
**PECULIARITIES OF THE LOW-FREQUENCY
RAMAN SCATTERING BY SUPRAMOLECULAR
INHOMOGENEITIES OF HYDROGEN-BONDED LIQUIDS****L.A. BULAVIN, M.M. BILYI, A.O. MAKSYMОВ, A.V. YAKUNOV**PACS 78.30.cd, 63.50.Lm
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The effective vibrational state density of hydrogen-bonded liquids is measured by the Raman scattering technique at room temperature. The existence of a linear region in the low-frequency spectrum on the log-log scale testifies to the applicability of the percolation model and the conception of fractals. The concentration dependences of the linear region's slope for different solutions are in good agreement with the behavior of other physicochemical parameters that depend on the hydrogen-bond network structure.

1. Introduction

In the recent years, the structure of amorphous substances such as aerogels, polymers, glass, and others is successfully simulated using the conception of fractals [1]. In particular, taking the scale invariance of inhomogeneities of a structure into account, one can explain the peculiarities of low-frequency regions in the vibrational spectra of the indicated substances [2–4].

For today, we possess experimental proofs of the existence of structural inhomogeneities (supramolecular formations) in liquids and liquid systems, whose molecules can form hydrogen bonds [5–7]. It turned out that, in water and in some aqueous and nonaqueous solutions, the inhomogeneity regions of a hydrogen-bond network have a substantial spread in dimensions — from tens to hundreds of nanometers. The attributes of the scale self-similarity within at least two orders of magnitude, as well as the formal similarity of the low-frequency vibrational spectra of amorphous media and hydrogen-bonded liquids [8], give grounds to consider the latter as media of the fractal structure.

In the given work, the peculiarities of the low-frequency Raman spectra of hydrogen-bonded liquids

and their binary solutions are considered from the viewpoint of the supramolecular structure fractality. Though much attention was paid to the study of such systems, the peculiarities of their structural dynamics and the nature of their numerous anomalies [9, 10] still remain unclear.

2. Percolation Model of a Hydrogen-Bonded Liquid

In hydrogen-bonded liquids and liquid systems, a complicated spatial energy structure of the pseudopolymer network type is formed and considerably affects such macroscopic parameters of the liquid as melting and boiling temperatures, heat capacity, viscosity, permittivity, *etc.*

At each time moment, the liquid state of a substance is similar to the amorphous one — with the close packing and a disordered arrangement of molecules. The instantaneous structure of the network changes within several picoseconds due to the thermal motion of molecules. That is why a liquid or a liquid system can be approximately presented as an amorphous medium with a variable structure.

The understanding of geometrical and topological features of the hydrogen-bond network and the validity of applying the fractal conceptions to it follow from the mathematical percolation theory. Its application to the structure of water [11, 12] helped one to explain its thermodynamic peculiarities in the bulk phase. The use of the percolation model for other liquids is possible only in the case of the existence of a certain (exceeding some critical value) number of hydrogen bonds per one molecule [13].

In the ordered phase (for example, crystalline ice), all potential bonds of the hydrogen network are involved. In the amorphous and liquid phases, a part of hydrogen bonds is broken, and the network looks like “crumpled rags” [1]. Moreover, the level of its damage depends on the temperature. The number of bonds, at which a skeleton of the hydrogen network still exists, corresponds to the so-called percolation limit.

Under these conditions, the liquid structure can be presented as an infinite percolation cluster (Fig. 1), whose cavities contain clusters of lower dimensions, small groups of bound molecules, and separate molecules. The cluster size distribution depends on the general number of involved bonds. The mean cluster size determines the dimension of a structural inhomogeneity and is called a correlation length ξ .

The scaling of the mass of an infinite cluster in the range of sizes exceeding the correlation length is described by a power law with the exponent corresponding to the dimension of the Euclidean space. In the case of smaller regions, the influence of a delicate space geometry typical of fractals takes place. The effective space dimension of the hydrogen-bond network calculated with the help of the Hausdorff and Kolmogorov algorithms [1] is called a fractal dimension that can be noninteger. Thus, the structure of a disordered medium on scales commensurable with or smaller than the correlation length is described in terms of the fractal geometry. The propagation of vibrational excitations in such a medium has its own features.

3. Low-Frequency Inelastic Light Scattering in a Disordered Medium

According to the quasimomentum conservation law, the light scattering by acoustic vibrational excitations is not observed in ideal crystals. Let us consider an ideal crystal lattice. An acoustic wave of elastic deformation makes a contribution to the local polarization fluctuation, moreover, this contribution is proportional to the elastic deformation gradient. The translation symmetry of the crystal causes a periodic space distribution of the polarization induced by vibrational excitations. Due to this fact, the contributions made to the polarization by translationally symmetric regions of the crystal compensate one another, and the total intensity of scattered light equals zero.

In the case of a disordered medium, the contributions of different regions to the scattering do not compensate each other due to the absence of the translation symmetry. The scattering by acoustic vibrational excitations

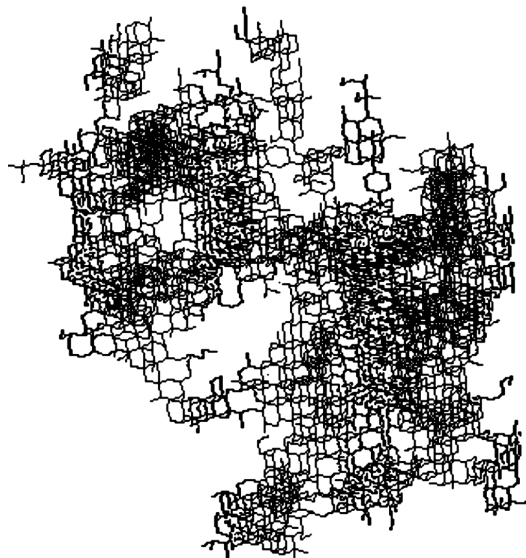


Fig. 1. Cluster which is close to the percolation limit and is constructed on the three-dimensional tetrahedral lattice that represents a skeleton of the pseudopolymer hydrogen-bond network in liquid water [14]

results in the appearance of the corresponding component in the low-frequency region of the vibrational spectrum.

The intensity of the Raman scattering observed in this case for the Stokes spectral component can be written down in the form proposed by Gammon and Shuker [15]:

$$I(\omega) = \frac{C(\omega)g(\omega)[n(\omega) + 1]}{\omega}, \quad (1)$$

where $C(\omega)$ denotes the function of coupling of light with vibrational modes, $g(\omega)$ is the vibrational state density, and $n(\omega)$ is the Bose–Einstein factor.

In a disordered medium, one can use the first coordination sphere (by analogy with a unit cell of a crystal) that allows one to estimate the spectral range of thermal vibrational excitations and the relative boundary between acoustic and optical excitations. Localized vibrational excitations collectively interact with photons, therefore such a medium should be considered as a whole. It is especially important for liquids because, in contrast to an amorphous medium with an invariable molecular structure, the fluctuation frequency of the network in liquids determined by the lifetime of hydrogen bonds is of the same order of magnitude as the oscillation frequency of the studied vibrational excitations.

According to the Debye approximation, the number of vibrational states in the interval $d\omega$ is proportional to

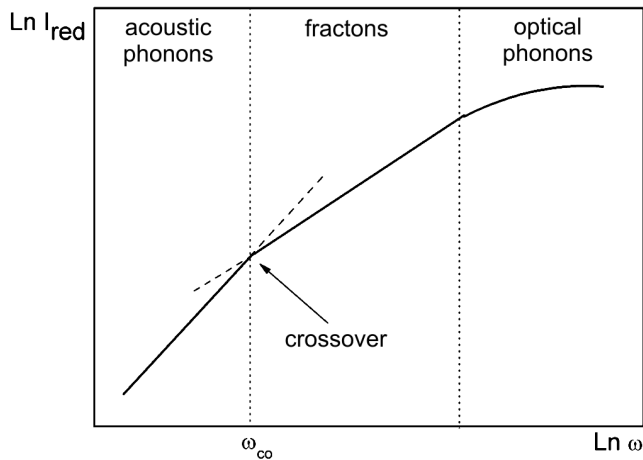


Fig. 2. Low-frequency region of the Raman spectrum of a fractal medium

the volume of the corresponding region of the reciprocal space $k^2 dk$. The use of this expression for a space of arbitrary dimension yields the expression

$$g(\omega)d\omega \propto k^{d_F-1} dk, \tag{2}$$

where d_F is the Hausdorff (fractal) dimension of space. The inhomogeneity of the medium determines the irregular (diffuse) pattern of the propagation of vibrational excitations. The time scaling parameter in the case of the propagation of excitations in a fractal medium is called the anomalous diffusion factor d_W . The corresponding dispersion relation has the form [2]

$$k(\omega) \propto \omega^{2/d_W}. \tag{3}$$

The substitution of (3) into (2) allows one to obtain the general form of the vibrational-state density function for vibrational excitations at fractals,

$$g(\omega) \propto \omega^{\bar{d}-1}, \tag{4}$$

where $\bar{d} = 2d_F/d_W$ stands for the spectral (fracton) dimension, while the corresponding vibrational excitations are called fractons. Thus, the fracton dimension reflects the fractal properties of a medium with respect to the propagation of waves in it.

Vibrational excitations with wavelengths exceeding some correlation length do not feel the fractality of a medium and therefore have a linear dispersion. The critical wavelength corresponds to the so-called crossover frequency. Vibrational excitations with smaller frequencies are acoustic phonons, while those with larger ones – fractons (Fig. 2). The crossover frequency manifests itself

in the form of a spectral peculiarity both in the Raman spectrum and in the corresponding region of the absorption spectrum. In particular, Majolino and co-authors demonstrated [16] that, for water at room temperature, $\omega_{co}/2\pi c \sim 1 \text{ cm}^{-1}$, which corresponds to $\xi \approx 10 \text{ nm}$ with regard for the dispersion law for phonons. In the dielectric loss spectrum of water, one observes a local maximum in the neighborhood of the same frequency [17].

Let us consider the contribution made to the low-frequency Raman spectra by the vibrational-optical coupling function $C(\omega)$.

It is known that the inelastic light scattering is caused by the polarization disordering of the medium. The momentum selection rules realized in crystals are violated in the case of a soft matter due to the spatial irregularity of the polarization, which yields a continuous spectrum in the low-frequency region. Thus, there exists a dependence of the vibrational-optical coupling function on the degree of disorder of the medium and, consequently, on the fractal characteristics of the hydrogen-bond network. The function $C(\omega)$ results from the averaging of the dielectric-modulation response function with respect to the vibrational modes with frequencies close to ω [15]:

$$C(\omega) = \frac{\sum_p C_p(\omega)\delta(\omega - \omega_p)}{\sum_p \delta(\omega - \omega_p)}, \tag{5}$$

where $C(p)$ is the response of the p -th mode that can be presented in the simpler form as

$$C_p = A_p l_p^D, \tag{6}$$

where l_p stands for the correlation length of the p -th mode that is much smaller in the case of liquid and amorphous media as compared to crystals and D is the effective space dimension that coincides with the Hausdorff one in the general case.

With regard for the dispersion law (3) and the validity of the power scaling law for both the wavelength and the correlation length, we obtain a power dependence of $C(\omega)$ on the frequency, which allows us to put down the effective vibrational-state density function in the following form:

$$g_{ef}(\omega) = g(\omega)C(\omega) \propto \omega^\alpha. \tag{7}$$

The exponent of ω that is equal to the angle coefficient of the rectilinear fracton spectral region on the log-log scale is sensitive to the relative orientation of molecules and characterizes the propagation of thermal vibrational excitations in a disordered medium. In the general case,

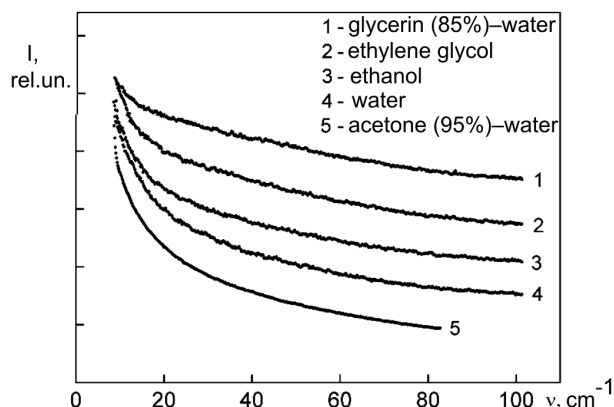


Fig. 3. Low-frequency regions of the Raman spectra of hydrogen-bonded liquids

the exponent α is determined by the fractal dimension of an instantaneous realization of the hydrogen-bond network and therefore can be determined as an integral parameter of the supramolecular structure.

4. Experimental Technique

We investigated the low-frequency ($10\text{--}100$) cm^{-1} regions of the Raman spectra of the following liquids: acetone, water, ethanol, ethylene glycol, glycerin, and some binary solutions. All solutions, except for the glycerin ones, were prepared using chemically pure substances. The error of preparing a certain volume concentration amounted to 1%. The samples with glycerin were prepared on the basis of a standard pharmaceutical 85% water-glycerin solution.

Our researches were performed with the help of a DFS-24 automatized spectrometer with a slit width of 0.1 mm. The Raman spectra were excited by radiation of an argon laser with a wavelength of 514 nm. The output power of the laser amounted to 100 mW. A laser beam passed vertically along the axis of a standard glass ampoule with liquid, whose volume was equal to 5 ml. The excitation region was projected on the entrance slit of the monochromator. The measurements were performed at room temperature.

5. Analysis of the Results

Figure 3 presents the fragments of the Raman spectra of the liquids (distilled water, ethanol, and ethylene glycol) and the liquid systems (acetone-water, glycerin-water) registered in the frequency range ($10\text{--}100$) cm^{-1} . The spectra of the reduced intensity of the same samples

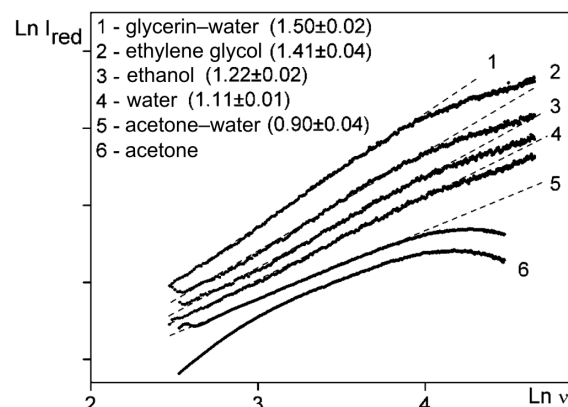


Fig. 4. Spectra of the reduced Raman intensity on the log-log scale. The corresponding values of the structural parameter averaged over several measurements are given in the parentheses

on the log-log scale are given in Fig. 4. One can see that the region ($10\text{--}50$) cm^{-1} is linear on the logarithmic scale, so it is described by a power dependence. The exponent equal to the slope corresponds to the above-introduced parameter α . It is worth noting that acetone had no rectilinear region in the investigated spectral range. The obtained value of the structural parameter for water, $\alpha = (1.11 \pm 0.01)$, coincides with the result of measurements [16] and is close to the values that were experimentally determined earlier for amorphous media with a tetrahedral structure of bonds, particularly for aerogels [3].

The absolute value of the parameter α cannot serve as an illustrative characteristic of the structure of the hydrogen-bond network. In the absence of a universal algorithm for the calculation of the function $C(\omega)$, the problem of searching for the correspondence between the structural parameter and the fractal dimension of a disordered medium is rather complicated in the general case. In order to establish quantitative relations, one should consider other parameters of the medium that can be obtained either from other experiments (for example, those on the neutron scattering) or by means of a computer modelling. In [16], the involvement of data from other sources allowed the authors to obtain quite a satisfactory agreement of α and d_F for water in the bulk phase.

New possibilities appear due to the comparison of the structural parameter for different liquids and liquid systems. Investigations of solutions of liquids with different molecular organizations and the same bond type allow one to eliminate the unknown parameters from consideration.

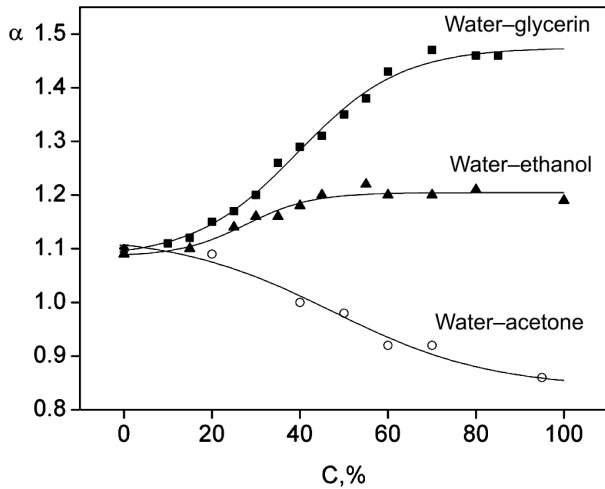


Fig. 5. Concentration dependences of the structural coefficient for the water solutions of glycerin, ethanol, and acetone

Investigations of the solutions have demonstrated that there exist at least two scenarios of the behavior of the structural parameter depending on the concentration of a binary molecular solution. The water solutions of glycerin, ethanol, or acetone manifest a sigmoid dependence in any case (Fig. 5), that is they have saturation regions and a point of inflection. At the same time, the similar dependences for the water–ethylene glycol or ethanol–glycerin solutions have no peculiarities (Fig. 6).

It is worth noting that the authors of work [16] (not dealing with the study of the concentration dependence of the water–ethanol solution) made conclusion about the effect of ethanol on the position of the crossover frequency, but not on the value of the structural parameter. Thus, the manifestation of the structural peculiarities of binary solutions in low-frequency Raman spectra was observed in our work for the first time.

To our mind, the general picture of formation of a transient (fracton) region in the Raman spectrum of binary solutions of hydrogen-bonded liquids can be as follows.

Polarization fluctuations consist of contributions made by each molecule. At the same time, the polarization of a separate molecule represents a sum of polarizations of its hydrogen bonds [18]. The contribution made to the summary polarization by each molecule will obviously depend on its symmetry. This statement can be extended to the level of the hydrogen-bond network. In the case where the symmetry of the arrangement of bonds in a molecule does not correspond to the close packing symmetry, the hydrogen-bond network principally cannot be constructed without breakages even in the

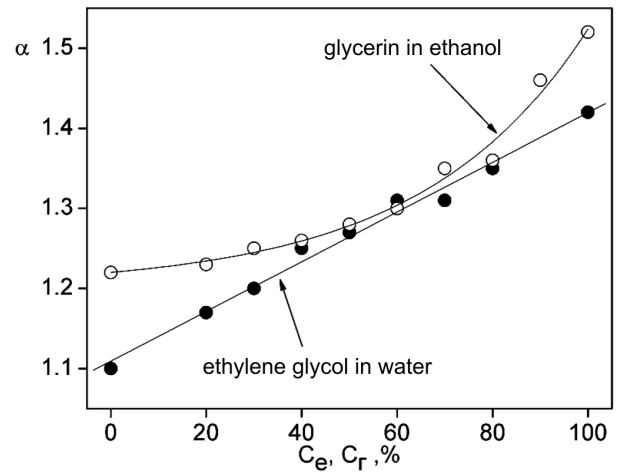


Fig. 6. Concentration dependences of the structural coefficient for ethanol-glycerin and water-ethylene glycol solutions

absence of thermal perturbations. If a hydrogen-bond network consists of molecules of different sorts, their resulting packing will depend not only on the symmetry of the constituent molecules, but also on their quantitative relation. For example, in the most general case, the fractal dimension of the hydrogen-bond network can be expressed in terms of the concentration of the binary solution as a function of the specific number of hydrogen bonds and the type of packing:

$$d_F = f[N_1, N_2, S_{12}(C)], \quad (8)$$

where N_1 and N_2 are the numbers of potential hydrogen bonds of molecules of the first and second sorts, correspondingly, $S_{12}(C)$ is the packing parameter for the given volume concentration of molecules of the first and second sorts that reflects the result of the mixing of molecules of different symmetries. In order to analyze the obtained concentration dependences, we suppose that the function $C(\omega)$ linearly depends on the concentration for all liquids [19]. Such an assumption allows one to qualitatively estimate the structural peculiarities of liquids and their solutions. For glycerin and ethanol, the average number of hydrogen bonds per one molecule is lower than for water and approximates 2. In spite of the fact that glycerin can form six potential hydrogen bonds, its complex molecular structure prevents it [5].

As one can see, the concentration dependence of the fractal dimension is more complex than a linear one. In particular, for the case of the water–glycerin solution, one can distinguish three regions corresponding to different structural phases: “depleted”, transient, and “enriched” ones, which is characteristic of micellar systems

[5]. That is, the structure of the water–glycerin solution at low and high concentrations of one of the components is realized in the form of the coexistence of a matrix-solvent and nanodimensional associates of other liquid, which is confirmed by data on high-frequency dielectrometry [20]. Vibrational excitations propagating in the percolation cluster of the solvent dominate in the formation of the energy spectrum as compared to excitations localized in associates. In the transient phase, some kind of a competition of the hydrogen bonds of water and glycerin takes place.

It is worth noting that the concentration corresponding to the most radical reconstruction of the hydrogen-bond network (the point of inflection in the concentration dependence) coincides with the anomaly of the density of the water glycerin solution. The water-glycerin mixture has a larger density than the sum of the partial densities of water and glycerin exactly in the neighborhood of the 40%-concentration [21]. This coincidence means that the increase of the density is caused by the reconstruction of the hydrogen-bond network related to the changes in the packing of molecules at this concentration. Such considerations completely agree with the experimental results of studying the supramolecular structure of liquids with the help of other methods [6, 7, 20]. The same logic can be applied to the water-ethanol solution, where it is also worth expecting density anomalies (possibly less pronounced).

For ethylene glycol molecules (the same way as for water ones), the number of hydrogen bonds formed per one molecule does not exceed four. That is why a change of the concentration of the solution results in the gradual incorporation of other molecules into the percolation cluster consisting of molecules of one sort. The fractal dimension of the cluster changes according to both the symmetry of molecules-substitutes and the space arrangement of their hydrogen bonds. Correspondingly, there is no competition of structures, which influences the monotonous character of the concentration dependence of the structural parameter. The ethanol–glycerin solution is practically three-component (due to the presence of water in glycerin). That is why the corresponding concentration dependence differs from the previous ones reflecting the domination of the hydrogen-bond structure of glycerin.

In contrast to the other investigated liquids, pure acetone has no hydrogen bonds able to form a percolation cluster. Formally, this fact is manifested in the absence of a rectilinear spectral region on the logarithmic scale. The adding of a small (5%) volume fraction of water favors the formation of a hydrogen-bond network of the

C–H···O type. In such a solution, there appear the attributes of a supramolecular structure with fractal properties: the low-frequency Raman spectrum acquires a rectilinear “fracton” region.

One can see that, for the investigated solutions, the low-frequency region of the Raman spectrum is sensitive to the concentrations of the corresponding substances. To our mind, this point can serve as a physical basis of a new rather accurate technique of determination of the solution concentration. Moreover, a sample under study can be measured in a sealed ampoule. The compounds can be easily determined from the spectrum of characteristic vibrations, whereas their concentration – from the low-frequency region.

6. Conclusions

The effective vibrational state densities of hydrogen-bonded liquids and their binary solutions have been measured at room temperature with the use of the Raman scattering method.

The existence of a transient (fracton) region in the low-frequency spectral range testifies to the correctness of applying the percolation model and the conception of fractals to the description of the structure of liquids and liquid systems. The angle coefficient of the fracton region on the log-log scale characterizes the propagation of thermal vibrational excitations in a disordered medium and can serve as an integral parameter of the supramolecular structure.

The results of studies of the binary molecular solutions revealed two scenarios of the behavior of the structural parameter as a function of the concentration that correspond to two different kinds of liquid systems. Water solutions of glycerin and ethanol (and acetone, to some degree) are characterized by the competition of the structures of hydrogen-bond networks. The critical values of the concentration confirm (in the case of glycerin) or predict (in the case of ethanol) the existence of anomalies of other physicochemical parameters in the corresponding concentration dependences.

The obtained data agree with the results of studies of the supramolecular structure of hydrogen-bonded liquids performed using other techniques (quasielastic light scattering, neutron scattering, high-frequency dielectrometry, and NMR).

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Received 04.02.10

Translated from Ukrainian by H.G. Kalyuzna

ОСОБЛИВОСТІ НИЗЬКОЧАСТОТНОГО
КОМБІНАЦІЙНОГО РОЗСІЯННЯ СВІТЛА
НА СУПРАМОЛЕКУЛЯРНИХ
НЕОДНОРІДНОСТЯХ РІДИН
З ВОДНЕВИМИ ЗВ'ЯЗКАМИ

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Резюме

Методом комбінаційного розсіяння світла за кімнатної температури виміряно ефективну густину коливальних станів рідин з водневими зв'язками. Наявність лінійної в подвійному логарифмічному масштабі ділянки низькочастотного спектра підтверджує застосовність перколяційної моделі та концепції фракталів. Залежність нахилу лінійної ділянки від концентрації для різних розчинів добре узгоджується з поведінкою інших фізико-хімічних параметрів, які залежать від структури сітки водневих зв'язків.