

DIODE LASER OVERTONE SPECTROSCOPY OF SOME POLLUTANTS

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ABSTRACT

High resolution spectroscopy of CH₄, NH₃, C₂H₂ near infrared overtone bands has been performed by using diode lasers. Direct, wavelength modulation and two-tone frequency modulation absorption techniques have been employed and their sensitivities compared.

1. INTRODUCTION

Observation of weak overtone absorption lines have been achieved in the past^{1,2} in the visible and near infrared (NIR) spectral regions by using very long optical path-lengths, but in a laboratory frame, as well as in pollution control stations, this condition is not easily fulfilled, so it is convenient to choose a sensitive technique, like diode laser frequency modulation (FM) spectroscopy³, which needs smaller dedicated volumes.

The use of diode laser (DL) for spectroscopy is suggested principally by its low cost and easy tuning, which is obtained by controlling the operating current and temperature.

DL spectroscopy can be performed also in the infrared (IR) and far infrared (FIR), where the fundamental vibrational modes give a higher absorption coefficient α , but it needs more expensive semiconductor lasers that work at low temperature. Moreover the IR and FIR spectroscopy needs expensive detectors operating at low temperature too.

Purpose of this work is to show the versatility of DL spectroscopy in a field where, at present, only the less selective solid state chemical sensors and more cumbersome and expensive laser systems (LIBS, LIDAR, DIAL) can work.

2. EXPERIMENTAL APPARATUS

Direct absorption (DA) technique is the easiest way to use the diode laser for spectroscopy. It works simply by scanning the diode laser emission wavelength around a gas resonance by varying the DL injection current. Unfortunately a change of the current involves also a variation of the emission power of the laser, giving a troublesome slope in the emitted intensity. This can be a big obstacle for extracting the signal from the background in case of very weak absorption.

Wavelength modulation (WM) technique uses a frequency modulation added to the sweep current that is much lower than the resonance linewidth. The detection of the in-phase signal is obtained by the aid of a lock-in amplifier. In this case the signal-to-noise ratio (S/N) is considerably higher as the system rejects many of the environmental interferences.

Two-tone frequency modulation (TTFM) technique⁴ uses a superposition of a high (1 GHz) and a low (10 MHz) frequency modulation of the laser and detects the low frequency beat signal. In such a way one can use slower and less expensive detectors, but still taking advantage of the high frequency to limit the $1/f$ noise. Absorbances as low as 10^{-7} – 10^{-8} have been detected⁵ by using TTFM spectroscopy.

In Fig. 1 the experimental apparatus is shown in the case of the WM technique application. In particular the Fabry-Perot serves to mark the frequency sweep of the laser, the mixer combines the sweep from an oscilloscope and the low frequency signal coming from the lock-in amplifier. The oscilloscope then displays the lock-in output. The "Ref. cell" contains the sampled gas at a constant pressure; this is used to get a reference absorption signal while varying the pressure in the measurement cell for broadening coefficient measurements.

The commercial cw DL is driven by the Melles Griot 06DLD201 current generator, and is thermally controlled less than 0.01 K by the Melles Griot 06DTC001 thermoelectric cooler. This control is very important since a variation of 1 K implies a laser emission wavelength drift of about 0.05 nm.

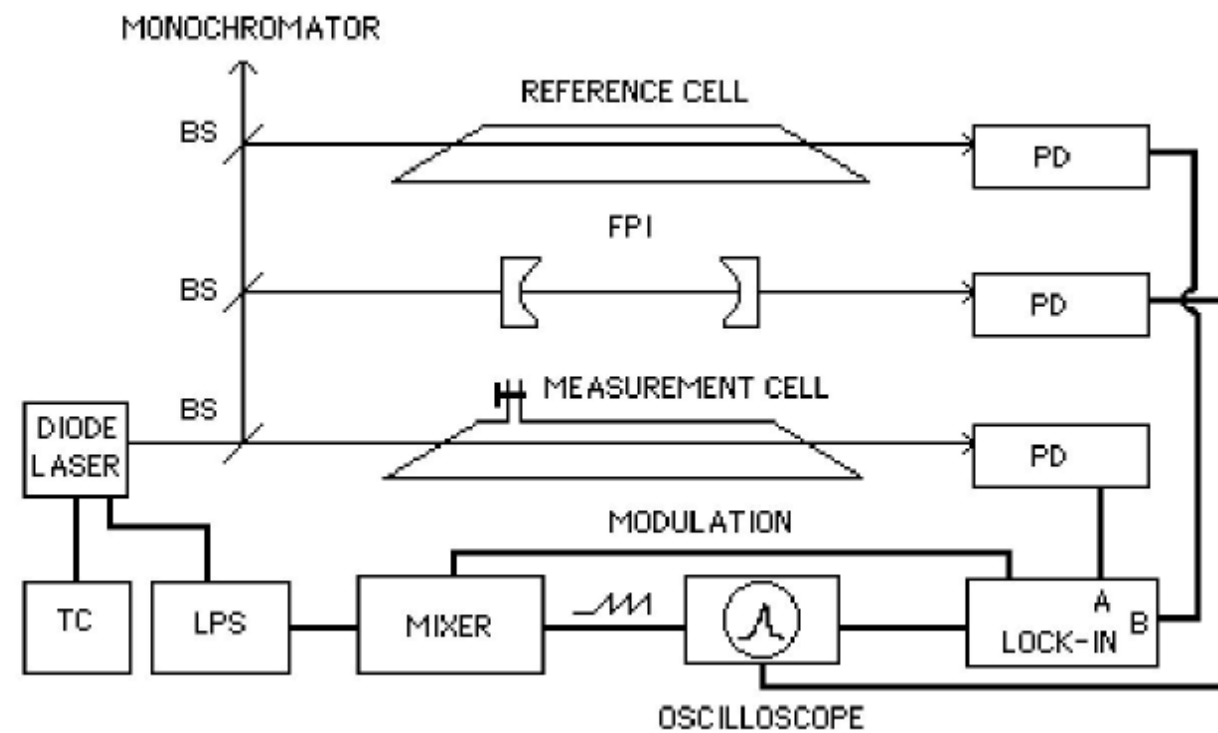


Fig.1. Outline of the experimental apparatus. PD: photo-diode; BS: beam splitter; FPI: Fabry-Perot interferometer; TC: temperature controller; LPS: laser power supply.

3. EXPERIMENTAL RESULTS

When using the WM spectroscopy and the "in-phase" detection technique of the modulated signal, in a first approximation the observed signal is the first derivative of the absorption feature.

Fig. 2 reports different measurements of the same ammonia absorption line. The WM spectroscopy, and the direct absorption results are shown in the graph. In the latter the slope is ought to the decreasing of the diode laser emission power while decreasing is injection current, as outlined previously.

More than 30 ammonia absorption lines belonging to the 790 nm band have been detected, among which the 789.305 nm and 789.317 nm have been observed for the first time.

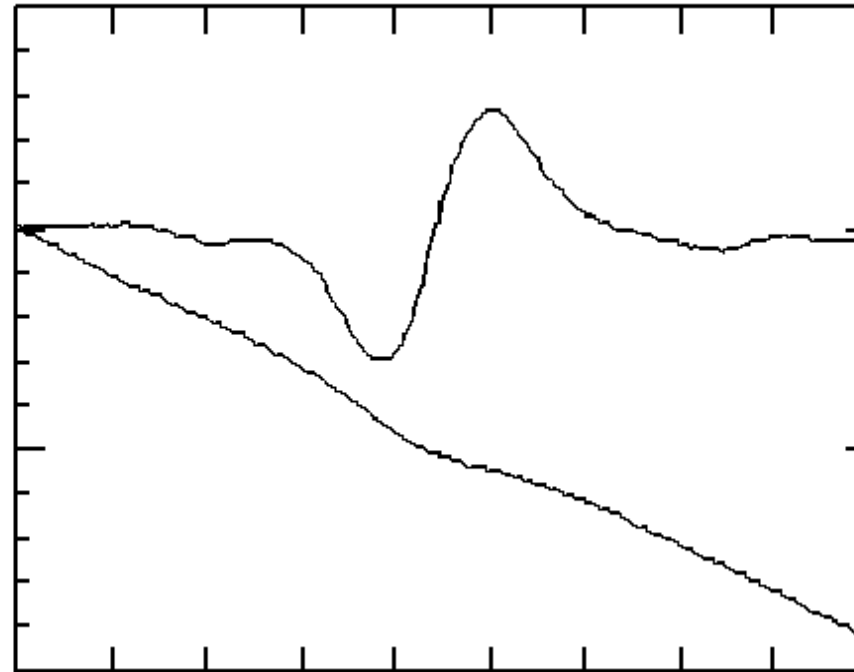


Fig. 2. Ammonia 791.690 nm absorption line observed at $p = 10$ Torr: lock-in output signal while using WM technique and the direct absorption curve (lower).

Line broadening from H_2 , He, air and self-broadening have been investigated for the strong ammonia line at 789.278 nm, and the collected full width at half the maximum (FWHM) relative broadening coefficients are:

$$\gamma_{H_2} = (8.7 \pm 0.3) \text{ MHz/Torr}, \quad \gamma_{He} = (4.0 \pm 0.2) \text{ MHz/Torr}, \quad \gamma_{air} = (10.8 \pm 0.3) \text{ MHz/Torr}, \quad \gamma_{self} = (24.4 \pm 0.3) \text{ MHz/Torr}.$$

The self-broadening coefficient has been obtained for the 792.851 nm line too:

$$\gamma_{self} = (25.4 \pm 0.1) \text{ MHz/Torr}.$$

Table I. List of the observed ammonia absorption lines. They belong to the combinations $4V_1(A_1)$, $2V_1+2V_3[A_1(+E)]$.

λ (nm)	ν' (cm ⁻¹)	Intensity ⁶	λ (nm)	ν' (cm ⁻¹)	Intensity	λ (nm)	ν' (cm ⁻¹)	Intensity
781.985	12784.45	medium	786.837	12705.61	strong	790.338	12649.33	strong
783.143	12765.55	medium	786.935	12704.04	weak	790.470	12647.23	weak
783.263	12763.59	medium	788.477	12679.19	strong	790.596	12645.21	strong
784.659	12740.88	strong	789.051	12669.96	strong	790.696	12643.61	strong
785.158	12732.78	medium	789.278	12666.32	strong	790.985	12638.99	strong
785.300	12730.48	medium	789.305	12665.89 ^a		791.089	12637.33	weak
785.384	12729.12	medium	789.317	12665.69 ^a		791.690	12627.73	very str.
785.468	12727.76	strong	789.356	12665.07	weak	791.902	12624.36	very str.
785.621	12725.29	medium	789.445	12663.65	strong	792.766	12610.59	medium
786.631	12708.95	strong	789.756	12658.65	strong	792.851	12609.24	strong
786.654	12708.57	strong	789.931	12655.86	strong	792.932	12607.96	medium
786.753	12706.98	weak	790.188	12651.74	medium	793.052	12606.04	medium

^a Lines observed for the first time, whose intensities are in the medium range.

For CH_4 we detected more than 30 lines in the 860 nm band, and three of them were observed for the first time⁷.

Table II. List of the observed **methane** absorption lines. The first six lines belong to the combination overtone $3\nu_1 + \nu_3 + (\nu_2$ or $\nu_4)$ band, the others to the $2\nu_1 + 2\nu_3$ band.

λ (nm)	ν' (cm ⁻¹)	Intensity ⁸	λ (nm)	ν' (cm ⁻¹)	Intensity	λ (nm)	ν' (cm ⁻¹)	Intensity
780.788	12804.06	0	859.418	11632.59	0	862.037	11597.25	2
781.179	12797.65	0	859.531	11631.06	0	862.497	11591.07	1
782.649	12773.61	0	859.748	11627.64	1	862.653	11588.97	0
783.041	12767.22	1	859.913	11625.89	1	862.959	11584.86	0
783.626	12757.68	0	860.726	11614.91	1	863.190	11581.76	3
783.767	12755.39	1	860.893	11612.66 ^b		863.494	11577.68	1
857.864	11653.64	2	860.923	11612.25 ^b		863.733	11574.48	4
858.327	11647.55	0	860.941	11612.01 ^b		864.188	11568.38	3
858.556	11644.27	0	860.964	11611.70	4	864.796	11560.26	2
858.819	11640.70	0	861.284	11607.39	1	865.210	11554.72	2
859.149	11636.23	0	861.641	11602.58	1	865.292	11553.63	2
859.298	11634.22	1	861.941	11598.90	3	866.361	11539.37	4

^b Lines observed and measured for the first time, having intensities comparable to that at 860.964 nm.

The S/N ratio of the measurements increased by another factor ten by using the TTFM technique, so that it allowed the extraction of weak signals from the background. An example of it is shown in Fig. 3, where near a strong acetylene resonance located at 787.298 nm (12698.18 cm⁻¹), one can observe a ~ 100 times less intense line at 787.307 nm (12698.03 cm⁻¹) not reported in literature. In direct absorption it was impossible to detect it.

Sixteen **acetylene** absorption lines belonging to the $\nu_1+3\nu_3$ overtone band have been observed by this technique. For the 786.791 nm (R15) line ($\alpha = 2.68 \times 10^{-5}$ cm⁻¹) the collisional broadening has been analysed:

$$\gamma_{\text{H}_2} = (6.6 \pm 0.1) \text{ MHz/Torr}, \quad \gamma_{\text{He}} = (3.7 \pm 0.2) \text{ MHz/Torr}, \quad \gamma_{\text{air}} = (5.8 \pm 0.1) \text{ MHz/Torr}, \quad \gamma_{\text{self}} = (10.98 \pm 0.05) \text{ MHz/Torr}.$$

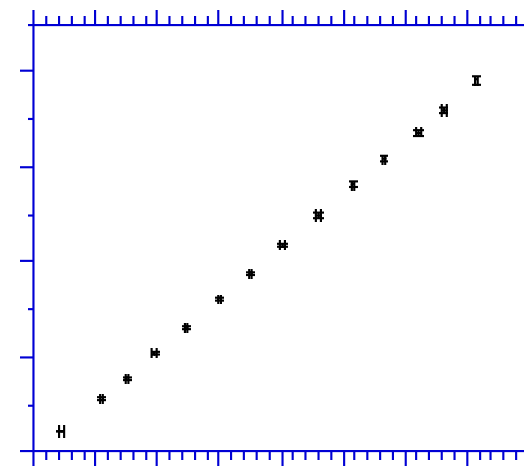
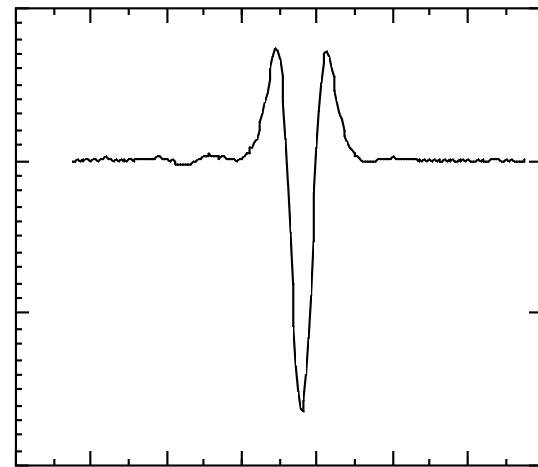


Fig. 3. Acetylene 787.298 nm absorption line observed by TTFM at $p = 50$ Torr and RT. 0.15 wavenumbers on the left of the strong resonance one can see a weaker one signed by the arrow.

Fig. 4. Acetylene lorentzian FWHM Vs pressure for the 786.791 nm absorption line at RT. It has been obtained from the Voigt fit of the resonance shape.

In Fig. 4 the result of C₂H₂ self-broadening measurement is shown for the R(15) line. In particular the lorentzian (collisional) FWHM is plotted as a function of the acetylene pressure in the measurement cell.

A sensitivity estimation has been done by standard DA technique in the 1 m long measurement cell filled with 50 Torr of methane. After three passes through the cell we collected an absorbance of 0.2%, with a S/N = 15 for the 860.964 nm line. From the Lambert-Beer equation $I_T = I_o \exp(-\alpha L)$, where I_T and I_o are the transmitted and incident intensities respectively, and L is the path-length: $\alpha \sim 10^{-5} \text{ cm}^{-1}$. By considering the gas density it means $k_V \sim 10^{-4} \text{ cm}^{-1} \text{ amagat}^{-1}$. By WM spectroscopy we observed the weaker 783.767 nm line, which has¹ $k_V \sim 10^{-5} \text{ cm}^{-1} \text{ amagat}^{-1}$. By TTFM spectroscopy also the less intense 780.788, 781.179, 782.649 nm lines have been easily discriminated from the background; they show $k_V \sim 10^{-6} \text{ cm}^{-1} \cdot \text{amagat}^{-1}$.

The minimum measured absorption coefficient for NH₃ has been $\alpha \sim 10^{-6} \text{ cm}^{-1}$, with a minimum detection limit of $2 \times 10^{15} \text{ molecules} \cdot \text{cm}^{-3}$, that is $6 \times 10^{-8} \text{ g} \cdot \text{cm}^{-3}$ of gas.

Tuning the DL in the C₂H₂ line at 786.791 nm, some mTorr of acetylene have been detected in the measurement cell, showing a sensitivity of 2.3×10^{-7} .

For many practical application, detection systems should work in open air at atmospheric pressure in noisy environments; in this case our apparatus detected **some ppm per meter** of NH₃ and C₂H₂ in air when working with TTFM and WM combined modes.

4. CONCLUSIONS

Diode laser absorption spectroscopy of NH₃, CH₄, C₂H₂ gases has been performed by using three different techniques with the goal of an enhancement of S/N. The results of their application have been shown from the viewpoint of resolution and sensitivity. All these results can be interpreted as a good encouragement to use this system for a fast and easy pollution control.

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5. REFERENCES

1. L.P. Giver, "Intensity Measurements of the CH₄ Bands in the Region 4350 Å to 10,600 Å", J. Quant. Spectros. Radiat. Transfer **19**, p. 311-22 (1978)
2. J.Y. Mandin, J.P. Chevillard, C. Camy-Peyret, J.M. Flaud, and J.W. Brault, "The High Resolution Spectrum of Water Vapor between 13200 and 16500 cm⁻¹", J. Mol. Spectr. **116**, p. 167190 (1986)
3. A. Lucchesini, L. Dell'Amico, I. Longo, C. Gabbanini, S. Gozzini, and L. Moi, "Diode Laser Spectroscopy: Water Vapour Detection in the Atmosphere", Il Nuovo Cimento D **13**, p. 677-685 (1991)
4. G.R. Janik, C.B. Carlisle, and T.F. Gallagher, "Two Tone Frequency-Modulation Spectroscopy", J. Opt. Soc. Am. B **3**, p. 1070-1074 (1986)
5. F.S. Pavone and M. Inguscio, "Frequency-Modulation and Wavelength-Modulation Spectroscopies: Comparison of Experimental Methods Using an AlGaAs Diode Laser", Appl. Phys. B **56**, p. 118-122 (1993)
6. S.H. Chao, "The Photographic Infrared Absorption Spectrum of Gaseous Ammonia", Phys. Rev. **50**, p. 27-37 (1933)
7. A. Lucchesini, I. Longo, C. Gabbanini, S. Gozzini, and L. Moi, "Diode Laser Spectroscopy of Methane Overtone Transitions", Appl. Opt. **32**, p. 5211-16 (1993)
8. H. Vedder und R. Mecke, "Das Rotationsschwingungsspectrum des Methans," Z. Phys. **86**, p. 137-156 (1933)