

Low-Energy Excitations in Water: A Simple-Model Analysis

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This paper demonstrates that characteristics of low-energy excitations in water observed in Raman scattering and inelastic neutron and x-ray scattering experiments follow naturally from a simple-model analysis, taking into account essential features of water structure in the center-of-mass system. It is shown that the modes associated with the lower band near 60 cm^{-1} are strongly localized with localization lengths of the order of their wavelength and the higher band near 180 cm^{-1} attributes to mesoscopically localized modes within the network connected by hydrogen bonds. [S0031-9007(97)05166-1]

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The realization of two broad bands in Raman spectra near 60 and 180 cm^{-1} in water is as old as the discovery of the Raman scattering itself [1,2]. A qualitative understanding has long been available for these low-energy bands. However, many key aspects of a detailed quantitative description, at the molecular level, are still missing despite focused experimental efforts in this decade [3]. Sette *et al.* [4] have very recently suggested the existence of collective excitations with a velocity of sound $3200 \pm 100\text{ m/s}$, more than twice larger than the ordinary speed of sound 1400 m/s , by measuring the dynamic structure factor $S(q, \omega)$ up to 200 cm^{-1} in the $q = 3\text{--}14\text{ nm}^{-1}$ range by means of high resolution inelastic x-ray scattering. The equivalent dispersive excitations at low energies for D_2O had been observed also by the coherent inelastic neutron scattering up to 120 cm^{-1} and $q = 6\text{ nm}^{-1}$ [5]. However, different interpretations for inelastic neutron scattering data are given [6] claiming that excitations observed in Refs. [4,5] are rather opticlike (dispersionless) excitations. Thus, the nature of low-energy collective excitations in water still remains controversial [7]. Since the energy range spanned by Raman spectra and inelastic x-ray and neutron-scattering data overlaps, the origin of low-energy excitations should be elucidated on the same basis. The present paper sets forth a new interpretation of low-energy excitations in water by a simple-model analysis. The model is abstract, but when discussing the physical origin of low-energy spectra in water, its significance becomes clear.

The commonly accepted overall picture of water structure is a tetrahedral random network totally connected by hydrogen bonds, isomorphous with that in quartz. This structural model originally proposed by Bernal and Fowler [8] has stimulated a lot of subsequent works on the microscopic structure of water. Recent experiments [9–13] and computer simulations [14] have suggested that the random tetrahedral network is not perfect but must contain defects which are characterized geometrically by the presence of an extra fifth molecule in the first coordination shell, or topologically by the presence of bifurcated hydrogen bonds (up to 40%).

When discussing the dynamic properties of water, there is an important time scale τ_c , which is of the order of 10^{-11} sec ($= 3.3\text{ cm}^{-1}$), distinguishing harmonic vibrations and relaxation processes [15]. On time scales shorter than τ_c , thermal motions of water molecules can be regarded as being of vibrations on a slowly moving network, while at time scales longer than τ_c slower displacements of the equilibrium positions become relevant. The energy regime $\omega \gg 1/\tau_c$ should be primarily associated with harmonic vibrations. Namely, liquid water at shorter time scales than $\approx 10^{-11}\text{ sec}$ resides in an approximately harmonic potential energy minimum (in configuration space) and the molecular motion can be described as being vibrational.

Walrafen *et al.* [16] observed the noticeable variation of intensities of 60 and 180 cm^{-1} bands with temperature and adding electrolytes in water, in which the Raman spectra of the 180 cm^{-1} band is insensitive to effects produced by hydration of cations, but it is very sensitive to the effects resulting from the hydration of certain anions. This result not only suggests that the connectivity of tetrahedral network via hydrogen bonds is much influenced, but also most importantly indicates that the modes associated with the 180 cm^{-1} band are related to the connectivity of the network. More recently, Tominaga and Miyoshi-Takeuchi [17] have performed high resolution Raman experiments and confirmed that the complete disappearance of the 180 cm^{-1} band with the concentration of dioxane in water of $\sim 0.7\text{--}0.8$ molar fraction. The molar fraction $\sim 0.7\text{--}0.8$ indicates an almost complete disconnectivity of a hydrogen bonded tetrahedral network. In addition, they have found [17] that the lower band near 60 cm^{-1} is not much affected by increasing the concentration of dioxane. The equivalent evidences had been obtained from the temperature dependence of the intensities of the 60 cm^{-1} band [16] and from data with aqueous LiCl solutions [18]. These results give a new insight to the description of the modes associated with 60 and 180 cm^{-1} , namely, the modes attributing to the 60 cm^{-1} band are “strongly” localized at least within several tetrahedral units and not associated with

the connectivity of tetrahedral network, while the modes attributing to the 180 cm^{-1} band are related to the connectivity via hydrogen bonds and not strongly localized ones. Here strongly localized modes imply the modes with the localization length $l_c(\omega)$ of the order of its wavelength $\lambda(\omega)$. It will be clarified later that our view mentioned above is consistent with recent inelastic neutron and x-ray scattering experiments [3–6].

We propose, at first, a simple structural model, taking account of essential features of water in terms of the center-of-mass system. This is because low-energy excitations treated here, below the Debye cutoff frequency ω_D (corresponding to that of ice I_h), are surely those associated with the center-of-mass dynamics. There is no long-range order in liquid water and the equilibrium positions are quite irregularly distributed in space. Figure 1(a) is the schematic illustration of our quasi-1D model, which takes into account characteristics of water structure such as disordered network-forming structure at any instant. This model consists of two main chains with a constant mass M of molecules and these are connected to their nearest neighbors by linear springs with constant strength K . The central hypothesis of our model is that in water there should be a certain number of extra vibrational states (e.g., corresponding to defect molecules suggested in Refs. [9–13] or librational motions of tetrahedra itself), which we attach to each main chain with the mass M by linear springs with the strength k_i at site i . The mass M and the force constant k_i are related to the characteristic frequency $\omega_i^2 = k_i/M$ of these additional states, where the parameters ω_i^2 are random quantities and assumed to be uniformly distributed in the range

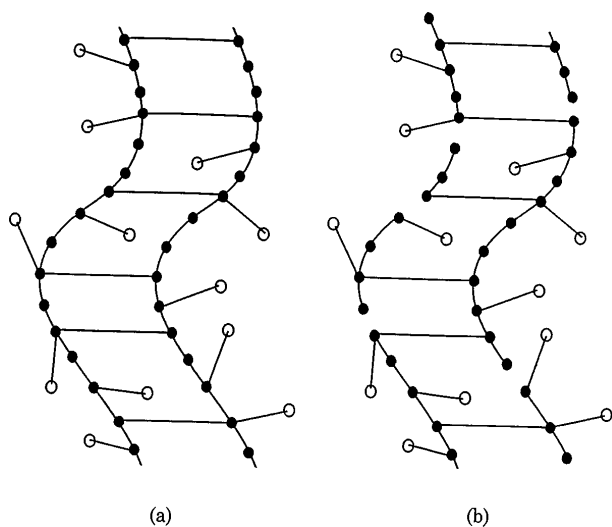


FIG. 1. Schematic illustration of a simplified (quasi-1D) water structure in the center-of-mass system. The network structure is composed of unit cells with six or eight molecules. (a) The number of extra vibrational states is 40% of the total number of main molecules, and they are randomly attached to two main chains. (b) The broken network model in which one bond in each unit cell with six or eight molecules is missing.

between ω_{\min}^2 to ω_{\max}^2 . The distribution of ω_i^2 arises from the local distortion and strain due to the disordered structure of water. We should emphasize that molecules connected by the spring constant k_i in Fig. 1(a) do not directly correspond to the true molecular arrangement in water. It simply means some kinds of low-energy vibrational states. It should be associated with extra vibrational states in the local potential minima with different curvatures ($k_i = M\omega_i^2$) due to the different environment of each defect. It is not worthwhile to give a strict picture for these entities from the two reasons: It depends on such factors as the particular configuration of molecules surrounding the extra vibrational state on local strains and potential energies (this is the very reason for taking the distributed ω_i^2).

The Hamiltonian for our model is expressed by

$$H = \sum_i \left[\frac{P_i^2}{2M} + \frac{p_i^2}{2M} + \frac{K}{2}(Q_i - Q_{i-1})^2 + \frac{k_i}{2}(q_i - Q_i)^2 \right], \quad (1)$$

where molecules have mass M , and Q_i and q_i are generalized coordinates representing displacements or changes of angle variable. The corresponding momenta are described by P_i and p_i , respectively. Capital letters denote quantities for main chains and lower letters are for additional vibrational states. Note that vibrations lose their pure longitudinal or transverse character in disordered systems like water, and direct coupling to density fluctuations with neutrons or x-rays probes the one-component projection of the vibrations. Thus, the scalar approximation in Eq. (1) is valid.

The dynamical structure factor $S(q, \omega)$ is expressed in terms of the Fourier transform of the correlation function of density fluctuations as $S(q, \omega) = (1/2\pi) \int dt e^{-i\omega t} \langle \delta\rho_{-q}(0) \delta\rho_q(t) \rangle$, where $\delta\rho_q(t)$ is the q component of the density fluctuation. The angular brackets $\langle \dots \rangle$ mean the thermal average. Decomposing $Q_i(t)$ [or $q_i(t)$] defined in Eq. (1) into normal modes, one obtains $\delta\rho_q(t) = -ie^{i\omega t} \sum_i qe_i(\lambda)e^{-iqr_i} + O(Q_i(t)^2)$, where r_i is the equilibrium position of the molecule at site i . Here $\{e_i(\lambda)\}$ is the eigenvector belonging to the eigenfrequency ω_λ . Substitution of this expression into the definition of $S(q, \omega)$ yields

$$S(q, \omega) = \frac{(n+1)}{\omega N} \sum_\lambda \delta(\omega - \omega_\lambda) \left| \sum_i qe_i(\lambda)e^{-iqr_i} \right|^2, \quad (2)$$

where n is the Bose-Einstein distribution function and N the total number of atoms, respectively. We employ the numerical method given in Ref. [19] to calculate $S(q, \omega)$. Calculated results for $S(q, \omega)$ with a system size $N = 12000$ are given in Fig. 2 in units of $M = 1$, and $K = 1$, where periodic boundary conditions are taken. The lower and upper limits for the distribution of the frequency ω_i^2

are taken to be $\omega_{\min}^2 = \frac{1}{4}$ (or equivalently $k_{\min} = \frac{1}{4}$) and $\omega_{\max}^2 = 1$ ($k_{\max} = 1$). The force constant K ($= 1$) should correspond to the (largest) stretching force constant $K_r \approx 1 \text{ eV \AA}^{-2}$ (in Keating's notation) between O-O within the network and the force constant k_i should be smaller than the strength of K . It is not easy to estimate meaningfully the value of k_i . However, for instance, the relevant force constant aside from K_r for network-forming structures is the bending one K_θ ($\approx 0.5 \text{ eV rad}^{-2}$). Thus, the above choice of the parameters k_i seems to be reasonable.

An important conclusion drawn from Fig. 2 is that there appear fairly two bands in the calculated spectra as observed in Raman scattering experiments. The lower peaks, being broadened by increasing the wave number q , are almost independent of q (nondispersive). The higher band depends strongly on q , indicating the modes contributed are "dispersive." By taking the spring constant $K = 1$ in Eq. (1) as the actual value of the stretching force constant $K_r \approx 1 \text{ eV \AA}^{-2}$ and M for the mass of water molecule, the peak energy of the higher band at ≈ 2 in Fig. 2 becomes $\approx 200 \text{ cm}^{-1}$ and that of the lower band at ≈ 0.5 in Fig. 2 does 50 cm^{-1} . Both of these values coincide with observed peak energies [16–18] in spite of a simple-model analysis. In addition, the velocity of the fast sound is estimated from the dispersion relation of the higher band depicted in Fig. 2 to be $v \approx 3 \times 10^3 \text{ m/sec}$. This value agrees fairly with observed values [4,5].

Figure 3(a) shows the eigenmode with $\omega_\lambda = 0.49801$, which provides the evidence of strongly localized modes

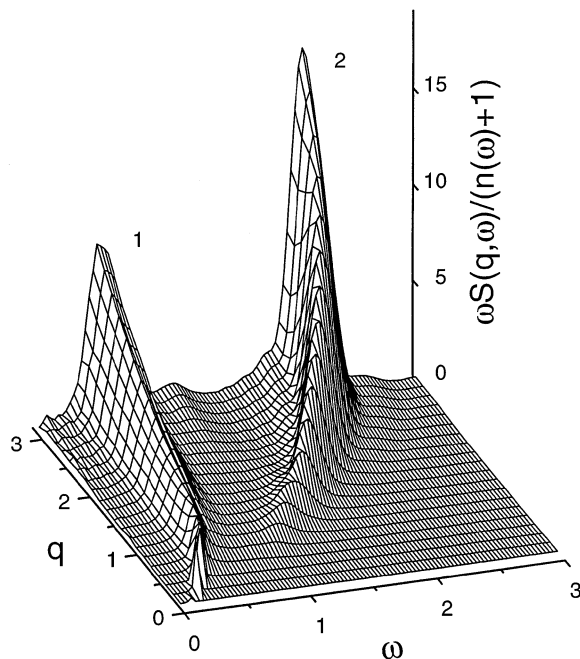


FIG. 2. The ω and the q dependence of $S(q, \omega)$ for the model of Fig. 1(a) with the total site number $N = 12000$. The strengths of force constants k_i are distributed between $k_{\max} = 1$ (or equivalently $\omega_{\min}^2 = 1$) and $k_{\min} = \frac{1}{4}$ ($\omega_{\min}^2 = \frac{1}{4}$). The system of units used is $M = K = a = 1$.

in the frequency region $\omega_{\min} < \omega < \omega_{\max}$. It should be noted that defect molecules and molecules belonging to main chains vibrate in antiphase (optical-like modes) [5]. The "strong" localization in the range $\omega_{\min} < \omega < \omega_{\max}$ originates from the resonance between excitations along main chains and extra vibrational states [20]. Note that the distributed ω_i^2 is the key element for the strong localization. Figure 3(b) is the eigenmode with $\omega_\lambda = 1.69910$ belonging to the higher band in Fig. 2. The mode pattern possesses quite different characteristics from those given in Fig. 3(a), indicating that only molecules in main chains vibrate remarkably, and extra vibrational freedoms do not follow the vibrations of main chains. In addition, these modes are dispersive [3,4] and are mesoscopically localized. Excitations below ω_{\min} will be dominated by a viscoelastic effect of water and this is beyond the scope of the present Letter.

We have calculated $S(q, \omega)$ for a "broken" network structure illustrated in Fig. 1(b). This is a model structure for the situation in which the network via hydrogen bonds are disconnected due to the hydration of anions [17,18] or increasing temperature [16]. Figure 4 clearly demonstrates that, with decreasing the connectivity of the network, the intensities of higher band (corresponding to the 180 cm^{-1} band) noticeably decrease and, in contrast, the lower band (60 cm^{-1} band) is insensitive to the connectivity. These results surely recover the tendency observed in Raman scattering experiments for 60 and 180 cm^{-1} bands [16–18].

Dispersive excitations observed in Refs. [4,5] had been interpreted as modes propagating within the hydrogen-bonded patches (O-O stretching) predicted by molecular dynamics calculations [21–25]. This interpretation agrees with our results in Fig. 3(b), but the most important consequence revealed by our calculations is the implication that those should be "mesoscopically" localized modes, not propagating over long distances. This feature should be subject to experimental tests. Bermejo *et al.* [6]

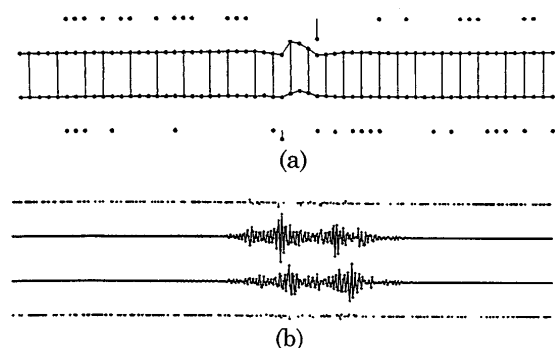


FIG. 3. Two types of mode patterns: (a) strongly and (b) mesoscopically localized modes. The upper and lower plots show the displacements of extra vibrational states, respectively. The displacements of main chains are given in two central curves. (a) The eigenmode with $\omega_\lambda = 0.49801$. (b) The eigenmode with $\omega_\lambda = 1.69910$.

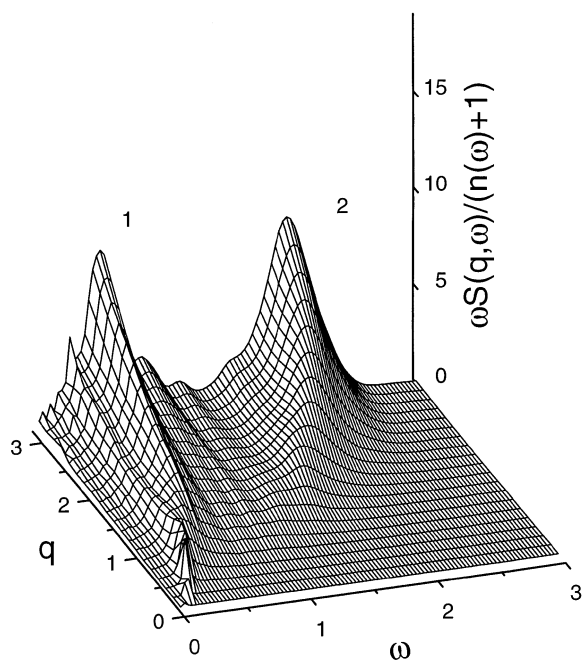


FIG. 4. The ω and the q dependence of $S(q, \omega)$ for the broken network model.

have reported the evidence of nondispersive modes around 60 cm^{-1} in terms of inelastic neutron scattering measurements. It seems to be natural to assign the nondispersive modes near 60 cm^{-1} observed by Bermejo *et al.* [6] as the modes belonging to the lower branch in our calculations in Fig. 2, which are strongly localized and nondispersive.

It is remarkable that the two-band feature at low energies has been also realized in network-forming glasses for a long time [26]. In glasses, the lower band near 50 cm^{-1} in the Raman spectra is the so-called boson peak and the higher band always appears close to the Debye cutoff frequency ω_D of the corresponding crystals [26]. The similarity of the Raman spectra between water and glasses, as well as the data of high-resolution inelastic x-ray scattering measurements between water [4–7] and glasses [27,28], suggests a common origin for the principal feature in their spectra. The present Letter will shed light on the elucidation of the properties of low-energy excitations in glasses as well.

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