

## Advanced photo-acoustic gas analyzer

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### Abstract

The gas analyzer based on optical parametric oscillators and laser photoacoustic spectroscopy is demonstrated in this paper. Optical parametric oscillator was pumped by compact nanosecond 1.053  $\mu\text{m}$  Nd:YLF laser.

**Key words:** laser photo-acoustic spectroscopy, optical parametric oscillator, trace gas detection,

### Introduction

At present analysis of the gas composition of atmosphere and human's breath is an actual direction in scientific researches. Registration and determination of the concentrations of various gases in the atmosphere plays an important role in biology and medical diagnostic. For last several years method of laser photo-acoustic spectroscopy (LPAS) has become an important method for monitoring of gaseous chemical compounds in atmosphere because of its simplicity of practical realization, safety, cost-effectiveness and extremely high sensitivity (ppb-ppt level) [1-2].

LPAS allows making measurements in real time with a minimal volume of gas sample. LPAS detectors do not require using of expensive high-reflectivity mirrors as opposed to cavity ring-down spectroscopy (CRDS) method. Capabilities of LPAS sensors generally increase with increasing laser energy as far as acoustic signal are proportional to optical power absorbed in detector. A major impact on the field of trace gas detection can be expected from new widely tunable solid-state laser systems working in the mid-IR spectral region. In this respect the recent realization and further improvement of optical parametric oscillators (OPOs) and quantum cascade lasers (QCL) could be an important breakthrough in the practical application of laser photo-acoustic spectroscopy (LPAS) in trace gas monitoring [3-7]. Optical parametric oscillation (OPO) is today one of the most widespread ways to produce tunable coherent radiation.

In this presentation we will show gas analyzer based on LPAS and OPO, which were designed by Special technologies, Ltd., in collaboration with V.E. Zuev Institute of Atmospheric Optics Russian Academy of Sciences, Siberian Branch.

### LPAS gas analyzer with a wide tunable optical parametric oscillator

Optical parametric oscillator (OPO) possesses broad wavelength coverage therefore we research new devices based on OPO for range extension of LPAS sensors. This technique will allow covering wide spectral range from 2.4 to 11  $\mu\text{m}$  as compared with other laser sources and, particularly, quantum cascade lasers (QCL).

The tuning range of nanosecond OPO based on PPLN crystal pumped with Nd:YLF laser is 2.4-3.9  $\mu\text{m}$  (idler wave). Expansion of the spectral range up to 11  $\mu\text{m}$  is possible by using nonlinear chalcogenide bulk crystal: LiGaSe<sub>2</sub>, LiInSe<sub>2</sub>, AgGaS<sub>2</sub>, and AgGaSe<sub>2</sub> [8-11].

We developed and researched experimental OPO setup combined with photoacoustic detector. The pump laser was Q-switched Nd:YLF laser operating at 1.053  $\mu\text{m}$  and providing up to 1.5 mJ (by Laser Compact Ltd.).

The experimental setup consists of pump laser and two OPO: PPLN OPO (2.4-4.3  $\mu\text{m}$ ) and AGS OPO with the same pumping. Photo-acoustic detector is used for registration of absorption spectra of tested gas samples.

The monolithic PPLN OPO cavity consist of two high-reflectivity mirrors at the signal wave. The output mirror is transparent at the pump and idler wavelengths; the input mirror has a high transmission coefficient at the pump wavelength. The step motor moves crystal in relation to pumping beam.

From Fig. 1 one can also see that the idler beam tunability of 2–4.3  $\mu\text{m}$  was achieved with PPLN crystal (the signal wavelength was tunable between 1.394 and 2.224  $\mu\text{m}$ , respectively).

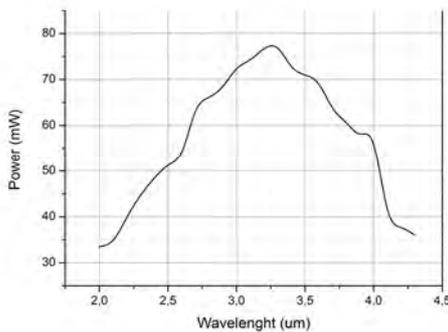


Fig. 1. PPLN OPO tuning curve (idler wave).

Use of chalcogenide crystals as a nonlinear medium for OPO allows the range from 2  $\mu\text{m}$  to 18  $\mu\text{m}$  to be overlapped. The advantages of these crystals are following: their relatively high thermal conductivity, large bandgap and, as a result, low two-photon absorption and low group velocities mismatching [9]. Optical parametric oscillator based on chalcogenide crystals allows covering wide spectral range from 2 to 11  $\mu\text{m}$ .

The advantages of OPO combined with photo-acoustic detector are:

- wide spectral range;
- OPO power in several times higher than diode laser power;
- response linearity of the device for variation of measured concentrations for 6 orders;
- real-time response at ppb level.

AgGaS<sub>2</sub> (AGS) crystal has high nonlinear optical coefficient and high optical transmission from 0.5–12.0  $\mu\text{m}$ , which makes it realistic to generate infrared parametric radiation. The monolithic AGS OPO cavity (Fig. 2) consists of two high-reflectivity mirrors at the signal wave. The output mirror is transparent at the pump and idler wavelengths; the input mirror has a high transmission coefficient at the pump wavelength. The designed monolithic block allows correcting the cavity length by means of changing the distance between two cylindrical holders in the flanges. The step motor moves crystal in relation to pumping beam. The crystal

in Figure 2 goes up to 4.2–11  $\mu\text{m}$ . It depends on orientation of the crystal.

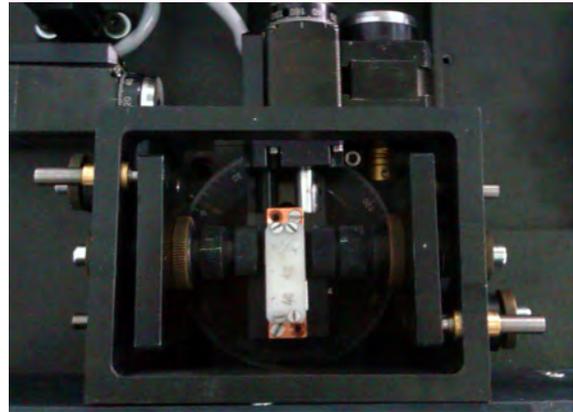


Figure 2. The OPO monolithic cavity OPO based on AGS crystal.

From Fig. 3 one can also see that an idler beam tunability of 4.2–10.6  $\mu\text{m}$  was achieved with AGS crystal (the signal wavelength was tunable between 1.169 and 1.405  $\mu\text{m}$ , respectively).

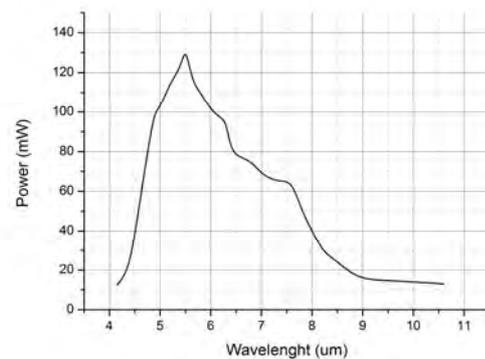


Figure 3. AGS OPO tuning curve (idler wave)

### Laser photo-acoustic spectral study

For excitation of photo-acoustic spectra we used the nanosecond mid-IR OPO described in previous part. More often in PA devices are used sinusoidally modulated radiation and resonant cells. In the pulsed photoacoustics, the system is illuminated with a laser pulse rather than with periodic modulation. In our experiments we used the photoacoustic resonant cell.

Absorption spectra of different gaseous mixture were studied with use of tandem OPO-PAD. Below these absorption spectra are presented. You can see absorption spectra of experimental gaseous mixture CH<sub>4</sub> (black line) in Fig. 4.

There are absorption spectra of different gaseous mixture present here (CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, atmosphere outside and inside) in range from 2.35 to 3  $\mu\text{m}$  (see Fig. 5).

Absorption spectra of different gaseous mixture are presented here ( $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , atmosphere outdoors and indoors) in the range from 3.30 to 3.6  $\mu\text{m}$  (see Fig. 6).

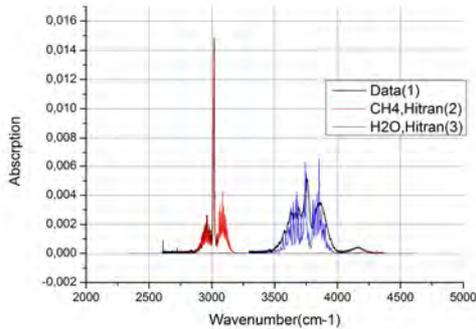


Fig. 4. Absorption spectra: absorption spectrum of experimental gaseous mixture  $\text{CH}_4$  (black line), absorption spectrum of  $\text{CH}_4$ , HITRAN (red line), absorption spectrum of  $\text{H}_2\text{O}$ , HITRAN (blue line).

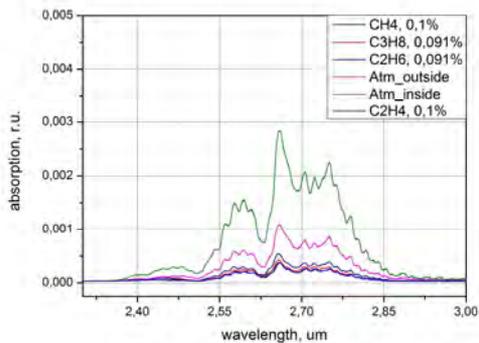


Fig. 5. Absorption spectra: absorption spectra of experimental gaseous mixture  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and absorption spectra of atmosphere outside and inside in the range from 2.35 to 3  $\mu\text{m}$ .

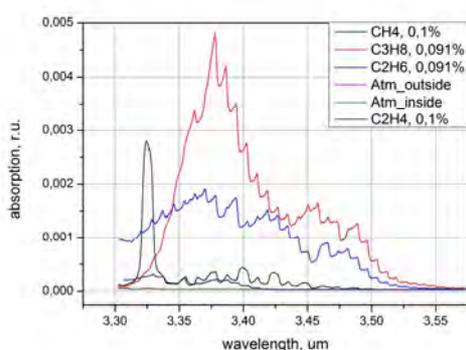


Fig. 6. Absorption spectra: absorption spectra of experimental gaseous mixture  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and absorption spectra of atmosphere outside and inside in the range 3.30 to 3.6  $\mu\text{m}$ .

Absorption spectra of human's breath (black line) and human's breath after smoking (red line) in the range from 2.3 to 3  $\mu\text{m}$  are presented in Fig. 7.

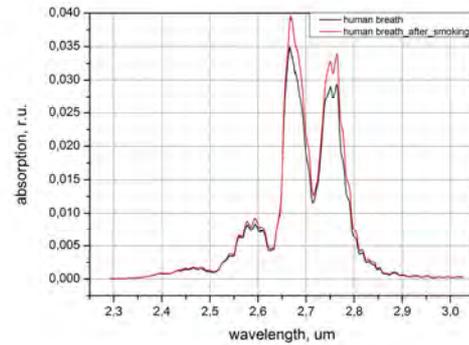


Fig. 7. Absorption spectra: absorption spectrum of human's breath (black line) and absorption spectrum of human's breath after smoking (red line).

## Conclusion

This work shows perspectives of using photoacoustic spectroscopy in medical and scientific practice. Compact analytical systems for different applications can be developed with use of this approach.

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## References

- [1] Photoacoustic Spectroscopy in Trace Gas Monitoring Frans J.M. Harren, Gina Cotti, Jos Oomens, and Sacco te Lintel Hekkert *Encyclopedia of Analytical Chemistry* R.A. Meyers (Ed.) pp. 2203–2226 Y John Wiley & Sons Ltd, Chichester, 2000
- [2] Miklos A, Hess P, Bozoki Z (2001) Application of acoustic resonators in photoacoustic trace gas analysis and metrology *Review of scientific instruments*, 72 (2001) pp. 1937-1955
- [3] A. Lyakh., R. Maulini, A. Tsekoun, R. Go, C. Pflugl, L. Diehl, Q. J. Wang, F. Capasso, and C. Kumar N. Patel, "3 W continuous-wave room-temperature single-facet emission from quantum cascade lasers based on non-resonant extraction design approach," *Appl. Phys. Lett.* 95,141113, 2009.
- [4] Anadi Mukherjee, Manu Prasanna, Michael Lane, Rowel Go, Ilya Dunayevskiy, Alexei Tsekoun, and C. Kumar N. Patel Optically multiplexed multi-gas detection using quantum cascade laser photoacoustic spectroscopy *Applied Optics* Vol. 47, Iss. 27, pp. 4884–4887 (2008)
- [5] Michael E. Webber, Michael Pushkarsky, and C. Kumar N. Patel Optical detection of chemical warfare agents and toxic industrial chemicals: Simulation *J. Appl. Phys.* 97, 113101 (2005)
- [6] K.N. Patel Laser photoacoustic spectroscopy helps fight terrorism: High sensitivity detection of chemical Warfare Agent and explosives Photoacoustic and Photothermal Phenomena *Journal The European Physical Journal - Special Topics* Volume 153, Number 1 / January, 2008

[7] Karapuzikov A.I., Karapuzikov A.A., Kashtanov D.A., Starikova M.K., Kistenev Yu.V. Photo-acoustic gas analyzer *Application for a patent RF № 201147362, 2011.11.21, patent owner – Special technologies Ltd.*

[8] Marchev G., Tyazhev A., Vedenyapin V., Kolker D., Yelisseyev A. Nd:YAG pumped nanosecond optical parametric oscillator based on LiInSe<sub>2</sub> with tunability extending from 4.7 to 8.7 μm // *Optics Express*, 2009, Vol. 17, Issue 16, P. 13441-13446.

[9] Petrov V., Zondy J.-J., Bidault O., Isaenko L., Vedenyapin V., Yelisseyev A., Chen W., Tyazhev A., Lobanov S., Marchev G., Kolker D. , Optical, thermal, electrical, damage, and phase-matching properties of lithium selenoindate *JOSA B*, 2010, Vol. 27, Issue 9, P. 1902-1927.

[10] Kolker D.B., Pustovalova R.V., Starikova M.K., Karapuzikov A.I., Karapuzikov A.A., Kuznetsov O.M., Kistenev Yu. V. Optical parametric oscillator within 2.4-4.3 mkm pumped with a nanosecond Nd:YAG laser// *Atmospheric and Oceanic Optics*, 2012, Vol. 25, No. 1, pp. 77-81

[11] Kolker D.B., Karapuzikov A.I., Karapuzikov A.A., Starikova M.K., Boyko A.A., Dukhovnikova N.Yu. Nanosecond optical parametric oscillator in the mid IR range with a two-pass pumping is based on the crystal AgGaS<sub>2</sub> *The 7th International Forum on Strategic Technology IFOST2012*, Tomsk, Russia, 2012 vol.2, p. 467-469