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Determination of a wide range of the spectrum of eigenfrequencies of the band of intermolecular vibrations of water 184 cm^{-1}; some properties of these frequencies

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Based on the previously developed method for determining the eigenfrequencies of intermolecular vibrations of liquid water using the previously obtained set of 65 Raman spectra, a set of eigenfrequencies for the hydrogen bond stretching mode was obtained, and the range and main properties of the eigenfrequencies were determined. For the given set were obtained all possible eigenfrequency values, located in a wide band of $169-209\,\mathrm{cm}^{-1}$, and some properties and structural features of the main characteristics in this band were determined.. The developed algorithm for dividing a two-dimensional distribution of a compact array of points into groups of points adjacent to the straight lines approximating them within a narrow strip is presented. The analysis of the ordered by magnitude eigenfrequencies and point densities per unit frequency interval in the group and the ordered by the strip width of the group of point densities per unit frequency interval was carried out. These characteristics were compared with the same characteristics of three sets of randomly scattered points with the same statistical characteristics as the spectral points of water. Distinctive features of water were revealed. It has been suggested that the reason for the discovered features is the existence of some structures in the water.

Keywords: intermolecular vibrations of water, hydrogen bond, band of eigenfrequencies, stretching mode, points on a plane, approximating line, point density, point extraction algorithm.

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1. Introduction

1.1. Initial stage of research into intermolecular vibrations

Low-frequency (LF) Raman spectra ($4-350\,\mathrm{cm}^{-1}$) of intermolecular (IM) vibrations of water reveal the dynamics and structure of the hydrogen bond network. This makes the study of these spectra in water and aqueous solutions relevant. Raman scattering (RS) has been discovered in 1928. In 1932, the use of RS in studies into the association of molecules has been proposed [1], and a review of RS research into „intermolecular interactions“ has been published in 1937 [2]. The author noted the extreme simplicity of observation of the effect (for that time), but added that it „*could only have been done on the basis of far-reaching theoretical ideas that matured only around the year 1928.*“ [3–5]. It was also noted in the same review that *the scientific understanding of the nature of the liquid state has evolved significantly in recent years. If liquid has previously been considered close to gas, the current theory ... evolves toward placing it closer to crystal. Namely the results of research undertaken using modern physical methods, such as X-ray diffraction and the Raman effect, shaped this new view of liquid. According to these concepts, most liquids are similar to crystals in the sense that molecules in liquids are not positioned in a completely random fashion relative to each other.*“ The frequencies of IM vibrations of water were examined in [6–8], and the correspondence between these frequencies of certain liquids and frozen crystalline structures was investigated in [9].

1.2. A word on the structure of molecular bonds in water

Modern views on the structure of water are presented in more detail in [10,11]. The idea of a continuous network of hydrogen bonds permeating the entire volume of water, which was first expressed in [12], is widespread. The structure of water is being studied extensively. Presented with the „structure of water“ AND „research“ search query in August 2024, *scholar.google.com* found 15 papers (including one review) within the 1930−1939 interval and 2410 papers (including 273 reviews) in 2023. However, as was noted in review [11] published in 2024, there is still no common understanding of the structure of water.

1.3. Dynamic susceptibility spectrum of water

The dynamic susceptibility (DS) spectrum, which is derived from the optical Raman spectrum by reduction [13,14] (see the references in [15] for more details), is examined in Raman studies of LF IM vibrations. This spectrum has the form of two broad bands with maxima at approximately

46 cm^{-1} (low frequency) and 170 cm^{-1} (high frequency, HF) [16,17]. These bands are normally approximated by Lorentz functions with three parameters each. Two of these parameters are frequency ones (the frequency of the maximum and the band width). To obtain a closer fit to the experiment within the entire examined frequency range, two terms were added to the approximating function, which expanded the spectral range significantly to 4–320 cm^{-1} [16] (cf. 250 cm^{-1} in [18]). It was noted in [19] that the bands are inhomogeneously broadened; i.e., the observed spectrum of the band features a certain ensemble of oscillator spectra with their eigenfrequencies and widths. At the same time, there are practically no indications in the literature about any structuring of these spectra. The bands were interpreted in [20]: the HF and LF components were associated with the hydrogen bond stretching mode and the bending mode of this bond, respectively. Other interpretations are discussed in literature [15].

Quite a large number of studies into different aspects of IM vibrations in water and aqueous solutions rely on the examination of shape, position of the maximum, and width of the bands of these vibrations based on the dependence of these parameters on variations of experimental conditions. Such studies were reviewed briefly in [21,22]. For example, examined were the effect of temperature on the spectral parameters of water with different oxygen and hydrogen isotope compositions [18], the effect of acetone on the structure of water [23], the assessment of the diameter of the distorted network of hydrogen bonds of water in the vicinity of a hydrogen peroxide molecule [24], etc. One result important for the present work was the detection of inhomogeneous broadening of the bands of IM vibrations of water [19].

1.4. On fluctuations of frequency spectral parameters and their correlations

We have found earlier that all spectral parameters fluctuate strongly, but the frequency parameters of each band fluctuate in a correlated fashion [21,25]. This was revealed by applying a new approach to the analysis of frequency properties of spectra, where the frequency parameters of the band for each spectrum are represented as a point in a two-dimensional coordinate system: the band width squared — the frequency of the maximum squared (spectral or frequency coordinates). A certain distribution of points in this coordinate system is obtained as a result. These points (for 65 water spectra) occupy a fairly large region in spectral coordinates with an average value of the frequency of the maximum squared of 28566 cm^{-2} (with a standard deviation (SD) of 511 cm^{-2}) and an average value of the band width squared of 29682 cm^{-2} (SD 1609 cm^{-2}; see Fig. 1). Notably, the points are distributed unevenly within this region: voids and crowded areas are visible [15]. Fluctuations are apparently associated with instabilities of hydrogen bonds, which translate into their constant breaking and re-emergement [10,26]. It should be noted that the instability of various characteristics of liquid water has long been well known (see, e.g., [27]). Thus, continuous structural rearrangements of the network of water molecule bonds proceed within the measured volume and are reflected in the distribution pattern of spectral parameters. The main objective of our research is to gain an insight into the features of structural bonds of water by analyzing these distributions. We have interpreted the linear correlation of spectral points of a hydrogen peroxide solution in spectral coordinates (the position of the band maximum squared — the width squared) for both low-frequency bands of IM vibrations [25] by invoking the properties of free oscillations of a classical damped oscillator [17]. The same correlation for a small number spectral points of water was demonstrated in the same study.

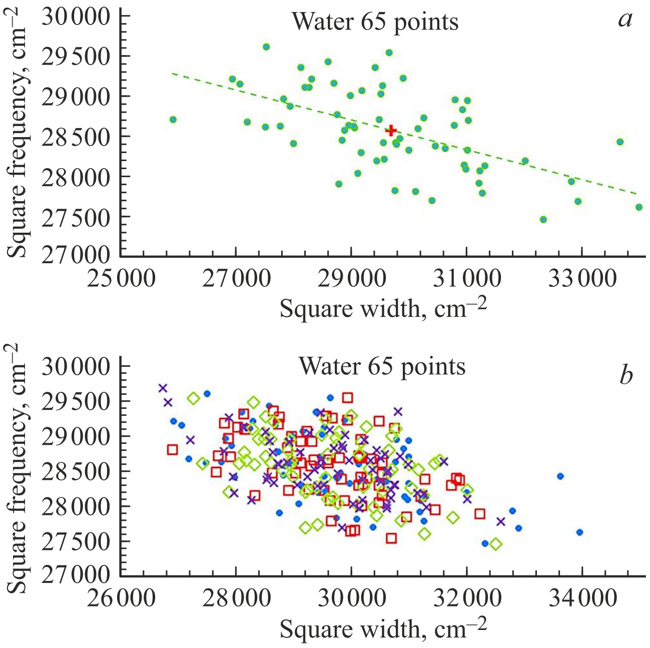

Figure 1. Sixty-five spectral points of water. (*a*) Inclined dashed line — approximating line of the effective oscillator; red straight cross — average value of all spectral points. (*b*) The same water points and three sets of 65 model points each: water (blue circles), model 2 (diamonds), model 3 (squares), and model 4 (oblique crosses).

1.5. Damped oscillators in the water bond network

A harmonic oscillator is characterized by eigenfrequency (EF) υ_0 and damping, which is associated with homogeneous spectral width γ. Frequency υ_m of the band maximum in the DS spectrum, band width Γ, and the eigenfrequency are related [16,17,28] in the following way:

$$\upsilon_0^2 = \upsilon_m^2 + 0.5\Gamma^2/K^2 \qquad (1)$$

Here, constant K, which is the ratio of observed width Γ to homogeneous width γ, is called the coefficient of inhomogeneous broadening (inhomogeneity coefficient, IC). It is evident that the relation between the observed width squared and the frequency squared in the coordinates observed band width squared — band maximum position squared (frequency coordinates) at a constant EF is linear with a negative slope. The slope ratio of the dependence of the position of the band maximum squared on the observed band width squared without inhomogeneous broadening ($K = 1$) is -0.5. In the case of inhomogeneous broadening, this ratio lies within the interval from -0.5 to 0 and sets the slope of the straight line. The EF squared is set by the coordinate of the point of intersection of this line with the axis of frequencies squared. These properties of the straight line approximating experimental points were used to determine the EF values of oscillators, which matched the frequencies of infrared (IR) absorption of water; the inhomogeneous band broadening; the homogeneous width values; and the damping times of oscillations. The straight line corresponds to an oscillator that is essentially an effective one for this group of points. Similar straight lines approximating the entire set of experimental points for hydrogen peroxide solutions were plotted in [28,22], and the lines for groups of points for water and peroxide were obtained in [15,22]. The parameters of the corresponding effective oscillator may also be calculated for each of these straight lines. The average damping times of free oscillations of effective oscillators were estimated. Thus, this approach provides a means to determine a significant number of parameters of real solutions.

The measured volume contains approximately $10^{15}-10^{16}$ water molecules (i.e., a very large number of strongly interacting oscillators). A solid body have density of the same order of magnitude, and structural features of its energy bands provide information about the material properties. Liquid lack crystal ordering. However, based on the concept of an elastic network of connections, it can be assumed that there is a significant number of EFs of IM vibrations, which also somewise reflect the structure of these connections, although they are fluctuating. It seems obvious that the EFs of such a system should occupy a fairly wide and rather densely packed range (i.e., a peculiar frequency band) [29]. The preliminary values of a number of EFs of IM vibrations of water and several aqueous solutions within the range from 170 to 210 cm^{-1} were presented in [29,30], and certain features of these EFs were reported briefly.

The aim of the present study is to obtain a set of EFs of the hydrogen bond stretching mode of IM water vibrations within a wide frequency range, estimate the range boundaries, demonstrate certain properties of the obtained EF distributions, and show the method for preparing such a set.

2. Studied set of frequency spectral parameters

The studies were carried out on spectra described and partially investigated earlier [15]. In the present study, we report the results for the 183 cm^{-1} HF band of IM vibrations of water obtained from 65 spectra recorded in sealed ampoules of medical-grade water for injections [31] at room temperature. The measurement process was detailed in [16,17,28]. Figure 1, *a* presents all 65 points considered here. The inclined dashed line is an approximation for all points obtained using the least squares method. Its parameters (slope, -0.1858; free term, 34082 cm^{-2}) were used to determine the parameters of the effective oscillator for the entire set of points: an EF of 184.6 cm^{-1} and an IC of 1.64. These values are fairly close to the parameters for the series of 51 points reported in [15] (all these points are incorporated into the set considered here). It should be borne in mind that the nature of scatter of spectral points is such that the indicated parameters of the effective oscillator of the entire set of spectral points pertain to average values. The values of the effective oscillator parameters do not affect the characteristics considered below. However, we note that the approximate estimates of standard deviations are 17% for the line slope and 3% for the EF squared. This yields approximately two times smaller deviations from the average values for the IC and EF.

Following [15], we compare the obtained results for spectral points of water with the results for model points scattered randomly over the same spectral plane with their statistical properties corresponding to those of the experimental set. These three model 65-point sets are shown in Fig. 1, *b* in spectral coordinates together with 65 experimental spectral points.

2.1. On the division of a set of spectral points into groups with a small deviation from the approximating line

Relying on different assumptions, we found in [15,31] that one and the same set of points with high frequencies from the upper part of the distribution (Fig. 1, *a*) is approximated well by two families of lines corresponding to different compositions of groups.

There is nothing unusual about this. The obtained values of the position of the maximum and the band width for the measured spectrum correspond to the experimentally observed pattern of a large ensemble of local homogeneously broadened spectra summed over the recording time. These parameters do not allow one to determine the EF and IC of the components of this ensemble. According to (1), they may correspond to a large set of parameters compliant with the permissible values of IC and EF. The emergence of a point with different coordinates implies that while the spectrum was recorded, the position of the maximum and the width of the distribution changed (i.e., rearrangements of a significant number of molecules occurred in the ensemble of local homogeneously broadened spectra). Thus, signals from the entire measured volume of liquid contribute to the formation of the spectrum, and the observed values of frequency and width characterize this entire volume. Connecting these two points with a straight line, we „localize“ EF and IC values present in these two ensembles of spectra. In other words, one may state that these values were indeed present with a certain probability in both ensembles.

If points are found near an already drawn straight line that may be combined statistically with the points of this group, we calculate the parameters of a straight line approximating a new set of points and determine the effective oscillator parameters of this group.

Performing such operations with all possible combinations of points, we construct all possible groups and identify all the EF and IC values. As for the remaining possible combinations of EF and IC, it can be stated that the probability of formation of ensembles with the corresponding parameters in experiments turned out to be small. As the number of measured spectra increases, other parameter values with non-zero probability will probably emerge.

It is convenient to factor in the probabilities of emergence of points in the spectral plane using the concept of density of points in a unit spectral interval introduced in [15]. This density was defined as the number of points in a strip divided by its spectral width. The strip width is understood here as the sum of distances from the straight line to two most distant points located on either side of it. Distances are measured in cm^{-2}. A proper comparison of densities determined with different numbers of processed spectra also necessitates the introduction of a normalized density of the number of points per unit spectral interval, which is the density defined above divided by the total number of spectra in the considered set [15]. In what follows, this quantity is the one referred to as density. In essence, this is the fraction of the total number of points within a unit spectral interval. Its dimension is $1/\mathrm{cm}^{-2}$. The density of points in the vicinity of approximating lines is one of the key parameters examined in the present study. Therefore, we consider groups containing at least three points. It should be borne in mind that some of the possible oscillators derived from straight lines drawn through two points are then replaced by averaged values, and a number of discovered oscillators with a lower probability of occurrence are neglected. The process of estimation of this reduction is fairly straightforward, but this is outside the scope of the present work.

Figure 2 illustrates how the EF values are obtained. It shows approximating straight lines representing 45 groups with the highest density of points that are extrapolated to the intersection with the axis of frequency squared. According to (1), the coordinates of these intersection points are the squares of the corresponding EFs. The range of squared EF values and the heterogeneity of their distribution within this range are visible.

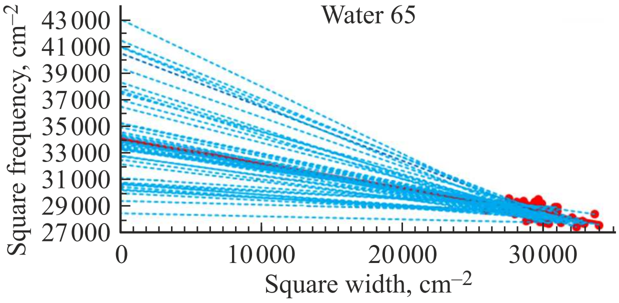

Figure 2. Lines approximating 45 groups of points. The thicker line in the center approximates the entire set of points.

2.2. Algorithm for dividing points into groups of oscillators

In accordance with the aim of the present study, we considered all ranges of possible group slope ratios from -0.5 to almost 0. At each slope value, a reference line with the current value was drawn through the center of the distribution of points, and distances in the spectral plane from this line to all spectral points were calculated. It is evident [15] that if a certain group of points is approximated by a straight line parallel to the reference one under consideration, the points of this group are concentrated within a compact distance interval from the line. This crowding of points disperses as the reference line rotates.

The algorithm was based on the following. Two points with a minimum distance between them, which is compared with the specified maximum allowable one (parameter 1), are selected from the considered array of distances for a given direction. If the comparison result is positive, these points serve as the basis for forming a group. To add points to a group, those closest to the interval formed by the points of the group are examined in a sequential order and checked for compliance with the inclusion criterion. Two criteria are used in the process: a simple one and a more complex statistical criterion. The simple criterion is as follows: a neighboring free point closest to the range occupied by the group being formed may be added to the group if the distance from this point to the nearest boundary of the range does not exceed the specified limit (parameter 2). The more complex statistical criterion for inclusion of a point into a group is as follows. The average distance from the base line and the standard deviation from the average value are calculated for all points already added to the group. The point closest to the group is included if its deviation from the average value does not exceed either the limits statistically acceptable for the accumulated number of points or the specified maximum distance from the group boundary (parameter 3). If neither of the two adjacent points are fit to be added to the group, the process of group formation is stopped. If the number of points considered in a cycle does not exceed 2, a group is not formed. If at least three points are suitable for inclusion into a group, this group is formed, and all relevant parameters are calculated:

the slope of the reference line; the density of points per unit interval for this section; the group slope, which specifies the IC and may differ significantly from the slope of the reference line; the EF; strip width $dr0$; distance $r2$ between the group and the center; number of points n and their density p in the group; and the composition of the group. If the point density for a given section exceeds the specified threshold value (parameter 4), this data set is marked for further study. If there are any free points left, the process of group formation starts again for them. With no free points left, we move on to a different slope ratio of the reference line.

The criterion for inclusion of a point into a group is chosen with regard to the limiting number of points in the group mp (criterion parameter (CP); for convenience, we denote its value on the right: e.g., $mp4$ means that the CP value is 4). The simple criterion is applied until this number is reached, and the statistical criterion is used when it is exceeded. At $mp2$, the statistical criterion is used straight away. It turned out that changing this parameter works as a kind of matched filter, leading to the selection of points when constructing a set, which provides additional opportunities for work.

Our primary goal is to obtain groups and their parameters for points closely adjacent to the approximating lines. However, the control parameters made it possible to obtain data for groups of points occupying large areas (up to the spectral interval of the entire set of points). It follows from the definition given at the end of Section 2.1 that the normalized density in this case is $1/w$ (in units of $1/\text{cm}^{-2}$), where w is the width of the interval occupied by points in the spectral space in the direction perpendicular to the straight line approximating all the points. Interval width w for 65 water spectral points with a slope ratio of -0.186 is $1768.8\,\text{cm}^{-2}$, and the average density is $0.000568\,1/\text{cm}^{-2}$. The obtained normalized densities may be compared with this average (background) point density. Groups with a density no lower than the threshold density of $0.001\,1/\text{cm}^{-2}$ were taken into account in calculations.

3. Results of dividing into groups of spectral points

3.1. Strips widths and number of points in a group

The software implementation of the algorithm did not include restrictions on the maximum number of points and the maximum strip width; the group strip widths for a number of slopes reached several tens and even hundreds of cm^{-2} (Fig. 3).

Data for the complete set of 340 strips obtained by processing our experimental set of 65 water spectral points are shown here. The indicated value is close to the estimate of the number of possible frequencies that would result from pairwise combinations. The data were obtained using only the complex (statistical) criterion for point inclusion into a group $mp2$ (CP $=2$). Figure 3, a presents the rank sequence of widths $dr0$ (i.e., the dependence of width on the number in this sequence). It is evident that the width increases at an ever-growing rate. The region shown in the inset is of interest to us. Figure 3, b shows the dependence of the number of points in a group for the same rank sequence. It is clear that groups with low order numbers (and, consequently, small widths) consist of just three points. Four, five, six, and seven points in a group appear at number 57 ($dr0 = 2.47$), 109 ($dr0 = 5.96$), 173 ($dr0 = 15.56$), and 197 ($dr0 = 19.58$), respectively. The results for wide strips are not needed to determine the frequency range and the nature of distribution of EFs, but it is important to estimate the frequency range considered. It should be borne in mind that as the strip width increases, the density of points in a strip decreases (Fig. 4). At $dr0 > 6$, the density is more than two orders of magnitude lower than the maximum.

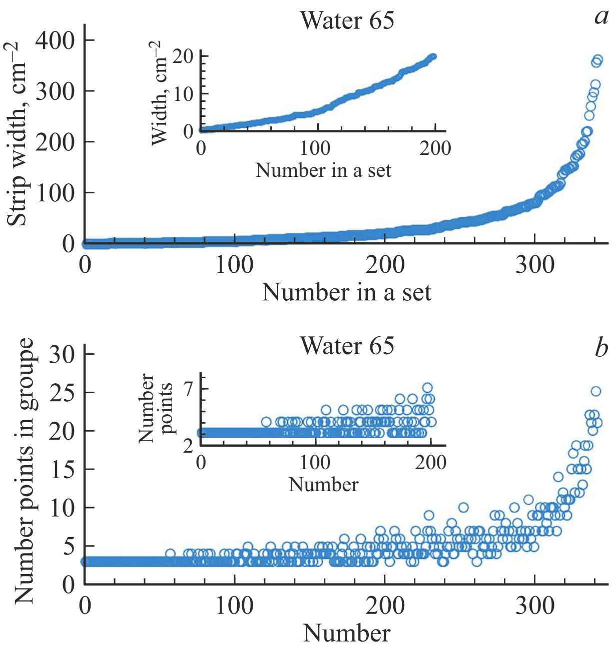

Figure 3. Dependencies of rank sequence of the width of a group of points (a) and the number of points in a group in a same sequence (b). The CP is 2 ($mp2$).

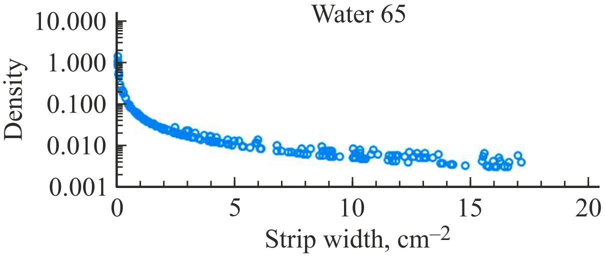

Figure 4. Dependence of the density of points in a strip on its width; CP = 2.

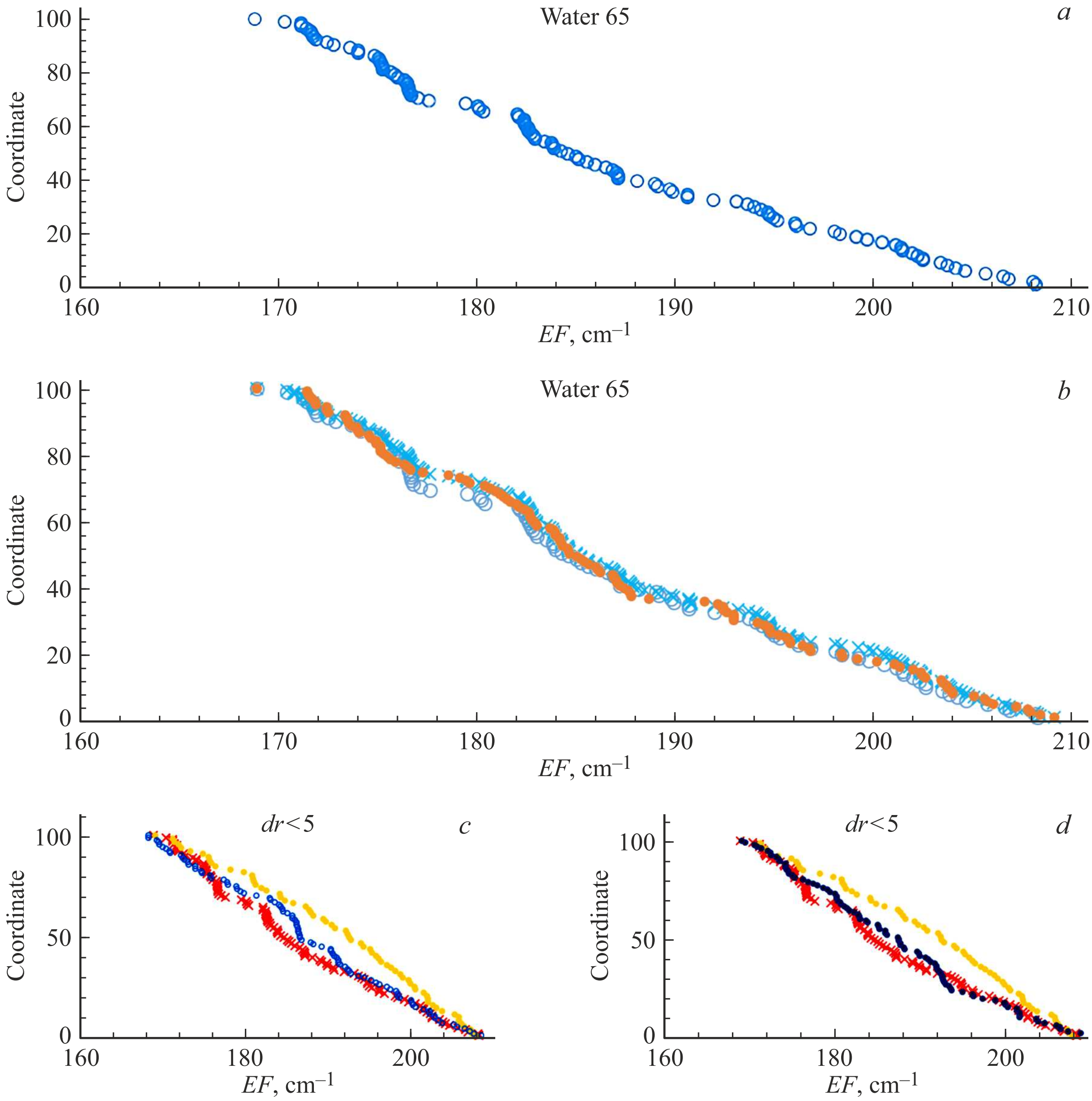

Figure 5. Relation for the normalized series coordinate for a sequence of EFs sorted in descending order and obtained for a set of 65 spectra of water: $mp2$ (a); comparison of rank sequences in series coordinates at different maximum strip widths at $mp2$ and $mp4$ (b); comparison of relations for water and three random sets with the same CP = 2 ($mp2$) and the same maximum band width: model 3 (c) and model 4 (d).

Note that the EF values obtained from wide strips are averaged over a larger frequency range than those derived from narrow strips.

3.2. Rank sequences of eigenfrequencies

The next characteristic is based on the relation between the EF value and its position in the rank sequence of EFs sorted in descending order. Figure 5, a shows the rank modified sequence of water EFs. To make an adequate comparison of series with different numbers of members possible, we use the modified normalized coordinate of the series instead of an order number: a value of 1 is assigned to the coordinate of the 1st number, and the last member has the coordinate 100. All members of the series are positioned uniformly. Only the statistical criterion was used here for the inclusion of points into a group (the limiting number of points for the statistical criterion is 2, $mp2$); with a maximum band width of 5 cm^{-2}, the minimum density of points in a strip was 0.0094, and the number of obtained EFs was 101. The EF interval extends from 168.8 to 208.2 cm^{-1}. Note that the maximum frequency is virtually coincident with the maximum of the Raman band of ice at about 207 cm^{-1} [28]. A discussion of this issue is beyond the scope of the present paper. For ease of comparison with other characteristics, EFs are plotted here along the abscissa axis (EF, cm^{-1}), while the series coordinates are plotted along the ordinate axis. The frequency distribution fills the range unevenly: in some places there are condensations, in others rarefactions, right up to obvious gaps. For example, large gaps are found near 178 and $181\,\mathrm{cm}^{-1}$. In addition, there are noticeable gaps at 192, 198, and $203\,\mathrm{cm}^{-1}$. Strong condensation is observed at the center of the pattern within the $182-188\,\mathrm{cm}^{-1}$ range. Several breaks are observed (specifically, in the region of gaps). Gently and steeply sloped sections are seen. It is beyond the scope of this study to analyze these features. Note also that the curve of this dependence is concave in general. This is visually evident and verified by the fact that the dependence has a slope ratio of -3.29 and -2.00 within the intervals of 169–$185\,\mathrm{cm}^{-1}$ and 185– $207\,\mathrm{cm}^{-1}$, respectively. Deviations from the approximating straight line in the high-frequency range are much smaller than those in the LF range.

When the maximum width was expanded to $17\,\mathrm{cm}^{-2}$, the number of points increased to 185, and the overall shape of the curve (Fig. 5, b, oblique crosses) was close to that of the water curve (circles). The key features remain at the same frequencies, but may shift along the series coordinate axis due to the nonuniformity of distribution of added points. Here, they are shifted upward. Some gaps may visually close, but the gaps at 178, 198, and $203\,\mathrm{cm}^{-1}$ remained.

With the criterion for including a point into a group adjusted to $\mathrm{CP} = 4$ ($mp4$), the number of groups with a small width and, consequently, a high density of points dropped sharply. At maximum width $dr0 < 5\,\mathrm{cm}^{-2}$, only ten groups with a point density of 0.00981 and above remained; at $dr0 < 17\,\mathrm{cm}^{-2}$, 65 groups with a point density of 0.00544 and above were found. Figure 5, b presents the data obtained at $dr0 < 50\,\mathrm{cm}^{-2}$ with 126 groups with a point density of 0.00119 and above. They are denoted by solid circles and located close to the first two dependences. No fundamental changes in the nature of dependences are apparent, although compared to the curve for narrow strips, the pattern becomes more distorted and necessitates additional analysis. Figures 5, c, d show modified rank distributions of EFs for narrow strips of water (oblique crosses in these figures denote the curve that was designated with open circles in the previous two figures) and „EFs“ for three random model signals. The dependence for model 2 differs most profoundly from the dependence for water. Almost all of its points are located above the points for water. Visually, along the model line 2 there are practically no condensations, such as for water. Wave-like oscillations are observed in the LF region, but they are significantly weaker than those corresponding to water, and the magnitude of deviation from the smoothed curve is smaller. As in water, two steps are observed in the $175-182\,\mathrm{cm}^{-1}$ region, but their shape is different: they are narrower and have a several times smaller difference in height. In the HF region, weak deviations are noticeable only at the ends of this interval. The dependence is convex in general. The other two dependences for model points are contained almost completely between the dependences for water and model 2 (and tend to be positioned closer to water). In the case of model 3 (Fig. 5, c), points lie below the water ones only in the LF section from 169 to $174\,\mathrm{cm}^{-1}$ and match the points for water within the range from $198\,\mathrm{cm}^{-1}$ to the end of the interval. Noticeable oscillations are seen at 180–$191\,\mathrm{cm}^{-1}$. Overall, the curve is slightly convex. As for model 4 (Fig. 5, d), the dependence is virtually coincident with the one for water within the 169–$175\,\mathrm{cm}^{-1}$ interval. These points lie noticeably lower than the points for water within the 192–$198\,\mathrm{cm}^{-1}$ section and effectively merge with them afterwards. The curve is slightly concave in general. All the features of model curves different in nature from those of the curves for water.

3.3. Influence of the points selection criterion parameter on the density characteristics

It was demonstrated in the previous section that the use of the simple criterion for point selection affects the group composition, which is manifested in rejection of a significant number of points and results in a reduction in the number of high-density points. Figure 6 illustrates the alteration of characteristics for water and model sets of randomly selected points induced by adjustment of the criterion parameter. Figure 6, a shows the dependences of density of water points on the order number in the rank sequence in ascending order of group strip width $dr0$ for four CP values ranging from 2 to 5. It is evident that four points with the highest density get left out of the groups as one switches from parameter $mp2$, when the statistical criterion is applied straight away, to $mp3$, when the simple criterion is applied to the third point and the statistical criterion is used for the following ones. The point with the highest density was the fifth one in the series constructed with parameter $mp2$. Its density is 0.44, which is almost 3 times lower than the maximum density (1.24) of the $mp2$ series. The sixth point in the $mp3$ series corresponds in density (0.0025) to the 44th point of the $mp2$ series; i.e., 38 points with the highest density from the $mp2$ series are missing from the $mp3$ series.

This is probably attributable to the specifics structure of EF arrangement. The first six points in these sequences with CP values from 3 to 5 were matching. The subsequent points of sequences $mp4$ and $mp5$ lie below the points of the $mp3$ sequence, but are close to each other.

With the $mp2$ criterion, the maximum density values are 0.41 for set 2 (Fig. 6, c) and 0.69 for set 3 (Fig. 6, d); i.e., they are noticeably lower than the corresponding value for water (1.24) (Figs. 6, a, b). The maximum for set 3 is 4.45 (significantly higher than the maximum for water). However, the transition to the $mp4$ criterion lowers the maximum value in the resulting set by more than an order of magnitude (specifically, by a factor of 12, 14, and 147 for sets 2, 3, and 4, respectively), and all densities for all

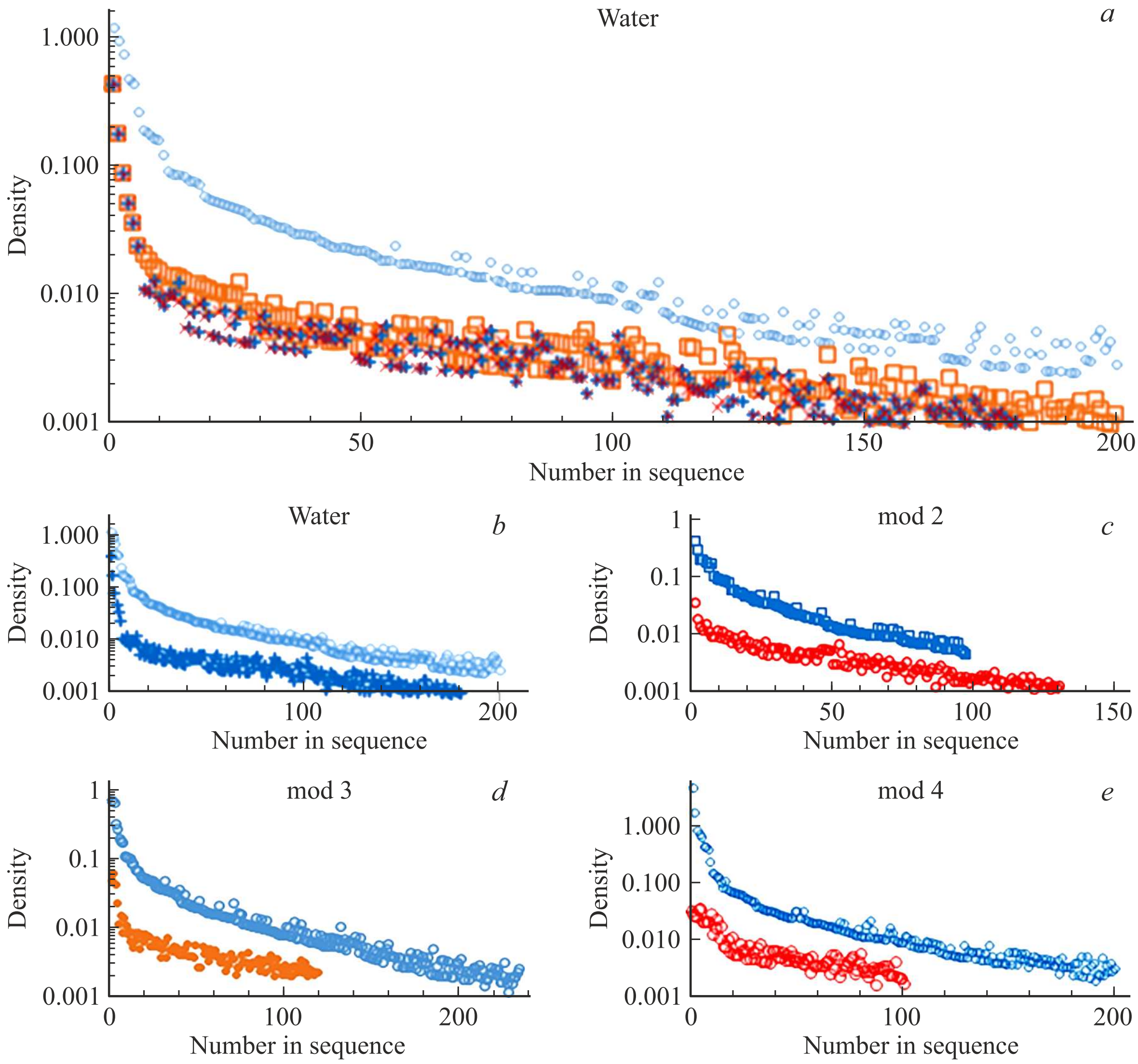

Figure 6. Dependences of the point density on the order number in the rank sequence in ascending order of the groups strip width: (*a*) for water and four CP values: *mp*2 — circles, *mp*3 — squares, *mp*4 — straight crosses, and *mp*5 — oblique crosses; for a CP equal to 2, 4 — for water (*b*) and models 2 (*c*), 3 (*d*), and 4 (*e*).

the model sets drop below 0.1. This may be a feature that distinguishes a real object (water) from a set of random points.

Figure 7, *a* shows the dependence of densities of points groups on the EF with criterion *mp*2. The parameters were chosen so as to include groups with a density greater than 0.002. Figure 7, *b* presents these dependences for four CP values considered above in the rank sequences. It is seen clearly, as in Fig. 6, *a*, that of all the points groups with densities higher than 0.021 found when applying the *mp*2 criterion, only six are included into the corresponding sets for each of the other three CP values; notably, they occupy the same places in all three series.

It is noteworthy that, in a first approximation, the complete set of points forms an almost smooth dome, which covers the entire set, contains approximately ten points (with the one with the maximum density belonging to the 180 cm^{-1} EF), and has a density decreasing toward the high-frequency boundary by almost two orders of magnitude. Notably, in the region of highest part of the dome (175–190 cm^{-1}), the points located below have a density an order of magnitude lower. In the LF region, the dome merges at a density level of 0.4 with a certain array of points that is located in the 0.1–0.4 interval and extends in the form of an inclined band to a density level of approximately 0.01 in the HF part, effectively merging there with the primary background of more closely arranged points with low densities. The upper edge of the latter is also inclined slightly and goes from 0.02 at the LF boundary to a level of 0.01 at 200 cm^{-1}. At the HF boundary, this background drops even lower in density to a value of 0.005.

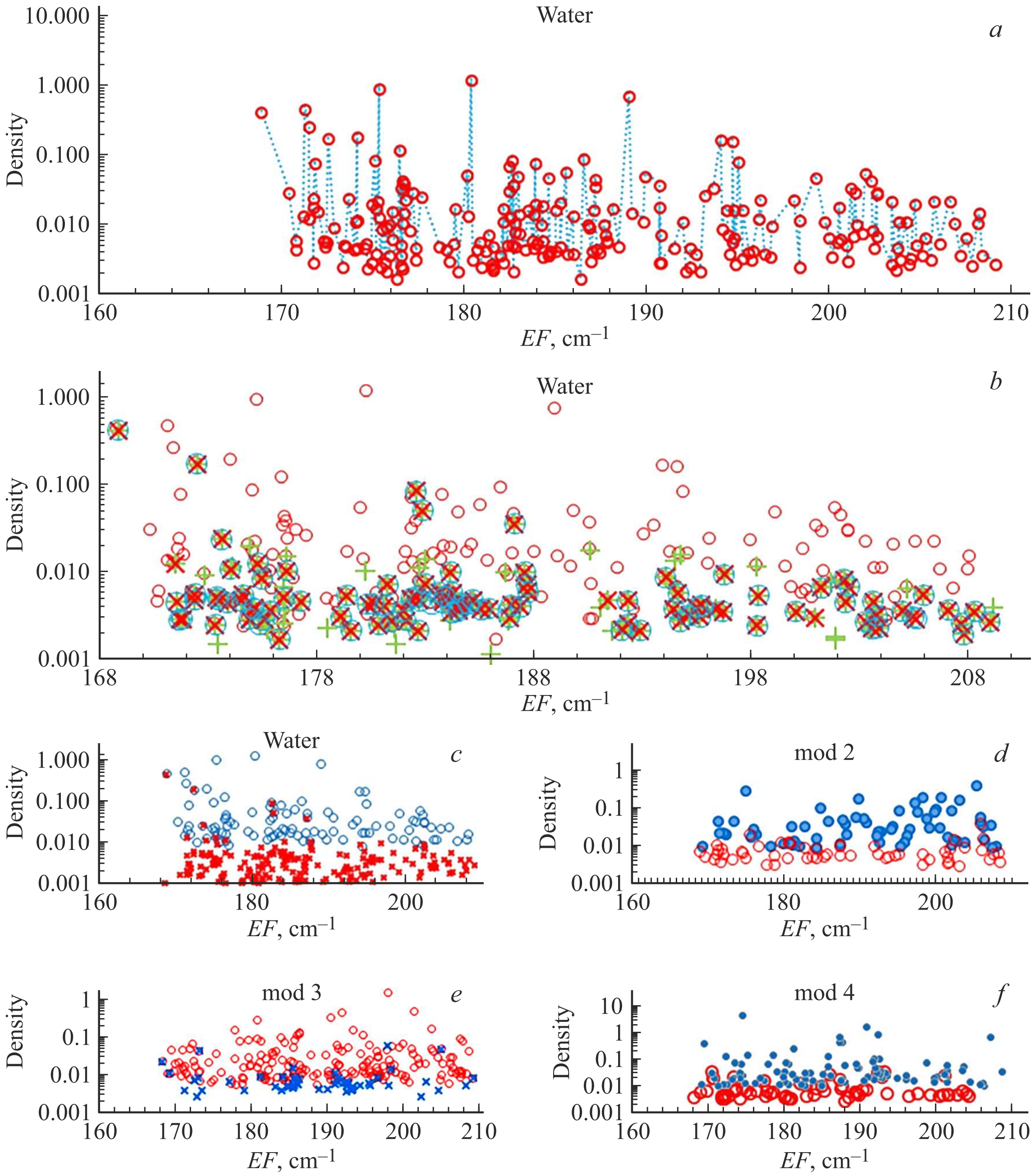

Figure 7. Dependences of the density of groups of points on the EF: (*a*) water, $mp2$; (*b*) $mp2$ — red circles, $mp3$ — straight green crosses, $mp4$ — oblique red crosses, and $mp5$ — green circles; (*c*) water, $mp2$ — blue circles and $mp4$ — red crosses; (*d*) model 2, $mp2$ — blue circles and $mp4$ — red circles; (*e*) model 3, $mp2$ — red circles and $mp4$ — blue crosses; and (*f*) model 4, $mp2$ — blue circles and $mp4$ — red circles.

Points obtained using the simple criterion at the first stage of grouping also behave in a similar fashion. In each of these three sets, five highest-density points of the six noted above belong to the mentioned inclined band lying between the upper points of the dome and the background. These six points in Fig. 7, *b* match in all three sets.

The overwhelming majority of background points found in the $mp5$ series also belong to the other three ones. Most points found in the $mp3$ series belong also to the $mp2$ series, but a noticeable number of them are missing from the other series. Considered separately, the series also reveal a drop in density as one moves from the LF edge to the HF one.

It should be clarified that the points shown in Fig. 7 are the positions of calculated EFs. Spectral coordinates (the width squared and the position of the Lorentzian maximum squared) are used to construct groups of points. The spectral bands themselves are wide, but they change consistently within a narrow strip (i.e., in a correlated manner) in transition to another point in a group. Note that the 45 highest-density lines shown in Fig. 2 belong to the highest-density layer and to the next (inclined) layer.

Figures 7, *c–f* present the results for criteria *mp*2 and *mp*4 for water and three sets of random points. In the case of model sets, the overwhelming majority of points obtained using the *mp*4 criterion belong to the background with the upper boundary slightly above 0.01; only a few of them rise above the level of 0.02. Notably, the density decreases slightly in the center of the range and increases insignificantly toward the edges (with a greater increase at the HF edge). In models 2 and 3, a marked increase toward the HF edge is seen for the points obtained with the *mp*2 criterion; in model 4, a reduction toward the HF edge is not observed.

It seems that the structuring of the distribution of points with a density of 0.03 and above distinguishes water from the model sets. Apparently, a strong reduction in density of points towards the HF edge is a characteristic feature of water. In general, the characteristic features of distributions for water become especially evident when one compares Figs. 7, *a* and *b* and are also manifested in Fig. 5, *a*: the frequencies of 178, 181, 187, 192, 197, 199, 203, and 206 cm^{-1}.

4. Summary

We have identified the eigenfrequency band of IM water vibrations within the 169–208 cm^{-1} region. The revealed spectral characteristics of the strip density suggest that the presence of certain special structures in water is the reason behind the observed behavior. It should be borne in mind that points discussed in this study represent just a very small sample from the actually existing vast array of eigenfrequencies of IM vibrations. Accumulating a more number of spectra would allow us to obtain a picture with a higher „resolution“ (although still incomplete). However, the boundaries of the EF range and the key features of the band structure are apparently fairly likely to be reproduced adequately even with the given number of initial spectra.

Conclusion

(1) An algorithm for grouping of points scattered within a compact region on a certain coordinate plane and enclosed within linear strips of a given maximum size (with at least three points found in each strip) running parallel to a straight line passing through the center of gravity of points was devised and presented.

(2) A program implementing this algorithm for grouping of an array of parameters of Raman spectra of IM water vibrations in „band width squared — position of the band maximum squared“ coordinates was developed. The operation of this program was demonstrated using the example of spectral parameters of the 184 cm^{-1} band obtained from an array of 65 Raman spectra of IM water vibrations. Rank sequences of widths of the obtained strips and the density of points per unit frequency interval were obtained.

(3) It was found that changes in the parameter controlling the criterion for inclusion of a point into a group may affect significantly the composition of the group and filter out strips with a high density.

(4) Rank sequences were constructed for water EFs with two different limiting strips widths and two values of the parameter governing the point inclusion criterion. It was demonstrated that the composition of points in groups changes, inducing a change in coordinates of points in the rank sequence; however, the key features at the same frequencies are preserved.

(5) Three model sets of randomly scattered points having the same statistical parameters (mean values and standard deviations in both coordinates) as the studied spectral points of water were processed. The rank sequences of „eigenfrequencies“ of these random sets differed from the sequence for water and differed greatly from each other, although two of them were close to the sequence for water.

(6) Sequences of point density in the groups strip ordered by increasing width of the groups strip were obtained for water and model sets at different values of the parameter governing the criterion for inclusion of the next point into a group. It was found that a group with a maximum value being almost 3 times lower than the one for $\mathrm{CP} = 2$ is formed for water as CP changes from 2 to 3, 4, 5. In the case of model sets, maximum density values being both higher and lower than the maximum density for water were obtained with $\mathrm{CP} = 2$. However, at $\mathrm{CP} = 4$, the maximum density for all model sets decreased sharply by more than an order of magnitude (by a factor ranging from 12 to 147).

(7) The obtained dependence of the point number density in a strip on the EF for water was stratified into three layers: the upper layer with a maximum density value of approximately 1.0 was an order of magnitude away from the middle layer with an approximate density of 0.1, and the lower background layer had a density of about 0.02. The densities of all layers decreased toward the high-frequency edge. Model sets revealed no density structuring of this kind (only its elements could be traced). A reduction in density toward the high-frequency edge was not observed; on the contrary, a trend toward an increase in density was noted. This behavior of the point density with a change in EF in a group gives reason to assume that there are some structures in water.

(8) Thus, it is fair to say that the EF band of IM vibrations of water within the 169–208 cm^{-1} range was discovered, and certain properties and structural features of this band were revealed.

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Conflict of interest

The authors declare that they have no conflict of interest.

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