

**LAPPEENRANTA UNIVERSITY OF TECHNOLOGY**  
**DEPARTMENT OF ELECTRICAL ENGINEERING**

**INVESTIGATION AND DATA ADAPTIVE ANALYSIS  
OF CARS SPECTRA**

Supervisor: Professor, Ph.D. Erik Vartiainen

Examiners: Professor, Ph.D. Erik Vartiainen  
Professor, Ph.D. Erkki Lahderanta

Lappeenranta 2008

Alexey Mironov  
Ruskonlahdenkatu 13-15 A 1  
53850 LAPPEENRANTA  
+358468932522

## **ABSTRACT**

Lappeenranta University of Technology

Department Of Electrical Engineering

Technical Physics

Alexey Mironov

### **Investigation and Data Adaptive Analysis of CARS Spectra**

Master's Thesis

2008

60 pages, 33 figures and 1 table

Examiners: Professor, Ph.D. Erik Vartiainen

Professor, Ph.D. Erkki Lahderanta

Keywords: CARS, Adaptive Analysis, Spectral Analysis

In this diploma work advantages of coherent anti-Stokes Raman scattering spectrometry (CARS) and various methods of the quantitative analysis of substance structure with its help are considered. The basic methods and concepts of the adaptive analysis are adduced. On the basis of these methods the algorithm of automatic measurement of a scattering strip size of a target component in CARS spectrum is developed. The algorithm uses known full spectrum of target substance and compares it with a CARS spectrum. The form of a differential spectrum is used as a feedback to control the accuracy of matching. To exclude the influence of a background in CARS spectra the differential spectrum is analysed by means of its second derivative. The algorithm is checked up on the simulated simple spectra and on the spectra of organic compounds received experimentally.

## **ACKNOWLEDGEMENTS**

First of all I want to thank Professor Erkki Lähderanta and Professor Erik Vartiainen for their guidance and support. Also I am grateful to the all staff of Lappeenranta University of Technology who provided my studying here, to Professors of St. Petersburg Electrotechnical University who gave me the broad basic knowledge and to all inhabitants of Lappeenranta for their hospitality.

Especially I wish to thank my parents.

Lappeenranta, May 2008.

Alexey Mironov

## TABLE OF CONTENTS

1. INTRODUCTION.....	4
1.1 Actuality of the problem.....	4
1.2 Aim of the work .....	6
2. CARS SPECTROMETRY IN MEDIUM ANALYSIS .....	7
2.1 Raman scattering .....	7
2.1 Coherent spectroscopy .....	8
2.2 Application of CARS for the medium analysis.....	14
2.3 Applying of stimulated Raman scattering for pumping in CARS.....	17
3. BASICS OF ADAPTIVE ANALYSIS .....	20
4. EXPERIMENTAL SECTION .....	24
4.1 CARS-spectrometer.....	24
4.2 Gained CARS-spectra .....	25
4.3 The used Raman spectra.....	28
5. DESCRIPTION OF THE ALGORITHM .....	30
5.1 Basic requirements to the algorithm.....	30
5.2 Description and the block diagram.....	31
5.3 Feedback module.....	34
5.4 Influence of a noise to the work of algorithm .....	41
5.5 Influence of the frequency shift on quality of measurements .....	45
6. CHECKING OF THE ALGORITHM ON REAL SPECTRA.....	48
7. CONCLUSIONS .....	53
REFERENCES .....	55

## Symbols and abbreviations

CARS	Coherent Anti-Stokes Raman Spectroscopy
RS	Raman Scattering
BLP	Biharmonic Laser Pumping
SRS	Stimulated Raman Scattering
$\Delta\nu$	Raman shift [Hz]
$E$	vibrational level energy
$h$	Planck's constant
$k$	wave vector
$\Delta\omega$	Raman shift
$q$	wave vector of diffraction grating
$v_p$	phase velocity
$\Omega_\sigma$	natural frequency of intramolecular oscillations
$\chi^{(3)}$	cubic susceptibility of medium
$\chi^{(3)R}$	resonant part of cubic susceptibility
$\chi^{(3)NR}$	not resonant part of cubic susceptibility
$I$	intensity of light
$n$	density of molecules
$\gamma$	cubic hyperpolarizability
$x$	input signal

$y$	output signal
$\varepsilon$	error signal
$d$	required response
$k$	coefficient of proportionality between CARS and Raman spectra
$S$	parameter of smoothness
$f$	differential function
$\alpha$	ratio between CARS and Raman spectra

### **Subscripts**

$s$	Stokes
$a$	anti-Stokes
$L$	pumping laser
$i$	discrete spectral element number
$C$	CARS spectrum
$R$	Raman spectrum
$CB$	background part of the CARS spectrum
$CN$	noise part of the CARS spectrum
$RN$	noise part of the Raman spectrum

## 1. INTRODUCTION

### 1.1 Actuality of the problem

One of the most powerful methods of nonlinear laser spectroscopy is the coherent active spectroscopy of Raman light scattering. The most spread variety of these methods has specific name - Coherent Anti-Stokes Raman Spectroscopy (CARS). This type of spectroscopy is closely related to the spectroscopy of spontaneous Raman Scattering (RS) and possesses practically all its advantages. However it considerably surpasses a spontaneous RS in the level of optical signal, in the spectral and space resolution, performance, in the much smaller level of optical noises and flares, in richness and completeness of the spectroscopic information about investigated material, gained with its help, etc.

This and other coherent non-linear optical methods are extremely perspective for non-disturbing local control of a composition, temperatures and pressures of gas intermixtures, sondage of an excited and non-steady gas mediums and aerodynamic streams, at examination of explosive and discharge processes in gases and plasma, etc. These methods together with a method of a spontaneous Raman effect form now exclusively powerful and manifold arsenal of laser methods of the gas and plasma diagnostic, keeping in themselves greater opportunities for applications.

The most significant goals of a Coherent Anti-Stokes Raman Spectroscopy and other non-linear methods, provided them wide prospects in a practical gas analysis, are following [1]:

1. In anti-Stokes variety of coherent active Raman spectroscopy, the signal has the frequency exceeding frequencies of pumping and, hence, gets in a spectroscopic range, free from parasitic flares of a Stokes luminescence and thermal light emission. The additional advantage of CARS is high collimation of coherently scattered beam (its divergence practically coincides with divergence of pumping beams) that allows to spend the exclusively effective space filtering of the useful signal from background

incoherent flares and noises (for example, originating because of diffusing light of pumping on a dust or aerosols in explored gas, light emissions of the firm corpuscles heated by laser radiation, etc.).

2. The spectral resolution of CARS is defined only by breadths of lines of pumping lasers and can attain  $0,001 \text{ cm}^{-1}$  whereas in spontaneous RS the resolution is restricted by a spread function of the spectroscopic device and usually lies over the range of several  $\text{cm}^{-1}$ . This property of CARS is especially important for investigation of dilute gases as they have a typical breadths of lines in range  $0,01^{-1} \text{ cm}^{-1}$ .

3. The spatial resolution of CARS is defined by an intersection size of focused beams and in a limit is restricted only by wave length of pumping. It allows to use CARS for investigation of microstructures in chemistry or biology [2, 3].

4. The temporal resolution is defined by duration of used laser pulses, and can attain values of 0,3 ps.

5. Because power of coherently scattered signal, depends on an equilibrium population difference of combination transition levels [4], CARS allows to make precise local measurings of vibrational and rotational temperatures of gases, including a flame, electric discharges, and plasma.

The main deficiency of CARS most clearly manifested at research of strongly constricted or overheated gases, and also at detecting of small concentration of impurity molecules in an aerosphere of buffer gases, is presence of non-dispersing background in the “active” spectra, connected with  $\chi^{(3) \text{NR}}$  – non-resonant part of a nonlinear susceptibility. If this non-resonant coherent background is not suppressed, the bottom detection limit of the majority of impurities is at a level  $1000 \text{ million}^{-1}$  and above.

High spatial, spectral and temporal resolution of CARS spectroscopy allows to get an extremely big amount of information in short time. However all this information is



absolutely useless without proper analysis. Thus, for nowadays the actual problem for CARS-spectrometry is the intelligent analysis of received data, what allows to reveal all advantages of the technology and to compensate its deficiencies.

## **1.2 Aim of the work**

**The aim of degree work** is development of the automated adaptive algorithm for the detection in the CARS-spectra of the spectral lines of components with known Raman spectra and measuring of their magnitude.

According to the aim of the work it is required to solve following problems:

- investigate applicability of methods of the adaptive analysis for processing of CARS spectra;
- develop the algorithm of search of known Raman line in CARS spectra and its quantitative analysis;
- test the algorithm on the spectra.

## 2. CARS SPECTROMETRY IN MEDIUM ANALYSIS

### 2.1 Raman scattering

Before starting to explain methods of CARS spectra analysis, it is necessary to state basics of the usual Raman scattering. Briefly the Raman scattering is a process of scattering of photons from molecules with change of their frequency. Generally scattering appears, when photon energy is firstly absorbed by molecule and then emitted back. In case of Raman scattering absorption and radiation happens on transitions between vibrational levels of molecules. Because scattering takes a very short time, the excited level may be not the real energy level, but the short lifetime virtual state. However if energy of incident photon matches to the transition between real vibrational levels, the scattering have a resonant maximum. The energy level diagram is presented on fig. 1 [4, 5].

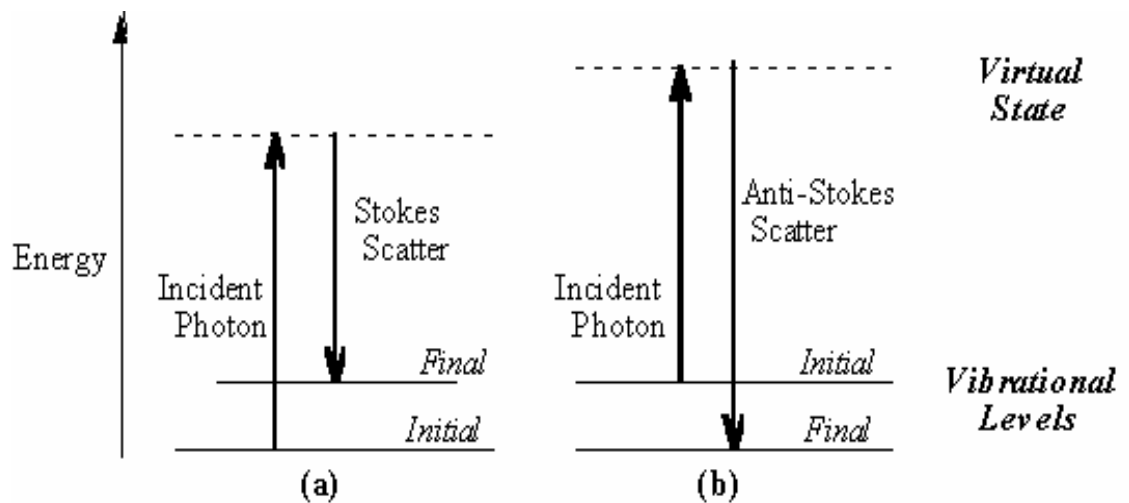


Figure 1. Energy level diagram for Raman scattering; (a) Stokes Raman scattering (b) anti-Stokes Raman scattering [4].

If radiation occurs on the same transition, on which absorption is happened, frequency of photon will not be changed. This is a normal scattering. If the emission transition happens between other pair of energy levels, than absorptive one, the emitted light will

have shifted wavelength. It is named Raman shift. Then the final level of emission transition have a higher energy than the initial level, the emitted light will have a lower frequency, than incident one. This case is named Stokes scattering. It is most probable variant of spontaneous Raman scattering, because in equilibrium state the population of lower energy levels is much higher than ones with higher energy. The opposite case, then the initial transition starts from the excited level and the emission one finishes on lower level, is called anti-Stokes. The frequency shifts of both Stokes and anti-Stokes components are equal and may be calculated by the following formula [6]:

$$\Delta\nu = (E_1 - E_2)/h,$$

where  $E_1$  and  $E_2$  are the energies of the high and low vibrational levels. That allows to investigate the vibrational levels structure of a material by measuring of the Stokes or anti-Stokes shift. Because each substance has its own unique vibrational levels structure the Raman scattering spectroscopy makes possible to determine the presence of some component in the medium.

## 2.1 Coherent spectroscopy

The traditional kinds of an optical spectroscopy which are based on measuring of spectrums of luminescence, absorption and diffusing of light are playing appreciable role in the science and technique owing to the unique diagnostic opportunities and high comprehension. Simultaneously they possess also the cardinal deficiency resulting from the expedient of extraction of the information about an explored system, based on measuring of a spectral distribution law of light intensity. It is possible to tell, that, as well as in optics before the invention of holography, in a traditional optical spectroscopy there is unresolved “phase problem” - a problem of restitution of the full information on studied object from essentially incomplete data containing in a spectral distribution of intensity of a light field after interacting with object.

The missing phase information completely lost at record of usual optical spectrums can be taken from data of a coherent active spectroscopy of scattering or absorption of light. In the coherent active spectroscopy the measuring of both amplitude and phase (or, that the same, of the real and imaginary components) of the interacted light can be realised.

As in a usual holography, here the record of the full spectroscopic information is carried out at an interference of coherent light beams. First of them is a light passed the interaction with explored object, other one is a specially inserted (or initially presented in the radiation leaving the explored specimen) coherent background, playing a role of reference wave. In other words, in the coherent active spectroscopy the heterodyning of a signal can be realized.

For realization of the full record of the actual physical information about the explored medium in all schemes of the active spectroscopy, the key value has a coherence of the signal light waves leaving a medium. That is provided by a coherence of the light waves radiated by phased elementary molecular oscillators of this medium. In turn phase synchronisation of molecular oscillators is provided by the stimulated character of oscillations. Moreover the amplitude and a phase of noted oscillations are set by amplitudes and phases of the coherent light waves (a pumping and probing), specially inducted in medium at measurement process of the coherent active spectroscopy.

The principle of the coherent spectroscopy of a Raman scattering (RS) can be illustrated by means of fig. 2. [7]

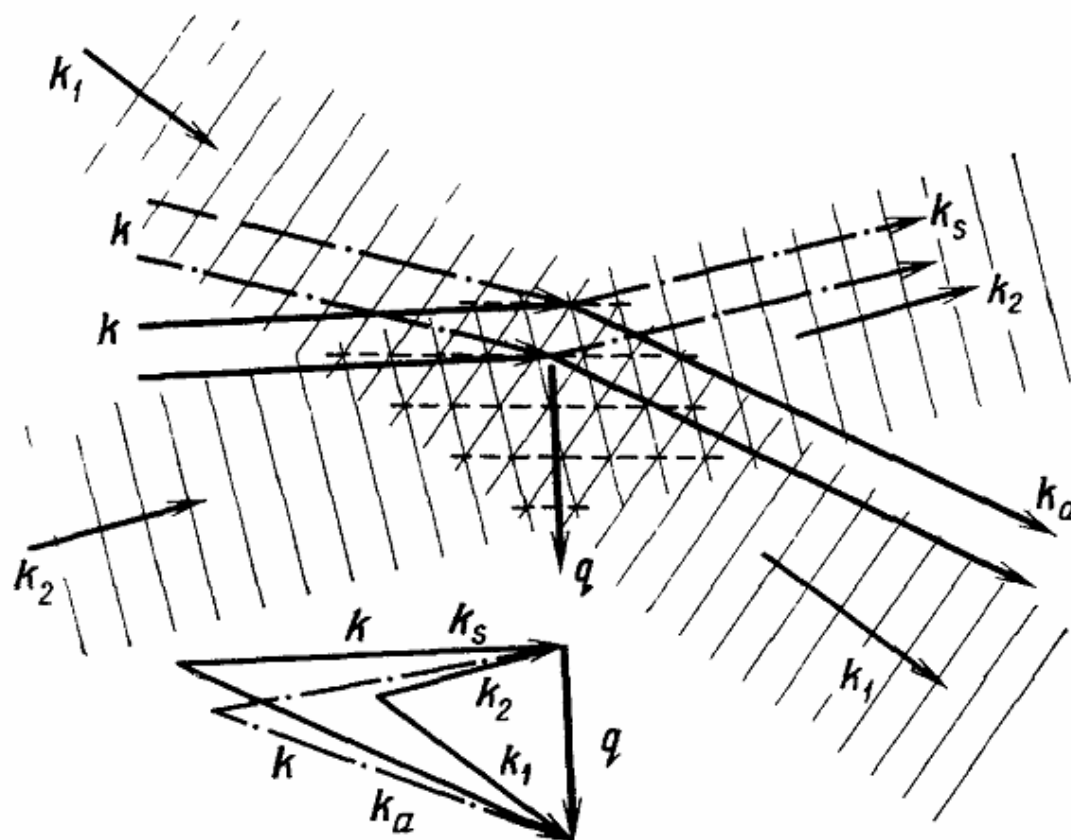


Figure 2. Principle of the coherent active spectroscopy of Raman scattering from the point of view of optical guidance of the running diffraction grating. On the bottom of figure:  $k_s$  – dash line,  $k_a$  – solid line [7].

Reflection of a probe wave  $k$  occurs with an angle defined by the Bragg condition (the diagram at the bottom illustrates relationships between wave vectors). Because of Doppler's effect the reflected waves have the frequencies shifted relative to frequency of a probe beam on  $\pm\Delta\omega = \pm(\omega_1 - \omega_2)$ . The Diffraction gratings connected with a coherent wave of intramolecular oscillations and with a wave of coherent perturbations of electronic shells of molecules, have equal frequencies and wave vectors. Therefore Stokes and anti-Stokes components of diffraction contain as informative (connected with diffraction on intramolecular oscillations), and basic (or “heterodyne”, connected with diffraction on lattices of electronic shells) components. As in usual holography,

the interference of informative and basic components of scattered light makes possible to rebuild the full information about properties and structure of the intramolecular oscillations, and thus to solve “a phase problem” of oscillatory molecular spectrum analysis.

The principle of signal reception in the active spectroscopy is very close to the principle of dynamic holography: two beams of light with flat phase fronts (wave vectors  $k_1, k_2$ ), being overlapped in nonlinear medium, “write down” the flat hologram, or in other words form the flat diffraction grating (wave vector  $q = k_1 - k_2$ ) on which a sondaing beam (wave vector  $k$ ) diffracts.

In practice various configurations of pumping, probe and anti-Stokes beams are used [8]. Most simple one is the collinear configuration presented on fig. 3, a. At such configuration of beams it is possible to gain interacting in maximum volume of a specimen, that considerably increases a level of an output signal, however it decreases the space resolution. Moreover at such configuration application of the filters separating an output signal, from beams of pumping is required. Thus in filters and other optical elements there can be a parasitic scattering.

At arrangement of beams with some angle (fig. 3, b), it is possible to increase considerably the space resolution and also simplify separation of the scattered beam from beams of pumping. However at such configuration exact convergence of three beams in one point is required. The coaxial arrangement of beams (fig. 3, c), at which the probe beam and a beam of pumping in any case will be crossed in one point, can solve this problem.

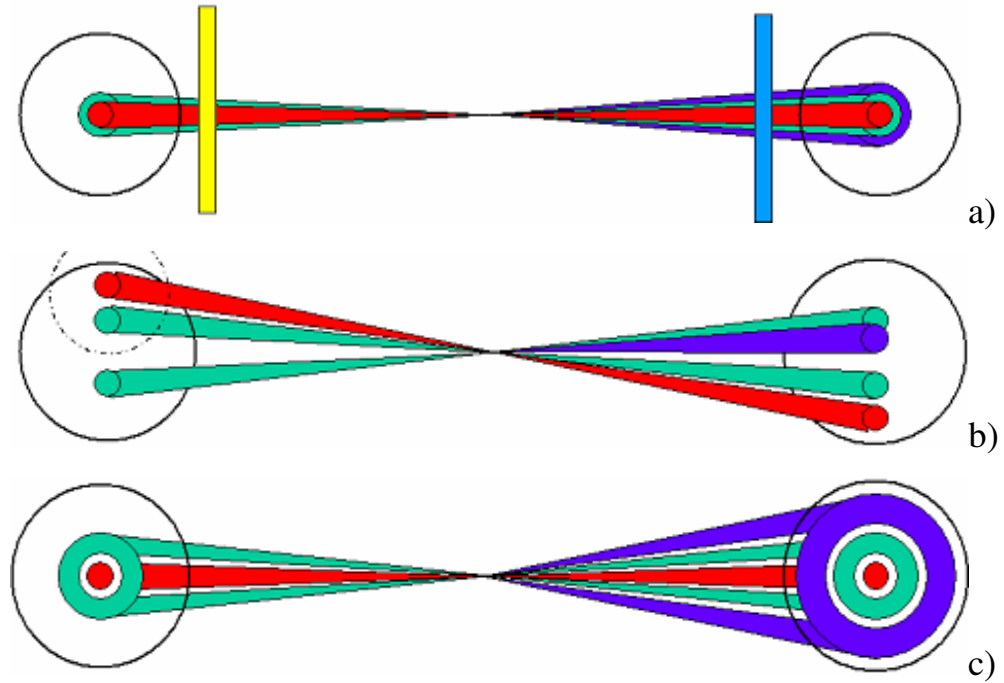


Figure 3. Various configurations of beams in CARS [6].

Diffraction is the most effective at accomplishment of conditions of synchronism between wave vectors of diffracted components  $k_s, k_a$  of a probing beam and wave vectors of the waves which are “writing down” and “reading out” the dynamic hologram:

$$k_s = k - q = k - (k_1 - k_2), \quad (1a)$$

$$k_a = k + q = k + (k_1 - k_2). \quad (1b)$$

Obviously, these conditions are equivalent to conditions of the Bragg diffraction in holography.

However essential difference of the scheme of diffraction in active spectroscopy from the usual holography is that waves with  $k_1, k_2$ , “writing down” the hologram (in active spectroscopy their named waves of pumping), have various frequencies  $\omega_1 \neq \omega_2$ , so a lattice oscillates with frequency  $\Delta\omega = (\omega_1 - \omega_2)$  and runs in medium with a phase

velocity  $v_p = q(\omega_1 - \omega_2)/|k_1 - k_2|^{-2} = q(\Delta\omega)/|q|^{-2}$ . Diffraction of a probing beam on such running lattice leads to a Doppler's frequency drift of diffracted components (they named Stokes and anti-Stokes, respectively):

$$\omega_s = \omega - qv_p = \omega - \Delta\omega = \omega - (\omega_1 - \omega_2), \quad (2a)$$

$$\omega_a = \omega + qv_p = \omega + \Delta\omega = \omega + (\omega_1 - \omega_2). \quad (2b)$$

When  $\Delta\omega$  coincides with any natural frequency of intramolecular oscillations  $\Omega_\sigma$  (or other internal micromotions of the investigated medium) active in a Raman scattering, the resonant change of a probing wave diffraction efficiency take place.

The intensity of an anti-Stokes wave measured in CARS may be defined by a formula:

$$I_a = |\chi_r + \chi_{nr}|^2 I_L^2 I_S,$$

where  $\chi^{(3)R} = n_I \gamma^r$ ,  $\chi^{(3)NR} = n_0 \gamma^{nr}$ ,  $I_L$ ,  $I_S$  - intensities of pumping and stokes waves with frequencies  $\omega_L$ ,  $\omega_S$ ;  $\chi^{(3)R}$ ,  $\chi^{(3)NR}$  - resonant and not resonant parts of a susceptibility of molecules,  $n_I$ ,  $n_0$  - densities of molecules of a detected impurity and buffer gas;  $\gamma^r$ ,  $\gamma^{nr}$  - cubic hyperpolarizability of investigated and buffer gases.

The last can be interpreted as resonant excitation of coherent intramolecular oscillations in medium by pair of traveling waves and the following scattering on this wave of a probing light beam. Thus there is a change of frequency in Stokes or anti-Stokes area, according to (2a) and (2b), with accomplishment of conditions of synchronism (1a), (1b). Presence of nonzero probing wave diffraction intensity in non-resonant case is connected with an excitation of forced (and, hence, coherent) non-resonant oscillations in the electronic shells of interacting molecules. Interfering of their radiation also generates not resonant components of probing beam diffraction. Obviously, at accomplishment of a resonance conditions  $\Delta\omega = \Omega_\sigma$ , there are both diffraction components in coherently scattered radiation which can interfere among



themselves. Not resonant component of diffraction represents the coherent displacement in an active spectrum on which resonant lines are placed.

It is necessary to note, that earlier the presence of a coherent background in Active spectra has been regarded as especially negative feature of coherent spectroscopy, leads to appearing of a high pedestal at investigated lines and complicates research of weak lines and overtones. Only after works in which ways of controlled suppression of a coherent background and active formation of a contour of spectral lines have been offered, qualitative specificity of the interference nature of the form of spectral lines in active spectroscopy has been reevaluated from the positive side.

For extraction of the information about the real and imaginary parts of cubic susceptibilities from CARS spectra, a numerical mathematical processing can be applied [9, 10, 11]. The most perspective method for today is a method of the maximum entropy [12, 13]. The given method allows to extract phase components from an amplitude signal without carrying out of additional measurements. However the gained spectrum requires special processing, because of presence in it of a variable background not carrying the information. Presence of this background does not allow to measure magnitude of various spectral lines quantitatively.

## **2.2 Application of CARS for the medium analysis**

The possibility to use CARS as a tool for quantitative and qualitative gas analysis and for a gas thermometry directly follows from abilities of the Raman scattering spectroscopy laying in its basis [14]. The new moments which the coherent methods introduce in area of a practical medium analysis, are connected with their advantages over spontaneous Raman spectroscopy in a high level of a registered signal, speed characteristics, high spectral and spatial resolution, the low sensitivity to optical noise and parasitic flares [15].

In works of J.-P. Taran group (France) [16, 17] CARS for the first time has been used for measurement of absolute concentration of impurity molecules in buffer gas ( $H_2$  in

aerosphere of  $N_2$ ), for measurement of local distribution of molecules of the certain type in stationary jets and a flame (in particular,  $H_2$  in a flame of a methane torch) and for measurement of a spatial distribution of temperature in a flame. The great advantages of this method have been illustrated.

Simultaneously in these and other works the difficulties originating at use of CARS for detection of extreme small impurity concentration have been found out also. They are result of presence in “active” spectrum of the pedestal produced by not resonant susceptibility  $\chi^{(3)NR}$  of molecules of buffer gas.

High signal strength in coherent spectroscopy and the unique high spectral resolution attaining  $0,001\text{ cm}^{-1}$  with using of narrow-band stabilized lasers for pumping also allows to obtain completely resolved thin structure of oscillatory-rotational spectra of rarefied gases.

It is necessary to note, that in the majority of experiments with high resolution CARS [18], as pumping lasers the continuous mode stabilized lasers with relatively small power (up to 10W) were used. Thereof signal strength in this case is rather insignificant and is at a level of a signal of spontaneous Raman scattering. The reason to use here the CARS is the possibility of reception of the ultrahigh spectral resolution.

Diagnostics of molecules on high electronic or oscillatory levels, and plasma of an electric discharge represents another example, where the CARS is extremely useful tool. Basic purpose of CARS here is measurement of distribution of population densities of excited states and, based on this information, temperatures of various subsystems of the energized molecules. The temperature of rotational and oscillatory subsystems of the energized molecules is defined by intensities of “hot” lines in active spectra [14].

One of the most perspective directions of application of CARS is distant non-disturbing local analysis of non-stationary gas jets, jet streams, and also the processes occurring in

explosive motors. High effectivity of traditional optical methods, especially spontaneous Raman spectroscopy, in the solution of these problems is well-known. However weakness of a signal of spontaneous Raman spectroscopy and impossibility of using of an effective space filtering of the useful signal strongly complicate or at all do impossible using of spontaneous Raman spectroscopy for diagnostic of dusty aerodynamic streams, combustion processes in conditions of clogging of a flame by firm corpuscles of fuel or black, etc. But just in these conditions using of CARS appears especially effective. This peculiarity of CARS recently attract the big attention from specialists in the field of aerodynamics and the engineers, engaged in development of jet and rocket engines [19]. In works [20, 21] the theory of this method is developed. It is shown, that application of CARS allows to develop an universal sensitive way of laser diagnostic of such local parameters of plasma as density, electronic and ionic temperatures, a direction and magnitude of a magnetic field, etc. It is important, what data about magnitudes of these parameters are taken from the analysis of coherently scattered light, whose intensity in  $10^5$ - $10^8$  times more, then in case of usual noncoherent scattering.

In many applications of CARS described above, the high speed of operation is characterised by very short times of exposure (down to duration of one laser pulse -  $10^{-8}$  -  $10^{-12}$  s) is required. In CARS for a rather long time ago the methods allowing to realize on a practice so fast operation are developed [22, 23, 24]. For this purpose it is necessary to pass from registration of spectra point-by-point to registration of spectra for one laser pulse, having taken advantages of broadband excitation. In this case one of pumping waves (let us assume, with frequency  $\omega_2$ ) should be presented by a laser radiation with very wide homogeneous spectrum “covering” in pair with a monochromatic wave of pumping  $\omega_1$  all spectral area, occupied by lines of a Raman scattering of the given medium interesting the experimenter. Spectrum of an anti-Stokes signal also becomes wide. Its form is defined by multiplication of spectrum contours of broadband pumping and spectral dependence of a square of the module of

medium cubic susceptibility  $|\chi^{(3)}|^2$ . As the broadband anti-Stokes spectrum as well as any “active” spectrum, is characterized by a high spectral luminance, it can be photographed without efforts or written down in memory of the optical multichannel analyser for one laser flash, in time equal to its duration (from  $10^{-8}$  till  $10^{-12}$ s).

### 2.3 Applying of stimulated Raman scattering for pumping in CARS

The original technique for selecting of spectral lines of target component in complicated spectrum was propounded by G. Miheev and T. Mogileva [25]. To measure only the target lines and exclude influence of other components in medium, they proposed to use pumping with spectral distribution equivalent to the spectral distribution of this line. For this purpose they proposed to use in pumping the stimulated Raman scattering in the same medium, which is required to select.

The technology of CARS assumes presence of two coherent laser beams which difference of frequencies is scanned about frequency of combinational transition of investigated material. Such biharmonic laser pumping (BLP) can be gained by means of two lasers, one of which works on a fixed frequency, and another one is a tunable frequency laser. When only the registration of one component concentration in a gas mix is needed, it is possible to gain specified BPL by using of stimulated Raman scattering (SRS) to shift a frequency of an only laser. Thus the laser part of installation becomes essentially simpler, because disappears necessity for the tunable laser and for overlapping of light pulses of two lasers in time and space. [25]

In gases at adjustment of the difference of frequencies  $\omega_L - \omega_S$  to the frequency of Raman transition of investigated molecules the relationship  $\chi^{(3)R} \gg \chi^{(3)NR}$  takes place. Thus intensity of an anti-Stokes wave sharply increases. According to this at research of a component concentration in a gas mix it is necessary to adjust in advance on a resonance so that the condition  $\omega_L - \omega_S = \Omega_\sigma$  was carried out during all experiment.

BLP fulfilling the given condition can be gained, using SRS. In this case all measurements are carried out by means of only one laser, works in a continuous mode. For these purposes the simple and effective single-mode laser can be used.

Principle of using SRS for a pumping is easier to present on the example. The diagram of such installation is presented on fig. 4 [25]. The only single-mode laser 1 is used for a pumping.

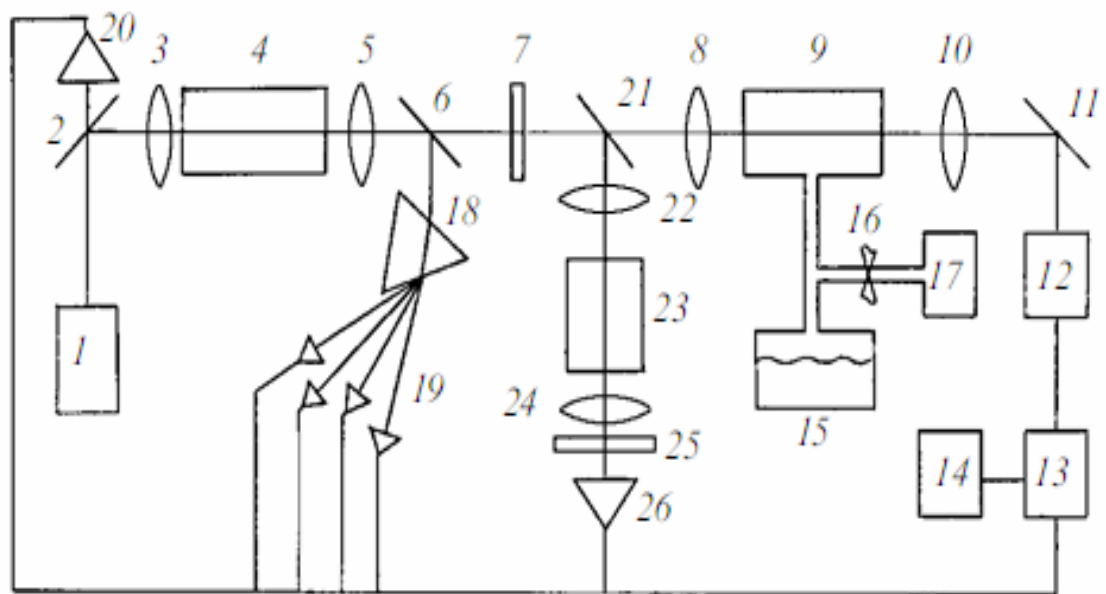


Figure 4. The CARS gas analyser with SRS pumping [25].

Target radiation by means of a rotary mirror 2 and lenses 3 is focused in the SRS-ditch 4. BLP, originating in a ditch 4, after the collimation lens 5 separates from others SRS component by means of a set of filters 7 and is focused in the measuring chamber 9 by objective 8. An anti-Stokes a component, originating in the chamber 9 by means of a lens 10 and mirrors 11 goes to the entry of the monochromator 12. Further the signal is registered by means of the detector 13 connected to the microcomputer 14. By a plate 6 a part of radiation from output of the SRS generator goes to the monitoring system of radiation pulses energy, consisting of a dispersing prism 18 and a set of the calibrated photo diodes 19. Photo diode 20 allows to measure energy of an input

pumping pulse. After splitting by a plate 21 a part of BPL is focused by a lens 22 in the center of basic ditches 23 with the fixed hydrogen pressure. The anti-Stokes component originating in a basic ditch 23, by a lens 24 goes to the photo diode 26. The set of filters 25 carries out its frequency selection. This additional optical branch consisting of elements 21-26, allows to normalise a signal originating in measuring ditch 9, and to eliminate agency of intensity fluctuations of the exciting laser.

Thus, application of SRS pumping in CARS spectrometry allows simple and effective means to analyse presence of the certain component in the investigated medium. However a basic deficiency of a method is its inflexibility which is not allowing by means of one device to analyse presence and a level of the contents of various components as it requires refilling of SRS ditch by the same substance which is supposed to be investigated.

### 3. BASICS OF ADAPTIVE ANALYSIS

One of the most important problems of the modern analysis is search of a way for overcoming of aprioristic vagueness at solving problem of reception and processing of the information. An effective way of the solution of the specified problem is using of the adaptive systems. There as adaptation are called a self-training, and also process of optimum reorganization of system structure according to a criterion of performance. Choosing of a criterion of optimization is defined by a system designated purpose.

Usually adaptive systems possess some or all listed below properties [26]:

1. They can adapt (self optimise) to a non-stationary change of environment conditions or requirements for system.
2. They can be trained for realization of the set type of a filtering and decision making. Systems with such properties can be synthesized automatically through training. In other words adaptive systems can be “programmed” due to process of training.
3. They do not require carefully developed methods of a synthesis usually necessary for not adaptive systems. On the contrary, it is possible to consider them as “self-organizing system”.
4. They can extrapolate model of behaviour for functioning in new conditions after training on usually small number of training signals or situations.
5. They can be restored to some degree. That means they can adapt to the certain internal flaws.
6. They are more complex for analysing, than not adaptive systems, but they allow to increase considerably area of functioning of system when parameters of an input signal are not known or vary in a time.

In the literature some ways of classification of adaptive systems are offered [26]. First of all adaptive systems can be divided into systems without a return coupling and with a return coupling. Process of adaptation without a return coupling consists of measurements of characteristics of an input signal or environment, introduction of this information into the formula or a computational algorithm and use of results for regulating of system parameters. At adaptation with a return coupling an output signal is also analysed to adjust system parameters.

Advantage of adaptation algorithms with a return coupling is their working capacity in many applications where analytical methods of a synthesis do not exist, or they are unknown. For example, such algorithms are used in cases of non-stationary signals or when physical parameters of components of system are variables or known inexactly.

The generalized circuit design of a feedback system is presented on fig. 5. Here  $x$  designates an input signal, and  $d$  is a required response (output signal) of adaptive system.

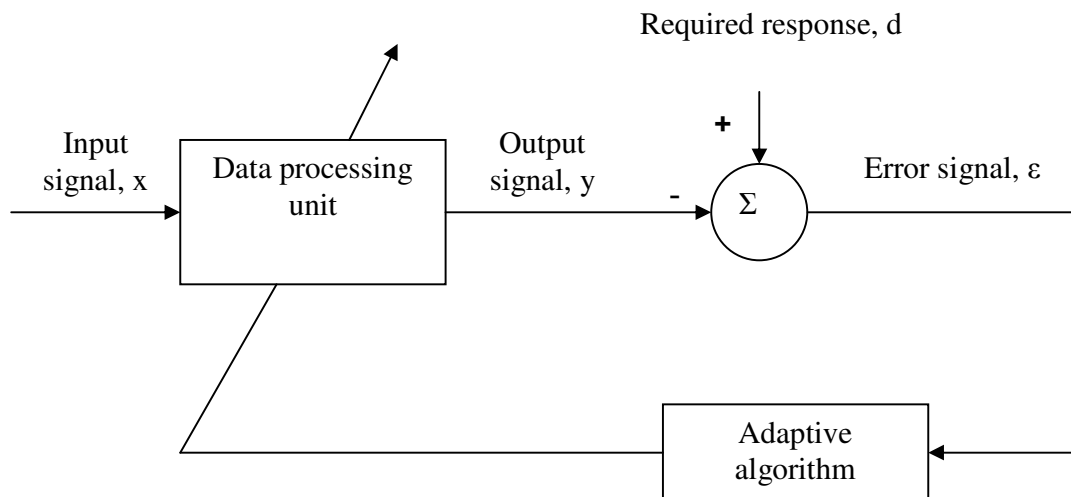


Figure 5. Signals in case of adaptation with feed-back.



The error signal  $\varepsilon$  is a difference between required and actual output signals of the adaptive system. By means of minimization of some parameter depending on an error signal, the adaptive algorithm allows to change characteristics of the response, that closing a loop of a functional return coupling.

On fig. 6 an example of application of adaptive system in a problem of system identification is presented. Here the signal  $X$  serves as an input signal for the adaptive processing system, and also for unknown “identified” system. For decrease of  $\varepsilon$  the adaptive processing system is aspired to reproduce a transfer function of identified system. After adaptation the identified system becomes “identified” in the sense that its transfer function becomes known. The adaptive filter is adjusted so that its output signal matches to an output signal of unknown system.

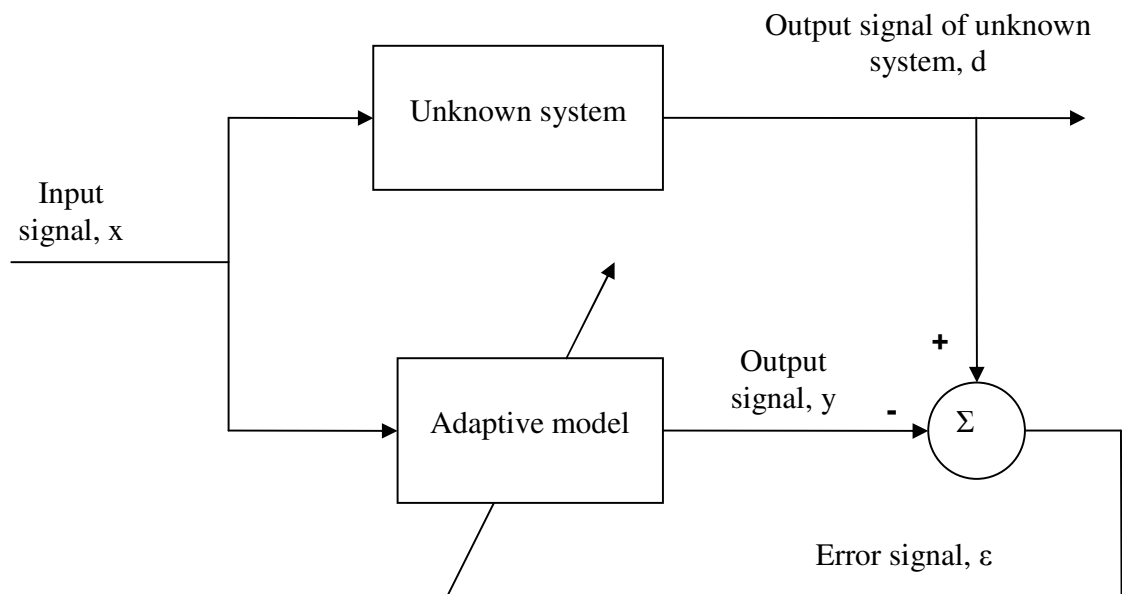


Figure 6. Identification of unknown system by adaptive model.

Close or probably full matching is possible when the adaptive system possesses sufficient pliability, i. e. has sufficient number of freedom degree (overhauled weight factors). After the adaptation the structure and parameters of the adaptive system can match or mismatch the structure and parameters of unknown system; however the intercoupling between an input and output signals will be the same. In this sense the adaptive system becomes model of unknown system.

## 4. EXPERIMENTAL SECTION

For further use in the work the experimentally obtained CARS-spectra are needed. Also Raman spectra of the same substances are necessary for their use as basic data for the analysis.

Below the descriptions of setups by which the spectra gained are presented.

### 4.1 CARS-spectrometer

The CARS-spectra used in this work are obtained on experimental setup of University of Amsterdam. The schematic diagram of the CARS-spectrometer is presented in a fig.

7

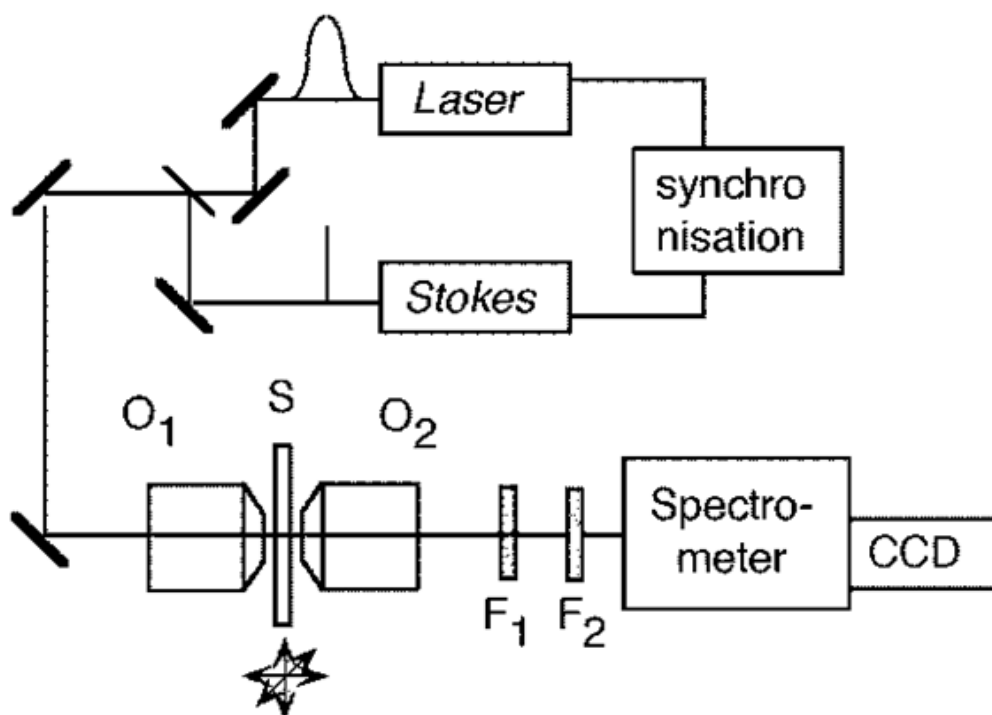


Figure 7. The schematic diagram of the CARS-spectrometer [27].

In this setup the two laser scheme is used. One of the lasers, marked out in figure as “LASER”, generates 10 ps impulses on a wave length 710 nm, with breadth of a spectrum  $1,5 \text{ cm}^{-1}$ . Second, marked out as “Stokes” - 80 fs pulses with breadth of a spectrum  $184 \text{ cm}^{-1}$  with a tunable wave length over the range 700-1000 nm, that allows to gain spectrums of vibrational levels over the range 0-4000  $\text{cm}^{-1}$ . Both of the beams are reduced together and focalized by microscope objective  $O_1$  on specimen S. The last radiation is agglomerated by microscope objective  $O_2$  and guided through filters  $F_1$  and  $F_2$  to a spectroscope with CCD matrix. Owing to a wide spectrum of the femtosecond laser and to using of CCD, all spectrum is gained due the one impulse of lasers.

Parameters of the used components of setup are presented in table 1[27].

Table 1.

Parameters of setup components

Component	Manufacturer	Parameters
Lasers:		
“LASER”	SpectraPhysics, Mountain View, CA	Ti/sapphire, $\lambda = 710 \text{ nm}$ , $\tau = 10 \text{ ps}$
“Stokes”	SpectraPhysics, Mountain View, CA	Ti/sapphire, $\lambda = 700\text{-}1000 \text{ nm}$ , $\tau = 80 \text{ fs}$
Filter $F_1$	Kaiser Optical Systems, Inc.	$\lambda_0 = 710 \text{ nm}$ , $D = 6$ , $\Delta\nu = 280 \text{ cm}^{-1}$
Filter $F_2$	Omega Optical, Inc.	$\Lambda_{\pi} = 710 \text{ nm}$ ,
Spectroscope	Oriel MS257, with CCD Andor V420-OE	$\Delta\lambda = 0,1 \text{ nm}$

## 4.2 Gained CARS-spectra

Gained CARS-spectra of intermixture AMP/ADP/ATP and solution of DMPC are presented on figures 8 and 9 respectively.

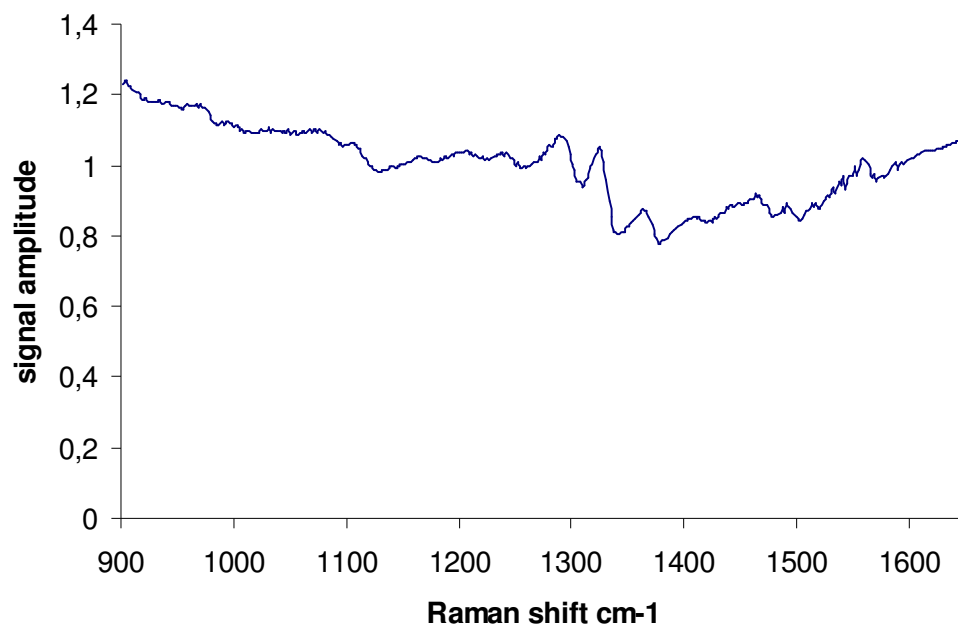


Figure 8. CARS-spectra of intermixture AMP/ADP/ATP.

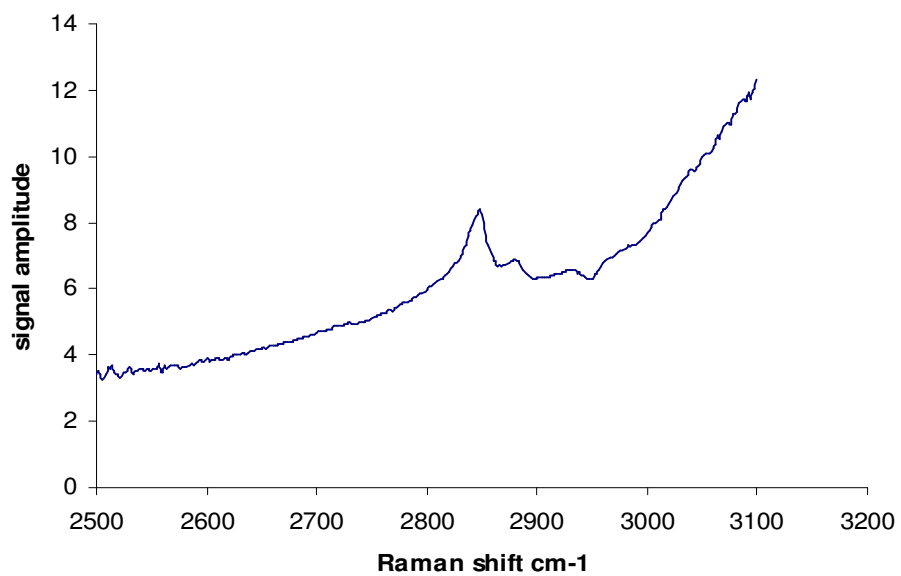


Figure 9. CARS-spectra of DMPC solution.

The imaginary parts of  $\chi(3)$  retrieved by the maximum entropy method are presented on figures 10 and 11.

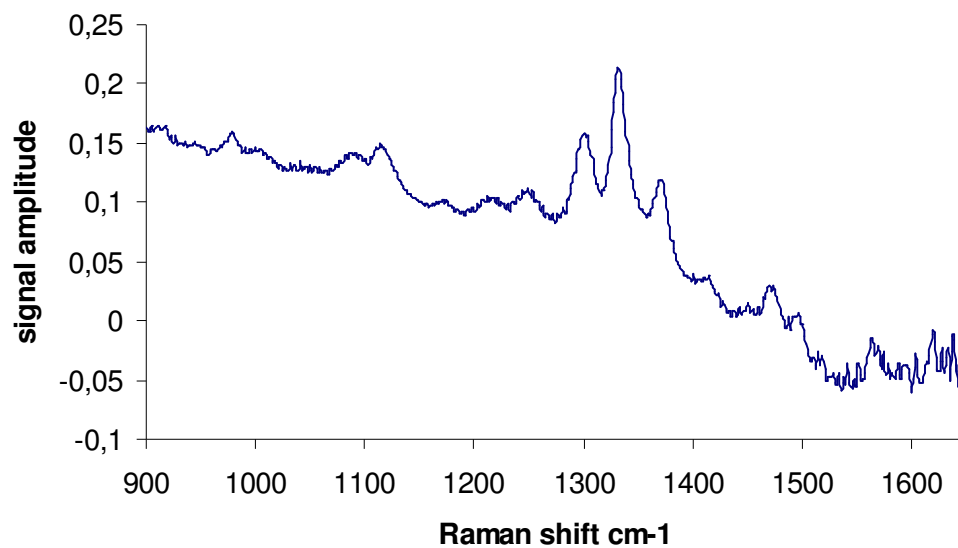


Figure 10. The imaginary parts of  $\chi(3)$  of intermixture AMP/ADP/ATP.

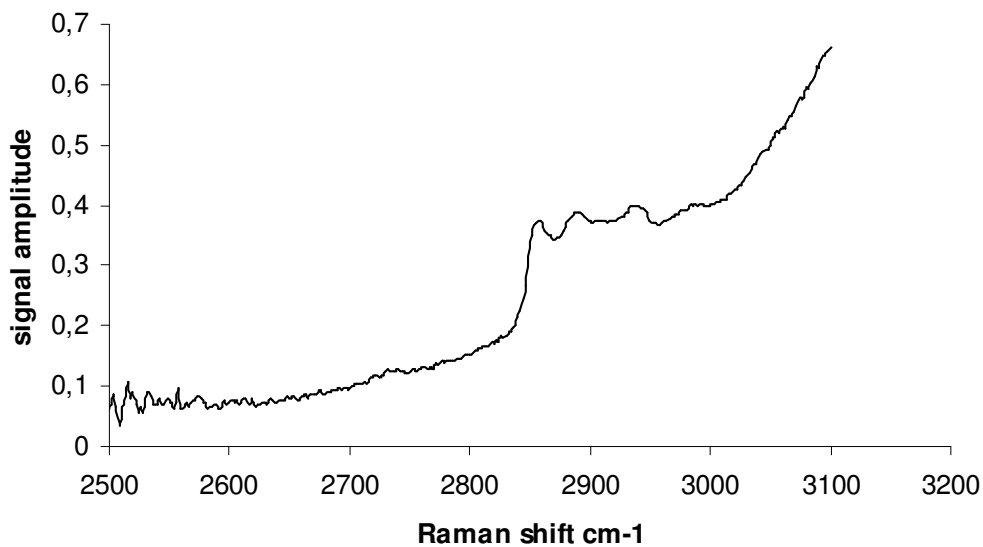


Figure 11. The imaginary parts of  $\chi(3)$  of solution of DMPC.

### 4.3 The used Raman spectra

The Raman spectra of the same substances are necessary for the following work.

The Raman spectra of intermixture AMP/ADP/ATP and solution of DMPC are presented on figures 12 and 13, respectively.

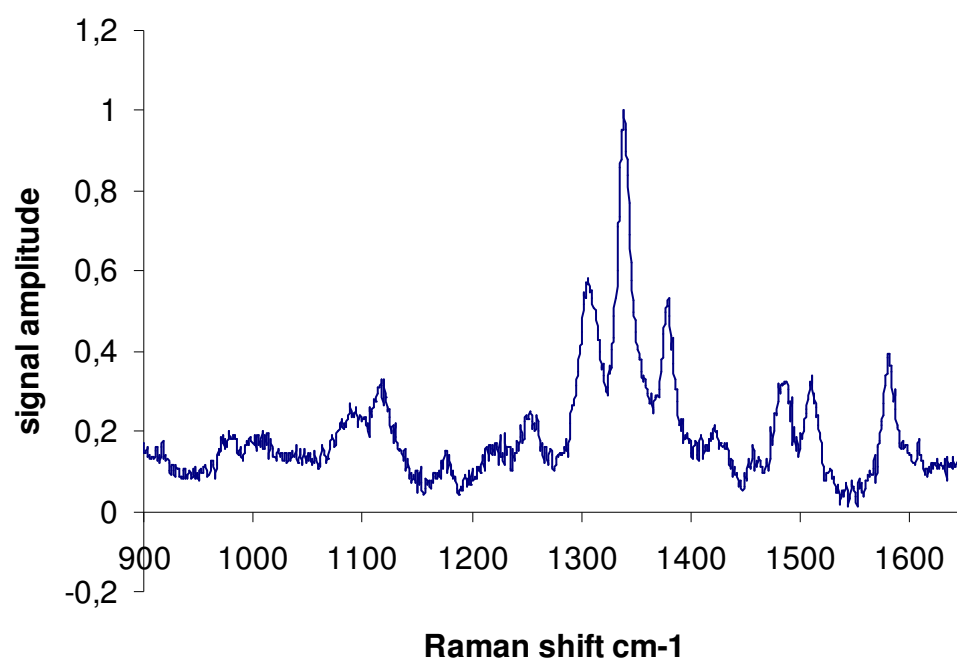


Figure 12. Raman spectra of intermixture AMP/ADP/ATP.

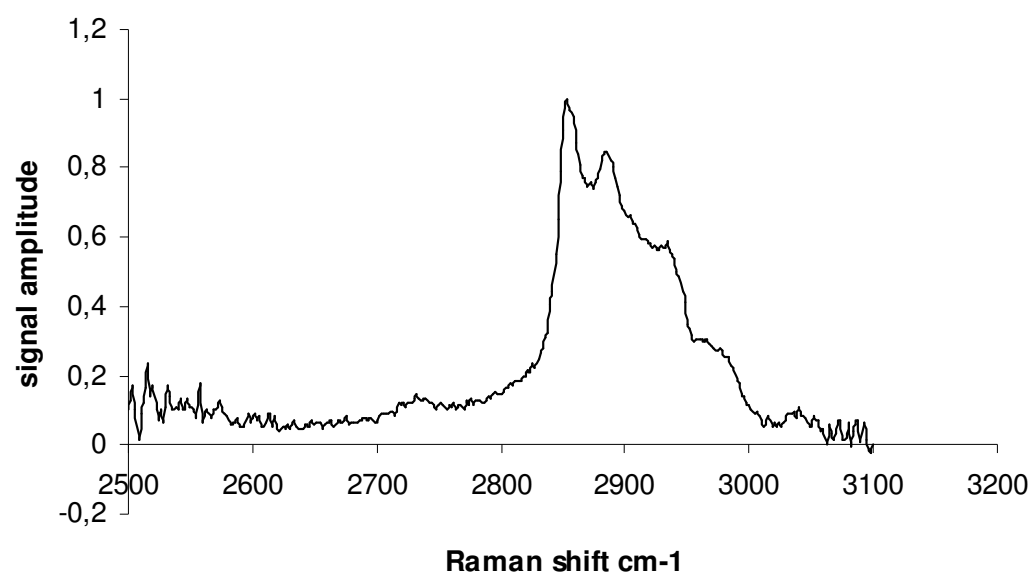


Figure 13. Raman spectra of solution of DMPC.



## **5. DESCRIPTION OF THE ALGORITHM**

### **5.1 Basic requirements to the algorithm**

The primary goal of developed algorithm is automatic detection and a quantitative analysis of concentration of interesting components in a spectrum of the complex substance gained by a CARS-spectrometer. Usually for these purposes the measuring of amplitude of a spectral line on certain, characteristic for required substance, wave length is used. Such method in itself has a row of deficiencies, namely:

- At presence of a noise in a spectrum the result of measurement will change considerably depending on that the maximum of a noise signal or its minimum will get on the measured wave length.

- At overlapping, even partial, a spectral maximum of an interesting component with lines of other components of investigated material, measurement will give incorrect result as magnitude of a signal on characteristic wave length will include the information on both components.

- If the spectrum has non-informative background displacement it is impossible to measure an absolute value of spectrum amplitude. It is necessary to determine firstly the magnitude of displacement on characteristic wave length. It creates the greatest problem at work with CARS spectra as they have displacement of the big magnitude, besides not constant on various wavelengths.

Hence it is possible to formulate the basic requirements to the developing algorithm:

- 1) Resistance against noise.
- 2) Ability to discriminate in a complex spectrum partially overlapped lines, or completely overlapped lines of the various form.

3) Resistance against presence of background displacement and independence of result on its magnitude.

For a possibility of use the algorithm in applications of the high-speed automated analysis, it is necessary also to meet the following requirements:

4) High performance of the method. The algorithm should be as much as possible simple. As the time of reading of one spectrum on CARS-installation can make shares of picoseconds, using of complex mathematical manipulations in an analysis algorithm becomes the factor restricting the general performance of system.

5) Full automation. Not only process of the analysis, but whenever possible and all supporting acts should be spent with minimal work of the operator.

## **5.2 Description and the block diagram**

To meet the above-named requirements the adaptive algorithm comparing investigated complex spectrum with obviously known spectrum of pure target substance is necessary. On-essence, such algorithm is analogous to application of stimulated Raman scattering for pumping, because it acts only on spectral components matching to the lines of the target substance. However, because it doesn't require any specific hardware, it may be used for selecting of any needed component without special configuring.

The algorithm is based on selection of coefficient of proportionality for a target substance spectrum. At multiplication on this coefficient, its form and size must as much as possible match to a form of line in an analysed spectrum. For definition of extent of conformity of spectra, at each stage of matching the difference between them is computed. The difference signal is processed in the feedback module on which exit the parameter reflecting smoothness of a spectral curve is generated. The result of analysis is the value of coefficient of proportionality at which this feedback parameter reaches a minimum (or maximum, depends on method of counting). Final conversion

this coefficient, in view of scales of spectra, will give required concentration of target substance.

Application for measuring concentration of the full spectrum of substance, instead of measuring amplitude of a spectrum on one wave length allows to solve the majority from termed above problems. As the line width in most cases considerably exceeds a spatial frequency of noise in coordinates of a wavelength, the proceeding will automatically average a noise on various lengths of waves. Besides if the shape of lines of different components considerably different, even if they have an equal central wavelength, it is possible to measure them separately owing to difference of lateral branches.

As the absolute value of spectral line amplitude is not measured in the given method, the result is absolutely noncritical to presence of background bias. Also then the target line overlapped by a lateral branch of other one, the second may be viewed as a background, that allows to separate them.

The general block diagram of algorithm is presented on fig. 14

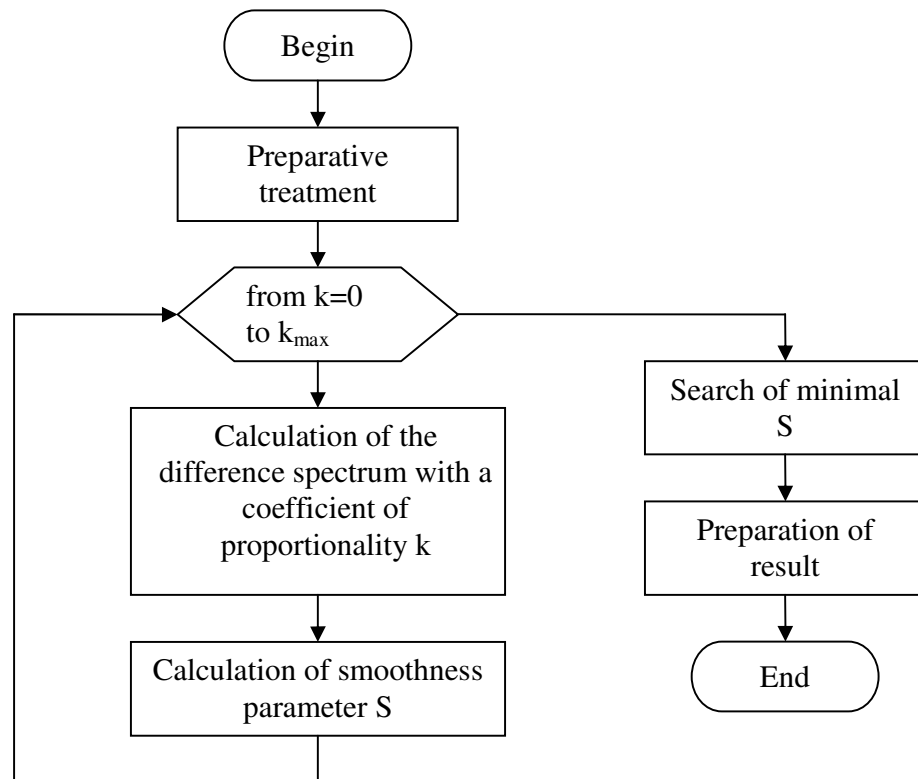


Figure 14. Block diagram of the developed adaptive algorithm.

The block of preparative treatment is necessary for reduction of initial data to a standard format. As the initial spectrum of pure substance can be gained on other installation (for example, on usual Raman spectrometer) rather than investigated complex spectrum, they can have various scale, a wave length step and interval. For correct work of the basic algorithm these parameters should be equal. Also the resolution of spectra may be decreased on that step. That will increase performance of analysis, what may be necessary in experiments, when the temporal resolution of a set of measurements is more important then the spectral resolution.

Search of a factor  $k$  can be carried out by various ways. The simplest method is a sequential search of values from 0, up to some maximum value defined by means of

the coarse analysis of initial spectra. In the simplest case as maximum there can be taken a factor at which maximum values of two spectra coincide. This is enough, because at the further magnification of a basic spectrum the differential spectrum will take negative values, that contradicts its physical nature. At such method of selection, it is possible to increase either a performance or an accuracy of analysing by changing a step of  $k$ . Increasing of both parameters is possible by using of more complicated methods of search, with variable pitch and continuous monitoring of parameter of feedback  $S$ . For example, the binary chop method may be used. . However in this case, if function  $S(k)$  has some local minima, there is a risk of that the result not with the least  $S$  will be chosen.

More important thing is to select the best algorithm of calculation of parameter  $S$ , because the applicability of all analysing method depends on its quality.

### 5.3 Feedback module

For definition of extent of “curvature” of a differential spectrum it is possible to use advantages of a frequency analysis by means of the Fourier-transformation or the wavelet analysis. However as it was noted above, such processing will noticeably lower speed of processing, that is undesirable. Much more sweepingly the extent of function curvature can be defined having analysed its second derivative. As more the value of the second derivative in the given point, as the graph is more strongly bent.

As the spectrum consists of a discrete set of points with equal intervals, it is possible to replace derivatives by a difference of values of neighbouring points.

$$f' = df(\lambda_i)/d\lambda := f(\lambda_i) - f(\lambda_{i+1})$$

$$f'' = d^2f(\lambda_i)/d\lambda^2 := df(\lambda_i)/d\lambda - df(\lambda_{i+1})/d\lambda$$

There  $f$  is a differential function. Let's define the spectral dependence of the imaginary part of CARS spectrum (hereinafter called simply CARS spectrum) as  $f_C$  and spectral dependence of a Raman spectrum as  $f_R$ . In this case the second derivative of the differential function may be described by the following formula.

$$f'' = d^2(f_C(\lambda) - k f_R(\lambda)) / d\lambda^2 = f_C'' - k f_R''$$

where  $k$  is a wanted coefficient of proportionality between CARS and Raman spectra. In turn, the CARS spectrum function may be divided in two parts:

$$f_C = \alpha f_R + f_{CB}$$

Where  $\alpha f_R$  is a Raman component of a CARS spectrum;  $\alpha$  is an unknown constant, which must be found by the developed algorithm to measure quantity of target component;  $f_{CB}$  is a background component of a CARS spectrum. Then the second derivative of the differential function will be:

$$f'' = \alpha f_R'' + f_{CB}'' - k f_R'' = (\alpha - k) f_R'' + f_{CB}''$$

The part  $(\alpha - k) f_R''$  has a variable sign and its sum by all spectrum is near the zero value, but the sum of its absolute values is not zero while  $(\alpha - k)$  is not equal to zero. Because background in CARS spectra is much more smooth than the spectral lines,  $f_{CB}''$  is negligibly small, and doesn't influence on the absolute value of Raman part while it is not zero. Thus the absolute value of differential function may be present in the following form:

$$|f''| = |(\alpha - k) f_R'' + f_{CB}''| = |(\alpha - k) f_R''| + |f_{CB}''|$$

It will have a minimum value when  $(\alpha - k) = 0$  and the coefficient of proportionality  $k$  will be equal to the unknown quantity  $\alpha$ .

The required parameter of smoothness  $S$  may be gained by summarising of the absolute values of the second derivative in each point.

$$S = \sum_{\lambda} |f''|$$

Having computed  $S$  at each value  $k$ , we shall gain curve  $S(k)$  providing a return coupling for search. Its minimal value matches to the maximum conformity of two spectra. In the theory of the adaptive analysis it is named error function.

Let's check the algorithm with simplest models. First of all we shall test it on synthetic spectra generated in program Spectral Assistant 8.0. On fig. 15 the spectrum (solid line) gained by superposition of the Gaussian contour with linear displacement is presented. The initial Gaussian curve will be used as a spectrum of target substance. It is presented in the same figure by a dot line.

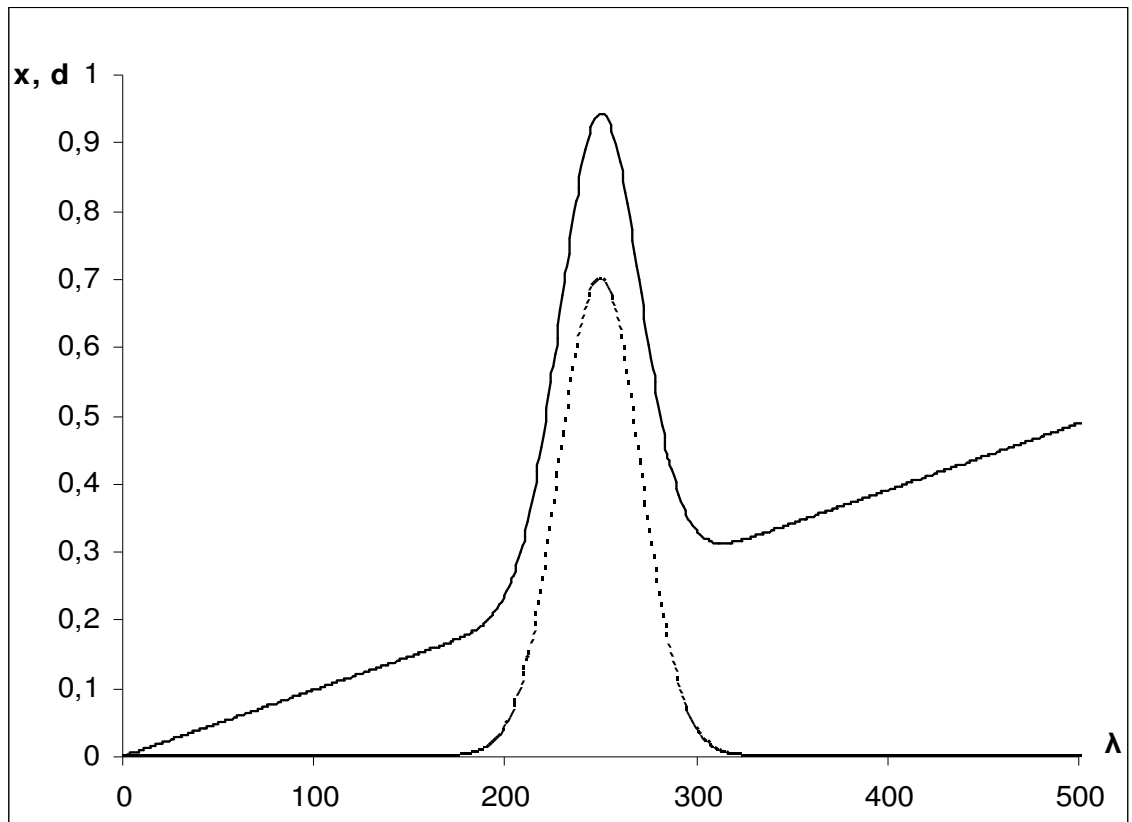


Figure 15 The Gaussian contour with linear displacement (solid line) and a target Gaussian curve (dot line)

As the scale of a contour was not varied at addition of displacement, minimum  $S$  should be gained at  $k=1$ . The differential spectra at various  $k$  are presented on the fig. 16. The function  $S(k)$  is presented on fig. 17. All calculations are made in program Excel.



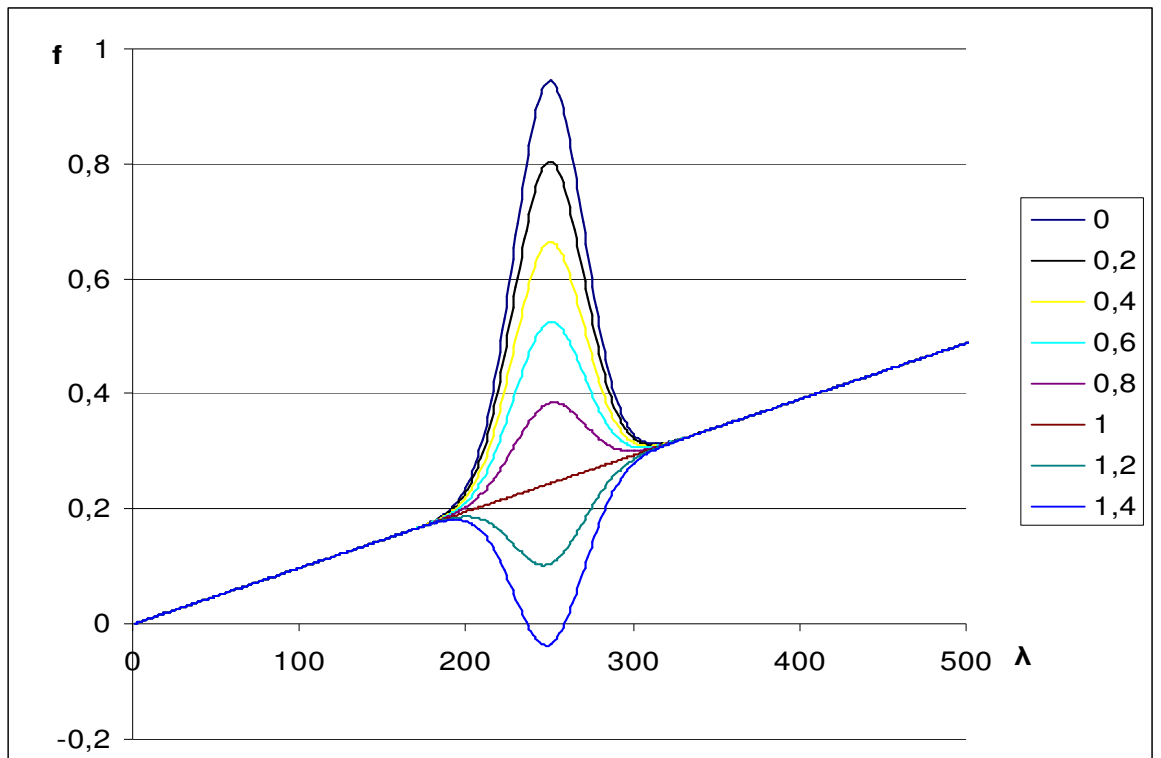
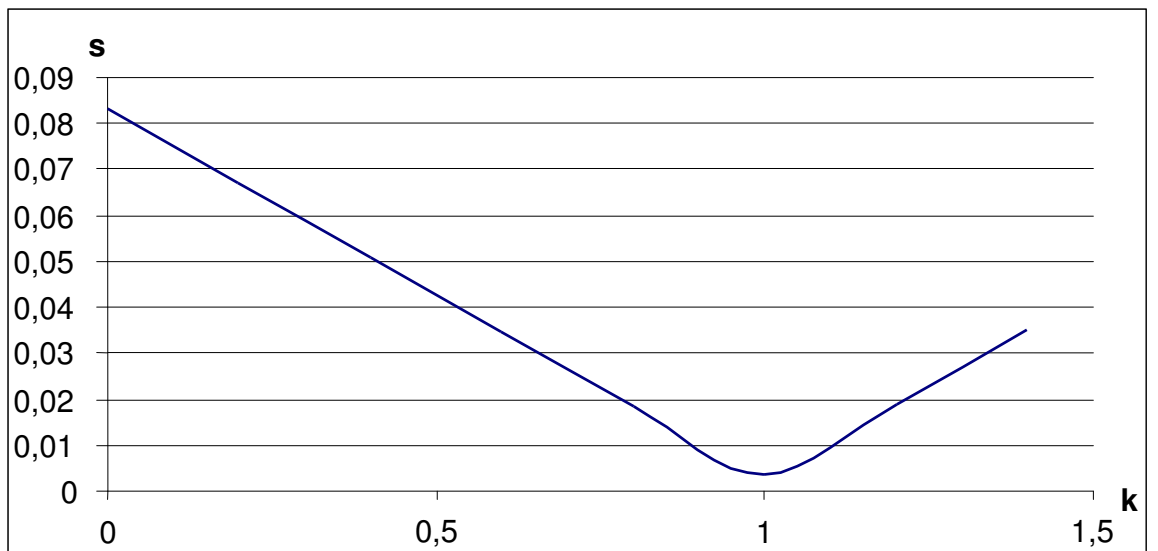
Figure 16. The differential spectra at various  $k$ 

Figure 17. Error function in case of simplest spectra

As may be seen, the minimum of the error function is really placed at point  $k = 1$ .

In figure 18 a more complicated synthetic spectrum is presented. In addition of linear displacement it has the second Gaussian contour partially overlapped with first one. As in previous example the first Gaussian contour (dot line) is used as a base spectrum.

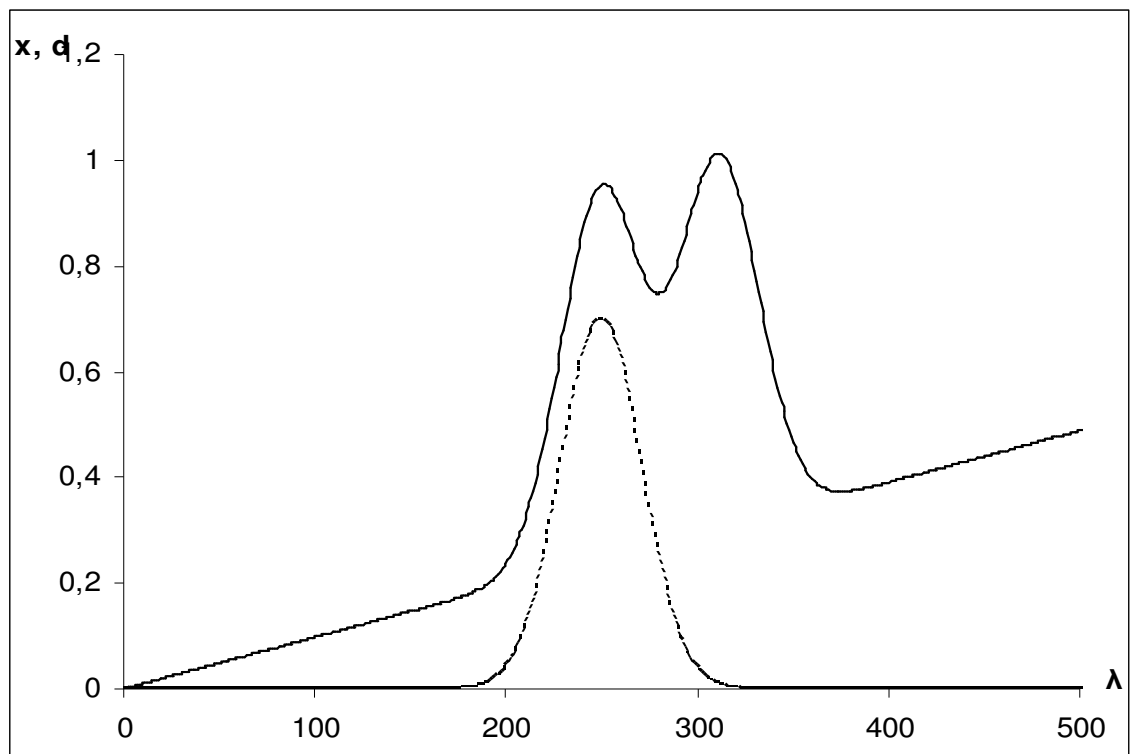


Figure 18. Two Gaussian contours and displacement (solid line) and a target Gaussian curve (dot line)

The differential spectra and error function for this case are placed on figures 19 and 20 respectively.

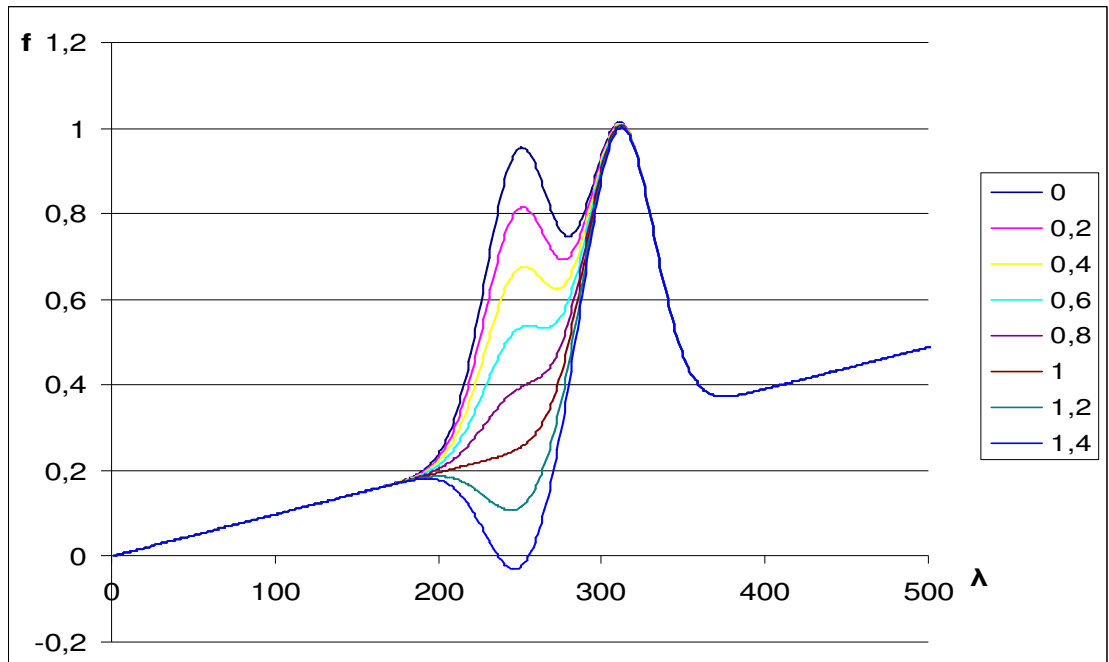


Figure 19. The differential spectra at various  $k$  for the case of two Gaussian contours and displacement.

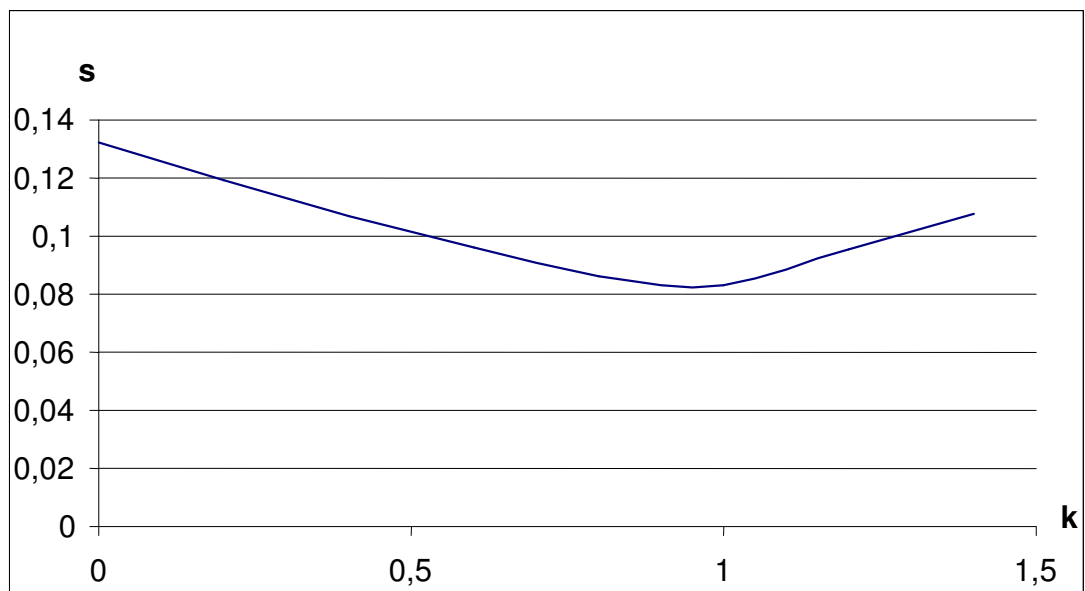


Figure 20. Error function for the case of two Gaussian contours and displacement.

In this case, as it is possible to see, the minimum of error function is expressed not so precisely, as in the previous elementary case, because the second contour always stays on a differential spectrum. Nevertheless, the minimum still is near the value  $k=1$ . Thus the differential spectrum represents the sum of background displacement and the second contour.

#### 5.4 Influence of a noise to the work of algorithm

The CARS and the Raman spectra may have a noise component with high spatial (in coordinates of wave length) frequency. In this case differential function will have additional components:

$$f'' = \alpha f_R'' + f_{CB}'' + f_{CN}'' - k(f_R'' + f_{RN}'') = (\alpha - k)f_R'' + f_{CB}'' + f_{CN}'' - kf_{RN}'',$$

where  $f_{CN}$  is a noise component of the CARS spectrum and  $f_{RN}$  is a noise component of the Raman spectrum.

Firstly let's look on the case of  $f_{RN} = 0$ . The background component as before may be neglected. The second derivative of the noise has a big values and variable sign. It takes a positive or negative sign with actually equal probability. Thus the sum of absolute values of the differential function may be described by the following equation.

$$\begin{aligned} S &= \sum_{\lambda} |f''| = \sum_{\lambda} |(\alpha - k)f_R'' + f_{CB}'' + f_{CN}''| = \\ &= \sum_{\lambda, (\alpha - k)f_R'' f_{CB}'' > 0} \{ |(\alpha - k)f_R''| + |f_{CB}''| + |f_{CN}''| \} + \sum_{\lambda, (\alpha - k)f_R'' f_{CB}'' < 0} \{ |f_{CN}''| - |(\alpha - k)f_R''| + |f_{CB}''| \} = \\ &= \sum_{\lambda, (\alpha - k)f_R'' f_{CB}'' > 0} \{ |(\alpha - k)f_R''| + |f_{CB}''| \} + \sum_{\lambda, (\alpha - k)f_R'' f_{CB}'' < 0} \{ -|(\alpha - k)f_R''| - |f_{CB}''| \} + \sum_{\lambda} |f_{CN}''| \approx \sum_{\lambda} |f_{CN}''| \end{aligned}$$

Thus, in this case the resulting parameter S will not depend on coefficient  $k$ . It means, that the algorithm will not work. This problem may be solved by changing of the absolute value by the squared value.

$$\begin{aligned}
S &= \sum_{\lambda} (f'')^2 = \sum_{\lambda} ((\alpha-k)f_R'' + f_{CB}'' + f_{CN}'')^2 = \\
&= \sum_{\lambda} ((\alpha-k)f_R'' + f_{CB}'')^2 + \sum_{\lambda} 2((\alpha-k)f_R'' + f_{CB}'')f_{CN}'' + \sum_{\lambda} f_{CN}''^2 = \\
&= \sum_{\lambda} ((\alpha-k)f_R'' + f_{CB}'')^2 + \sum_{\lambda} 2((\alpha-k)f_R'' + f_{CB}'') \sum_{\lambda} f_{CN}'' + \sum_{\lambda} f_{CB}''^2 \approx \\
&\approx \sum_{\lambda} ((\alpha-k)f_R'' + f_{CB}'')^2 + \sum_{\lambda} f_{CN}''^2
\end{aligned}$$

The second term of the trinomial was excluded because the sum of noise second derivative on whole spectrum is equal to zero.

Thus using of the squared value instead of absolute one allows to exclude influence of the noise in CARS spectra on the result of analysis. This may be illustrated by the following example. The spectrum analogous to previous, but with addition of a pseudo-random noise is presented on fig. 21.

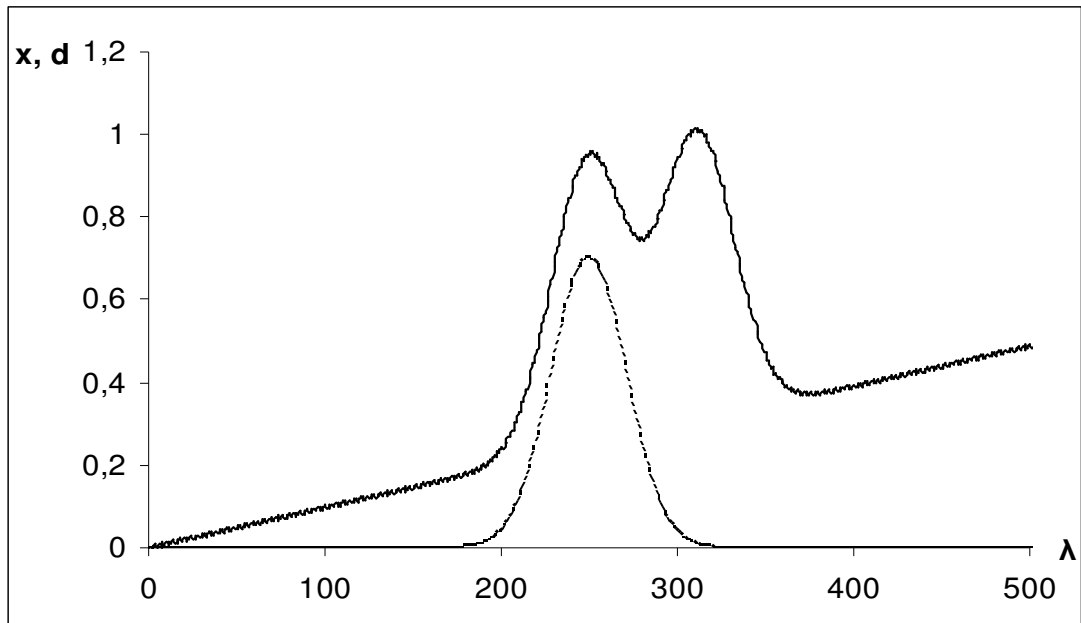


Figure 21. Spectrum with pseudo-random noise (solid line) and a target Gaussian curve (dot line).

The differential spectra for this case are placed in figure 22.

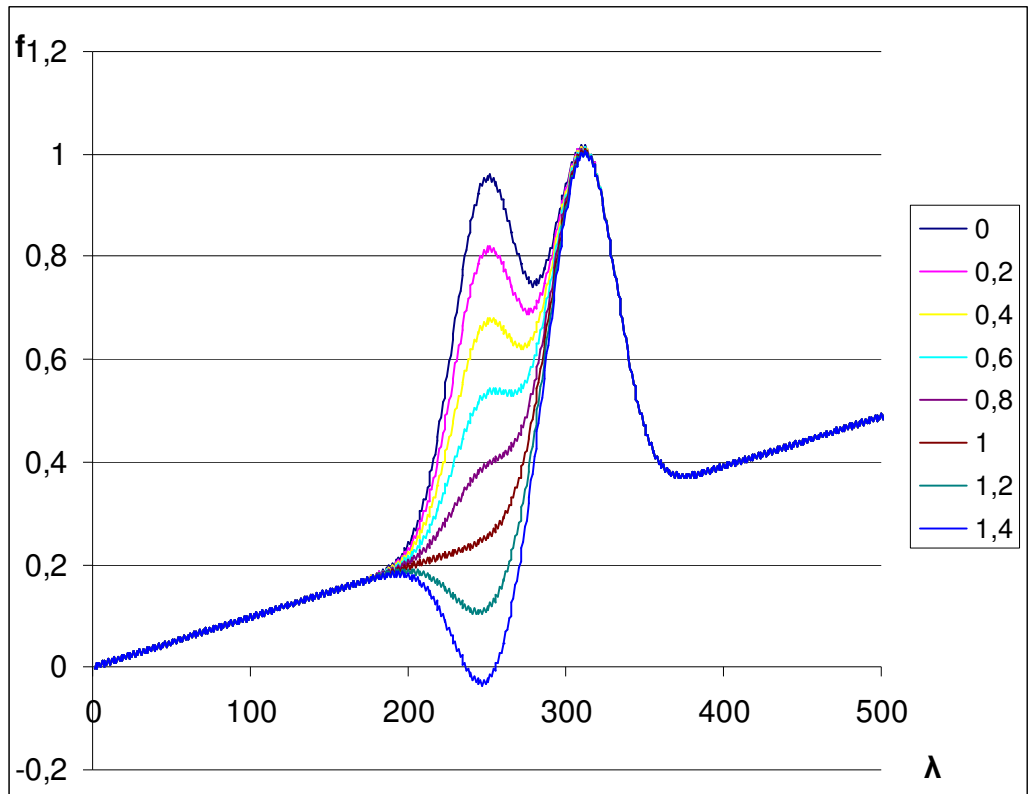


Figure 22. The differential spectra at various  $k$  for the case spectrum with noise.

The error functions gained at use of absolute value and squared value of the second derivative of differential function are presented on figures 23 and 24, respectively.

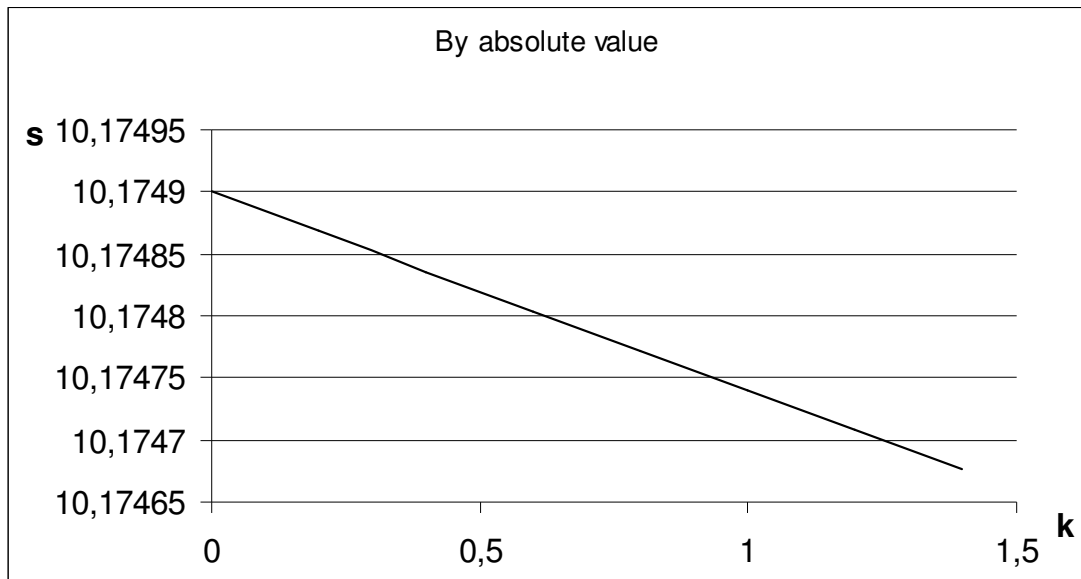


Figure 23. The error functions gained at use of absolute value the second derivative.

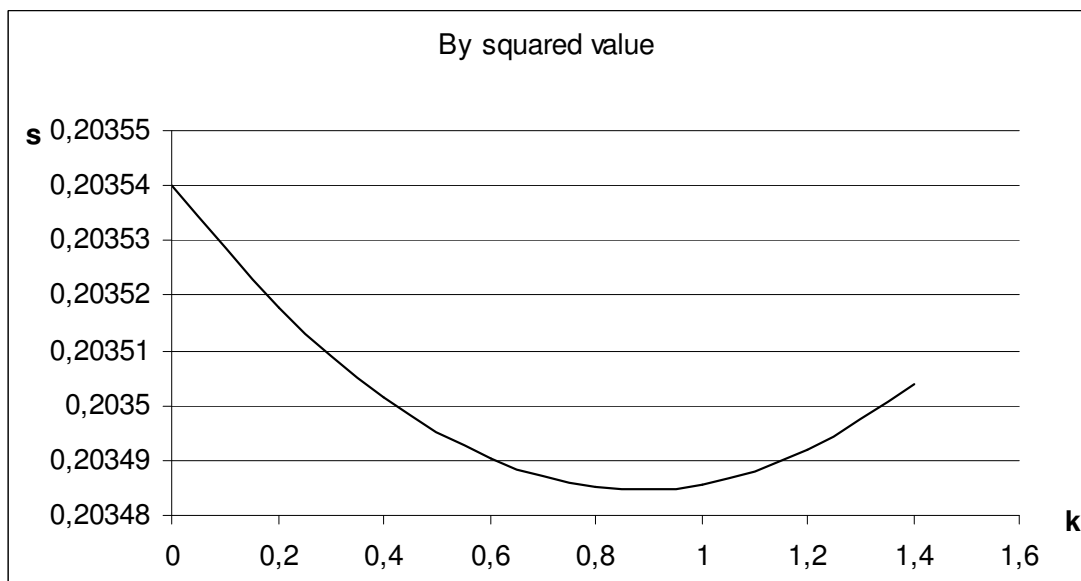


Figure 24. The error functions gained at use of square of the second derivative.

As may be easily seen, in first case the result is absolutely incorrect. In same time, using of square of the second derivative gives the quite correct error function with minimum around point  $k=0,9$ .

If the basic Raman spectra include a noise not correlated with noise of CARS spectra, its term ( $-k f_{RN}$ ) in the equation of second derivation will significantly increase the total value of parameter  $S$ , as soon as  $k$  becomes different from zero. Thus the minimum of the error function will be shifted toward the zero as close as high the noise level. The only way to suppress this effect is to smooth out the Raman spectra. The simplest way for it is point-by-point averaging, when each point of an averaged spectrum is calculated as mean value of several neighboring points. The amount of needed point depends on spectral resolution and may be from 1 – 2 periods of noise fluctuations and higher, but not higher then width of measured spectral line.

### **5.5 Influence of the frequency shift on quality of measurements**

Let's analyse what will happen if the Raman spectrum will be shifted by frequency. On the fig. 25 the differential spectra of the same pair of spectrums like on fig.18 are presented, but there the Raman spectra are shifted on two steps in each direction. The parameter  $k$  is a constant and equal to unit, that corresponds to a best matching in case of not shifted spectra.



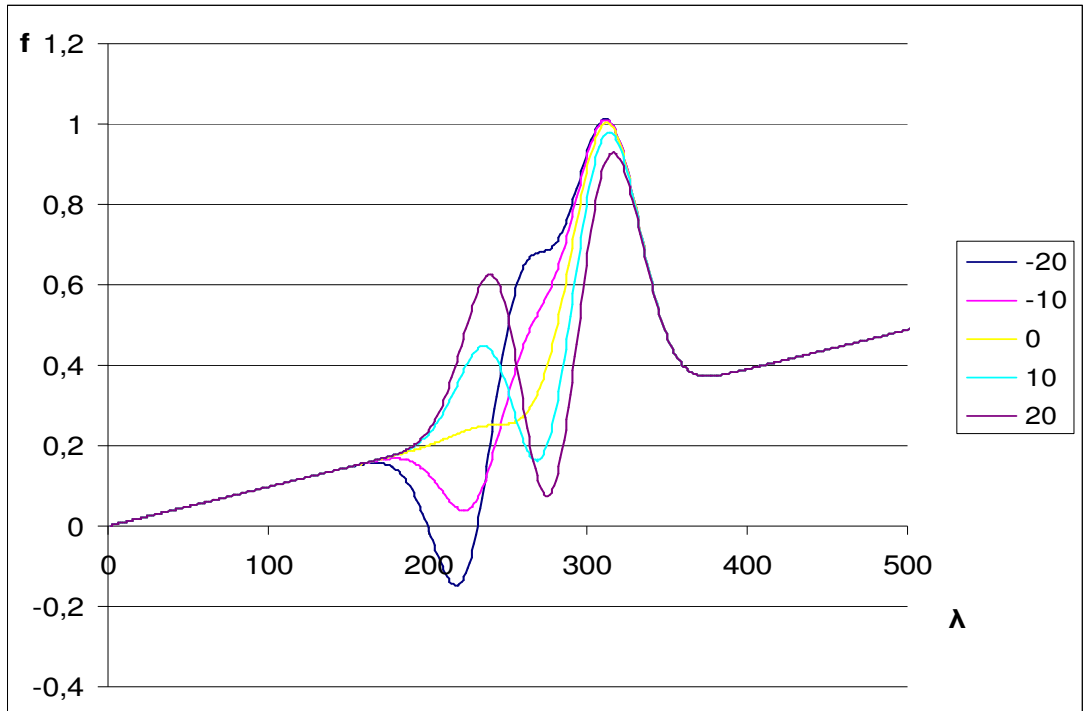


Figure 25. Differential spectra with shifted Raman spectrum. The numbers indicate a value of shift.

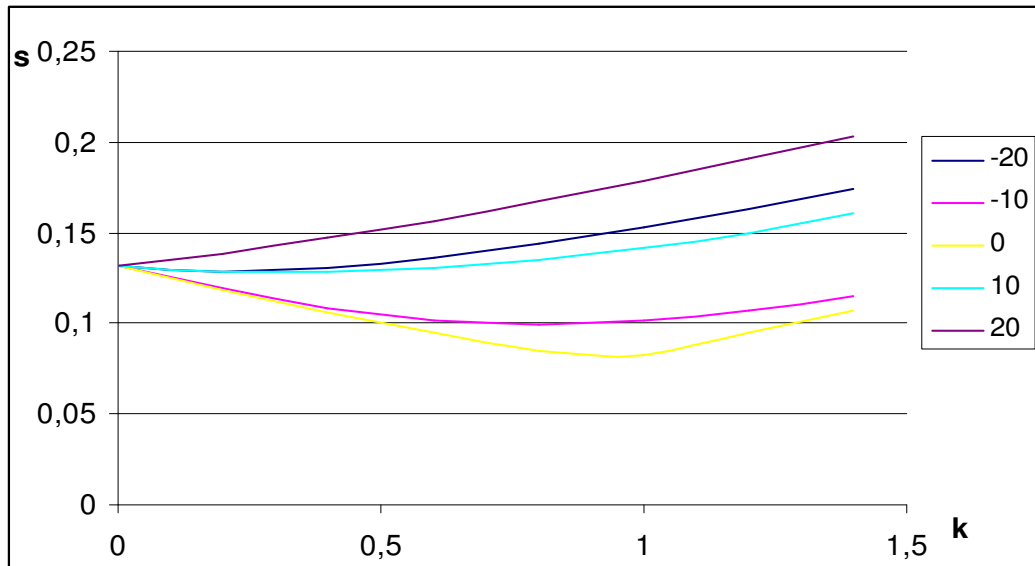


Figure 26. Series of error functions with shifted Raman spectrum.

As may be easily seen, even small shift on  $1/5$  of a Gaussian line half-width (50 points) seriously distort the form of the differential function. This behavior may be explained by the fact, that the spectra become not correlated. This distortion dramatically influences on the result of measuring. On the fig. 26 the series of error functions according to the different values of shift is presented.

Then Raman spectrum has a small frequency shift, minimum of error function moves to the smaller values of  $k$ . Then spectra became fully uncorrelated the minimum of  $s$  becomes placed in point  $k=0$ . This means, that no components with such shifted spectral line are presented in CARS spectra.

If it is known, that one of the pair of spectra is shifted, then it possible to select the correct position. For that purpose the series of error functions like on fig. 26 must be made. The one of them, which has a minimum at higher  $k$  match to the best position of the spectra.

## 6. CHECKING OF THE ALGORITHM ON REAL SPECTRA

The next step is a checking of algorithm on experimentally gained spectra of AMP/ADP/ ATP intermixture and solution of DMPC. The Raman and CARS- spectra of these solutions are presented on fig. 9, 10, 12 and 13. As concentrations of substances are not known, correctness of operation of algorithm can be estimated by the shape of differential function, which at the correct selection of coefficient  $k$  should be a curve of background bias.

The CARS and Raman spectra of AMP/ADP/ATP intermixture are presented on figure 27. The differential spectra and the error functions are presented on fig. 28 and 29 respectively.

As it is possible to see, the minimum of  $S$  occurs near the value  $k = 0,075$ . The differential curve at this value do not has the smoothest form. The reason for it is the considerable disparity of the lateral parts of spectra. The result may be significantly improved by limiting of analysed band to range from  $1200 \text{ cm}^{-1}$  to  $1400 \text{ cm}^{-1}$ . The error function gained in that range presented on figure 30. In this case the minimum placed between the points  $k=0,15$  and  $k=0,2$ , that correspond to the most smooth lines on fig. 28.

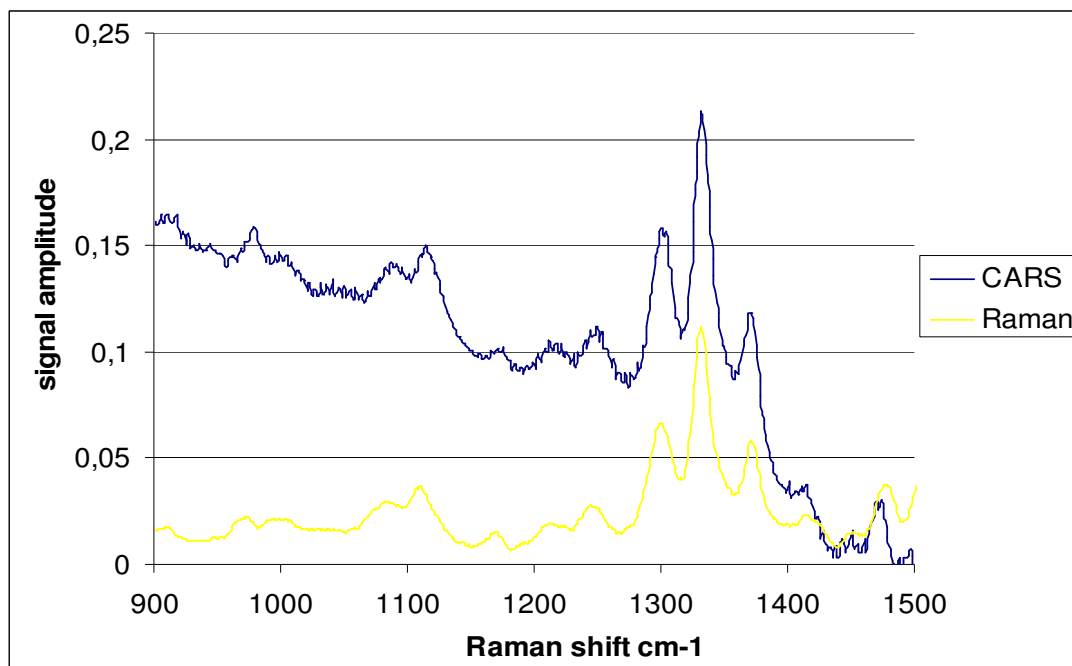


Figure 27. The CARS and Raman spectra of AMP/ADP/ATP intermixture

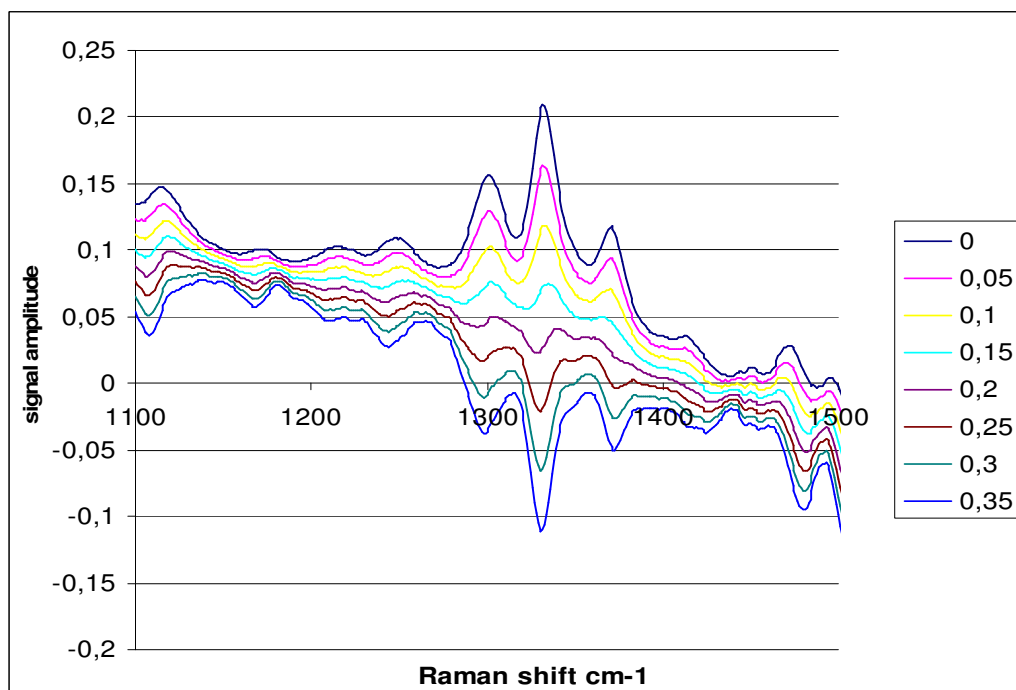


Figure 28. The differential spectra for AMP/ADP/ATP intermixture at various  $k$

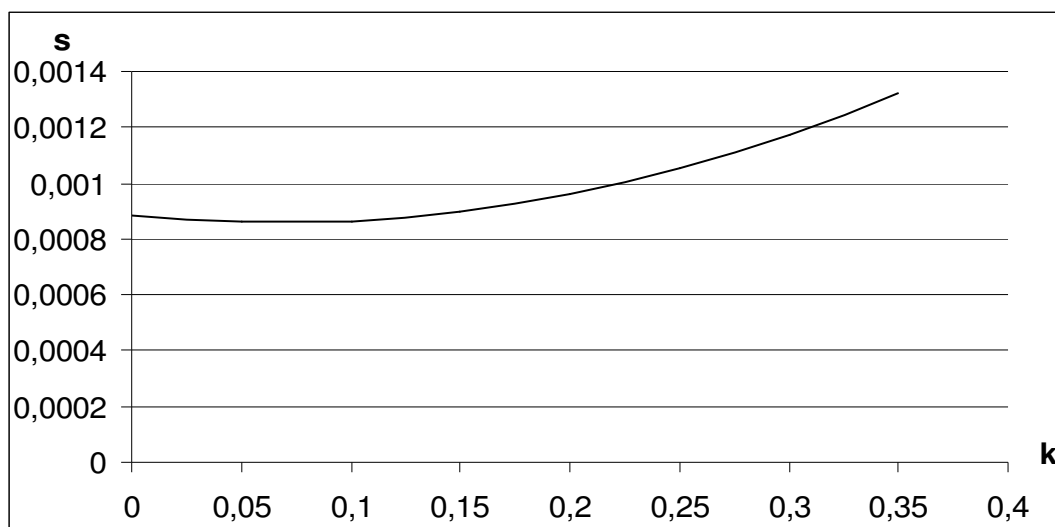


Figure 29. Error function for intermixture AMP, ADP and ATP

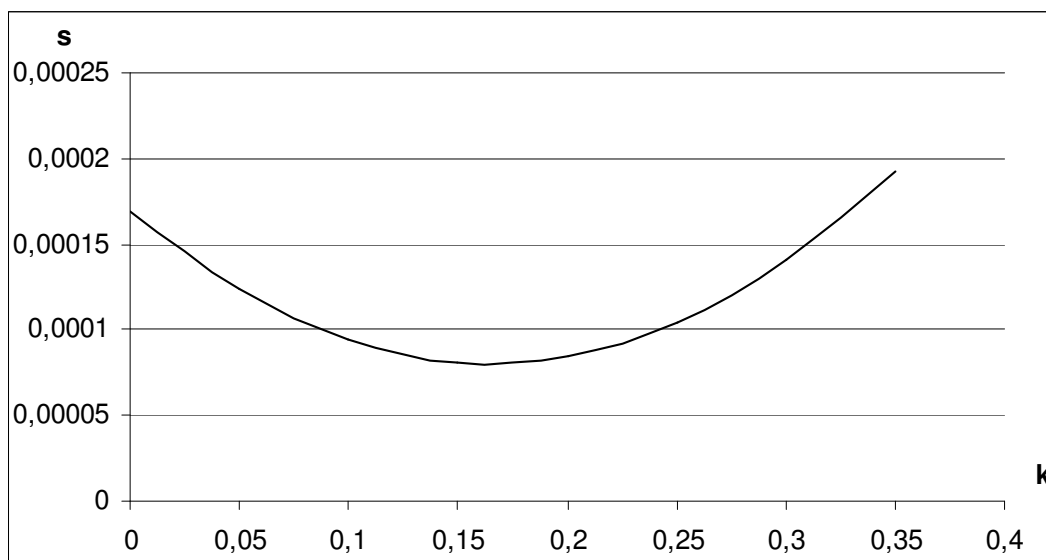


Figure 30. Error function for intermixture AMP, ADP and ATP gained in spectral range  $1200 \text{ cm}^{-1} - 1400 \text{ cm}^{-1}$ .

At the pictures 31, 32 and 33 the analogues spectra for the solution of DMPC are presented.

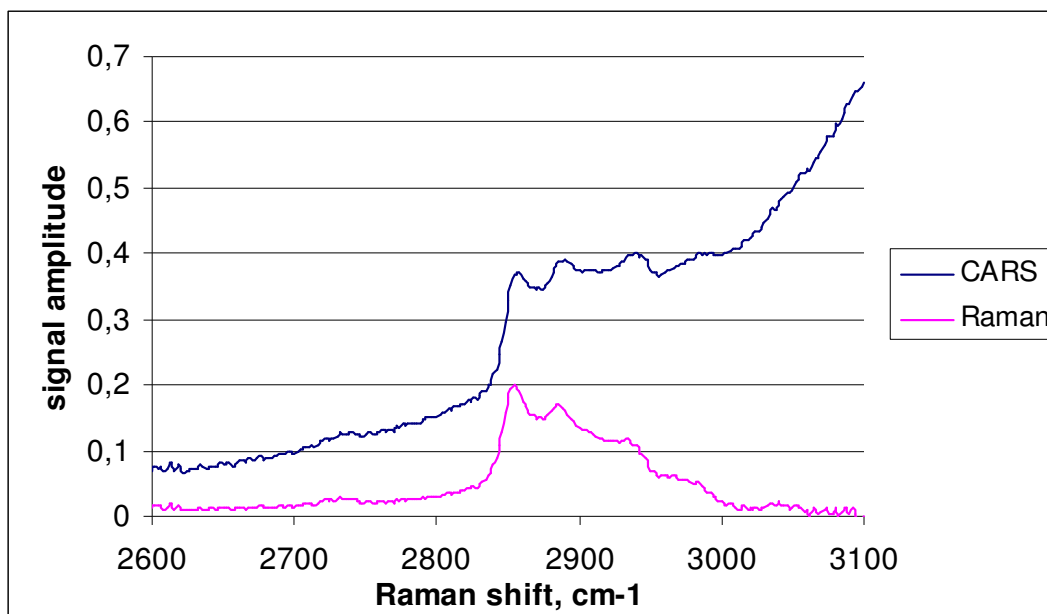


Figure 31. The CARS and Raman spectra of solution of DMPC.

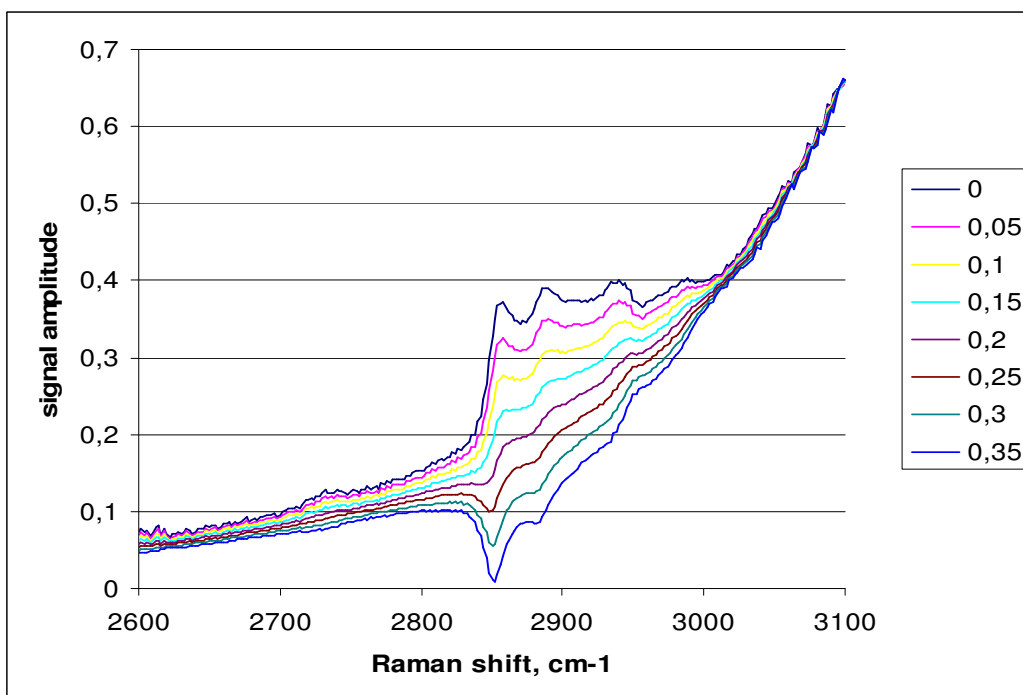


Figure 32. The differential spectra for solution of DMPC at various k

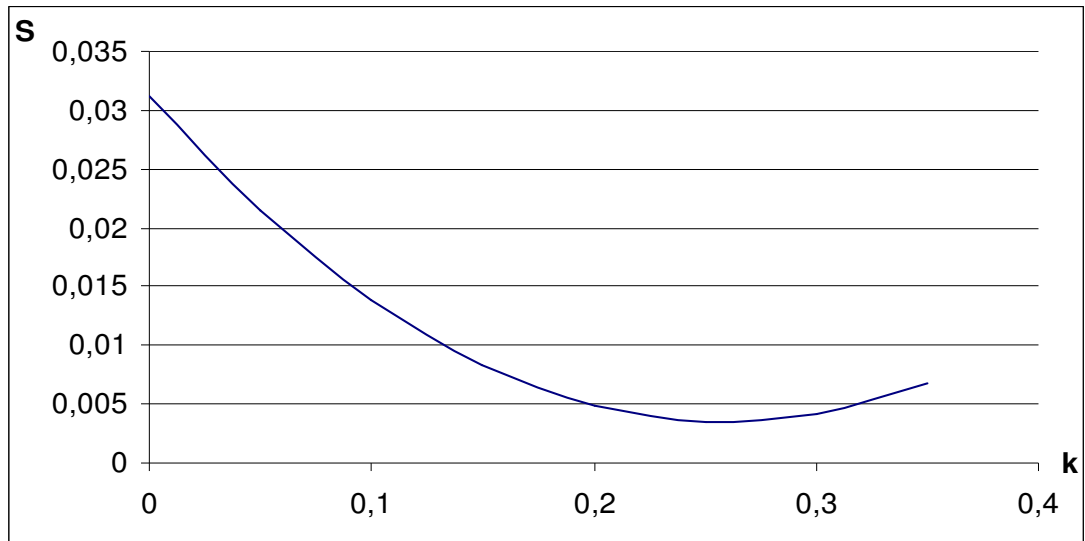


Figure 33. Error function for solution of DMPC

The value  $k = 0,25$ , at which  $S$  has a minimum, well corresponds to the most smooth line on figure 30. That confirms the efficiency of the developed search algorithm.

## 7. CONCLUSIONS

In the presented work some ways of using of CARS spectroscopy for the analysis of composition and parameters of investigated medium have been observed. However all of them have the certain deficiencies. In particular, the method of search of the certain component in gases with application of RS pumping, at all advantages, does not allow to investigate various components by one device, without serious customising. Processing of CARS-spectra by means of a method of the maximum entropy allows to gain the full information on the analysing object, but presence in the gained spectrum of variable background displacement considerably complicates their automated processing. From experimental data it is easy to see, that the spectra are considerably distorted. So the analyzing of such spectra in most cases requires handwork, what considerably retards researches. Application of methods of the adaptive analysis allows to automate this process hence makes it much faster and cheaper.

The algorithm of the automated quantitative analysis developed in this work allows to measure spectral lines, ignoring presence of background bias in a spectrum. Also it allows to measure magnitudes of partially overlapped lines. These advantages are based on the fact, that in the given method consecutive trimming of a scale of the whole spectrum of pure target substance to a spectrum of an explored intermixture is used, instead of measuring of an absolute value in one point with the characteristic for the given substance wavelength. For a quality control of trimming operation the algorithm for a quantitative evaluation of smoothness of a differential spectrum based on the analysis of its second derivative is used.

During the trial of algorithm for the elementary simulated models and real spectra its serviceability has been confirmed. The resistance to a noise in CARS spectrum has also been proved. However it has been found out, that at presence of noise in a Raman spectrum the measurement accuracy considerably decreases. It is necessary to apply smoothing of the spectrum. The simplest way to solve this problem is a point-by-point averaging. The influence of the frequency shift between CARS and Raman spectra on



precision of measurements was also investigated. It is found that comparing of measurements results with various values of shift allows to find a correct matching of spectra.

On the example of AMP/ADP/ATP intermixture it was found that selecting of the most correct spectral range is necessary to get the maximum precision. Including of the non-correlated parts to the comparing range significantly decreases the gained result.

## REFERENCES

1. A. F. Bunkin, N. I. Koroteev, Nelineynaya lazernaya spectroscopiya gazov, gazovyh potokov i nizektemperaturnoy plazmy, (rus), Uspekhi Fizicheskikh Nauk, 134, 93 (1981).
2. M. D. Duncan, J. Reintjes, and T. J. Manuccia, Scanning coherent anti-Stokes Raman microscope, OPTICS LETTERS 8, 350 (1982).
3. Ji-Xin Cheng, X. Sunney Xie Coherent Anti-Stokes Raman Scattering Microscopy: Instrumentation, Theory, and Applications. J.Phys. Chem. 108 827 (2004).
4. Raman Spectroscopy Tutorial. <http://www.kosi.com/raman/resources/tutorial/>
5. O. Svelto, Principy lazerov, (rus.), Moscow: “Mir”, (1990)
6. D. L. Mills, Nonlinear Optics: basic concepts,(1991)
7. N. I. Koroteev, Interferencionnye yavleniya v kogerentnoy aktivnoy spektroskopiya rasseyaniya i pogloshcheniya sveta: golograficheskaya mnogomernaya spektroskopiya Uspekhi Fizicheskikh Nauk, 152 493 (1987).
8. Lecture notes on Laser Spectroscopy at the ERCOFTAC summer school “Introduction to Numerical and Experimental Methods in Combustion Research” ETH Zьrich, March 15-21, 2002. 4.Coherent anti-Stokes Raman Spectroscopy (CARS). <http://cdg.web.psi.ch/Summerschool/chap4.pdf>
9. E. M. Vartiainen. Analysis of coherent Raman spectra. J. Opt. Soc. Am. B/Vol. 7, No. 5 (1990).
10. Erik M. Vartiainen. Phase retrieval approach for coherent anti-Stokes Raman scattering spectrum analysis. J. Opt. Soc. Am. B/Vol. 9, No. 8 (1992).

11. Erik M. Vartiainen,\* Kai-Erik Peiponen, And Toshimitsu Asakura, Phase Retrieval in Optical Spectroscopy: Resolving Optical Constants from Power Spectra, APPLIED SPECTROSCOPY Vol. 50, No. 10 (1996).
12. E. M. Vartiainen, H. A. Rinia, M. Müller, and M. Bonn, Direct extraction of Raman line-shapes from congested CARS spectra, Opt. Express 14, 3622 (2006)
13. H. A. Rinia, M. Bonn, M. Müller and E. M. Vartiainen. Quantitative CARS spectroscopy using the maximum entropy method: the main lipid phase transition. Submitted to: JOSA B, (2006).
14. Lecture notes on Laser Spectroscopy at the ERCOFTAC summer school “Introduction to Numerical and Experimental Methods in Combustion Research” ETH Zürich, March 15-21, 2002. 3 Application of Raman spectroscopy: Species concentration and temperature measurements for catalytically stabilized combustion.  
<http://cdg.web.psi.ch/Summerschool/chap3.pdf>
15. Georgi I. Petrov, Rajan Arora, Vladislav V. Yakovlev, Xi Wang, Alexei V. Sokolov, and Marlan O. Scully. Comparison of coherent and spontaneous Raman microspectroscopies for noninvasive detection of single bacterial endospores. PNAS vol.104 no.19, 7776 (2007).
16. Regnier P. R., Taran J. P. E — Appl. Phys. Lett., 23, 240 (1973).
17. Atta1 B., Pealat M., Taran J. P. E. CARS Diagnostics of Combustion: Paper presented at the AIAA 18th Aerospace Science Meeting Pasadena. USA, AIAA Paper 80-0282 (1980).
18. Kozlov D. N., Prokhorov A. M., Smirnov V. V, J. Mol. Spectr., 77, 21 (1978)
19. Paul Scherrer Institute Combustion Research Laboratory <http://crl.web.psi.ch/>

20. F. V. Bunkin, F. V. Kalinin, P. P. Pashinin, *Kvant. elektron. (rus)* 5, 468 (1978).
21. F. V. Bunkin, F. V. Kalinin, *Fiz. plazmy (rus)* 5, 745 (1979).
22. A. M. Zheltikov, *Femto i attosekundnaya spektrokronografiya (rus)*, UMP, Fizfak MGU, (2006)
23. S. A. Akhmanov, V. A. Vysloukh, A. S. Chirkin. *Optika femtosekundnyh lazernyh impul'sov (rus)*. (1988)
24. N. Blombergen. *Nelineynaya optika (rus)*. (1966).
25. G. M. Miheev, T. N. Mogileva. *Optimizaciya i primenenie VKR-generatora dlya kontrolya vodoroda metodom KARS, Kvant. elektron. (rus)*, 23, 943 – 946 (1996).
26. B. Widrow, S. Stearns, *Adaptivnaya obrabotka signalov (rus)*, Moskow, (1989).
27. Michiel Muller, Juleon M. Schins. *Imaging the Thermodynamic State of Lipid Membranes with Multiplex CARS Microscopy. J. Phys. Chem. B* 106, 3715-3723 (2002).