International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.4, pp 1957-1964, 2015

Using pulsed Optical Parametric Oscillator to detect the absorption lines of CO2 molecules

Sinan Al-Jalali, and Moustafa Sayem El-Daher*

Higher Institute for Laser Research and Applications, Damascus University, Damascus, Syria

Abstract: In this work we detected multi absorption lines of gas molecules simultaneously using a set of apparatuses consists of powerful optical parametric oscillator (OPO) Laser as light source, multipass cell with absorption length of 30 m, and monochromator with photomultiplier tube (PMT) as detector.
We choose CO2 molecule to investigate its absorption line in weak band because of two important reasons: its important influence on environment, and because CO2 molecule is the most investigated molecule so we can validate our results according to previous standard results.
Keywords: OPO lasers, CO2 gas, Herriott type multipass cell, Infrared Spectroscopy, Absorption Spectroscopy, Band width, Absorption lines.

1. Introduction

Carbon dioxide (CO2) is one of the most important gases in atmosphere, it is the second greenhouse gas after water vapour , and is responsible for global warming of the atmosphere [1],[2]as CO2 absorbs thermal radiation of infrared spectrum while water vapour doesn't. Because of human activities CO2 concentrations are continuously increasing in the ambient air and thus playing very important role in climate changes [3].

There are many spectroscopic studies for CO2 ranging from near infrared (NIR) to far infrared (FIR) regions, and those studies find applications majorly in space sciences, biological purposes[3], atmosphere and environmental monitoring[4][3]. The availability of NIR laboratory equipment (in general) makes this region very desirable for CO2 spectral studies, those studies include different spectroscopic techniques as tunable diode laser absorption spectroscopy (TDLAS)[5],cavity ring down spectroscopy (CRDS), intra-cavity laser absorption spectroscopy (ICLAS), Fourier transform infrared spectroscopy (FTIS)[6], and photo acoustic(PA) detection technique [7], [8]. Where various works were based on theoretical calculations of absorption lines. The most of those spectral studies depend on very narrow bandwidth source lasers(0.1 cm^{-1}as example) such as tunable diode lasers and continuous or pulsed Periodically Poled Lithium Niobate (PPLN) OPO laser, this approach can investigate only one of absorption lines of each molecules gases species.

Infrared spectrum divided into three main regions: Near region NIR (0.8-2.5μm), Mid region MIR (2.5-20μm) and Far infrared region FIR bigger than (20-1000μm)[9][6].

Gases molecular detection in FIR and MIR regions based on molecule's vibrational fundamental bands excitations. Where small amount of power few tens of micro watts are able to excite that bands[4], [10].

Detection in this area is very effective because of the very high absorption strength of laser photons, but Laser sources work in those region such as semiconductor laser (based on lead-salt PbS, PbSe and PbTe) generally require very low operation temperature as liquid nitrogen, more than this it's detectors should be cryogenically cooled, these matters are not easy to deal with, or sometimes can't be available [10].

These reasons make detection in FIR and NIR regions is not practical for example industrial applications seldom use this laser sources and these regions for gases detection [4], [10].

For more practical applications and easy treatment with apparatus and equipments inside or outside laboratories gases detection in NIR region is the most popular and uses. Where laser sources and its detectors work near normal temperature [7], [9], [6].

Gases molecular detection at NIR region based on molecular vibration overtone and combination-overtone bands excitation. But absorption strength of these bands is weaker than that of fundamental bands about 100 times in average [5], [7], [6].

To overcome this problem there are some available solutions like: using long absorption path (multipass cell[11]), increasing laser power (tens of milli-watts can excite that bands), wavelength modulation and using detectors such as silicon photodiode for wavelength shorter than 1μm, and indium-gallium-arsenide (InGaAs) photodiode up to 2.6μm[6].And way the former detection methods based on tunable diode lasers or PPLN OPO lasers [12].

Our work suggests direct absorption technique with a setup composed of the following parts: Herriott multipass cell (with absorption path of 30 m), monochromator with photomultiplier tube (PMT) as detector, and pulsed OPO source laser with broad bandwidth (5 cm^{-1}at the studied infrared range)to detect multi absorption lines simultaneously. The gas molecules inside Herriott cell absorb the incident photons of broad bandwidth laser beam at their specific lines of absorption spectrum, the output beam directed to high resolution Monochromator which implies a high sensitive PMT detector.

A post processing of the spectrum was done using Matlab. In total, we were able to bypass the limitation (which presented in many former methods) of being limited to investigate only one absorption line of spectrum, and we were able to investigate many absorption lines simultaneously with the discussed setup.

2. Experimental setup

We used the experimental setup depicted in figure (1).

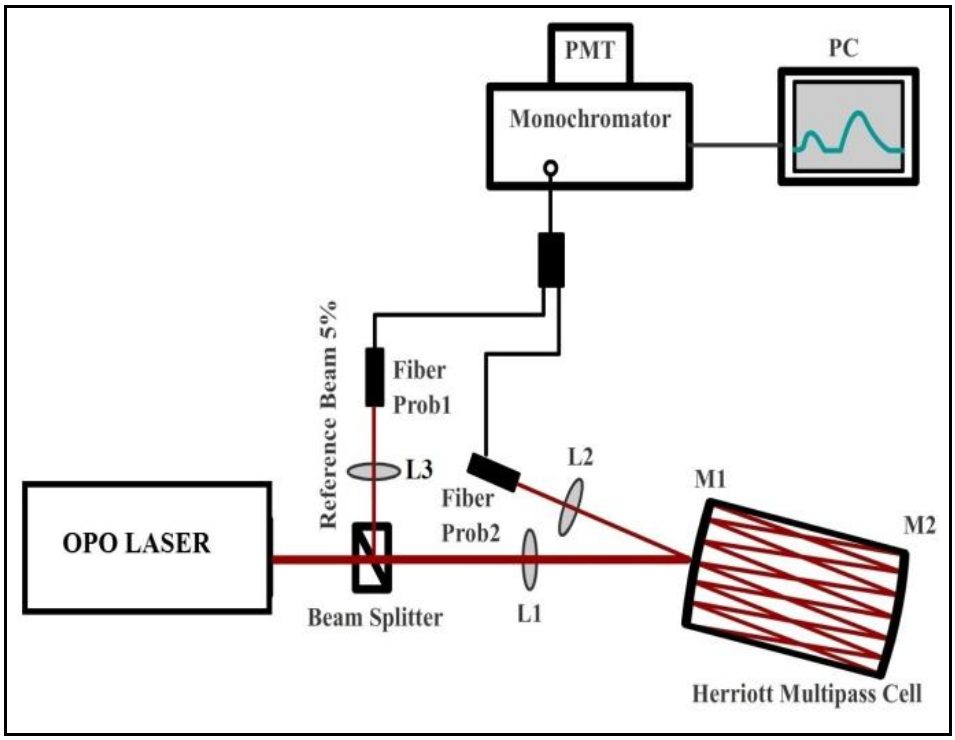

Figure (1): Experimental Setup and Optical Scheme

We used the experimental setup that is depicted in figure (1). The utilized instruments were:

1- *OPO laser from Ekspla* with the following specifications:
- Wavelength range: 210 – 2600 nm

- Bandwidth: Less than 5 cm^{-1}.
- Optical pulse repetition rate: 1- 20 Hz.
- Pulse duration: 6 nSec

2- Multipass cell by specifications of:
- Herriott design, configuration.
- Distance between mirrors: 40.4 cm.
- Total number of passes: 74 pass.
- Optical path length: 29.91 m.
- Operation pressure: 10^{-3} - 760 Torr.
- Mirror reflectivity: ($\lambda > 1$ μm) > 98.2 %.
- Inner volume: 900 Cm^3.

3- *Monochromator* with the following specifications:
- Designed at Horizontal Czerny-Turner configuration.
- Focal length: 75 cm.
- Grating: 400 graves by mm, with blaze at 1200 nm.
- Smallest Scan step: 0.0042 nm.

4- Photomultiplier PMT with the following specifications:
- Photocathode material: InP/InGaAs.
- Spectral range: 950 -1700 nm.
- Operating temperature: -60 C^o.
- Supply (DC) voltage: (-500 to -900).

5- Energy meter.

6- Anti-reflection (AR) coated lenses by focal length: L1=500mm, L2=L3=100 mm.

7- Beam splitter.

8- Pressure gauge. (0-1 bar).

9- Gas flow meter.

10- *Evacuation pump*.

3. Results and discussion

As we mentioned before, the major goal of this work is to detect multi CO2 gas absorption lines simul taneously at weak absorption band for most of atmospheric gases near 1432 nm.

We achieved that with the following preparation procedures:

1- Adjust monochromator Configuration as the following: the grating was [400;1200], scan range [1431 – 1434] nm smallest scan step 0.0042 nm.

2- Adjust OPO laser configuration as the following: Output wavelength 1432 nm, $\Delta K=5\ cm^{-1} \rightarrow \Delta\lambda \approx 1.5$ nm. Pulse energy: 5 mJ. So we scan round the 1432 nm as a central line [1431–1434] nm.

3- Coupling the laser beam and the multipass cell as the following:
- Focusing Laser beam to the center of the Herriott-type multi-pass cell by an AR coated lens (L1 = 500 mm).
- Focusing diffracted output beam onto a fiber Probe by a short focal AR coated lens (L2 = 100mm).
- Utilizing beam splitter to get reference beam (5% from main beam), and focusing it onto another fiber probe by a lens of (L3 = 100mm).

4- Evacuate multipass cell several times, then fill it by CO2 gas with concentration of 99.99%, pressure of 1 bar, ambient temperature about 20C^o.

After the preparation procedures, we can divide our work into sixmain steps.

First step:

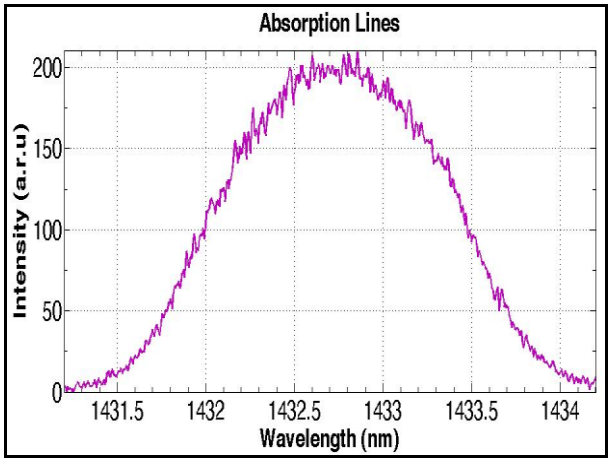

Figure (2) some spectrum results of experiments for first set up

- Adjust laser energy to E= 5 mJ.
- Keep gas pressure in multipass cell at constant value equal to 1 bar.
- Change pulse repetition rate within the range [10- 20] Hz.

We could not distinguish any absorption line. Figure (2) shows a sample of spectrum results of those experiments.

Second step:

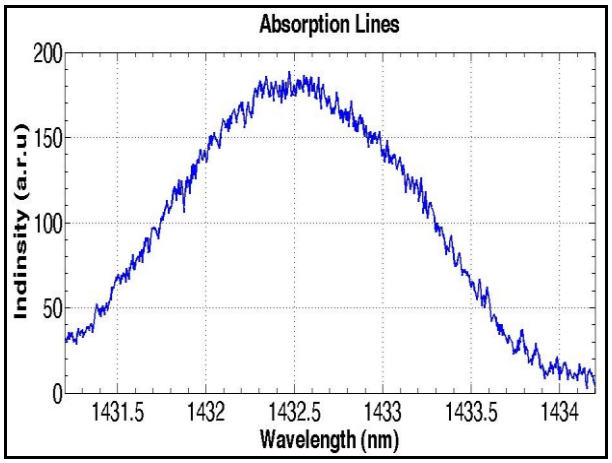

Figure (3) some spectrum results of experiments for second set up

- Keep laser energy at E= 5 mJ.
- Reduce gas pressure in multipass cell to 0.5 bar.
- Change pulse repetition rate within the range [10 - 20] Hz.

We could not distinguish any absorption line. Figure (3) shows a sample of spectrum results of those experiments.

Third step:

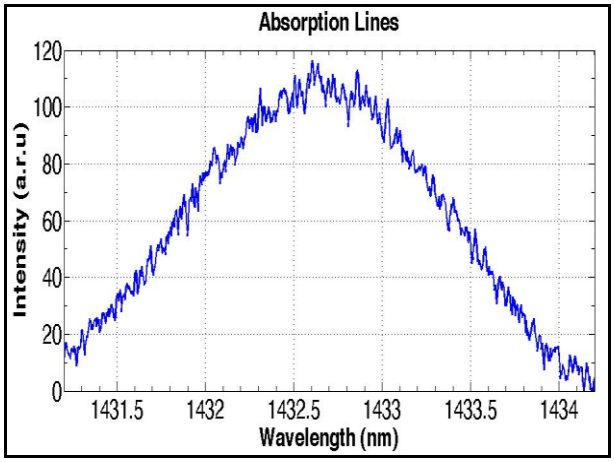

Figure (4) some spectrum results of experiments for third set up

- Reduce laser energy to E= 2.5 mJ.
- Keep gas pressure in multipass cell at the constant value equal 0.5 bar.
- Change pulse repetition rate within the range [10 - 20] Hz.

We could not distinguish any absorption line. Figure (4) shows a sample of spectrum results of those experiments.

Fourth step:

- Keep laser energy E= 1mJ.
- Keep gas pressure in multipass cell at constant value equal to 0.5 bar.
- Adjust pulse repetition rate at10 Hz.

We could distinguish some wide absorption lines. Figure (5) and table (1) show spectrum results of this experiment.

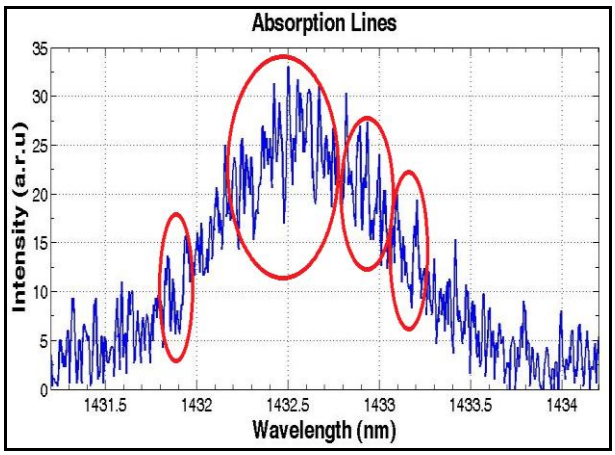

Figure (5) some spectrum results of experiments for fourth set up

Table (1): Experimental result of fourth step.

Max Wavelength:1432.5024 nm Intensity: 33 a.r.u				
Absorption Lines		$\frac{S_{min}}{S_{max}}$ %	**Hitran**	**Difference**
nm	**Cm^{-1}**		**Cm^{-1}**	**Cm^{-1}**
1433.1737	6977.521287	25.254	6977.52344	0.002152804
1432.6494	6980.074818	57.576	6979.943523	-

				0.131295026
1432.4774	6980.912927	51.512	6980.65933	-0.253597492
1432.3103	6981.727353	46.467	6981.713509	-0.013844354
1432.2303	6982.117331	43.436	6982.067847	-0.04948427
1431.8821	6983.815218	17.176	6983.896231	0.081013253

Where S_{max}, S_{min} are intensities of peak wavelength and absorption line respectively.

Fifth step:

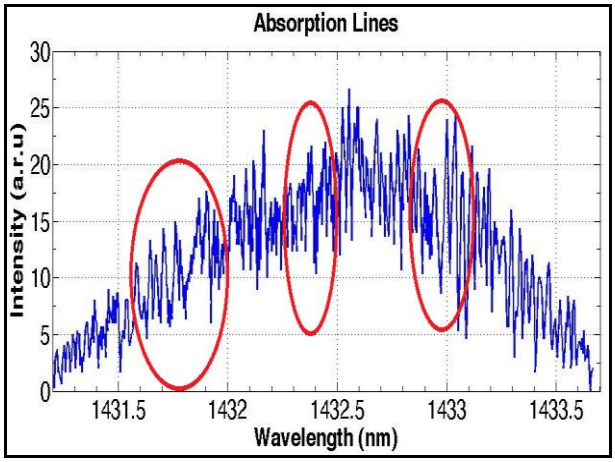

Figure (6) some spectrum results of experiments for fifth set up

- Keep laser energy E= 1 mJ.
- Keep gas pressure in multipass cell at the constant value equal 1 bar.
- Adjust pulse repetition rate at 2 Hz.

We could distinguish some wide absorption lines, figure (6) and table (2) show spectrum results of this experiment.

Table (2): Experimental result of fourth step.

Max Wavelength: 1432.5534 nm Intensity: 26.666 a.r.u				
Absorption Lines		$\frac{S_{min}}{S_{max}}$ %	**Hitran**	**Difference**
nm	**Cm^{-1}**		**Cm^{-1}**	**Cm^{-1}**
1433.0896	6977.930759	17.498	6977.52344	-0.40731883
1432.9726	6978.500496	32.498	6978.65836	0.157863898
1432.4023	6981.278933	38.742	6981.33155	0.052617398
1432.0712	6982.893029	39.998	6982.693142	-0.199887341
1431.8071	6984.181039	23.746	6983.93036	-0.250679471
1431.736	6984.527874	21.248	6984.47918	-0.048693854
1431.631	6985.04014	17.498	6985.04655	0.006410467

Sixth step:

- Keep gas pressure in multipass cell at constant value equal to 0.5 bar.
- Keep laser energy E= 1 mJ.

- Adjust pulse repetition rate at 2Hz.

We could clearly note some absorption lines. Figures (7), (8), and table (3) show spectrum results of this experiment.

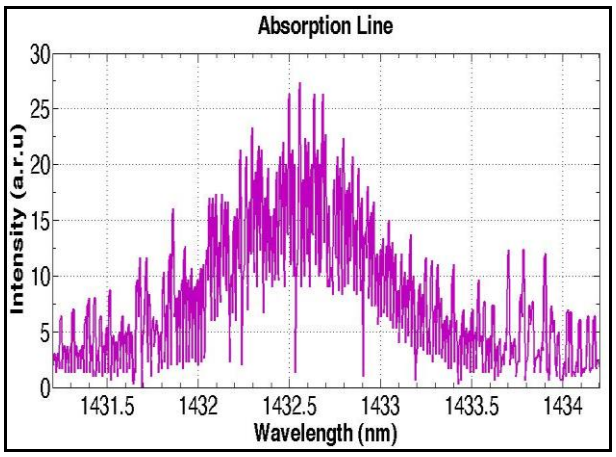

Figure (7): Absorption Lines

Table (3): Experimental result of fifth stage

Max Wavelength: 1432.5574 nm Intensity: 27.334 a.r.u				
Absorption Lines		$\frac{S_{min}}{S_{max}}$ %	**Hitran**	**Difference**
nm	**Cm^{-1}**		**Cm^{-1}**	**Cm^{-1}**
1433.1817	6977.482339	2.444	6977.52344	0.041101229
1432.9046	6978.831668	3.658	6978.77044	-0.061228207
1432.5324	6980.644905	4.88	6980.65933	0.014424517
1432.2383	6982.078332	7.317	6982.067847	-0.010484518
1432.1712	6982.405455	8.539	6982.4647	0.059244563
1431.69	6984.752286	0	6984.69939	-0.05289576

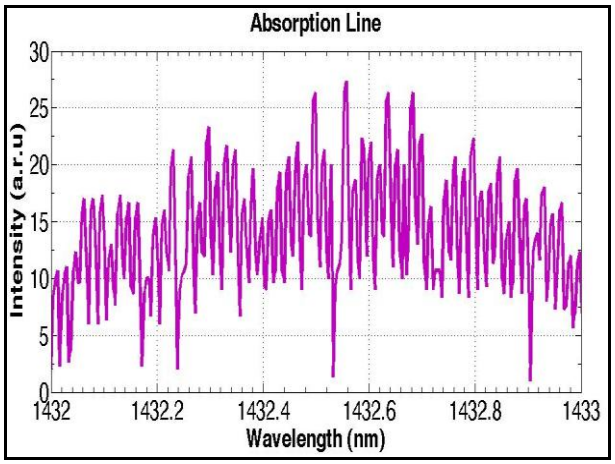

Figure (8): Absorption Lines Shape

According to the former result we could see clearly the absence of absorption lines at high values of laser parameter (energy and pulse repetition rate)in both cases of pressure values (0.5 and 1 bar), steps (1,2,3). This is due to saturation of absorption lines.

But at relatively low values of laser parameters (energy and pulse repetition rate), steps (4,5)we could distinguish some wide absorption lines which has been broadening due to thermal and pressure broadening. Where the sequence powerful pulses will rise gas temperature so gas pressure inside the cell, which yield that broadening.

At good convolution of laser parameters and gas pressure (as in sixth step) we could clearly note multi absorption lines simultaneously as we planned.

We compare detected lines with HITRAN database. They showed good coincidence with a shift due to thermal effect on absorption lines.

The important role of pulse repetition rate is clearly noted, which control the thermal effects on gases molecules inside the cell. These effects influence absorption lines as shift, broadening, and even the absence of these lines.

Conclusions

In this work we had detected multi absorption lines of CO2 gas around 1432 nm simultaneously. At the same time we specified suitable parameters of OPO laser and gas pressure to do. Where we implemented sensitive PMT attached to high resolution monochromator and pulsed OPO laser.

The detected absorption lines were compared to HITRAN database where they showed good agreement.

This work proves benefits of utilizing powerful broadband width wavelength to detect multi gases absorption lines simultaneously and thus it can be applied to multiple applications.

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