

## A Method for Distinguishing between Liquid Samples by Calculation of the Initial Moments Using Their Infrared Spectra

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**Abstract**—In this paper, a method for distinguishing between liquid samples that are sensitive to the influence of low-intensity physicochemical factors is described. It is based on the calculation of the initial moments of the intensity distribution series in their infrared spectra and comparison of the obtained values with each other. Reliable signs of the coincidence of liquid samples that were obtained in the experiment were used to distinguish distilled water at  $-0.5 \pm 0.5$  and  $-3.0 \pm 0.5 \pm C$ , and at  $-3.0 \pm 0.5$  and  $-5.0 \pm 0.5^\circ\text{C}$ , and to distinguish between distilled and tap water at  $25.0 \pm 0.5^\circ\text{C}$ . For each sample, the moments were calculated for the bending ( $1640\text{ cm}^{-1}$ ), combination ( $2090\text{ cm}^{-1}$ ), and stretching ( $3370\text{ cm}^{-1}$ ) water absorption bands. It was found that when comparing distilled water at  $-0.5 \pm 0.5$  and  $-3.0 \pm 0.5^\circ\text{C}$  the greatest differences are observed for the bending band (50%). When considering distilled water at  $-3.0 \pm 0.5$  and  $-5.0 \pm 0.5^\circ\text{C}$ , the greatest differences occur for the stretching band (54%). When comparing distilled water at  $25.0 \pm 0.5^\circ\text{C}$  and tap water at  $25.0 \pm 0.5^\circ\text{C}$ , the greatest differences were observed for the bending band (86%).

**Keywords:** calculation of the initial moments, distinguishing between liquid samples, IR spectra, low-intensity physicochemical factors.

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### INTRODUCTION

The technique of infrared (IR) Fourier spectroscopy provides an informative and rapid method of investigating the structure and properties of water. However, the resolution of some modern IR Fourier spectrometers does not make it possible to reveal changes in the spectra of liquid samples using standard methods of spectra processing, as the temperature of the samples is elevated or reduced by units of degrees or after the impact of other low-intensity physicochemical factors which have a nonthermal effect on them. The authors of [1–5] obtained results at a step of  $5\text{--}10^\circ\text{C}$  and higher during the investigation of the temperature dependences of the IR spectra of water samples, since a smaller temperature step makes distinguishing between spectra significantly problematic. To study the temperature dependences of the IR spectra of water samples at a step of  $1^\circ\text{C}$  and smaller, setting of the resolution at  $0.5\text{--}1\text{ cm}^{-1}$  is required, which, in its turn, makes the experiment significantly longer. A prolonged experiment duration leads to changes in the sample properties. The MIDAC M4000 IR Fourier spectrometer does not allow one to distinguish

between distilled and tap water at  $25^\circ\text{C}$  by the standard methods of spectra processing.

One of the most widespread techniques for analysis and processing of IR spectra is the decomposition of spectral absorption bands into components [6–9], which is widely used for the interpretation of the spectra of water. Commonly, each of the components into which the studied spectral band is decomposed can be related to a certain water structure. Therefore, this method enables the investigation of structural changes in the samples under the actions of differing physical and chemical factors. However, it does not show sufficient sensitivity in distinguishing between samples that are subjected to low-intensity factors. Low-intensity nonthermal physicochemical factors should be considered as the actions of weak electric, magnetic, and acoustic fields, which do not result in changes in the sample temperature, and the addition of small concentrations of salts, heavy and light water, etc. to water.

To sum up, the development of special sensitive techniques of spectral data processing remains topical.

# 1. A METHOD FOR DISTINGUISHING IR SPECTRA USING CALCULATION OF THE INITIAL MOMENTS

In the present study, a method for distinguishing the IR spectra of water media based on the calculation of the initial moments of the distribution series of intensities in a spectrum and comparison of the obtained values with each other is proposed. The initial moments are sensitive to the shape of the curve that is formed by the set of all points in the studied spectral region. The initial moment of the  $h$ th order is calculated using formula [10]

$$m_h = \frac{\sum_{j=1}^k \left( \frac{x_j - x_a}{c} \right)^h n_j}{n},$$

where  $x_j$  is the maximum intensity value in the group  $j$ ,  $x_a$  is the selected initial intensity value,  $c$  is the rank value,  $n_j$  is the respective repetition rate of the value,  $n$  is the sum of all frequencies  $n_j$ ,  $k$  is the number of groups into which the experimental intensity values in the spectrum are divided, and  $h$  is the order of the moment.

The rank value  $c$  is given by the following expression:

$$c = \frac{x_{j_{\max}} - x_{j_{\min}}}{k},$$

where  $x_{j_{\max}}$  and  $x_{j_{\min}}$  are the maximum and the minimum intensity values in the IR spectra, respectively.

The initial intensity value  $x_a$  is defined as

$$x_a = \frac{\sum_{j=1}^k x_j n_j}{n}.$$

This technique for the selection of the initial intensity value did not contradict the following criterion of the correctness of its choice [10]:

$$-0.5 < m_1 < +0.5.$$

The experimental intensity values were grouped using the following algorithm:

1. The values  $x_{j_{\max}}$  and  $x_{j_{\min}}$  are determined.
2. The number of groups  $k$  is specified.
3. The  $x_j$  value belongs to the group  $j$  if it meets the following criteria:

$$x_j \leq j \cdot \frac{x_{j_{\max}} - x_{j_{\min}}}{k},$$

and

$$x_j > (j - 1) \cdot \frac{x_{j_{\max}} - x_{j_{\min}}}{k}.$$

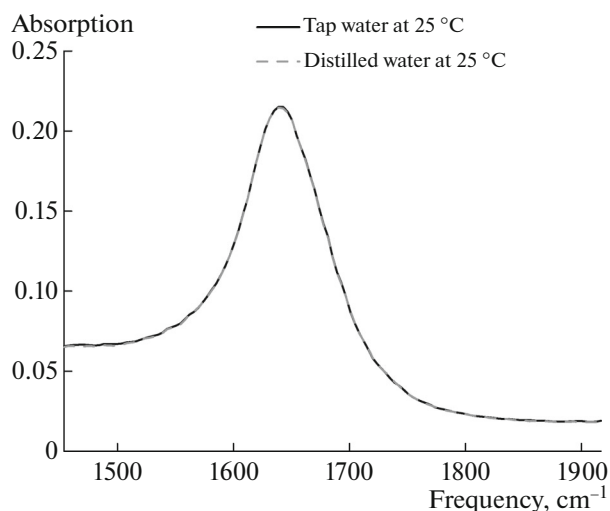
As a result, the values of the moment depended on the intensities in the IR spectrum and the number,  $k$ , of groups.

For the implementation of this method, the authors wrote a special program in the Visual Basic language. The program allows simultaneous processing of two differing experimental data sets, each of these is a set of spectra of the same sample that were obtained under the same conditions. For each spectrum, the moment values were computed and the average value of each moment and its confidence interval were computed over the entire data set. The confidence interval value is determined according to the formula  $\Delta_{cc} = t_{\alpha, n-1} S_m$ , where  $t_{\alpha, n-1}$  is the Student's coefficient for the chosen confidence coefficient  $\alpha$ ,  $S_m$  is the selective standard deviation of the arithmetical mean, and  $n$  is the number of spectra in the set (in all experiments  $n = 20$ ). The program compares the respective moments for two data sets; the output is the number, list, and values of differing and coinciding moments for each of the groups. The values of the compared respective moments differ if their confidence intervals do not intersect. The confidence coefficient  $\alpha$  is taken to be 0.95 in the present work.

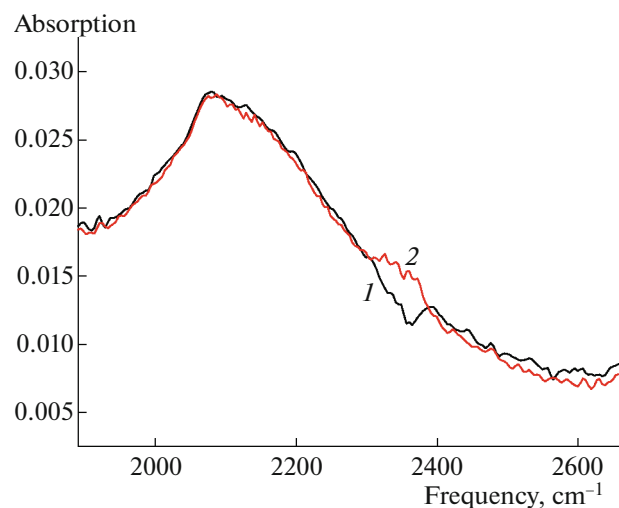
Using this program, the calculation can be carried out with a number of groups from two to the number of points in the studied spectral region and a number of moments from 1 to 50.

The initial IR spectra were obtained on a MIDAC M4000 IR Fourier spectrometer by the attenuated total reflectance (ATR) method with multiple beam reflection. The spectra were recorded with a resolution of  $8 \text{ cm}^{-1}$ ; a cell with a germanium (Ge) crystal was used. Using this cell, the spectrometer operating region is in the range of  $780\text{--}4000 \text{ cm}^{-1}$ . For cooling and heating of the sample to a desired temperature, a temperature regulating metal bar that was designed by the authors that was connected via hoses to a KRIO-VT-01 low-temperature liquid temperature regulator was used. The bar was positioned onto the surface of the cell where the studied sample was placed. The temperature of the bar was regulated by passing coolant from the temperature regulator through it. The sample temperature was measured using a Kelvin-IKS Indikatorom remote-sensing infrared thermometer with an error of  $0.5^\circ\text{C}$ . For these investigations, distilled water that was obtained on a DE-4 distiller (ZAO Zavod Elektromedoborudovanie, Russia) and ordinary water from the tap were used. This experimental apparatus was described in greater detail in [11, 12].

For calibration of the parameters of the method, two similar sets of experimental data, namely, two sets of spectra of distilled water at  $25.0 \pm 0.5^\circ\text{C}$ , were processed. The parameters of the method were selected that provide a reliable coincidence of moments in the given data sets. The computation of the moments was carried out for each of the three water absorption bands in the mid IR-region, viz., the bending ( $\nu_2$ )



**Fig. 1.** The bending absorption band of tap (solid line) and distilled (dashed line) water at 25°C (1450–1917  $\text{cm}^{-1}$ ) (resolution of 8  $\text{cm}^{-1}$ ).

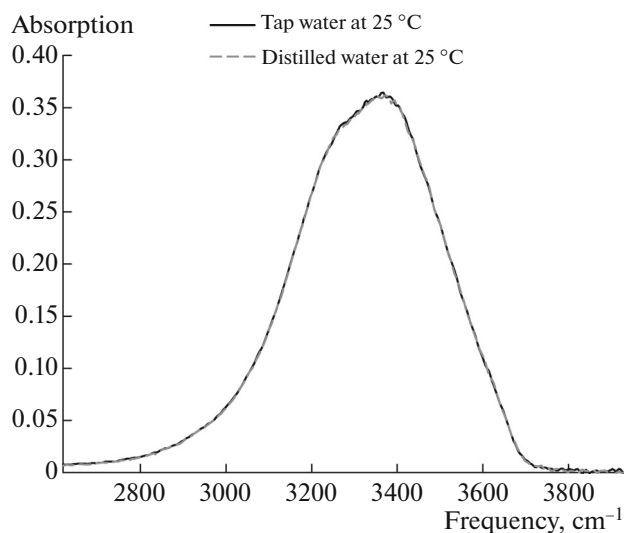


**Fig. 2.** The combination absorption band of tap (curve 1) and distilled (curve 2) water at 25°C (1917–2619  $\text{cm}^{-1}$ ) (resolution of 8  $\text{cm}^{-1}$ ).

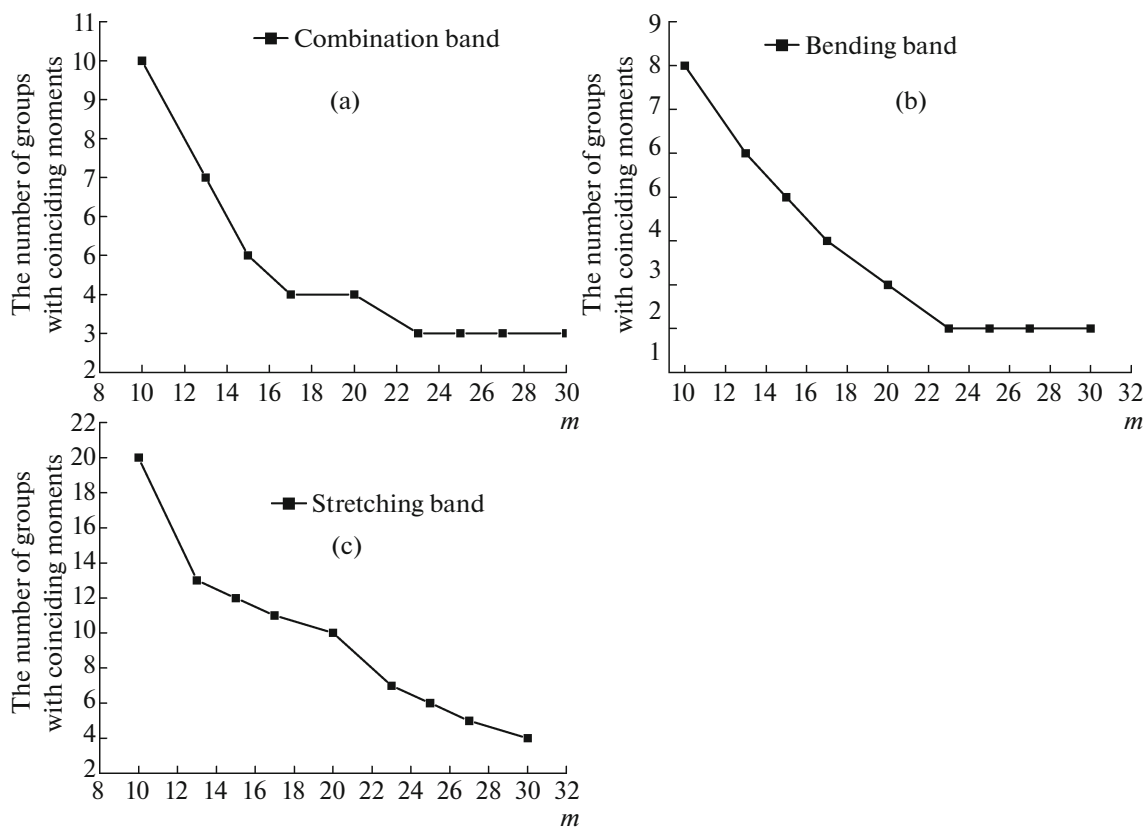
(1450–1917  $\text{cm}^{-1}$ ) (Fig. 1), combination ( $\nu_2 + \nu_L$ ) (1917–2619  $\text{cm}^{-1}$ ) (Fig. 2), and stretching ( $\nu_1$ ,  $\nu_3$ , and  $2\nu_2$ ) (2619–3930  $\text{cm}^{-1}$ ) (Fig. 3) bands, from the 1st to the 50th moment for each of them. The number of groups was from two to the number of points in the studied spectral region. For the bending band, the number of groups was from 2 to 122; for the combination band, it was from 2 to 183 and for the stretching band it was from 2 to 341. The dependences of the number of groups with coinciding moments on the minimum number,  $m$ , of points in each group were plotted. For the combination and bending bands, at  $m = 23$  the dependences change their behavior and reach a plateau, while at  $m = 25$ , 27, and 30, the number of groups with coinciding moments remains constant. For the stretching band, as the number of points changes from 23 to 30, the number of such groups decreases by 3 (from 7 to 4) after the analogous change along the ordinate axis from  $m = 20$  to  $m = 23$  (Fig. 4). The decrease in rate of change of the values of the groups with coinciding moments became a criterion for the choice of the value  $m = 23$  for the stretching band. Therefore, to optimize the algorithm, viz., to decrease the number of the varying parameters of the method, in further investigations we only use the value  $m = 23$ .

Thus, during the choice of the most reliable parameters, the following conditions were taken into account. First, the number of points in a group should be 23 or higher; consequently, only those numbers of groups that comply with this requirement were taken into consideration; that is, the number of groups was restricted to a certain maximum number. For the bending band, the number of such groups was taken to be lower than 6; for the combination band it was lower

than 8 and for the stretching band it was lower than 15. Second, among these numbers of groups for which the moments coincided, those were selected at which the number of coinciding moments lies in the interval from  $N - 10$  to  $N$ , where  $N$  is the number of moments for which the calculations were made. In our case, at  $N = 50$ , the considered interval spans from 40 to 50. Thus, among the number of groups for which the moments coincide, the following were selected: 3 and 4 for the bending band (Fig. 5a); 2, 3, and 4 for the combination band (Fig. 5b); and 2, 7, 8, 9, 12, 13,



**Fig. 3.** The stretching absorption band of tap (solid line) and distilled (dashed line) water at 25°C (2619–3930  $\text{cm}^{-1}$ ) (resolution of 8  $\text{cm}^{-1}$ ).



**Fig. 4.** The dependence of the number of groups with coinciding moments on the minimum number of points,  $m$ , in a group for two identical samples of distilled water at  $25.0 \pm 0.5^\circ\text{C}$ .

and 14 for the stretching band (Fig. 5c). The selected parameters are considered to be reliable and were used during further distinguishing between the spectra of various samples.

Next, two sets of IR spectra were processed for differing samples. The calculation was performed for the same water absorption bands. Among the moments for which the difference was obtained, moments were selected for which a coincidence occurred for two identical samples. Among the number of groups, those were selected at which the number of differing moments lies in the interval from  $N_{\text{dif}} - 10$  to  $N_{\text{dif}}$ , where  $N_{\text{dif}}$  is the maximum number of differing moments for the given spectral range. The empirical constant 10 indicates a tolerance for a small deviation from their maximum value. Upon processing of two differing experimental data sets, the moments were compared separately for each band for those groups in which a reliable coincidence occurred for two identical samples. The total number of moments,  $M_{\text{tot}}$ , within the framework of the given groups in each band of one sample was taken as 100%. The program computed the number of differing moments,  $M_{\text{dif}}$ , corresponding to them for the second sample. As a result, within the bands that were chosen for the investigation, the level

of difference between two samples in percent was defined as  $(M_{\text{dif}}/M_{\text{tot}}) \times 100\%$ . Thus, one can determine the spectral ranges in which the greatest differences occur.

On the whole, by performing the calculations for various absorption bands of samples that were subjected to low-intensity influences, conclusions about the modifications of molecular vibrations corresponding to certain bands can be drawn from the changes in the parameters of the method.

## 2. RESULTS OF THE APPLICATION OF THE METHOD FOR DISTINGUISHING IR SPECTRA FOR THE DETERMINATION OF SIGNS OF DIFFERENCES BETWEEN WATER SAMPLES

The main task of our investigation was to distinguish between water samples at negative temperatures. The studied temperature range is of special importance, since it is the range of the supercooling of water, within which it exhibits a number of interesting properties. In this case, water becomes metastable and its structure rearranges in time continuously; thus, even a small action can lead to its crystallization at any nega-

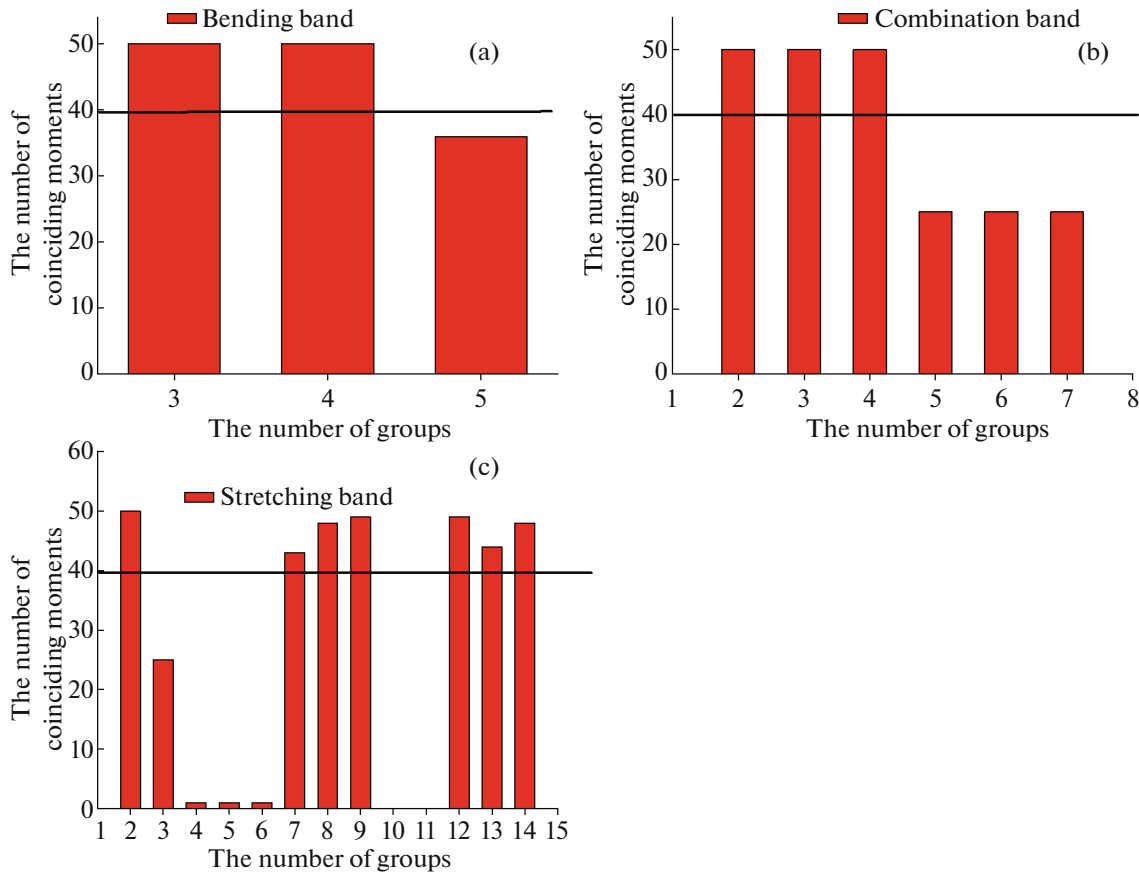


Fig. 5. The parameters at which coincidence occurs for two identical data sets of distilled water at  $25.0 \pm 0.5^\circ\text{C}$ .

tive temperature. A temperature of  $-0.5^\circ\text{C}$  was used for the studies as it is the closest to  $0^\circ\text{C}$  with allowance for the measurement error. The temperatures of  $-3.0$  and  $-5.0^\circ\text{C}$  were used for the investigations of the temperature dependence of the spectra at a step of 1 and  $1.5^\circ\text{C}$  (with allowance for the measurement error).

Two series of experiments were conducted. In the first of them, the sets of spectra were obtained for distilled water at  $-0.5 \pm 0.5$ ,  $-3.0 \pm 0.5^\circ\text{C}$ , and  $-5.0 \pm 0.5^\circ\text{C}$ . In the second, the sets of spectra were obtained for distilled and tap water at  $25.0 \pm 0.5^\circ\text{C}$ . According to the technique that was described in Section 1, the moments of distilled water at  $-0.5 \pm 0.5$ ,  $-3.0 \pm 0.5^\circ\text{C}$ , and  $-5.0 \pm 0.5^\circ\text{C}$  were computed and compared.

Among the numbers of groups for which differences in the moments were obtained, the groups which met the above criteria were selected. In the comparison between distilled water at  $-0.5 \pm 0.5$  and  $-3.0 \pm 0.5^\circ\text{C}$ , the numbers of groups which met these requirements were as follows: 4 for the bending band (Fig. 6a), 4 for the combination band (Fig. 6b), and 2 and 12 for the stretching band (Fig. 6c). These parameters were utilized further to reliably distinguish between these samples. Let us calculate the level of differences for each of the studied absorption bands.

The level of differences for the bending band is 50% and the same values for the combination and stretching bands are 16 and 28%, respectively.

In the comparison between distilled water at  $-3.0 \pm 0.5$  and  $-5.0 \pm 0.5^\circ\text{C}$ , the numbers of groups that agree with the above criteria are given in the table. In this case, for the bending and combination absorption

The numbers of the groups with differing moments for water samples at various temperatures

Absorption band	The numbers of the groups with differing moments
The numbers of the groups with differing moments for distilled water samples at $-3.0 \pm 0.5$ and $-5.0 \pm 0.5^\circ\text{C}$	
Bending	0
Combination	0
Stretching	2, 7, 9, 12
The numbers of the groups with differing moments for distilled and tap water samples at $25.0 \pm 0.5^\circ\text{C}$	
Bending	3, 4
Combination	4
Stretching	7, 8, 9, 12, 13, 14

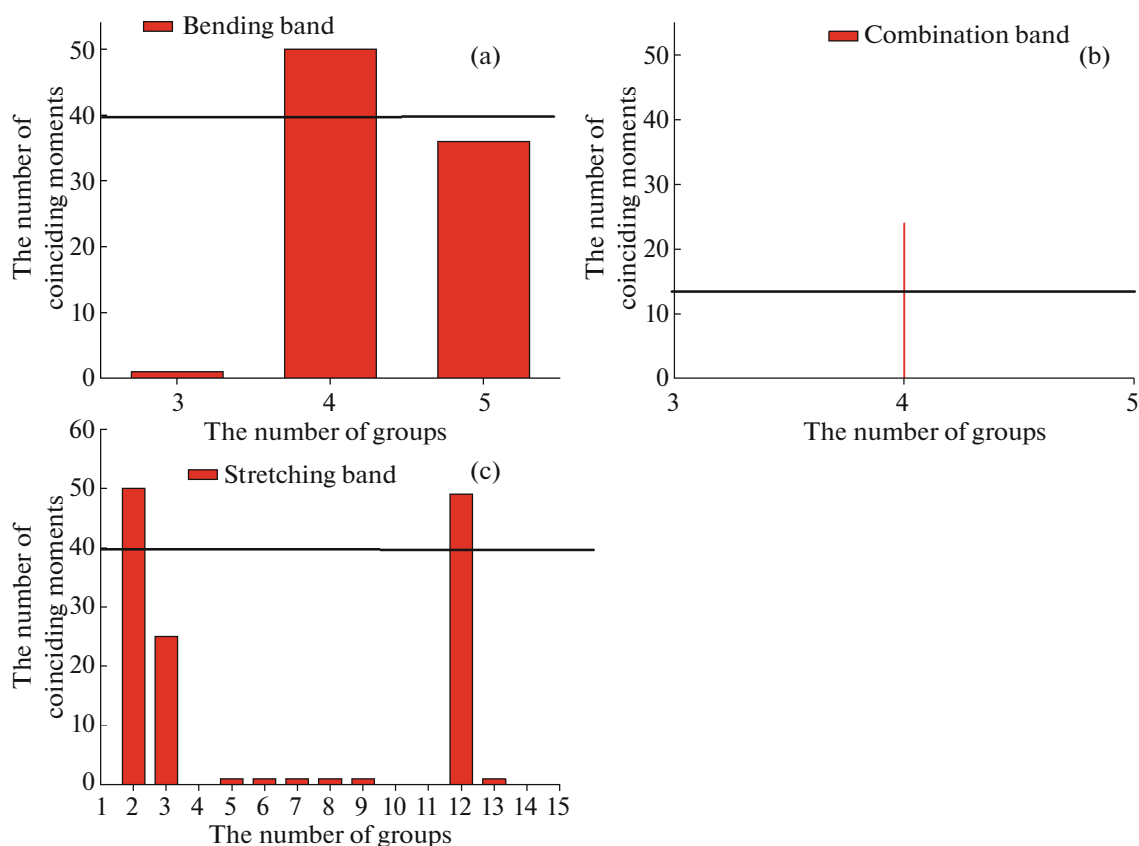


Fig. 6. The parameters at which differences occur for the experimental data sets of distilled water at  $-0.5 \pm 0.5$  and  $-3.0 \pm 0.5^\circ\text{C}$ .

bands, the level of differences is zero; for the stretching band it is 54%.

These changes in the water spectra at  $-0.5$  and  $-3^\circ\text{C}$ , and  $-3$  and  $-5^\circ\text{C}$  are apparently connected with changes in the water structure.

Comparison between distilled water at  $25.0 \pm 0.5^\circ\text{C}$  and tap water at  $25.0 \pm 0.5^\circ\text{C}$  revealed the numbers of groups with differing moments, which are also shown in the table. The level of the differences for the bending, combination, and stretching bands was 86, 32, and 80%, respectively. These results can be explained by the elevated contents of impurities in the tap water compared to those in the distilled water. Their low concentration could not be detected by the standard methods of spectral processing on a MIDAC M4000 spectrometer. The impurities affect the spectra of the samples by displacing lines and distorting the line shapes. The results that were obtained for the studied water absorption bands confirmed this fact.

## CONCLUSIONS

The proposed method via the analysis of IR spectra that were obtained on a MIDAC M4000 IR Fourier spectrometer at a resolution of  $8\text{ cm}^{-1}$  allowed us to distinguish between distilled water samples at tem-

peratures that differed by units of degrees and between distilled water and tap water samples, which was not achievable using the standard methods of spectra processing, even at the highest resolution of  $0.5\text{ cm}^{-1}$ .

Thus, the proposed method enables the enhancement of the sensitivity to the concentration of impurities (at a temperature of  $25.0 \pm 0.5^\circ\text{C}$ ) while preserving the same temperature sensitivity (in the range between  $-0.5 \pm 0.5$  and  $-5.0 \pm 0.5^\circ\text{C}$ ) of the experimental techniques for the investigation of the spectra of the samples. Taking the fact into account that at a lower spectrometer resolution the duration of one measurement is reduced, this method makes it possible to shorten the duration of an experiment.

It was revealed that when considering distilled water at  $-0.5 \pm 0.5$  and  $-3.0 \pm 0.5^\circ\text{C}$ , the greatest level of differences was observed for the bending band (50%). It was established that when the temperature of distilled water changes from  $-3.0 \pm 0.5$  to  $-5.0 \pm 0.5^\circ\text{C}$ , the greatest level of differences is observed for the stretching band (54%). It was also revealed that when comparing distilled water at  $25.0 \pm 0.5^\circ\text{C}$  and tap water at  $25.0 \pm 0.5^\circ\text{C}$  the greatest level of differences is observed for the bending band (86%).

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