CoRa: An Innovative Software for Raman Spectroscopy

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An innovative software CoRa with friendly user interface for Raman spectroscopy has been developed. The interface and functionality of CoRa have been discussed in this paper. Two examples of practical usage of CoRa for data analysis of amorphous $Ge_3Sb_2Te_6$ and CdP_2 singly crystal have been demonstrated.

Keywords: Raman spectroscopy, Program, Data analysis.

PACS numbers: 81.70. − q, 78.20. − e

1. INTRODUCTION

Optical spectroscopy is a powerful tool of studying the properties of physical objects based on measuring their interaction with visible, ultraviolet, or infrared light. It is an important technique in modern scientific and industrial fields [1].

Fitting of IR and Raman spectra gives great power to the researcher. The correct interpretation of the experimental data enables to extract information about the optical properties, chemical composition of studied object [1, 2].

The market offers plenty of programs aimed to treat the experimental IR and Raman data. They can be divided into two main groups: first group comes from independent software developers, other are offered by hardware manufacturers. Most of the products posse rich functionality can solve many different spectroscopic tasks, but few of them can boast about their usability. Someone considers that the user interface is like a joke: it is not good anymore if you have to explain it. Many of researchers who have experience in fitting of IR and Raman spectra may agree that, on one hand it does not have to take much time to understand the program's interface, on the other hand all necessary functions must be present.

Once working with experimental Raman data we decided to develop own software tool, which will combine the all these features and which might simplify the work of other spectroscopists. Proposed program CoRa – Cologne Raman Tool – was named after the city where it was programmed. Firstly, it is to develop the software which can treat experimental data, fit it and can be able to export results as a graph or a table to be used in papers, presentations, reports, etc. As program's logo Raman spectrum of one of the typical samples was chosen. The spectrum is very resembling to the profile of the Cathedral of Cologne which is very recognizable.

2. THEORY

Raman and absorption peaks can be described by well-known Gaussian and Lorentzian profiles [2]. A Gaussian function is used in the program in following form:

$$f(x) = a \exp\left(-\frac{(x-b)^2}{2c^2}\right),\qquad(1)$$

where the parameter a is the height of the curve's peak, b is the position of the center of the peak, c controls the width of the "bell".

Lorentzian profile has a following form:

$$f(x) = \frac{bgx/x_0^2}{\left(1 - (x/x_0)^2 + gx/x_0^2\right)},\qquad(2)$$

where the parameter g controls the height of the curve's peak, x_0 is the position of the center of the peak and b is responsible for the width of the peak. It also has "bell" shape, but has longer wings.

As shown above, both Gaussian and Lorentzian profiles are characterized by three parameters: location (frequency), height (intensity) and line width (broadening) [2]. The location of a peak is controlled first by the natural vibrational frequency of the isolated molecule. The height of a peak depends on the number of molecules present (concentration) and the strength of the absorption.

Resulting Raman spectrum is a sum of Gaussians and Lorentzians, which describe active phonons. In order to find the best agreement between the calculated spectra and the experimental data, the least-square deviation δ was minimized:

$$\delta = \frac{\sqrt{\sum_{i=1}^{N}\left(R_{i\exp} - R_{icalc}\right)^2}}{N},\qquad(3)$$

where $R_{i\exp}$, R_{icalc} are the values of experimental and calculated reflectance in the i-th point of the spectrum, and N is the number of measurement points in the spectrum.

The area of the peak is an indicator of concentration, because the final peak profile is the sum of all the individual elements. In some cases, the peak height can be changed by some broadening mechanisms, but the area will remain constant as the total number of molecules is constant. To calculate the peak area the trape-

zoidal rule was used. The trapezoidal rule works by approximating the region under the graph of the function $f(x)$ as a trapezoid and calculating its area [2]:

$$\int_a^b f(x)\,dx \approx (b-a)\left[\frac{f(a)+f(b)}{2}\right]. \qquad (4)$$

Line widths are normally reported as full width at half height. The line width is the richest in information content. At a simple level, the line width is inversely proportional to the effective lifetime. Rapid loss of the excitation results in broad peaks; a long lifetime leads to narrow peaks. The parameter c from (1) is related to the full width at half maximum (FWHM) of the peak according to

$$FWHM = 2\sqrt{2\ln 2}\,c \approx 2.35482c. \qquad (5)$$

3. PROGRAM INTERFACE

The key point of the interface of CoRa is its simplicity and usability. One does not need to spend time to understand the interface of CoRa. The program's window (Fig. 1) consists of graph, where the experimental and calculated spectra are plotted, toolbar with buttons to load and to export the data and the functional block with 3 parts: *Data processing, Data modeling* and *Graph settings.*
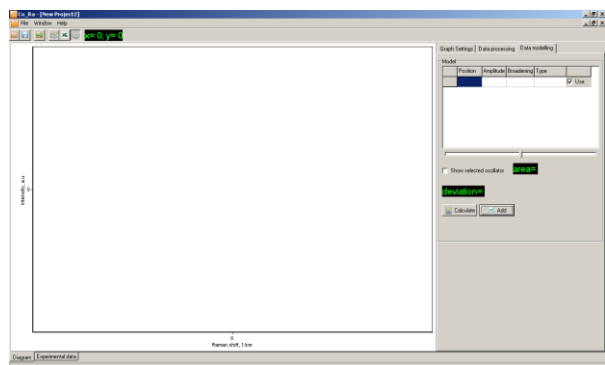

Fig. 1 – Appearance of CoRa Window

The raw data after the measurement need to be treated before the fit procedure. Following tools are included in the section *Data processing* in CoRa (Fig. 2):

1. *Smoothing of the experimental spectrum.* If it is needed, it is possible to remove noise from the data. User should be careful with it and not to remove real peaks from the spectrum.

2. *Cutting area from the experimental spectrum.* By using this tool user can narrow the frequency range of an experimental spectrum. Desired frequency range should be defined, then *Apply* button need to be clicked.

3. *Area integrating.* The area of the peak is an indicator of concentration, because the peak profile is the sum of contribution of all vibrating molecules. By using *area integrating* it is possible to evaluate the area in the defined range which may include one or several peaks.

4. *Background subtracting.* User may substrate the background of the experimental spectrum in CoRa. Use may chose Lorentzian, Gaussian or linear profile.

5. *Calculator* implements arithmetical operations

with experimental spectrum.

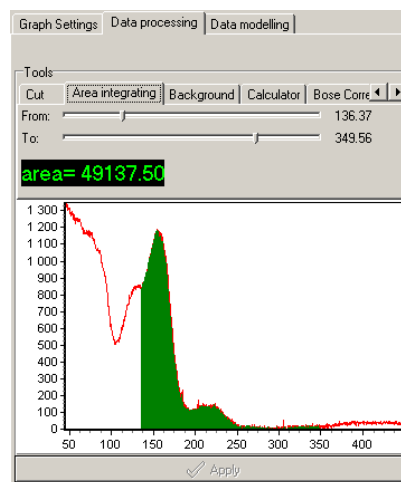6. *Bose correction* is needed to obtain reduced Raman spectra.

Fig. 2 – User interface with tools to treat experimental data

It is possible to preview the result in a small graph below the *Data processing* section. By clicking the *Apply* button, selected function will be applied to the experimental spectrum.

Data modeling is aimed to perform fit of the experimental data, i.e. make a mathematical model of the experimental spectrum by varying of the parameters of Gauss and Lorentz oscillators and minimizing the difference between experimental and calculated spectra (Fig. 3).
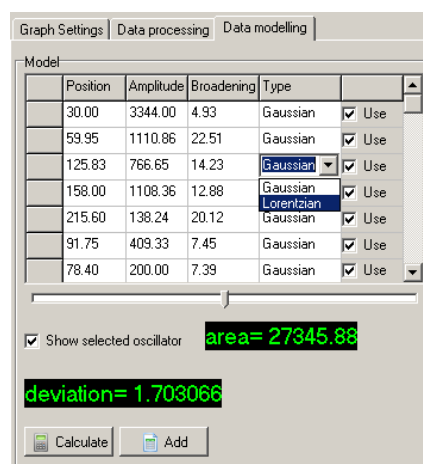

Fig. 3 – User interface with *Data modeling* block with oscillators' table

User can choose the number of oscillators, their type (Gaussian or Lorentzian) and to vary their parameters.

Graph settings (Fig. 4) help to set up the appearance of the graph: colors and styles of curves and background. The graph can be exported as a graphic file and used in presentations, papers, etc.

Results of the fit can be exported to the Microsoft Excel or saved as a *.dat file. All user's settings together with imported experimental data and fitted spectrum can be saved in a file *.crp (CoRa project). CoRa is a multi-document program, i.e. several projects can be open and treated simultaneously. This is

Table 1 – The parameters of oscillators used for fit of the $Ge_3Sb_2Te_6$ spectrum.

| No	Position	Amplitude	Broadening
1	30.00	3344.00	4.93
2	59.95	1110.86	22.51
3	125.83	766.65	14.23
4	158.00	1108.36	12.88
5	215.60	138.24	20.12
6	91.75	409.33	7.45
7	78.40	200.00	7.39
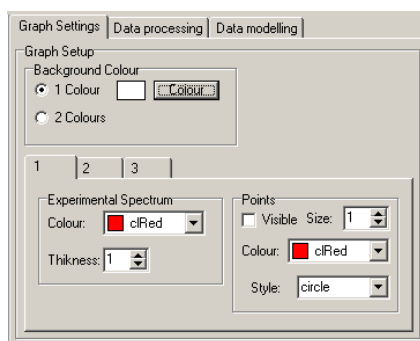
Fig. 4 – User interface with *Graph settings* block

very convenient especially when several resemble spectra (for example results of in-situ experiment) need to be treated.

4. EXAMPLES OF DATA ANALYSIS

Firstly, we used CoRa to analysis of Raman spectrum of amorphous $Ge_3Sb_2Te_6$ [3]. $Ge_3Sb_2Te_6$ belongs to phase change materials which show profound change in their optical and electrical properties between amorphous and crystalline phases due to the presence of resonant bonding in their crystalline phase [4]. There is a strong peak at 160 cm^{-1} with a shoulder at 130 cm^{-1} and small peak at 218 cm^{-1} (Fig. 5).
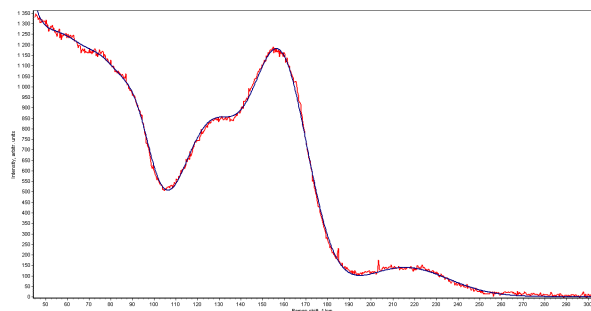
Fig. 5 – Experimental and fitted Raman spectrum of amorphous $Ge_3Sb_2Te_6$ exported from CoRa (red line – experimental spectrum, blue – fit)

Strong increase of the intensity towards small wavenumbers caused by laser radiation, as the intensity of other peaks is relatively low. 7 oscillators were used to fit the experimental spectrum: one Lorentzian was used to describe the laser radiation and other 6 Gaussians describe phonons. The deviation coefficient is equal to 0.64. The parameters of corresponding oscillators are shown in the Table 1.

The second example is the Raman spectrum of CdP_2 single crystal. Cadmium diphosphide CdP_2 is a promising material for the application in intensity stabilizers and pulse stretchers for solid state lasers, optical and thermal sensors and polarizing prisms for thin-film waveguides [5]. The spectrum shows 8 peaks, which were modeled by Gaussian oscillators. The deviation coefficient is equal to 0.11. Experimental and calculated spectra are shown in Fig. 6.
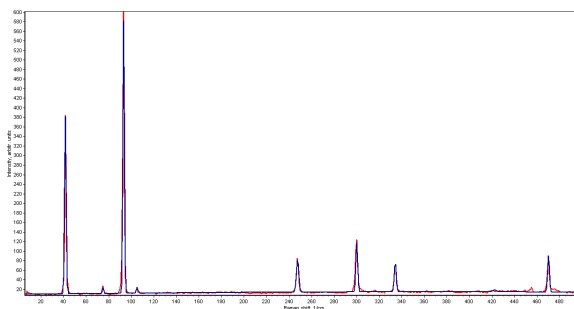
Fig. 6 – Experimental and fitted Raman spectrum of CdP_2 single crystal exported from CoRa (red line – experimental spectrum, blue – fit)

5. CONCLUSIONS

Thus, CoRa software with proposed friendly interface can be used for fitting Raman and absorption spectra of different materials, for example, amorphous and crystalline types. The demo version of the program can be downloaded from www.shportko.com and it has several functional limitations. CoRa can be modified to satisfy different users' demands and you are kindly welcome to contact us to discuss your specific task and needs.

CoRa: іноваційний програмний інструмент для Раманівської спектроскопії

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Іноваційний програмний продукт з дружнім користувацьким інтерфейсом CoRa для Раманівської спектроскопії був нами розроблений. Інтерфейс та функціональність програмного продукту CoRa були обговорені в цій статті. Два приклади практичного використання CoRa для аналізу експериментальних даних аморфного $Ge_3Sb_2Te_6$ та кристалічного CdP_2 були продемонстровані.

Ключові слова: Раманівська спектроскопія, Програма, Аналіз даних.

CoRa: инновационный программный инструмент для спектроскопии комбинационного рассеивания

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Инновационный программный продукт с дружественным пользовательским интерфейсом CoRa для спектроскопии комбинационного рассеивания был нами разработан. Интерфейс и функциональность программного продукта CoRa были обсуждены в этой статье. Два примера практического применения CoRa для аналіза экспериментальных данных аморфного $Ge_3Sb_2Te_6$ и кристаллического CdP_2 были продемонстрированы.

Ключевые слова: Спектроскопия комбинационного рассеивания, Программа, Анализ данных.

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