QCL spectroscopy combined with the least squares method for substance analysis

D A Samsonov¹, A S Tabalina², I L Fufurin³

¹Department of Physics student, Bauman Moscow State Technical University, Moscow, Russia
²Department of Physics student, Bauman Moscow State Technical University, Moscow, Russia
³Cand. Sc. (Phys.), Assoc.Professor, Department of Physics, Bauman Moscow State Technical University, Moscow, Russia

Email: blitzar90@gmail.com, ast_295@mail.ru, igfil@mail.ru

Abstract. The article briefly describes distinctive features of quantum cascade lasers (QCL). It also describes an experimental set-up for acquiring mid-infrared absorption spectra using QCL. The paper demonstrates experimental results in the form of normed spectra. We tested the application of the least squares method for spectrum analysis. We used this method for substance identification and extraction of concentration data. We compare the results with more common methods of absorption spectroscopy. Eventually, we prove the feasibility of using this simple method for quantitative and qualitative analysis of experimental data acquired with QCL.

1. Introduction

Nowadays spectroscopy is one of the most used research methods in different areas [1-5]. Infrared spectroscopy plays a crucial role in identification and qualitative analysis of organic and inorganic substances.

Quantum Cascade Laser (QCL) [6] is a semiconductor laser that emits due to electron transitions between multiple quantum well heterostructures. This technology makes it possible to achieve a wide range of radiation wavelengths. It was first introduced in 1994 and is used today in many research areas [8-10].

Distinctive features of QCLs are:
- radiation frequency manipulation by setting the appropriate active layer thickness in the heterostructure;
- frequency manipulation by changing the voltage applied to the superlattice.

The main goal of this paper was to apply QCL IR-spectroscopy in the range of 5.14 to 12.8 μm for qualitative and quantitative analysis of gases and thin films of test substances. To achieve this goal, the research team had to perform the following tasks:
- setting up a QCL-based experiment;
- registering absorption spectra of test substances;
analysing the data acquired by means of the least squares method (LSM) in matrix form;

estimating the efficiency of substance identification and concentration determination.

2. Experimental set-up

Figure 1 demonstrates the experimental set-up used in the investigation.

![Figure 1. Experimental set-up](image)

1 - QCL, 2 - external photodetector, 3 - QCL-detector channel, 4 - QCL-PC channel, 5 - PC with specialised software, 6 - gas container.

During the experiments, the distance between the QCL and the photodetector was 50 cm. It is possible to use a greater distance with corner reflectors [10].

This experimental set-up can acquire absorption spectra of substances in the gas phase as well as those of films that are up to several dozen μm thick.

3. Spectrum analysis

For spectrum analysis we chose one of the simplest methods for quantitative and qualitative spectroscopy, the least squares method in matrix form (LSM). Works [11, 12] describe its theoretical foundation.

We used Python 2.7 for all the computations and visualisation. The main idea of the method consists of solving a matrix equation for $C_j$:

$$B_{ij}C_j = E_i,$$

where $C_j$ is the resulting vector of concentrations, $B_{ij}$ is the matrix of base substance optical densities and $E_i$ is the experimental spectrum of optical density. Index $i$ is the wavelength (0..1023 cm$^{-1}$) and $j$ is the number of the substance in the base substance matrix $B_{ij}$.

The data which comes from the QCL is a normed experimental spectrum of absorbance $I_i$. The base $W_{ij}$ is a matrix of normed base spectra. Transforming absorbance spectra into optical density, we get the $B_{ij}$ and $E_i$ quantities that we use in the expression (1).

$$D_i = -ln(I_i),$$

where $D_i$ is the corresponding optical density at the $i$-th wavelength.
To solve (1) we need to get $B_{ij}^{-1}$. Generally $i \neq j$ so $B_{ij}^{-1}$ is a pseudoinverse of the matrix $B_{ij}$, which has the required property $B_{ij}^{-1}B_{ij} = I$, where $I$ is the identity matrix. So the solution of the equation (1) becomes:

$$B_{ij}^{-1}E_i = C_j$$  \hspace{1cm} (3)

4. Results
We used the Pearson correlation coefficient ($r$) [14] to perform our qualitative analysis. While quantitative description was provided by the LSM (expression (3)), where the $j$-th place in the $C_j$ vector shows the corresponding concentration of the substance $j$ in the base. This method measures the concentration in the units of concentration of the corresponding base spectrum.

Figures 2, 3 and 4 present examples of the spectra acquired and their analysis.

![Figure 2](image)

**Figure 2.** Aceton detection

1 - experimental spectrum, 2 - base spectrum. $r = 0.97$, $c = 64 \text{ g cm}^{-3}$, SNR = 7.4.
Figure 3. Polystyrene detection

1 - experimental spectrum, 2 - base spectrum. $r = 0.91$, $c = 5.6 \mu m$, SNR = 28.7.

Figure 4. Lavsan (PET) and polyethylene mixture detection

1 - experimental spectrum, 2 - base polyethylene spectrum, 3 - base lavsan spectrum. $r_2 = 0.96$, $r_3 = 0.27$, $c_2 = 10.4 \mu m$, $c_3 = 5.7 \mu m$, SNR2 = 33.2, SNR3 = 19.5.

We performed mixture analysis as shown in figure 4 the following way. We analysed the most relevant spectrum using the correlation coefficient $r$, then we subtracted it from the experimental spectrum with the corresponding concentration value, then the procedure was repeated and all the remaining substances were identified.
5. Concentration error estimation

We conducted the following experiment to estimate errors. We prepared three identical polyethylene films of a known thickness (8 μm). Then we obtained absorption spectra of one, two and three films in sequence. Adding a film means that absorption lines on a normed spectrum should become deeper. This effect is evident in figure 5, and table 1 shows the results of estimating the concentration error.

![Figure 5. Concentration error estimation](image)

C - 1 polyethylene film, 2C - 2 polyethylene films, 3C - 3 polyethylene films.

| Number of films | LSM width, μm | Real width, μm | Relative error, % |
|----------------|--------------|---------------|------------------|
| 1              | 7,870        | 8             | 1,62             |
| 2              | 13,251       | 16            | 17,18            |
| 3              | 20,233       | 24            | 15,67            |

6. Conclusion

This paper presented mid-infrared absorption spectra acquired with QCL. We showed the possibility to successfully conduct quantitative and qualitative spectrum analysis with the LSM. Moreover, we were able to analyse mixtures. This method gives a relative concentration error under 30% and may be a reliable method for substance identification. In real-world conditions, which are far from laboratory conditions, noise could have a critical effect. To this end, future research may be aimed at QCL noise analysis and ways of identifying substances in the natural environment.

References

[1] Morozov A.N and Svetlichniy S I 2016 *Osnovi furie-spectroradiometrii* [Fundamentals of Fourier spectroradiometry] (Moscow: Nauka) 456 p

[2] Golyak Ig S, Golyak Il S, Karfidov A O, Korolev P A, Morozov A N, Mironov A I, Strokov M A, Tabalin S E and Fufurin I L 2014 *Panoramniy furie-spekrtroradiometr PHRDD-4* [Panoramic Fourier spectroradiometer PHRDD-4] *Pribory i tekhnika eksperimenta* Instruments and Experimental Techniques 6 119-20
[3] Morozov A N, Svetlichniy S I, Tabalin S E and Fufurin I L 2013 Fizicheskie osnovi rascheta interferometra s vrashchayuscheyysya plastinkoy [Principal physics for design calculations of an interferometer with a rotating plate]. Opticheskiy zhurnal - Journal of Optical Technology 80(8) 37-41

[4] Zaytsev K I, Gavdush A A, Karasik V E and Yurchenko S O 2014 Highly accurate reconstruction of spectral optical characteristics of a medium using terahertz pulsed spectroscopy. Vestn. Mosk. Gos. Tekh. Univ. im. N.E. Baumana, Estestv. Nauki - Herald of the Bauman Moscow State Tech. Univ., Nat. Sci. 3 69-92

[5] Bashkin S V et al 2016 Experimental results of investigating a panoramic Fourier transform infrared spectrometer. Vestn. Mosk. Gos. Tekh. Univ. im. N.E. Baumana, Estestv. Nauki -Herald of the Bauman Moscow State Tech. Univ., Nat. Sci. 2 51–64 DOI: 10.18698/1812-3368-2016-2-51-64.

[6] Kazarinov R F and Suris R A 1971 O elektromagnitnihsvostvahpoluprovdnikov so sverhreshetkoy [On electromagnetic properties of semiconductors with superlattice]. Fizika i tehnika poluprovdnikov - Semiconductors 5(4)

[7] Herman M A 1986 Semiconductor Superlattices (Berlin: Akademic-Verlag)

[8] Schwaighofer A, Alcaráz M R, Araman C, Goicoechea H and Lendl B 2016 External cavity-quantum cascade laser infrared spectroscopy for secondary structure analysis of proteins at low concentrations. Scientific Reports 6

[9] Deutsch E R, Kotidis P, Zhu N, Goyal A K, Ye J, Mazurenko A, Norman M, Zafiriou K, Baier M and Connors R 2014 Active and passive infrared spectroscopy for the detection of environmental threats Advanced Environmental, Chemical, and Biological Sensing Technologies XI

[10] Volkov V G 2016 Quantum Cascade Lasers and their Application in Safety and Communication Systems Systems of Control, Communication and Security 1

[11] Kozintsev V I, Belov M L, Gorodnichev V A and Fedorov Yu V 2006 Lazerny optiko-akusticheskii analiz mnogokomponentnyh gazovyh smesey [Optoacoustic laser analysis of multicomponent gas mixtures] (Moscow: Bauman Moscow State Technical University) 387 p

[12] Tsej R and Shumafov M M 2011 Matrix condition number as a stability characteristic in solving applied problems Trudy FORA - Works of the Adygheya Republic Physical Society 16

[13] Pearson K 1895 Notes on regression and inheritance in the case of two parents. Proceedings of the Royal Society of London

[14] Morozov A N, Kochikov I V, Novgorodskaya A V, Sologub A A and Fufurin I L 2015 Statistical estimation of the probability of the correct substance detection in FTIR spectroscopy Computer Optics 39(4) 614-21 DOI: 10.18287/0134-2452-2015-39-4-614-621.

[15] Fufurin I L 2010 Research on method and algorithm of substance recognition in the atmosphere for one measurement of fourier-spectroradiometer Cand. phys. sc. diss. (Moscow)