Dynamic type Fourier spectrometer development for Raman spectra detection

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Abstract. The dynamic Fourier spectrometer model for Raman scattering (RS) is developed. The working spectral range is 800–1050 nm. The excitation source is the laser with the wavelength $\lambda = 785$ nm. In the spectrometer the “white light” channel for summing interferograms over several scans is implemented. Also the reference channel with a sampling frequency of $\lambda / 4$ is realised. The developed layout in experiments of the chemical compounds registration is approved. The signal-to-noise ratios for recorded Raman spectra are also calculated. The work shows the RS spectra of stilbene ($C_{14}H_{12}$) and 1,4-bis (5-phenyl-2-oxazolyl) benzene (POPOP, $C_{24}H_{16}N_2O_2$) recorded on the model spectrometer. An experimental research of the registration of the minimum amount of stilbene ($C_{14}H_{12}$) dissolved in acetone using the Raman spectroscopy method was carried out.

1. Introduction

Raman scattering (RS) spectroscopy is widely used to identify unknown chemical compounds [1]. Based on the previously created Raman spectral database it is possible to analyze unknown substances. The field of active use Raman spectroscopy is associated with express analysis, where it is necessary to identify substances in real time. The advantages of the method consist of high selectivity, which guarantees the probability of correct recognition, as well as in spectral databases of thousands of substances [1-4]. The method limitation is in low sensitivity, which makes it necessary to use high aperture systems.

The paper considers the use of a dynamic Fourier spectrometer for reconstructing the Raman spectra of substances in the 800–1050 nm wavelength range [8–10]. The source of exciting radiation is a laser with the wavelength $\lambda = 785$ nm and a spectral width $\Delta \lambda = 0.15$ nm [9, 10].

2. Optical scheme

The layout of the dynamic Fourier spectrometer was developed in the Scientific and Technological Center of Unique Instrumentation of the Russian Academy of Sciences. The spectrometer is designed to obtain Raman spectra in the visible and near-IR spectral range.

The layout is shown in figure 1. The spectrometer consists of four main parts: a measuring channel, a "white light" channel, a reference channel and a Raman attachment for excitation and collection Raman scattering of light.
To excite the Raman spectra, a semiconductor laser with a wavelength $\lambda = 785$ nm, an optical power of 1500 mW and a spectral linewidth $\Delta \lambda = 0.15$ nm is used.

![Figure 1. The layout of dynamic Fourier spectrometer.](image)

1,2,3,16,17 – plane mirrors; 3 – beamsplitter; 5,6 – triangular corner reflectors; 7,11 – focusing lenses; 8 – detector; 9 – while light channel source; 10 – expanding lens; 12 – white light channel detector; 13 – laser with wavelength 785 nm; 14 – reference channel splitter; 15 – dihedral retroreflectors; 18 – reference channel detector; 19 – laser with wavelength 976 nm.

Michelson's interferometer is the main element of the developed instrument layout. In the arms of the interferometer mirror, triangular corner reflectors with an angular aperture of 2.5 inches and an angular deviation of 1 sec are used as reflectors. One triangular corner reflector is mounted on a movable carriage, moving through a magnetoelectric motor. The system to measure the path difference with a frequency $\lambda / 4$ in the reference channel is implemented. That helps to increase sampling accuracy [9]. For the accumulation and summation of interferograms over several scans, in order to increase the SNR, the white light channel is implemented.

3. Results
The Raman spectra of the test substances POPOP, stilbene were recorded. The emission spectra in the wavelength region 800-1100 nm are observed. This corresponds to frequencies of 200-3500 cm$^{-1}$.

Figure 2 shows the Raman spectra of the POPOP and stilbene substances obtained on the model of the dynamic Fourier spectrometer when excited by a 1500 mW laser. The exposure time during the registration of the Raman spectra was 0.25 sec with one frame. The distance from the test substance to the fiber was 8 mm.
Figure 2. Raman spectra recorded on a dynamic Fourier spectrometer. (a) – POPOP spectrum, (b) – stilbene spectrum.

In figure 2a the POPOP spectral lines are on the following frequencies $\nu$: 1610 cm$^{-1}$, 1510 cm$^{-1}$, 1490 cm$^{-1}$, 1140 cm$^{-1}$ and 1060 cm$^{-1}$. In figure 2b the emission maxima in the RS spectrum of stilbene are at the following frequencies $\nu$: 1635 cm$^{-1}$, 1594 cm$^{-1}$, 1193 cm$^{-1}$, 1000 cm$^{-1}$.

The SNR ratio in the POPOP spectrum was 1922, and in the stilbene spectrum – 632.

Evaluation of the sensitivity of the layout of the Fourier spectrometer was conducted on the basis of experiments to detect the minimum concentration of a substance.

The minimum concentration was determined from the RS spectra of stilbene ($C_{14}H_{12}$) dissolved in acetone. For this, solutions with next concentrations were prepared: 5%, 1% and 0.5%. The solution was placed in a glass transparent cuvette. The power of laser radiation in the experiment was 1500 mW, the recording time of the full interferogram was 0.6 sec, which corresponds to a spectral resolution of 8 cm$^{-1}$.

The Raman spectrum of a 0.5% stilbene solution is shown in figure 2. On the spectrum of figure 3 visible lines corresponding to stilbene at frequencies: 1000 cm$^{-1}$, 1193 cm$^{-1}$, 1594 cm$^{-1}$, 1635 cm$^{-1}$. In addition to stilbene spectral lines, there are lines corresponding acetone Raman spectrum.

Figure 3. Raman spectrum of 0.5% stilbene solution.
4. Conclusion

The layout of the dynamic Fourier spectrometer model for Raman scattering is presented. Main features of the spectrometer are the “white light” channel and the reference channel with a sampling frequency of $\lambda / 4$. The Raman spectra with a short exposure time of the test compounds are presented. Spectral resolution of the recovered spectra is 8 cm$^{-1}$. Signal-to-noise ratio in test substances spectra is 1922 for POPOP and 632 for stilbene. The possibility of recording the Raman spectra of substances at low concentrations is shown.

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