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Spectral evidence of connected structures in liquid water: Effective Raman density of vibrational states

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We present experimental results of the effective Raman density of states showing that water both in normal and supercooled states has a fracton behavior. We have unambiguously determined a crossover frequency ω_{co} between the phonon and fracton regimes. The obtained spectral results and the temperature behavior of ω_{co} are consistent with the correlated-site percolation model indicating the existence of four-bonded patches whose spatial extent increases with decreasing temperature. This picture for the water system is confirmed from the spectral results of two different water-alcohol mixtures; the first one with ethanol, which acts as a "patch-breaking" impurity, and the second one with butoxyethanol, which can be considered as a "patch-increasing" impurity.

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I. INTRODUCTION

It is well known that liquid water is a singular system in its physical and chemical properties. Many peculiar behaviors in the stable state as well as in the metastable deeply supercooled region, where structural effects are dominant [1,2], can be understood if dynamical clustering processes are taken into account. Such extended structures of macroscopic extent are built up through a growth mechanism in which the H bond (HB) plays the main role.

The mechanism of growth of such "dynamical clusters" has been studied in the past from a theoretical point of view; more precisely, Stillinger and Weber [3] propose that polyhedra appear in the inherent structure with spatial extents ranging up to tens of angstroms. However, beside the different theoretical models proposed in order to describe the anomalous behavior of water, if compared with that of other liquids, is the percolation theory (PT), developed in terms of the connectivity of HB's and proposed by Stanley and Teixeira. This theory successfully explains many thermodynamical properties of bulk water [4–6] as well as the temperature behavior of the isothermal compressibility of the constant-pressure specific heat and the thermal expansivity. In particular, this model describes an instantaneous structure of water as a dynamic "gel" (random network of HB's) that continuously modifies its structural configuration through the breaking and reforming of the HB's. As an example, it has been stressed that the structural superarrangements due to the organization of pentagons in polyhedra are topologically favorable and that the process of their formations tends to be autocatalytic [2]. Furthermore, recently the analysis of the distribution of lifetimes in an extensive molecular-dynamics (MD) simulation has shown that the characteristic times of the HB and the gel network increase strongly when the temperature is lowered [7]. The representation in terms of the PT implies an increase in the degree of HB connectivity as the temperature is reduced into the deeply supercooled region. More properly, since water, considered in terms of the random-bond percolation theory, is well above its gelatin threshold, Stanley and Teixeira have developed a percolation model based upon connectivity concepts from correlated-site PT, which explains the behaviors and the well-known singularities of many physical quantities [4–6] of the system. The resulting picture is the following: in terms of bond connectivity, water appears as a large macroscopic space-filling HB network subject to continuous restructuring; in fact, at any instant of time, there are many strained and broken bonds. Instead, if four-bonded molecules ("sites") are taken into account the system can be considered as having certain clustering features. Water appears as a myriad of tiny patches of four-bonded molecules embedded in a highly connected network or gel. These patches have a local density and a local entropy lower than the global density and the global entropy of the network; in particular, they are characterized by highly ramified shapes, just as in the random site percolation. As the temperature is lowered the patches increase in number and size.

From a general point of view the existence in water of extended structural networks is confirmed in several different experiments, as light [8], x rays [9,10], neutron scattering [11], and MD [6]. Brillouin [12] and Landau-Placzek [13] ratio results are successfully explained if the presence of extended structures (such as polygons and their superarrangements in polyhedrons) is taken into account. Such an interpretation of the experimental results, based on the hypothesis that dynamical processes in supercooled water are cooperative in character, has been confirmed by recent MD experiments [14] that show, taking into account for the first time, to our knowledge, three- and four-body correlations, a dispersion of the acoustic velocity. Furthermore, recent MD studies [15] accurately explain x-ray results assuming both fast restructuring networks and the fact that water molecules can exist in distinct configurations characterized by either four or five neighbors in the first coordination shell.

On the other hand, the anisotropic quasielastic light scattering (Rayleigh wing) [12] shows a fine structure in which at least two symmetric central contributions are present. The intensities and linewidths of such contributions are connected to the decay of the local order due to the centers of gravity correlations triggered by the presence of the H bond . In particular, the faster one has been related to the time evolution of H bonds, whereas the slower one has been related to the dynamical evolution of more extended structures (polyhedra) in close analogy with the results obtained by the analysis of the Landau-Placzek ratio. The whole body of the obtained dynamical information allows us to consider the supercooled liquid water, as far as the high-frequency response is concerned, like a frozen-in glass in which water molecules have high HB connectivity. When temperature decreases the order of magnitude of such extended structures has been estimated in the past: von Blanckenhagen [16] explained the features of the frequency distribution of vibrational modes obtained by an inelastic incoherent neutron-scattering experiment in liquid water hypothesizing that the short-range order existing in ice *I* persists in the fluid. In particular, in this work the correlation length on which the "acoustic" waves can propagate in phase was estimated to be 25 Å in liquid H_2O ($T=2\,^{\circ}\mathrm{C}$).

Finally, neutron-scattering experiments (elastic and quasielastic) [11] and x rays [9,10] made by Teixeira and co-workers, giving a direct evidence of such collective excitations in a water system, confirm such a physical picture proposed by percolation and light-scattering data. In fact, the time-averaged structure of deeply supercooled water shows characteristics that indicate a greater complexity in the spatial correlations compared with those of normal water. In particular, neutron data [11] give evidence of an increase (decreasing the temperature) in the spatial correlations that coincides with a growth in the size of the hydrogen-bonded assembly, a behavior implicit in the concept of transient hydrogen-bonded patches predicted by PT and supported experimentally by the observation of small-angle x-ray scattering [9].

Results obtained in recent careful and detailed studies [17–20], made in glass-forming systems having a structural network based on tetrahedral tile as water, suggested an investigation of the density of vibrational states of bulk water from the stable region ($T=70\,^{\circ}\mathrm{C}$) to the deeply supercooled one ($T=25\,^{\circ}\mathrm{C}$) by analyzing the low-frequency anisotropic light-scattering features, and, if possible, to connect the findings obtained with the above-mentioned percolating HB environments. From such experimental studies performed with different techniques by Courtens and co-workers (neutron [17–19] and light scattering [20]) and by Kieffer and Angell (by means of computer simulation [21]), it was found that these systems have a fractal-like geometry, and in particular their dynamic behavior shows a crossover from a phononlike regime to a fracton one. These latter works on tetrahedral systems with percolation connectivity and Teixeira's results of neutron-scattering experiments cited above suggest that in liquid water, particularly in the deeply supercooled region, the dynamical behavior of the system can be usefully described using self-similarity concepts. The final goal should be to test if the percolation mode with its scaling behavior, successfully applied to the study of inhomogeneous materials, can be applied to our system too.

II. LIGHT SCATTERING FROM PERCOLATING SYSTEMS

It is well known that percolating or fractal systems are characterized by well-defined scaling behavior [22] in the vibrational density of states $g(\omega)$; in fact, such a quantity, obtainable from spectral measurements (neutron- or light-scattering), follows the scaling law

$$g(\omega)\sim\omega^{\bar{\bar{d}}-1}f(\omega/\omega_{\mathrm{co}}) , \tag{1}$$

where ω_{co} is a crossover frequency between the phonon [Debye-like, $g(\omega)\sim\omega^2$] and fracton regimes; $\bar{\bar{d}}$ is the so-called spectral or fracton dimension, and f is the scaling function. In particular, in the fracton regime ($\omega\gg\omega_{\mathrm{co}}$)

$$g(\omega)=g_{\mathrm{fr}}(\omega)\sim\omega^{\bar{\bar{d}}-1} . \tag{2}$$

The crossover frequency ω_{co} can be related to a characteristic fractal length ξ, i.e., the crossover distance from the fractal behavior to the homogeneous one, through

$$\omega_{\mathrm{co}}\sim\xi^{-(1+\theta/2)} , \tag{3}$$

where θ is a characteristic dynamical index related to the scaling properties of the elastic constant [23]. For percolating systems, when we are dealing only with the infinite cluster, θ is connected to the spectral dimensionality $\bar{\bar{d}}$ by [23]

$$\bar{\bar{d}}=\frac{2D}{(2+\theta)} , \tag{4}$$

where D is the Hausdorff dimension. When we are dealing with a system in the presence of the infinite and finite clusters,

$$\bar{\bar{d}}=\frac{2d}{(2+\theta)} , \tag{5}$$

where d is the Euclidean dimensionality. Direct calculations for percolating systems give [24] $\bar{\bar{d}}\simeq\frac{4}{3}$ and $\theta=0$, 0.8, 1.5, and 2.7 for $d=1,2,3,4$.

These results hold only for a formulation of the fracton theory that considers as a model the scalar elasticity. A more proper study considering a tensorial analysis in elastic forces can change, in a significant way, the obtained results for $\bar{\bar{d}}$. This has been shown in a percolating system with rotationally invariant elastic forces [25], and observed for silica aerogels from neutron scattering [26]. In particular, two distinct elastic regimes in the fracton range can be observed, which are associated, respectively, with bending and stretching vibrations [26].

In comparison with inelastic neutron scattering, allowing for a direct measurement of the true density of states $g(\omega)$ [26], depolarized light-scattering data give the so-called effective spectral density of states $g^r_{\text{eff}}(\omega)=C(\omega)g(\omega)$, where $C(\omega)$ is the electron-vibron coupling function. In fact, the measured anisotropic spectrum $I^{\text{vibr}}_{\text{anis}}(\omega)$ is [27]

$$I^{\text{vibr}}_{\text{anis}}(\omega)=(\omega_0-\omega)^4\frac{[n(\omega,T)+1]}{\omega}C(\omega)g(\omega)\ , \tag{6}$$

where ω_0 is the laser wave number and $n(\omega,T)=[\exp(\hbar\omega/kT)-1]^{-1}$ is the Bose-Einstein statistical factor. In our case, as shown below, only with this data reduction are we able to obtain the temperature behavior of $g^r_{\text{eff}}(\omega)$ in the water system.

Recently, Alexander [28] developed a general model for light scattering where the implications of the self-similar scaling structure for the vibration spectrum are discussed. The relationship between fracton picture, elastic-scattering theory, and Anderson localization are considered, giving the following forms for the structure factors, respectively, for the high- and low-frequency regions (above and below the crossover frequency):

$$S(\kappa,\omega)\sim\omega^{2(\bar{\sigma}-1)} \tag{7}$$

and

$$S(\kappa,\omega)\sim\omega^{2(\bar{\sigma}-1)}(\omega/\omega_\lambda)^{\bar{\bar{d}}}\ , \tag{8}$$

where ω_λ is a matching frequency for the two results [Eqs. (7) and (8)] and $\bar{\sigma}$ is a scaling index defined by the strains of the network structure. This latter can be written as $\bar{\sigma}=(\bar{\bar{d}}\sigma/D)$, where σ is an internal length dimension that quantifies the fractal microstructure [26,29]. In comparison with Eq. (8) derived with some approximations, Eq. (7) is unique and follows from general scaling assumptions, and its frequency dependence should be interpreted, for Raman scattering, as a measurement of $\bar{\sigma}$ rather than a check on the value of $\bar{\bar{d}}$. Although its validity has not yet been definitively established, Eq. (8) explains the observed scaling behavior with ω of the measured spectra in the phonon regime [28]. From Eq. (7) we find that the fracton regime $g^r_{\text{eff}}(\omega)$ must scale as [28]

$$g^r_{\text{eff}}(\omega)\propto\omega^{2\bar{\sigma}-1}=\omega^{2(\bar{\bar{d}}\sigma/D)-1}\ . \tag{9}$$

This result, different from Eq. (2), takes into account the effects on the Raman spectra of the coupling function $C(\omega)$. Therefore it represents the form used in the present work in order to study the properties of bulk water in the normal and supercooled water by the fitting of the experimentally obtained spectra.

III. EXPERIMENTAL RESULTS AND DATA ANALYSIS

The depolarized light-scattering measurements were performed in samples of 10 cm^3 contained in a vial. The water was of high purity, triple distilled, deionized, and dust-free. The optical thermostat used was specially built in order to avoid unwanted stray-light effects and allows one to collect data with a good signal-to-noise ratio. The sample temperature was held constant within $\pm0.005\,^\circ\text{C}$ in the full range of measurements, -27 to $70\,^\circ\text{C}$, for periods of hours, using a proportional temperature controller monitored by a platinum resistor connected to a high-precision resistance bridge. The main interest of this optical setup was to realize a good index refraction matching, which allowed us to measure scattered intensities with very good accuracy. All the scattered spectra were measured using two fully computerized high-resolution spectrometers: a Spex triple monochromator and a double monochromator double pass (SOPRA model DMDP 2000) with a half-width-at-half-maximum (HWHM) resolution of respectively, 2 GHz and 700 MHz. The SOPRA monochromator is especially designed for a very high resolution and stray rejection. This instrument has an exceptionally high stray-light rejection. The depolarized spectra were measured in the frequency range -50 to $+50$ cm^{-1}. We worked in a classical scattering geometry with a scattering angle of 90° and the incident beam reached the sample vertically polarized with respect to the scattering plane, while the scattered light was collected through a Glan-Thompson polarizer with an extinction coefficient better than 10^{-7}. As exciting source we used the 5145-Å line of a unimode Ar^+ laser working at a mean power of 1 W. The spectra were taken at different temperatures, in normal and supercooled regions. Acquisition time was chosen in order to obtain good-quality spectra, mainly in the far-wing region. Normalization for incident-beam intensity fluctuations and correction for the density ρ and refractive index n (ρ and n data are taken from literature) has been finally performed on our experimental data.

Using Eq. (6) the effective spectral density of states $g^r_{\text{eff}}(\omega)=C(\omega)g(\omega)$ was obtained from the scattered intensity. As can be observed in Fig. 1, where we plot the ω dependence of this quantity, in a log-log scale at the temperature of $22\,^\circ\text{C}$, because of the very low quasielastic contribution, identical results are obtained with [Fig. 1(a)] and without [Fig. 1(b)] the subtraction of the quasielastic (Rayleigh) contribution. This result shows that the obtained spectra can be analyzed without any manipulation, indicating therefore that the observed scaling behavior above (solid line) and below (dotted line) a certain crossover frequency are due only to the physical properties of the system. On this basis, we study the spectral properties of water for many different temperatures, covering a range that goes from the normal region ($70\,^\circ\text{C}$) to the deeply supercooled one ($-27\,^\circ\text{C}$).

In Fig. 2 are reported, in a log-log scale, four different spectra showing the effective spectral density of states $g^r_{\text{eff}}(\omega)$ at the temperatures: -25, -4, 27, and $70\,^\circ\text{C}$. From these plots, which show behaviors analogous to the data reported in Figs. 1(a) and 1(b), it is possible to assert, by just looking at the best fit of the experimental data in both the high- and low-frequency regions, respectively, the following.

(i) In all reported spectra two well-defined regions exist with a crossover frequency, the first one characterized by a quadratic frequency dependence (ω exponent $\sim2\pm0.1$). This shows unambiguously that, for small ω,

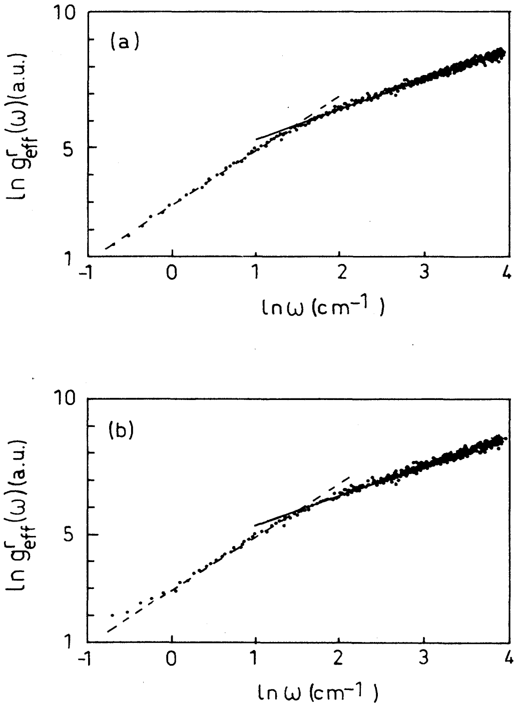

FIG. 1. Log-log plot of $g^r_{eff}(\omega)$ vs ω at $T=22\,°C$, with (a) and without (b) the subtraction of the quasielastic (Rayleigh) contribution.

$g^r_{eff}(\omega)$ follows a powerlike behavior. Such a "phononlike" dynamics persists in all the temperatures spanned in this experiment and its ω extension is restricted, lowering T by the existence of a lower-slope region.

(ii) At higher frequency $g^r_{eff}(\omega)$ behaves like ω^n with $n \simeq 0.9 \pm 0.1$. In particular, this value for n is obtained for all temperatures of the experiment.

(iii) The crossover frequency between the two above-mentioned regions shifts towards lower values, going from the stable liquid region ($T \geq 0\,°C$) to the supercooled one ($T < 0\,°C$).

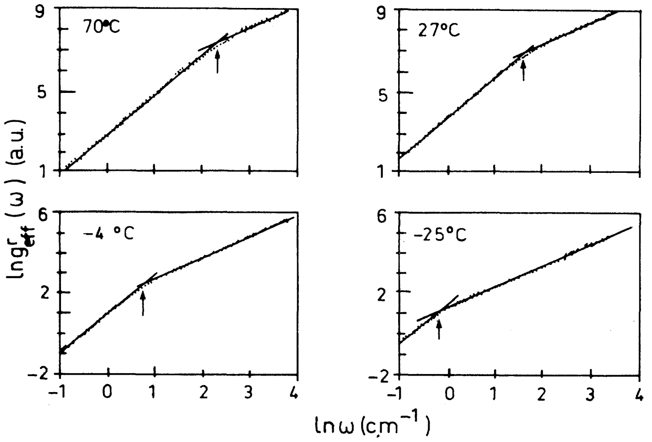

FIG. 2. Log-log plot of Raman spectral density of states vs frequency shift at $T=70$, 27, -4, and $-25\,°C$. Straight lines represents least-squares best-fit results; the two resulting slopes are 2 ± 0.1 and 0.9 ± 0.1, respectively. Arrows indicate the crossover frequency ω_{co}.

Such an overall behavior can be rationalized only if a percolating structural network exists in liquid water. In particular, in terms of the proposed models, localized excitations are present in the system. Considering that for percolation the fractal dimension $D=2.5$, the obtained value for $\bar{\sigma}$ is consistent $[\bar{\sigma}=(\bar{\bar{d}}\sigma/D)]$ with the fracton dimension $\bar{\bar{d}}$ and the internal lengths σ measured for analogous tetrabonded systems ($\bar{\bar{d}} \sim 1.7$ and $\sigma \sim 1.4$). As far as the fracton dimension is concerned, the obtained value is different from that corresponding to the percolation ($\bar{\bar{d}}=\frac{4}{3}$), but agrees with the value measured from analogous systems (tetrahedral structures such as silica aerogels [26]). In these latter systems the tensorial character of the elastic strains in a percolating system with rotationally invariant elastic forces [25] is considered. In particular, $\bar{\bar{d}} \sim 1.7$ is the value obtained in the frequency region where the vibrational dynamics is due to elastic stretching contributions [28]. Considering that, for Raman scattering in water, stretching vibrations dominate the bending contributions [30], the obtained result $\bar{\bar{d}} \sim 1.7$ is noticeable. Finally, the obtained internal length dimension σ agrees with the theoretical predictions [26,28,29], and it can be observed that values significantly larger than 1 suggest a very fractal (percolating) microstructure [26,28,29].

Although these results cannot be considered conclusive on the fracton behavior of water (this would require a separate determination of the fracton index $\bar{\bar{d}}$ from a direct evaluation of the density of states, using, if possible, neutron-scattering or molecular-dynamics simulation), the reported data give significant results on the scaling behavior of the system and consequently on its percolating behavior. In this respect, two findings can be considered as interesting goals: (a) the temperature insensitivity in the frequency dependence of $g^r_{eff}(\omega)$ in both the high- and low-frequency regions and (b) the lowering of the crossover frequency while decreasing the temperature. This latter result is shown in Fig. 3(a).

Equation (3) connects the crossover frequency ω_{co} to the characteristic length ξ, a quantity that, for percolating systems, represents the "connectivity coherence length." In fact, we obtain the indication that the correlation length ξ increases with decreasing T, in agreement with the behavior of the spatial extent of water clusters with high connectivity.

This result can be studied in a more substantial way considering that the buildup of such structures is due to the HB. In particular, the growth mechanisms of the patches could be driven by a thermally activated process through the HB. In this respect we plot, in Fig. 3(b), ω_{co}^{-1} [directly related to ξ through the exponent $(1+\theta/2)$ of Eq.(3)] vs $1/T$ obtaining as a result that the observed process has a well-defined Arrhenius behavior. The best fit of the data gives an activation energy of ~ 20 kJ mol^{-1}. Assuming for θ the value of 1.5 [24,30] we have for ξ an activation energy value that agrees with the value of the hydrogen-bonding interaction energy as recently calculat-

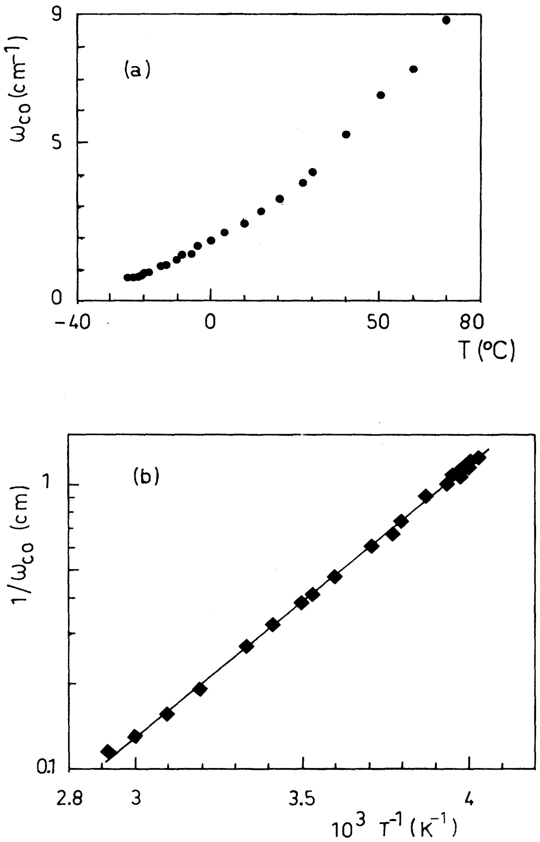

FIG. 3. (a) Plot of the crossover frequency ω_{co} vs T; solid line is a guide for eye. (b) ω^{-1} vs $1/T$.

ed in a careful MD experiment by Sciortino, Geiger, and Stanley [31] and measured in many different experimental studies [32]. This result constitutes another important finding that agrees with the structural picture, in terms of the transient ramified patches of four-bonded molecules, proposed for water by PT [4] and supported experimentally by neutron scattering [11], x-ray scattering [9,10], and MD simulations [6].

As previously reported, the correlated-site percolation model well explains "paradoxical facts" in some thermodynamical quantities at sufficiently low temperatures [4,5]. The presence of patches, with local properties different from the global properties of the HB network as a whole, provides the mechanism for the anomalies observed in the specific volume, isothermal compressibility, and constant-pressure specific heat of water by changing the temperature [4,5,33]. These anomalies are enhanced in the supercooled region. The ansatz of the model is the local density and the local entropy of the patch must be less than the global density and entropy of the network. Both such local quantities are consistent with the presence of a local structure that is able to support the localized vibrational modes observed in the effective density of states. Since all water molecules in a given patch are tetrahedrally bonded, the patch density is different (smaller) from the global or mean density. Furthermore, the water molecule being extremely nonspherical, with a consequently highly directional HB, implies a significant reduction of angular degrees of freedom in the patch (where all molecules are four bonded), creating a local (patch) entropy smaller than the mean entropy of the network. In these terms PT is also able to give qualitative predictions on the pressure and temperature behaviors of the above-reported thermodynamical quantities, adding "patch-breaking" or "patch-increasing" impurities. In particular, it is expected that patches increase in size and number by diluting in water a certain quantity of D_2O. This is because, in this isotope, the fraction f_4 of four-bonded molecules is larger than the same quantity in pure water at a given temperature [6]. Correspondingly, one observes for D_2O a value of p_B (the fraction of linear HB) larger than that for H_2O at the same value of T [6]. On the contrary, upon diluting in water patch-breaking impurities, such as ethanol, which can form essentially three bonds for a molecule rather than four, the patches decrease in size and number. In particular, relatively few molecules of this second component should considerably decrease both size and number of these structures. In order to test these effects on the water structure and to confirm the interpretation of the presented experimental data based on the presence, in water, of well-defined local structures, we performed additional measurements of the effective density of states in a water-ethanol mixture (patch-breaking) and on a system for which the presence of well-established supramolecular structures has been shown in detail by means of different experimental techniques [34–37]. In this second case we used a water-butoxyethanol (BE) mixture in which small-angle neutron scattering (SANS) [36] and light scattering [37] gives direct evidence of the presence of supramolecular structures with a spatial extent (gyration radius) that increase from 20 to 55 Å, increasing the temperature in the range 5–45 °C. Such aggregates have micellarlike BE-rich structures. In particular, the SANS experiment (in the concentration range, mole fraction of BE, 0.035–0.09) shows that such structures can be of the type h $[(H_2O)_4\text{-BE}]$ with h increasing with T from tens to several hundreds on passing from $-5\,^\circ$C to higher temperatures.

In Fig. 4 we report the log-log plot of $g^r_{\text{eff}}(\omega)$ vs ω for

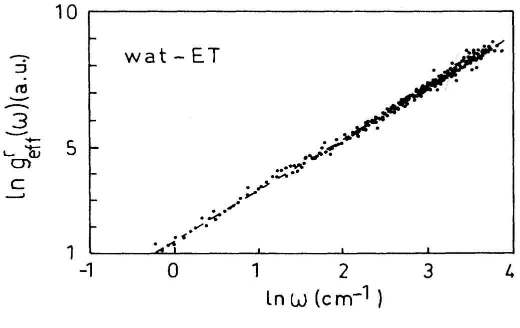

FIG. 4. Log-log plot of $g^r_{\text{eff}}(\omega)$ vs ω for the water-ethanol solution at $T=22\,^\circ$C; the concentration in mole fraction of alcohol is $x=0.025$.

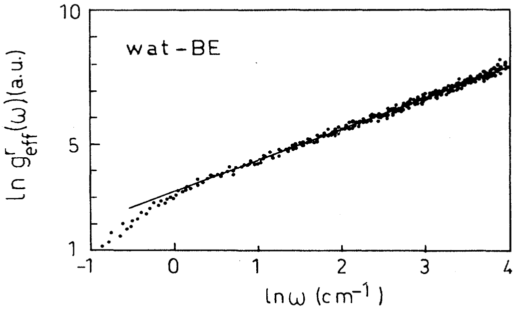

FIG. 5. Log-log plot of the effective Raman density of states measured in the water-BE mixture (BE concentration $x=0.035$ and $T=22\,^{\circ}\mathrm{C}$).

the water-ethanol solution at $T=22\,^{\circ}\mathrm{C}$; the concentration in mole fraction of alcohol is $x=0.025$. As can be observed, all the data fall in the entire explored frequency range around the dotted line obtained as the best fit of the experimental points. The slope of this line is about 2 ± 0.1 indicating that the Debye-like behavior persists in the whole frequency region. From this we have the indication that alcohol molecules really act as patch-breaking impurities. In fact, by replacing a water molecule belonging to the full tetrabonded patch with such an impurity, forming essentially three bonds per molecule, the local structure is destroyed. The behavior observed in an analogous plot (Fig. 5) of the effective Raman density of states measured in the water-BE mixture for the BE concentration $x=0.035$, in the same experimental conditions ($T=22\,^{\circ}\mathrm{C}$ and same spectral range) is much different. In such a case we obtain a behavior which is opposite that shown by the water-ethanol mixture. Figure 5 shows a scaling behavior $[g^r_{\mathrm{eff}}(\omega)\sim\omega^n]$ in $g^r_{\mathrm{eff}}(\omega)$ which covers about the entire explored frequency range. The measured slope $n\simeq1\pm0.1$ is slightly different from the value obtained for pure water. This represents a confirmation that the BE molecule behaves as a patch-increasing impurity. In fact, in supramolecular aggregates $h[(H_2O)_4\text{-BE}]$ the water molecule plays the determinant role (the structure is built up via the HB). The significant result is however that for this latter mixture the crossover between the two vibrational regimes moves towards the lowest frequencies if compared with water at the same temperature ($T=22\,^{\circ}\mathrm{C}$). In this condition pure water shows the frequency crossover at about 3 cm^{-1}, while for the water-BE mixture it is $\omega_{\mathrm{co}}\sim1$ cm^{-1}. Considering that Eq. (3) connects the crossover frequency ω_{co} to the "size" of the structure, and assuming that in the water-BE mixture this latter quantity is related to the extension of the micellarlike aggregatus (35 Å from SANS data for $T=22\,^{\circ}\mathrm{C}$), we can hypothesize a rough estimate of the water patch dimensions [Eq. (3)] of about 10 Å.

IV. CONCLUSIONS

In this paper we have studied the effective density of vibrational states measured by depolarized Raman light scattering in pure bulk water in the normal and deeply supercooled regions. We observe that the present data provide a striking confirmation of the theoretical conjectures (correlated-site percolation model [4–6]) concerning the nature of structural changes that occur in water. In particular, the results of the reported spectral measurements give evidence of percolating structures with a scaling (fracton) behavior reflected in the vibrational dynamics of the system.

The exposed results of effective spectral density of states are summarized in two unambiguous experimental findings: a persisting scaling behavior for high and low frequencies with a well-defined crossover between a phononlike regime to a fracton one on the vibrational modes of the system, and the decrease of such crossover frequencies while decreasing the temperature. Such localized modes and the ω_{co} behavior as a function of temperature can be explained, in accordance with PT, only if the existence in water of tiny patches, with a local density and a local entropy lower than the global density and entropy, is hypothesized.

By studying the temperature behavior of the crossover frequency and considering, in an appropriate way (fracton theory [22–24]), that ω_{co} is directly connected with the correlation length ξ, the connectivity coherence length for percolating systems, we show that the growth mechanisms of the patches must be derived by a thermally activated process through the HB. This is directly confirmed by the measured values for the activation energy that is of the same order of the hydrogen-bonding interaction energy.

Confirmation of the presence in the system of the tiny patches of four-bonded molecules embedded in a highly connected water network is drawn from the results relative to some water-alcohol mixtures. In particular, for a solution of ethanol in water, we observe that the alcohol molecules behave as patch-breaking impurities, while in the micellarlike mixture water-butoxyethanol, we observe the opposite behavior: BE molecules are patch-increasing impurities.

In conclusion, we remark that the presented data give important indications about the fractal character of water. The present interpretation of the spectral data and the above exposed experimental findings are able to give indications of the possible presence in this complex system of self-similar structures (transient ramified patches of four-bonded molecules). However, definitive confirmation of this respect can be obtained only through direct structural measurements or molecular-dynamics simulation experiments.

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