Pokrowsky et al. [4] as a sensitive technique for measuring weak absorptions and has also illustrated the potential applications of this method in reading frequency-domain optical memories.

In the wavelength-modulation technique an ac component is added to the injection current of the diode laser; the frequency of modulation must be smaller than the linewidth of interest, so that the absorption is probed simultaneously by a number of sidebands. If the modulation frequency is increased to exceed the linewidth, only one sideband will be absorbed at a time, giving rise to a characteristic heterodyne beat signal at the modulation frequency. If the modulation index is chosen so that only one higher sideband and one lower sideband have appreciable amplitude, we have the case of frequency-modulation spectroscopy.

This technique was first applied by Bjorklund [5] using a single-mode cw dye laser. Osterwalder and Rickett [6] first reported frequency-modulation of double heterostructure GaAlAs lasers at microwave frequencies (up to 2.25 GHz), and Lenth [7] used frequency and amplitude modulation at 2.6 GHz of a GaAlAs laser to study water-vapor absorption in the near-IR region (816–818 nm).

A new technique of FM spectroscopy at very high modulation frequencies was applied by Janik et al. [8]. In this technique, called two-tone FM, the laser emission is simultaneously modulated at two distinct but closely spaced frequencies (i.e., 490 and 510 MHz). Likewise here a heterodyne signal is obtained, but it occurs at the difference frequency between the two sidebands (i.e., 20 MHz) eliminating the need of high speed detectors and making possible large linewidth detections.

The application of dye lasers to FM spectroscopies [9] offers the advantage to reduce the laser amplitude noise by orders of magnitude by working at higher detection frequencies. For semiconductor lasers, considering their power spectrum [10], the amplitude noise difference between low- and high-detection frequencies is less pronounced. On the other hand, the sidebands can be produced directly from the source with semiconductor lasers making it possible to work at higher frequencies, which is useful for Doppler-broadened detections, compared to the electro-optic modulators used with dye lasers.

A first experimental work that compares wavelength- and frequency-modulations of AlGaAs diode lasers was performed by Wang et al. [11]. In this work they found a difference in sensitivity of two orders of magnitude between the high-wavelength and two-tone frequency-modulation. They obtained (in absorbance units): 2.8×10^{-4} for the wavelength-modulation at 1 kHz, 3.1×10^{-4} for the wavelength-modulation at 100 MHz and 2.4×10^{-6} for two-tone FM at 1 GHz $\pm$ 10 MHz. These results differ from the theoretical predictions of Silver [12] for lead salt diode detections, where he found that the sensitivity of the high wavelength-modulation should be of the same order of magnitude as the two-tone frequency-modulation technique. In the experimental work, performed by the same group [13] on lead salt diodes, they measured minimum detectable absorbances in the low-to-mid 10^{-7} range for the high-frequency modulation technique, while for the two-tone frequency-modulation the poorer result (1×10^{-6}) was justified by the excess detector noise and inefficient rf modulation of the laser.

The application of these high-frequency detection techniques with near-IR diode lasers offers two advantages over mid-IR lasers as laser powers and both the laser and matching detectors are well suited to higher modulation frequencies.

In a recent work [14] we have measured, using a stabilized GaAlAs diode laser, a minimum detectable absorption on a third-overtone transition of acetylene of 7 in 10^5 with a S/N of about 10 and a detection bandwidth of 100 Hz performed by a low-wavelength modulation technique. This result was consistent rather with the values obtained by Silver et al. [13] than with those of Wang et al. [11].

Considering all this, we decided to compare the sensitivities of the low-wavelength modulation (1 kHz), the high-wavelength modulation (100 MHz) and the two-tone frequency-modulation (390 $\pm$ 5 MHz) techniques by means of a GaAlAs diode laser by observing a test transition at a third overtone of methane at 886 nm. Our results show a sensitivity of the same order of magnitude in absorbance units for the HWHM and TTFM, while the value referred to the LWM is about one order of magnitude less with respect to the previous ones.

1 Experimental

We used a Mitsubishi laser (model ML 5101A), emitting 20 mW at 886 nm. Frequency tuning was achieved by changing the laser temperature (tuning of about 1 Å/K). The temperature was stabilized within 1/100 K by means of a miniaturized Joule-Thomson refrigerator in a copper block to which the diode laser was attached. In the laser beam path we avoided any lenses or orthogonal windows (using Brewster angle) to prevent etalon effects.

In Fig. 1 the scheme of the apparatus for the low-wavelength modulation technique is shown.

The laser beam from the beam splitter is utilized for frequency analysis. Sample pressure in the absorption cell (1.5 m long) was monitored by two capacitance manometers in the range 760 – 1 Torr and 10 – 10^{-3} Torr, respectively.

The ac signals were added to the laser bias current by means of a proper driver for frequency scanns. Very slow modulation (about 1/10 Hz) was used to scan the absorption line, while the 1 kHz modulation signal was used for phase sensitive detection. In this case we used a third-harmonic detection.

The detector signal was preamplified and demodulated by a lock-in amplifier whose output was sent to a digital scope and stored by a computer or plotter.

The second detection technique utilized was the high-wavelength modulation as shown in Fig. 2.

The idea of this technique is exactly the same as for the LWM; in this case the ac fast modulation signal (100 MHz) was added to the laser current by means of a bias-tee to avoid back-current to the sweeper from the laser power supply. The same sweeper signal (sweeper model HP 8341B) was dou-

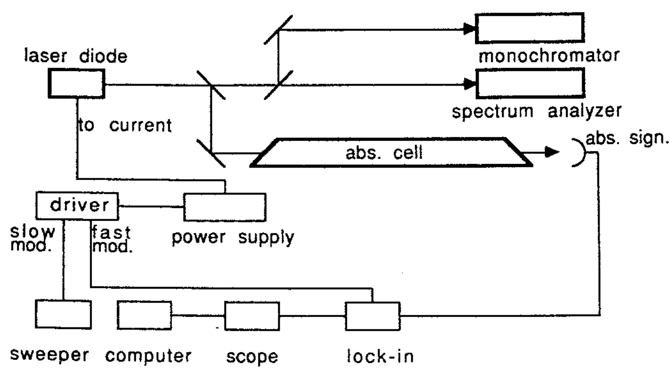

Fig. 1. Experimental setup for LWM

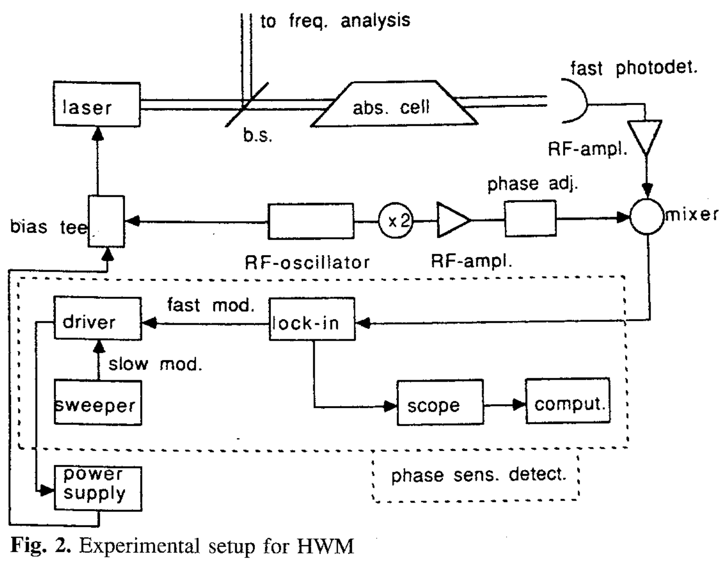

Fig. 2. Experimental setup for HWM

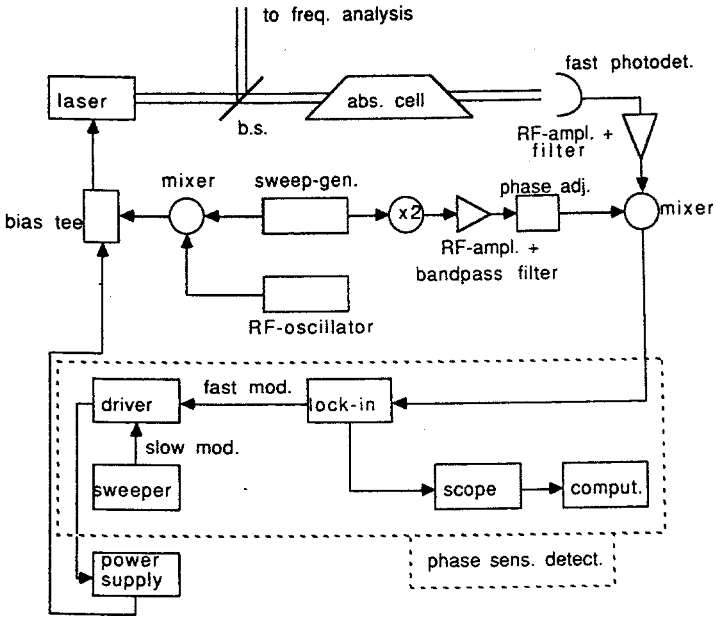

Fig. 3. Experimental setup for TTFM

bled (minicircuit component) for the second-harmonic detection, preamplified (Stanford SR 440), appropriately shifted, and sent to the local oscillator of the demodulation mixer. Laser light was detected by a fast photodetector (Telefunken BPW 28, efficiency $\mu = 50\%$, gain bandwidth higher than 20 GHz) whose signal was amplified (low-noise fast amplifier Miteq, model M/N-AU-4A-0150, amplification 60 db, noise figure 1 db) and sent to the demodulation mixer (minicircuit component). To obtain a narrowband detection we used a phase sensitive detection of the mixer signal by means of a lock-in amplifier whose reference modulation (1 kHz) was added by means of a driver to the slow scanning (1/10 Hz) and by means of the bias-tee to the fast modulation (100 MHz). The output of the lock-in amplifier was monitored by a digital scope and then stored by a computer or plotter. The experimental scheme of the two-tone frequency modulation is depicted in Fig. 3.

In this case two modulations were added by means of the bias-tee to the laser current. A sweeper signal at 390 MHz and another at 5.3 MHz were mixed to generate the couple of sidebands for the two-tone detection. The 5.3 MHz signal was also doubled, amplified, filtered (audio filter at 10.7 MHz, 300 kHz bandpass), appropriately shifted, and sent to the demodulation mixer. The photodetector signal was filtered (low-noise filter, insertion loss = 0.25 db, dc −50 MHz), amplified (Miteq low-noise amplifier as above), and sent to the demodulation mixer. Its output was phase sensitive detected as described previously and monitored by a digital scope.

2 Results and Discussion

As said before, we have chosen as test transition for the application of the different modulation techniques a component of a combination band of methane corresponding to a third overtone at 886 nm. This transition is the strongest among the combination bands in this wavelength region [15];

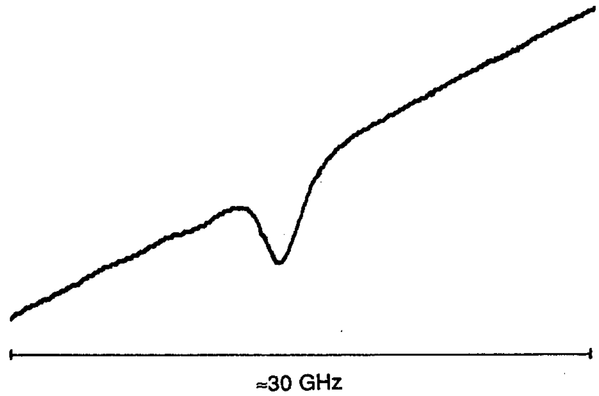

Fig. 4. Pure absorptioin signal on the third overtone of methane at 100 Torr (1.5 m pathlength)

furthermore, methane is of obvious interest because of environmental applications. Figure 4 shows a pure absorption signal corresponding to an absorbance of 3.6% at 100 Torr with a 1.5 m pathlength.

2.1 Low-Wavelength Modulation Technique

We have used a modulation frequency of 1 kHz and slow-frequency scanning of about 1/10 Hz.

Figure 5 shows a third-derivative signal at 100 mTorr corresponding to an absorption of 3.6×10^{-5} with a S/N of 10 (lock-in time constant = 10 ms).

As demonstrated by Werle et al. [16], it is possible to reduce the noise and detection bandwidth by means of an averaging procedure. The electronic noise deriving from the laser-amplitude fluctuations is inversely proportional to the square root of the number of averaged recordings n, if it is caused by random fluctuations of photons or charge carriers, and the detection bandwidth is reduced according to the relation

$$\Delta f_{\text{eff}} = \Delta f / n .$$

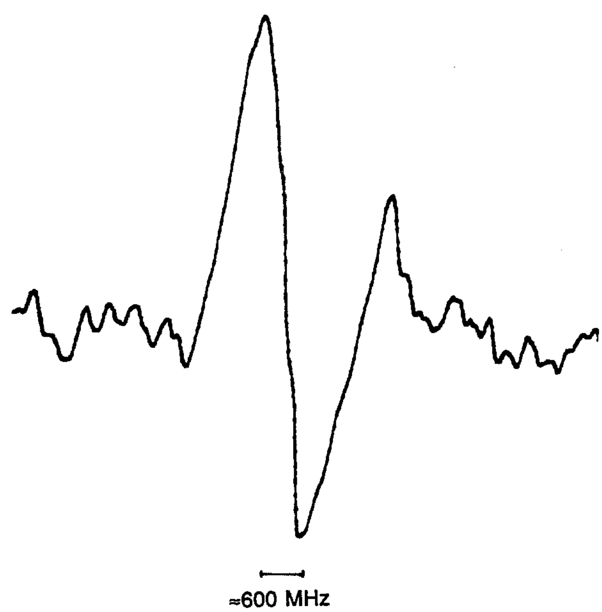

Fig. 5. Third-derivative signal with the LWM technique at 100 mTorr

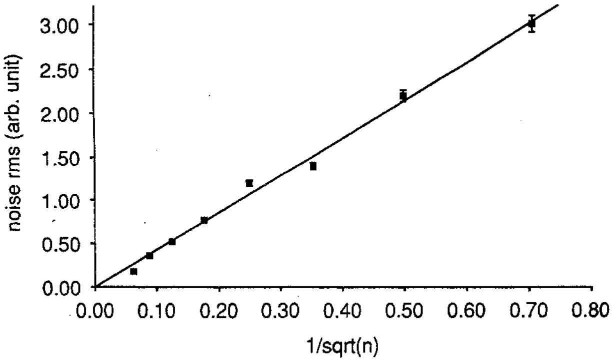

Fig. 6. rms noise vs number of averages

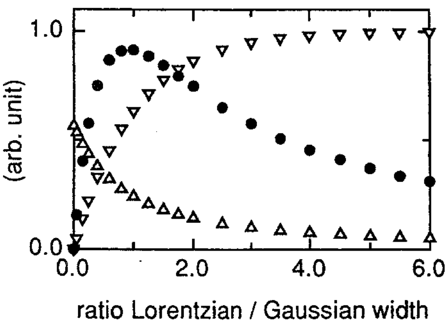

Fig. 7. (△) Voigt-peak contribution, (▽) nonlinear absorption, and (•) total absorption

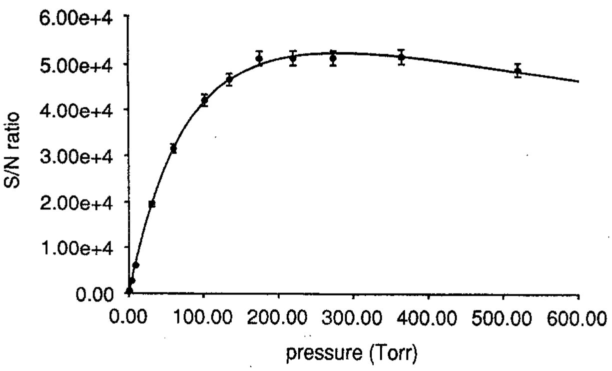

Fig. 8. S/N ratio vs pressure fitted by the theoretical absorption curve

We have applied this averaging procedure by means of a digital scope. Figure 6 reports the rms noise versus the $1/\sqrt{n}$.

Thus is possible, by an appropriate choice of the number of averages, to reduce the bandwidth to 1 Hz. This is of course not the only way to obtain 1 Hz bandwidth detection.

The purpose of this work is to measure the detection limit of the apparatus. For this reason we have studied the S/N behavior versus sample pressure to extract the limit of detection with $S/N = 1$ obtained with this technique. The S/N ratio, which is proportional to the absorbed signal, scales with pressure because of two main effects.

The first is related to the presence of a nonlinear absorption; it saturates at higher pressure and shows a depence on the molecular density N of the form $(1 - \mathrm{e}^{-bN})$, where the constant b is related to the absorption cross section and pathlength; the second effect depends on the variation of the Voigt profile of the absorbed line with pressure. In this case, in fact, increasing the pressure, the Lorentzian contribution increases, leading to the broadening of the line and lowering its peak value. This behavior, in the case of narrower laser line, means a decrease of absorption.

Considering now the product function of the two contributions we obtain a behavior of the absorption versus sample pressure as depicted in Fig. 7 (obtained for $b = 1$).

Figure 8 shows the experimental S/N values (1 Hz bandwidth detection) fitted with the function described above.

Calculating the pressure value for which $S/N = 1$ from the fitting curve and considering the absorbance of 3.6% at 100 Torr, the minimum absorbance extracted has a value of $4.5 \times 10^{-7} \pm 0.1$.

2.2 High-Wavelength Modulation Technique

The modulation frequency was 100 MHz (1 dbm). We used a second-harmonic detection and for the final phase-sensitive detection with the lock-in amplifier we used the same data as described in the previous technique. The S/N versus pressure fitting procedure (described in the previous section) in this case gives as minimum absorbance a value of $9.7 \times 10^{-8} \pm 0.3$.

2.3 Two-Tone Frequency Modulation

The two modulation frequencies used in this technique were 390 MHz and 5.35 MHz. The data for the final phase-sensitive detection with the lock-in amplifier were already discussed. The modulation powers utilized were chosen for the best performances giving a frequency-modulation index β of 1.2. In this case, from the S/N versus pressure fitting procedure, it was possible to measure a minimum detectable absorbance of $6.4 \times 10^{-8} \pm 0.2$.

Figure 9 presents a recording at 500 mTorr corresponding to an absorption of 1.8×10^{-4} (1.5 m pathlength, 1 Hz detection bandwidth) with a measured S/N ratio of a few thousands.

We considered at this point the behavior of the minimum detectable absorption versus the index of modulation. From a theoretical point of view its analytical expression is [17]:

$$\alpha_{\min} = \frac{\mathbf{A}}{2\sum_n \mathbf{J}_n^2 \mathbf{J}_{n-1}^2},$$

where $\alpha_{\min}$ is the minimum absorption detectable with an $SNR = 1$, J are the Bessel functions depending on the index β, A is a coefficient which depends on noise

Fig. 9. Derivative lineshape of a two-tone recording at 500 mTorr

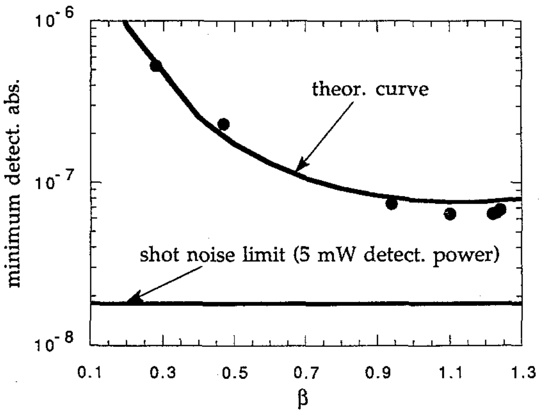

Fig. 10. Minimum detectable absorption vs frequency-modulation index

parameters of the apparatus and has the form:

$$A = \left(\frac{2e\Delta f \left[\left(\frac{e\eta}{h\nu_0}\right) \langle P_0 \rangle \left(1 + \frac{M^2}{2}\right) + \frac{2kT_{\text{eff}}}{eR_{\text{L}}} \right]}{\left(\frac{e\eta}{h\nu_0}\right)^2 2\langle P_0 \rangle^2} + \frac{\sigma_{P_0}^2 M^4}{\langle P_0 \rangle^2} \right)^{1/2},$$

where P_0 is the laser power, T_{eff} is the preamplifier effective noise temperature, R_{L} is the photodetector load impedance, η is the photodetector efficiency, Δf is the detection bandwidth, σ_{P_0} is the laser-power low-frequency excess noise, and M is the amplitude modulation index. The constant A contains sources of noise such as the photodetector-induced shot noise, detector and preamplifier thermal noise, and residual amplitude-modulation noise. Figure 10 reports the experimental points relative to the minimum detectable absorption versus the modulation-index values β.

The solid line represents the theoretical curve discussed above with a particular value of the constant A of $3.2(1) \times 10^{-8}$.

From the value of this constant, knowing the values of the parameters R_{L}, T_{eff}, η, P_0, Δf, being $50\,\Omega$, 30 K, 0.5, 5 mW, 1 Hz, respectively, it was possible to extract a value for the amplitude-modulation index equal to 0.02. In this calculation we have considered a value for the prameter $\sigma_{P_0}/\langle P_0 \rangle$ equal to 10^{-4} at 1 Hz detection bandwidth from pure absorption detection measurements. The contribution of the laser $1/f$ excess noise at this detection frequencies is negligible with respect to other factors, such as detector-induced shot noise, detector and preamplifier noise, and residual amplitude-modulation noise. The latter one is indeed the predominant part of the noise sources.

The single contributions contained in the square root of the constant A are, respectively, 8×10^{-17} for the detector-induced shot noise, 3×10^{-18} for the thermal noises, and 10^{-15} for the residual amplitude-modulation noise. Considering the absorption limit derived by the calculated shot noise (lower solid line in Fig. 10), the minimum detectable absorptions measured in the high-frequency detection techniques are about 6 db higher than this value.

3 Conclusions

In this work we have compared three different detection techniques by measuring, in each case, the sensitivity limit on third-overtone methane transition.

We have measured the minimum detectable absorption for the low-wavelength modulation (1 kHz), high-wavelength modulation (100 MHz) and two-tone frequency modulation (390 ± 5 MHz) techniques obtaining $4.5(1) \times 10^{-7}$, $9.7(3) \times 10^{-8}$, and $6.4(2) \times 10^{-8}$, respectively. In the first case the detection limit is determined by the laser amplitude $1/f$ excess noise, while in the other two cases this noise contribution is negligible with respect to other ones, such as detector-induced shot noise, thermal and RAM noises. The detection limits well agree with the calculated "quantum-limited" values based on measured laser power, modulation index, noise figure of the electronic components, and other parameters of the apparatus.

This trend in the different detection limits with different modulation techniques is consistent with the results obtained by Silver et al. [12, 13] on lead salt diodes and on their theoretical predictions for the near-IR detection while it differs from the Wang et al. measurements [11] on AlGaAs diode laser.

We can conclude that because of the semiconductor-lasers noise spectrum, the advantage of using high-frequency detections with respect to low-frequency detections is less pronounced compared to dye lasers; therefore, it is possible with this compact and inexpensive sources to perform very sensitive trace-gas–species detection for environmental purposes using a simple experimental configuration.

Acknowledgements. We would like to thank for the stimulating discussions Dr Leo. Hollberg, NIST Boulder, CO, Dr. Peter Kauranen, Univ. of Lund, Sweden, Dr. I. Longo, IFAM, Pisa, Italy, Dr. G. Tofani and Dr. M. Catarzi, Inst. of Astrophysics, Florence, Italy.

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