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Incoherent inelastic neutron scattering from liquid water: A theoretical investigation

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A theory of incoherent inelastic neutron scattering from liquid water is presented, and recent experimental data obtained by employing the spallation sources are interpreted. This theory is a statistical theory, similar to those describing optical spectra of liquids. The experimental spectra of liquid H_2O and D_2O are reproduced theoretically. The incoherent neutron- and light-scattering spectra of water are compared. The suitability of this type of experiment to study high-frequency modes of translational-rotational motion of molecules in liquids is emphasized.

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I. INTRODUCTION

Until recently, the production of neutrons for scientific use was centered on fission reactors in which the neutrons are generated in a continuous stream by the fission of the uranium in the reactor core. As the needs of the scientific community have grown, an alternative neutron production method has been developed. A high-energy accelerator is used to bombard the ^{238}U target with pulses of high-energy protons. In the resulting process of spallation, neutrons are produced, which can then be used for experiment. Combined with strongly improved neutron detection technology, this new method has permitted considerable progress in various fields of neutron spectroscopy. For information on spallation sources, see Refs. [1–3].

The inelastic incoherent neutron-scattering studies of water began in 1958 when Brockhouse, using a reactor source, observed the low-energy part of the inelastic-scattering spectra of this liquid [4]. Eleven years later, in 1969, Harling measured its high-energy component due to internal vibrations [5]. However, the flux of epithermal neutrons was too weak, and the momentum transfer too large, to get more than a mere detection of the vibrational effect on the neutron scattering. An important step was accomplished when Chen *et al.* applied spallation-source technology to this problem [6]. The experimental method was further developed by Toukan *et al.* [7], and was also employed by Giordano, Salvato, and Wanderling [8]. The similarity between the neutron- and light-scattering spectra then appeared clearly. One could then envisage performing a band-shape analysis.

As far as the theory is concerned, the first attempt to interpret the inelastic incoherent neutron scattering of slow neutrons from water was published by Nelkin [9]. Starting from the theory of Zemach and Glauber [10, 11] and considering hindered rotations of the water molecules as harmonic oscillations, he examined the low-energy part of the inelastic spectrum. Harling [5] applied the Egelstaff-Schofield theory of incoherent neutron scattering [12] to the region of bending motions. Later Stillinger and Rahman [13] and Toukan and Rahman [14] published computer-simulation studies of water in which they calculated the proton velocity autocorrelation function. Finally, Bansil *et al.* [15] and Toukan *et al.* [7] carried out a molecular-dynamics calculation of the **k**-dependent proton density of states $G_S(\mathbf{k},E)$. Models have also been proposed to refine the analysis [16, 17]. Although the analytical theories refer to polycrystalline materials rather than to liquids, and the classical simulations are not really adapted to study internal vibrations, these calculations permitted an interpretation of high-energy data. Nevertheless, a genuine liquid-state theory of these processes is still lacking.

The purpose of the present paper is to fill this gap by transposing the statistical theories of band shapes in liquids from light [18, 19] to neutron scattering, and to interpret the new material collected by employing spallation-source technology. Experimental neutron spectra of normal and heavy water are discussed and are compared to the corresponding optical spectra. The suitability of the neutron spectroscopy for analyzing librational motion is emphasized. A preliminary account of this research was published elsewhere [20].

II. BASIC FORMULATION

A. Description of the model

The problem to be investigated is the incoherent inelastic scattering from a system formed by a sample of liquid water. The following model is used to study this problem. (i) The internal vibrations of the tagged water molecule are described by three normal coordinates n_ν, $\nu = 1,2,3$. They are perturbed by a potential $V(\mathbf{n},t)$ expressing the effect of intermolecular forces on molecular vibrations. The Hamiltonian

$$H(\mathbf{n},t)=\sum_{\nu=1}^{3}\{(\tfrac{1}{2}p_\nu^2+\tfrac{1}{2}\lambda_\nu n_\nu^2)+[V_\nu(t)n_\nu+\tfrac{1}{2}V_{\nu\nu}(t)n_\nu^2]\}$$
$$=\sum_{\nu=1}^{3}(H_0^{(\nu)}+V^{(\nu)})=\sum_{\nu=1}^{3}H^{(\nu)}(n_\nu,t) \qquad (1)$$

is a quantum-mechanical operator where $\lambda_\nu = \omega_\nu^2$ and ω_ν is the νth normal frequency of the water molecule, $V_\nu = \partial V/\partial n_\nu$, $V_{\nu\nu} = \partial^2 V/\partial n_\nu^2$, etc. (ii) The molecules of the liquid execute classical reorientation and translation, which makes $V(\mathbf{n},t)$ and $H(\mathbf{n},t)$ time dependent. (iii) The correlations between vibration and translation-rotation are neglected.

The above model is a semiclassical model in which the translational and rotational degrees of freedom are treated classically. These degrees of freedom are in fact quasiclassical in liquid water, but their quantum characteristics cannot be wholly neglected in neutron-scattering experiments and are examined in Sec. III C. Other comments are as follows. The resonant vibrational interaction that couples the vibrations of different molecules is certainly present in a dense liquid [21], but, as only the self-motions are probed in an incoherent neutron-scattering experiment, it is not expected to play a major role in this problem. Moreover, the symmetry of the water molecule forbids the presence of any coupling term $V_{\nu\nu'}$ other than that between the symmetric hydrogen stretching and bending modes. As this interaction is nonresonant, it can safely be neglected. $H(\mathbf{n},t)$ can thus be written as a sum of three Hamiltonians associated with the three normal modes. Finally, the separability of vibrational and rotational-translational motion has been checked by detailed calculations [22, 23]. Thus, the assumptions of the present model do not seem really restrictive.

B. Description of the scattering process

If a monochromatic beam of neutrons is scattered by a liquid sample, the incoherent-scattering cross section is expressible as a Fourier transform of the intermediate scattering function $I(\mathbf{k},t)$ [24]:

$$\left(\frac{\partial^2\sigma}{\partial\omega\partial\Omega}\right)_{\text{inc}}=\frac{1}{2\pi}\frac{k_s}{k_i}2Na_{\text{inc}}^2\int_{-\infty}^{+\infty}dt\,e^{-i\omega t}I(\mathbf{k},t), \qquad (2a)$$

$$I(\mathbf{k},t)=\langle e^{-i\mathbf{k}\cdot\mathbf{r}(0)}e^{i\mathbf{k}\cdot\mathbf{r}(t)}\rangle_{\text{av}}. \qquad (2b)$$

Here, a_{inc} is the incoherent scattering length of the proton, $\mathbf{k}_i$ and $\mathbf{k}_s$ are the wave vectors of the incident and scattered neutrons, respectively; $\mathbf{k}=\mathbf{k}_i-\mathbf{k}_s$, and $\mathbf{r}(t)$ is a Heisenberg operator of the position vector of an arbitrarily chosen proton in an arbitrarily chosen water molecule. The problem thus reduces to the determination of the correlation function (2b). The details of this calculation are given below.

III. THEORY

A. The intermediate scattering function $I(\mathbf{k},t)$ for liquids

The first problem is to extend the Zemach-Glauber theory from gases to liquids. The following steps are involved in this operation. Considering the semiclassical nature of the present theory in which rotation-translation is classical whereas vibration is quantum mechanical, the averaging operation $\langle\,\rangle_{\text{av}}$ in Eq. (2b) is executed separately for these two groups of degrees of freedom. The first is represented by an angle bracket, and the second by the trace operation Tr. The vibrational density matrix ρ_0 is built on the nonperturbed vibrational wave functions of $H_0^{(1)}$, $H_0^{(2)}$, and $H_0^{(3)}$. Then, (i) recalling that in all cases of practical interest, only the vibrational ground state is populated, and (ii) writing $\mathbf{r}=\mathbf{R}+\sum_{\nu=1}^{3}\boldsymbol{\rho}_\nu$, where $\mathbf{R}$ indicates the equilibrium position of one of the two protons of a specified molecule, whereas $\boldsymbol{\rho}_\nu$ describes its displacement in the normal vibration ν, one can write

$$\begin{aligned}I(\mathbf{k},t)&=\left\langle e^{-i\mathbf{k}\cdot[\mathbf{R}(0)-\mathbf{R}(t)]}\mathrm{Tr}\rho_0\prod_{\nu=1}^{3}e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_\nu(0)}e^{i\mathbf{k}\cdot\boldsymbol{\rho}_\nu(t)}\right\rangle\\
&=\langle e^{-i\mathbf{k}\cdot[\mathbf{R}(0)-\mathbf{R}(t)]}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_1(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_1(t)}]_{00}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_2(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_2(t)}]_{00}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_3(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_3(t)}]_{00}\rangle\\
&\quad+\langle e^{-i\mathbf{k}\cdot[\mathbf{R}(0)-\mathbf{R}(t)]}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_1(0)}]_{01}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_1(t)}]_{10}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_2(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_2(t)}]_{00}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_3(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_3(t)}]_{00}\rangle\\
&\quad+\langle e^{-i\mathbf{k}\cdot[\mathbf{R}(0)-\mathbf{R}(t)]}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_1(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_1(t)}]_{00}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_2(0)}]_{01}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_2(t)}]_{10}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_3(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_3(t)}]_{00}\rangle\\
&\quad+\langle e^{-i\mathbf{k}\cdot[\mathbf{R}(0)-\mathbf{R}(t)]}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_1(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_1(t)}]_{00}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_2(0)}]_{00}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_2(t)}]_{00}[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_3(0)}]_{01}[e^{i\mathbf{k}\cdot\boldsymbol{\rho}_3(t)}]_{10}\rangle\\
&\quad+\text{higher-order terms.}\end{aligned} \qquad (3)$$

The matrix elements $[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_\nu}]_{\beta\beta'}$ are taken between the eigenfunctions of $H_0^{(1)}$, $H_0^{(2)}$, and $H_0^{(3)}$. The first term of this expansion describes the quasielastic neutron scattering, and the three others, the inelastic scattering in which the first, second, and third normal vibrations are singly excited. Higher-order excitations are not treated explicitly.

The second step of calculation consists of determining the matrix elements $[e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_\nu(t)}]_{\beta\beta'}$ that appear in the above series. One has $\boldsymbol{\rho}_\nu(t) = \mathbf{l}_\nu(t)n_\nu(t)$ where $\mathbf{l}_\nu(t)$ indicates the direction of the proton motion in the normal vibration ν; this vector depends on the orientation of the tagged molecule. As the Hamiltonian $H(\mathbf{n},t)$ is additive in $H^{(\nu)}(n_\nu,t)$, the calculation of the matrix elements can be performed separately for each normal vibration. The theory is further simplified by the fact that the vibrational energy levels are widely spaced as compared with $k_B T$: the adiabatic approximation is thus appropriate. Then, dropping for convenience the subscripts or superscripts ν in $H^{(\nu)}$, n_ν, ρ_ν, l_ν, and denoting ω_0 and $\Delta\omega = \hbar^{-1}([V]_{11} - [V]_{00})$ the nonperturbed vibrational frequency and the interaction induced shift, respectively, one can write

$$\begin{aligned}\frac{d}{dt}[n(t)]_{00} &= \frac{i}{\hbar}\{[H(t)]_{00}[n(t)]_{00} - [n(t)]_{00}[H(t)]_{00}\}\\ &= 0; \Rightarrow [n(t)]_{00} = [n(0)]_{00}\,,\end{aligned} \tag{4a}$$

$$\begin{aligned}\frac{d}{dt}[n(t)]_{10} &= \frac{i}{\hbar}\{[H(t)]_{11}[n(t)]_{10} - [n(t)]_{10}[H(t)]_{00}\}\\ &\Rightarrow [n(t)]_{10}\\ &= [n]_{10}\, e^{i\omega^{(0)}t} \exp\left(i\int_0^t dt'\Delta\omega(t')\right).\end{aligned} \tag{4b}$$

Similar equations govern the time evolution of $n^2(t)$, $n^3(t)$, ..., and, as a consequence, that of the operator $1 + i\mathbf{k}\cdot\boldsymbol{l}(t)n(t) + 1/2[i\mathbf{k}\cdot\boldsymbol{l}(t)n(t)]^2 + \cdots = \exp[i\mathbf{k}\cdot\boldsymbol{l}(t)n(t)]$. Only the diagonal matrix elements $[H]_{\alpha\alpha}$ have been retained in Eqs. (4a) and (4b), in agreement with the adiabatic approximation. Then, applying the above equations to the present problem and integrating over the harmonic-oscillator wave functions involved in the transition gives

$$\begin{aligned}&[e^{i\mathbf{k}\cdot\boldsymbol{l}(t)n(t)}]_{00} = e^{-1/2[\mathbf{k}\cdot\mathbf{L}(t)]^2},\\ &[e^{i\mathbf{k}\cdot\boldsymbol{l}(t)n(t)}]_{10} = i(\mathbf{k}\cdot\mathbf{L}(t))e^{-1/2[\mathbf{k}\cdot\mathbf{L}(t)]^2}e^{i\omega^{(0)}t}\\ &\qquad\times\exp\left(i\int_0^t dt'\Delta\omega(t')\right),\end{aligned} \tag{5}$$

where $\mathbf{L}(t) = \boldsymbol{l}(t)\,[n]_{01}$ is the vibrational amplitude of the proton.

The final expressions may be obtained by collecting the partial results given in Eqs. (4) and (5) and inserting them into Eq. (3). Let $I_Q(\mathbf{k},t)$ designate the intermediate scattering function appropriate to the low-energy spectrum, and $I_\nu(\mathbf{k},t)$ that associated with the fundamental ν. The following formulas may be found in this way:

$$I_Q(\mathbf{k},t) = \langle \exp\{-i\mathbf{k}\cdot[\mathbf{R}(0)-\mathbf{R}(t)]\} \prod_{\nu'=1}^{3} \exp\{-\tfrac{1}{2}[\mathbf{k}\cdot\mathbf{L}_{\nu'}(0)]^2 - \tfrac{1}{2}[\mathbf{k}\cdot\mathbf{L}_{\nu'}(t)]^2\}\rangle, \tag{6}$$

$$\begin{aligned}I_\nu(\mathbf{k},t) = {}&\left\langle \exp\{-i\mathbf{k}\cdot[\mathbf{R}(0)-\mathbf{R}(t)]\}\,[\mathbf{k}\cdot\mathbf{L}_\nu(0)]\,[\mathbf{k}\cdot\mathbf{L}_\nu(t)] \prod_{\nu'=1}^{3} \exp\{-\tfrac{1}{2}[\mathbf{k}\cdot\mathbf{L}_{\nu'}(0)]^2 - \tfrac{1}{2}[\mathbf{k}\cdot\mathbf{L}_{\nu'}(t)]^2\}\right\rangle\\ &\times \exp(i\omega_\nu^{(0)}t)\left\langle \exp\left(i\int_0^t dt'\Delta\omega_\nu(t')\right)\right\rangle.\end{aligned} \tag{7}$$

The quantities $\mathbf{L}_\nu$, $\omega_\nu^{(0)}$, and $\Delta\omega_\nu$ have the same meaning as in Eqs. (4) and (5), but refer to a specific normal vibration ν. Similar expressions can be derived for overtone and combination bands.

The above theoretical results merit some comments. (i) The quantum and the classical degrees of freedom of this problem are disentangled in Eqs. (6) and (7). As the translations and rotations are essentially classical, these equations are well adapted to molecular-dynamics simulations. If desired, semiclassical corrections may be introduced; compare with Sec. III C. (ii) Although the present theory is developed for liquids, it has several features in common with the Zemach-Glauber theory of neutron scattering in gases; compare e.g., Eqs. (6) and (7) of this paper with Eqs. (3.21)–(3.22) of Ref. [10]. The main difference between the two theories is the presence of a factor in Eq. (7) describing the vibrational relaxation: the delta peaks of a Zemach-Glauber spectrum thus spread into bands.

B. Application to water

The present theory takes a particular form in the problem under study. In fact, the experiment [6] of Chen *et al.* is characterized by large $\mathbf{k}$ vectors with a modulus between 5 and 10 Å^{-1}. As the length scale probed in a neutron-scattering experiment is of the order of $1/k$, molecular motions are followed only over a fraction of an angstrom and over very short, subpicosecond time intervals. The above experiment is thus a short-time experiment in which only internal and rapid external vibrations are detectable. This simplifying feature makes the theory practicable without any restrictive assumption.

It is convenient to start the analysis by noticing that, for large k, the dynamical variables $e^{-i\mathbf{k}\cdot\mathbf{R}(t)}$, $\Delta\omega_\nu(\mathbf{R}(t))$, and $e^{-(1/2)[\mathbf{k}\cdot\mathbf{L}_\nu(t)]^2}$ behave very differently. The correlation times of the former two quantities are $\tau_1 \sim 1/kV \sim 10^{-14}$ sec and $\tau_2 \sim d^2/6D \sim 10^{-12}$ sec, where V is the mean thermal velocity of the proton, D the diffusion constant of a water molecule, and d a length of the order of intermolecular distances. Moreover, the variable $e^{-(1/2)(\mathbf{k}\cdot\mathbf{L}_\nu)^2}$ is virtually constant in the time interval of interest. As slow and fast variables are effectively decorrelated, it is possible to average them separately. It is even legitimate to suppress the time dependence of the slow variables altogether. Then, designating the proton velocity in absence of any internal vibration by $\mathbf{V}$, Eqs. (6) and (7) may be rewritten in the following way:

$$I_Q(\mathbf{k},t) = \left\langle \exp\left(i\mathbf{k}\cdot\int_0^t dt'\mathbf{V}(t')\right)\right\rangle \times \left\langle \prod_{\nu'=1}^{3} \exp[-(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2]\right\rangle , \tag{8}$$

$$\begin{aligned} I_\nu(\mathbf{k},t) = e^{i\omega_\nu^{(0)}t} &\left\langle \exp\left(i\mathbf{k}\cdot\int_0^t dt'\mathbf{V}(t')\right)\right\rangle \\ &\times \left\langle (\mathbf{k}\cdot\mathbf{L}_\nu)^2 \prod_{\nu'=1}^{3} \exp[-(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2]\right\rangle \\ &\times \langle \exp(i\Delta\omega_\nu t)\rangle . \end{aligned} \tag{9}$$

It remains to determine expressions (8) and (9). Their translational-rotational factor may be calculated by recalling that, at the short times typical of this experiment, Gaussian characteristics of the variable $\mathbf{V}$ are dominating. The cumulant expansion may thus be employed and truncated after its second-order term. There results

$$\begin{aligned} &\left\langle \exp\left(i\mathbf{k}\cdot\int_0^t dt'\mathbf{V}(t')\right)\right\rangle \\ &\quad = \exp\left(-\frac{k^2}{6}\int_0^t\int_0^t dt'dt'' \langle \mathbf{V}(t')\mathbf{V}(t'')\rangle\right) \\ &\quad = \exp\left(-\frac{k^2}{3}\langle V^2\rangle \int_0^t d\tau(t-\tau)\phi(\tau)\right) , \end{aligned} \tag{10}$$

where $\phi(\tau)$ is the normalized proton velocity autocorrelation function. This function decays in several translational-rotational modes. As only short times are detectable by the present experiment, the time dependence may, here too, be suppressed in all but the fastest librational modes. These modes correspond to restricted rotational motions of H_2O in the H-bond network of liquid water. Then, attributing to them a single decay constant λ_0 where $\mathrm{Re}\lambda_0 \ll \mathrm{Im}\ \lambda_0 = \omega_0$ and defining L by $L^2 = 2\xi_0\langle V^2\rangle/\omega_0^2$, one finds

$$\begin{aligned} \phi(t) = \sum_\rho \xi_\rho e^{\lambda_\rho t} &= \sum_\rho{}' \xi_\rho + \xi_0\left(e^{i\omega_0 t} + e^{-i\omega_0 t}\right) \\ &= (1-2\xi_0) + 2\xi_0\cos\omega_0 t , \end{aligned} \tag{11}$$

$$\begin{aligned} &\left\langle \exp\left(i\mathbf{k}\cdot\int_0^t dt'\mathbf{V}(t')\right)\right\rangle \\ &\quad = \exp\left(-\tfrac{1}{3}k^2L^2\right)\exp\left[-\tfrac{1}{6}k^2\left(\langle V^2\rangle - \omega_0^2L^2\right)t^2\right] \\ &\qquad \times \left(I_0\left[\tfrac{1}{3}k^2L^2\right] + 2\sum_{\mu=1}^{\infty} I_\mu\left[\tfrac{1}{3}k^2L^2\right]\cos\mu\omega_0 t\right) . \end{aligned} \tag{12}$$

In these equations,

$$\exp(z\ \cos\theta) = I_0[z] + 2\sum_{\mu=1}^{\infty} I_\mu[z]\cos\mu\theta$$

and $I_\mu\,[z]$ is the modified Bessel function of order μ. Moreover, ξ_ρ is the amplitude of the mode ρ, ξ_0 the amplitude summed over the three librational modes, ω_0 their average frequency, and L is the average amplitude of the proton motion in these three librational modes. The above development relies heavily on the fact that $\mathbf{k}$ is large. The expansion of $\phi(t)$ is not a phonon expansion and ξ_ν, λ_ν are averaged properties of the liquid. No quasicrystalline model is required to calculate L.

The vibrational factors of Eqs. (8) and (9) can be determined by employing the cumulant expansion techniques again. In fact, the cumulant expansion in $(\mathbf{k}\cdot\mathbf{L}_\nu)^2$ is expected to be rapidly convergent: in the experiment of Chen *et al.*, as well in all others in which the vibrational structure is well resolved, all $\mathbf{k}\cdot\mathbf{L}_\nu$ are less than 1. The cumulant expansion in $\Delta\omega_\nu$ is also expected to converge rapidly, although the underlying argument is different: $\Delta\omega_\nu$ can be thought of as being composed by a number of more or less uncorrelated increments, and by virtue of the central-limit theorem it can be taken as approximately Gaussian. Then,

$$\left\langle \exp\left(-\sum_{\nu'}(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2\right)\right\rangle = \exp\left(-\sum_{\nu'}\langle[(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2]\rangle_c + \tfrac{1}{2}\sum_{\nu'\nu''}\langle[(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2][(\mathbf{k}\cdot\mathbf{L}_{\nu''})^2]\rangle_c + \cdots\right) , \tag{13}$$

$$\begin{aligned} &\left\langle (\mathbf{k}\cdot\mathbf{L}_\nu)^2 \exp\left(-\sum_{\nu'}(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2\right)\right\rangle \\ &\quad = -\left[\frac{\partial}{\partial\lambda_\nu}\left\langle \exp\left(-\sum_{\nu'}\lambda_{\nu'}(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2\right)\right\rangle\right]_{\boldsymbol{\lambda}=1} \\ &\quad = -\left[\frac{\partial}{\partial\lambda_\nu}\exp\left(-\sum_{\nu'}\lambda_{\nu'}\langle[(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2]\rangle_c + \tfrac{1}{2}\sum_{\nu'\nu''}\lambda_{\nu'}\lambda_{\nu''}\langle[(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2][(\mathbf{k}\cdot\mathbf{L}_{\nu''})^2]\rangle_c + \cdots\right)\right]_{\boldsymbol{\lambda}=1} \\ &\quad = \left(\langle[(\mathbf{k}\cdot\mathbf{L}_\nu)^2]\rangle_c - \sum_{\nu'}\langle[(\mathbf{k}\cdot\mathbf{L}_\nu)^2][(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2]\rangle_c + \cdots\right) \\ &\qquad \times \exp\left(-\sum_{\nu'}\langle[(\mathbf{k}\cdot\mathbf{L}_\nu)^2]\rangle_c + \tfrac{1}{2}\sum_{\nu'\nu''}\langle[(\mathbf{k}\cdot\mathbf{L}_{\nu'})^2][(\mathbf{k}\cdot\mathbf{L}_{\nu''})^2]\rangle_c + \cdots\right) \end{aligned} \tag{14}$$

$$\langle \exp(i\Delta\omega_\nu t)\rangle = \exp(i\,\langle\Delta\omega_\nu\rangle\, t - \tfrac{1}{2}\langle(\Delta\omega_\nu)^2\rangle_c t^2 + \cdots), \tag{15}$$

where the symbol $\langle\,\rangle_c$ designates ordinary cumulants and $\boldsymbol{\lambda} = 1$ is a shorthand notation for $\lambda_1 = \lambda_2 = \lambda_3 = 1$. The calculation of the cumulants which appear in Eqs. (13) and (14) is straightforward and does not need a further explanation. This is no longer true for those in Eq. (15) and no attempt was made here to determine them *a priori*.

The final expressions may be obtained by combining Eqs. (8)–(15). Only the leading cumulant is retained in the exponentials of Eqs. (13) and (14) as well as in the prefactor of Eq. (14). The omitted terms were found to be one order of magnitude smaller than those which were retained. Let then $I_l(\mathbf{k},t)$ designate the intermediate scattering function describing the librational portion of spectrum, $I_\nu(\mathbf{k},t)$ that associated with the fundamental ν, and let $I_{l\pm\nu}(\mathbf{k},t)$ refer to the combined vibrational and librational motions. Then

$$I_l(\mathbf{k},t) = I_1\left[\frac{k^2L^2}{3}\right]\exp\left[-\tfrac{1}{3}k^2\left(L^2+\sum_{\nu'}L_{\nu'}^2\right)\right]\exp\left(i\omega_0 t\right)\exp\left[-\tfrac{1}{6}k^2\left(\langle V^2\rangle-\omega_0^2L^2\right)t^2\right], \tag{16}$$

$$\begin{aligned} I_\nu(\mathbf{k},t) = {}& \left(\frac{k^2L_\nu^2}{3}\right)\; I_0\left[\frac{k^2L^2}{3}\right]\exp\left[-\tfrac{1}{3}k^2\left(L^2+\sum_{\nu'}L_{\nu'}^2\right)\right] \\ & \times\exp\left(i\,\langle\omega_\nu\rangle\, t\right)\exp\left[-\tfrac{1}{2}\left(\frac{k^2}{3}\left(\langle V^2\rangle-\omega_0^2L^2\right)+\left\langle\Delta\omega_\nu^2\right\rangle_c\right)t^2\right], \end{aligned} \tag{17}$$

$$\begin{aligned} I_{\nu\pm l}(\mathbf{k},t) = {}& \left(\frac{k^2L_\nu^2}{3}\right)\; I_1\left[\frac{k^2L^2}{3}\right]\exp\left[-\tfrac{1}{3}k^2\left(L^2+\sum_{\nu'}L_{\nu'}^2\right)\right] \\ & \times\exp\left[i(\langle\omega_\nu\rangle\pm\omega_0)t\right]\exp\left[-\tfrac{1}{2}\left(\frac{k^2}{3}\left(\langle V^2\rangle-\omega_0^2L^2\right)+\left\langle\Delta\omega_\nu^2\right\rangle_c\right)t^2\right], \end{aligned} \tag{18}$$

where $\langle\omega_\nu\rangle = \omega_\nu^{(0)} + \langle\Delta\omega_\nu\rangle_c$. These formulas represent the final result of the theory as far as the translation and rotation is treated classically.

C. Semiclassical corrections

Although the translational and rotational motions of molecules in liquid water are essentially classical, their quantum characteristics cannot be neglected altogether. The simplest way to describe them would be to apply the Schofield [25], Egelstaff [26], or Rosenbaum-Zweifel [27] prescriptions. Unfortunately, the energy of the librational modes is comparatively high, which makes a series expansion in powers of $\hbar$ impracticable. An alternative approach is thus employed resting, once more, on the fact that, for time scales characteristic of this experiment, the proton velocity $\mathbf{V}$ is a quasi-Gaussian, quasiclassical process. Then

$$\begin{aligned} &\left\langle e^{-i\mathbf{k}\cdot\mathbf{R}(0)}e^{i\mathbf{k}\cdot\mathbf{R}(t)}\right\rangle \\ &\quad = \exp\left(\frac{k^2}{6}\langle[\mathbf{R}(0),\mathbf{R}(t)]\rangle \right. \\ &\qquad \left. -\frac{k^2}{6}\int_0^t\int_0^t dt'dt''\langle\mathbf{V}(t')\mathbf{V}(t'')\rangle\right). \end{aligned} \tag{19}$$

This expression may be obtained by writing the left-hand side of Eq. (19) in the form $\langle e^z\rangle$ and by expanding z, with the help of the Baker-Campbell-Hausdorff formula [28], into a series involving the noncommuting operators $\mathbf{R}(0)$, $\mathbf{R}(t)$. It is next expressed by introducing a series of commuting cumulants [29]. As the process $\mathbf{V}$ is quasiclassical, only the leading "quantum-mechanical" term of this expansion, i.e., a term that vanishes when $\hbar \to 0$, needs to be retained; and as the process $\mathbf{V}$ is quasi-Gaussian, only the second-order "classical" term, i.e., a term which survives when $\hbar \to 0$, must be considered. Compare the expression (19) with its classical analog (10).

The practical evaluation of Eq. (19) involves the following steps. (i) The argument of the exponential on the right-hand side of Eq. (19) is transformed into the form

$$\tfrac{1}{6}k^2\langle[\mathbf{R}(0),\mathbf{V}(0)]\rangle\, t - \tfrac{1}{3}k^2\int_0^t dt'(t-t')\langle\mathbf{V}(0).\mathbf{V}(t')\rangle\,.$$

The commutator $\langle[\mathbf{R}(0),\mathbf{V}(0)]\rangle$ is then approximated by applying the standard commutation formula between two conjugated variables $\mathbf{R}$, $\mathbf{P}$. (ii) The semiclassical expression for the proton velocity autocorrelation function is obtained by using the well-known relation $G_{\rm as}(\omega) = 2(1+e^{-\beta\hbar\omega})^{-1}G_{\rm sym}(\omega)$ between the Fourier transforms of the asymmetric and symmetrized corre-

TABLE I. Raman data on liquid water [30, 33, 34]: $\tilde\omega_0$ indicates the average librational Raman frequency, $\tilde\omega_\nu$ the frequency of the fundamental ν, and $(\Delta\tilde\omega_\nu)_{1/2}$ its half-width (in cm^{-1}).

	$\tilde\omega_0$	$\tilde\omega_1$	$(\Delta\tilde\omega_1)_{1/2}$	$\tilde\omega_2$	$(\Delta\tilde\omega_2)_{1/2}$	$\tilde\omega_3$	$(\Delta\tilde\omega_3)_{1/2}$
H_2O	600	3225	250	1640	126	3431	250

lation functions $G_{\mathrm{as}}(t) = \langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle$ and $G_{\mathrm{sym}}(t) = \langle \frac{1}{2} [\mathbf{V}(0) \cdot \mathbf{V}(t) + \mathbf{V}(t) \cdot \mathbf{V}(0)] \rangle$, and by replacing the latter by the classical velocity autocorrelation function $\langle V^2 \rangle \, \phi(t)$ of Eq. (10): $G_{\mathrm{sym}}(t)$ is a real and pair function of time as are the classical autocorrelation functions, but this is not the case for $G_{\mathrm{as}}(t)$. The calculation is straightforward and does not need to be reproduced here.

The final results take the simplest form if the quantity $k^2L^2/3\cosh(\frac{1}{2}\beta\hbar\omega_0)$, which appears in the general expression of $I(\mathbf{k},t)$, is much smaller than unity. The formulas (16)–(18) for $I_l(\mathbf{k},t)$, $I_\nu(\mathbf{k},t)$, $I_{\nu\pm l}(\mathbf{k},t)$ may then be replaced by the expressions

$$\begin{aligned} I_l(\mathbf{k},t) = {} & \frac{1}{1+e^{-\beta\hbar\omega_0}} \left(\frac{k^2L^2}{3} \right) \exp \left[-\tfrac{1}{3}k^2 \left(L^2 + \sum_{\nu'} L^2_{\nu'} \right) \right] \\ & \times \exp \left(it\{\omega_0 + \tfrac{1}{6}k^2 \left[\hbar\beta \langle V^2 \rangle - 2\omega_0 L^2 \tanh \left(\tfrac{1}{2}\beta\hbar\omega_0 \right) \right] \} \right) \exp \left[-\tfrac{1}{6}k^2 \left(\langle V^2 \rangle - \omega_0^2 L^2 \right) t^2 \right] , \end{aligned} \tag{20}$$

$$\begin{aligned} I_\nu(\mathbf{k},t) = {} & \left(\frac{k^2L_\nu^2}{3} \right) \exp \left[-\tfrac{1}{3}k^2 \left(L^2 + \sum_{\nu'} L^2_{\nu'} \right) \right] \exp \left(it\{\langle \omega_\nu \rangle + \tfrac{1}{6}k^2 \left[\hbar\beta \langle V^2 \rangle - 2\omega_0 L^2 \tanh \left(\tfrac{1}{2}\beta\hbar\omega_0 \right) \right] \} \right) \\ & \times \exp\{ -\tfrac{1}{2} \left[\tfrac{1}{3}k^2 \left(\langle V^2 \rangle - \omega_0^2 L^2 \right) + \langle \Delta\omega_\nu^2 \rangle_c \right] t^2 \}, \end{aligned} \tag{21}$$

$$\begin{aligned} I_{\nu\pm l}(\mathbf{k},t) = {} & \frac{1}{1+e^{\mp\beta\hbar\omega_0}} \left(\frac{k^2L^2}{3} \right) \left(\frac{k^2L_\nu^2}{3} \right) \exp \left[-\tfrac{1}{3}k^2 \left(L^2 + \sum_{\nu'} L^2_{\nu'} \right) \right] \\ & \times \exp \left(it\{\langle \omega_\nu \rangle \pm \omega_0 + \tfrac{1}{6}k^2 [\hbar\beta \langle V^2 \rangle - 2\omega_0 L^2 \tanh \left(\tfrac{1}{2}\beta\hbar\omega_0 \right)] \} \right) \\ & \times \exp\{ -\tfrac{1}{2} \left[\tfrac{1}{3}k^2 \left(\langle V^2 \rangle - \omega_0^2 L^2 \right) + \langle \Delta\omega_\nu^2 \rangle_c \right] t^2 \}. \end{aligned} \tag{22}$$

As expected, Eqs. (20)–(22) take into account the constraint of detailed balancing; they also describe the recoil effect, i.e., the frequency shift

$$\frac{k^2}{6} \left[\hbar\beta \langle V^2 \rangle - 2\omega_0 L^2 \tanh \left(\tfrac{1}{2}\beta\hbar\omega_0 \right) \right]$$

which is absent in the classical treatment. If $\frac{1}{2}\beta\hbar\omega_0 \ll 1$, these corrections reduce to those given by the abovementioned prescriptions. Equations (20)–(22), together with similar expressions obtained for overtone and coordination bands, are employed in the analysis of the experiment of Chen *et al.* which follows.

IV. RESULTS AND DISCUSSION

A. Choice of parameters

The above theory was applied to the study of the neutron-scattering spectra in the following conditions. The frequencies ω_0, $\langle \omega_\nu \rangle$, and $(\langle \Delta\omega_\nu^2 \rangle_c)^{1/2}$ of H_2O were taken as equal to the Raman frequencies $\tilde{\omega}_0$, $\tilde{\omega}_\nu$, and $(\Delta\tilde{\omega}_\nu)_{1/2}$ [30] (Table I); the amplitudes L_ν of internal vibrations were calculated by performing the normal-coordinate analysis with a force field associated with the frequencies $\tilde{\omega}_\nu$; and the mean-square velocity $\langle V^2 \rangle$ of a proton was expressed in terms of the molecular mass M of H_2O, the mass m of a proton, and the temperature T. The resulting formula is

$$\langle V^2 \rangle = \frac{3k_BT}{M} \left(1 + \frac{M}{2m} \right) . \tag{23}$$

The quantity L was considered as an adjustable parameter and was extracted from the spectral data. The corresponding quantities for D_2O were calculated by reducing the values of ω_0, $\langle \omega_\nu \rangle$, $(\langle \Delta\omega_\nu^2 \rangle_c)^{1/2}$, L_ν^2 by a factor of $\sqrt{2}$; moreover, Eq. (23) was applied with the new values of m and M, and L was adjusted again (Table II). This theory thus contains only one adjustable parameter, the mean amplitude L of the proton motion in the librational modes; all other quantities are either calculated or are transferred from optical spectra.

B. Results

The theoretically reconstructed incoherent, inelastic neutron scattering spectra of the liquid H_2O and D_2O at $\theta = 8°$ are illustrated in Figs. 1 and 2. The calculated quantity is the $\mathbf{k}$-dependent proton density of states $G_S(\mathbf{k},E) = (E^2/K^2)S_S(\mathbf{k},E)$, where $S_S(\mathbf{k},E)$ is the dynamical structure factor. The proton amplitudes

TABLE II. Amplitude of the proton and the deuteron motions in the librational, the symmetric stretching, the bending, and the antisymmetric stretching modes, respectively (in angstroms). The temperature is 313 K for H_2O and 298 K for D_2O.

	L	L_1	L_2	L_3
H_2O	0.16	0.05	0.07	0.05
D_2O	0.11	0.04	0.06	0.04

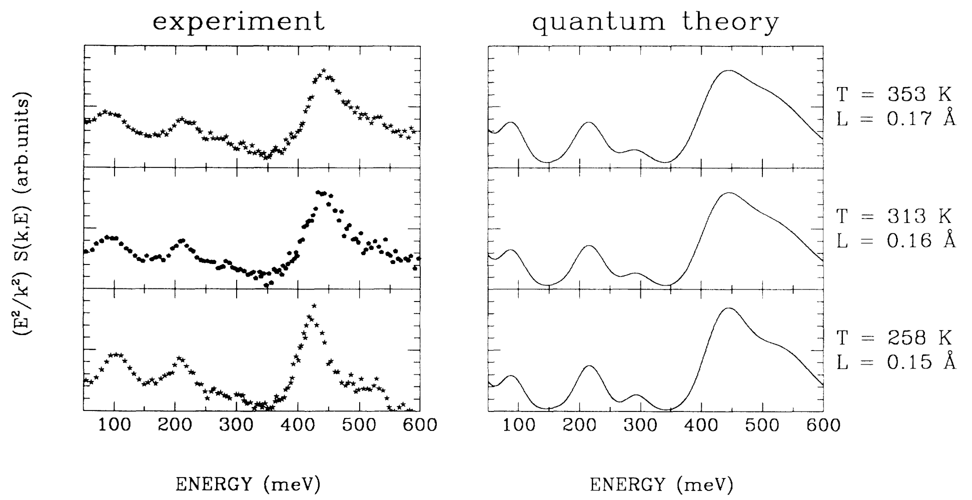

FIG. 1. Quantum-mechanical reconstruction of the k-dependent proton density of states $G_S(\mathbf{k}, E)$ for liquid water (H_2O) and its comparison with the experiment. The energy of the incident neutrons is equal to 800 meV and $\theta = 8°$. In order to facilitate the comparison, the theoretical spectra are convoluted with an instrumental function corresponding to Fig. 1 of Ref. [7].

L and L_ν involved in this calculation are those of Table II. In order to facilitate comparison with experiment, the theoretical spectra were convoluted with an instrumental function corresponding to Fig. 1(c) of Ref. [7]. These calculations are in good agreement with the experiment of Toukan *et al.* [7]. Our theory is thus successful in interpreting the new information provided by the spallation-source technology. The early data by Harling [5] are correctly reproduced too; this is illustrated in Fig. 3.

A second important point is the comparison of the neutron- and light-scattering spectra. Figure 4(a) illustrates the neutron spectrum of water generated by the present theory, and Fig. 4(b) its experimental Raman analog, reproduced by assigning to each band a Gaussian profile [31]. The following points are worth noticing.

(i) The energies occurring in these two spectra are similar, but not identical. In the experiment of Toukan *et al.*, the differences are of the order of, or smaller than 10 meV. This effect is due to the k^2 dependent molecular recoil; compare with Eqs. (20)–(22).

(ii) The band intensities of the two spectra are entirely different. The Raman intensities depend on the polarizability tensor α of the water molecule and on its derivatives $\partial\alpha/\partial n_\nu$ with respect to the normal coordinates n_ν. On the other hand, the spectral intensities of the neutron spectra are given by the following formulas, obtained by combining Eqs. (2) and (20)–(22):

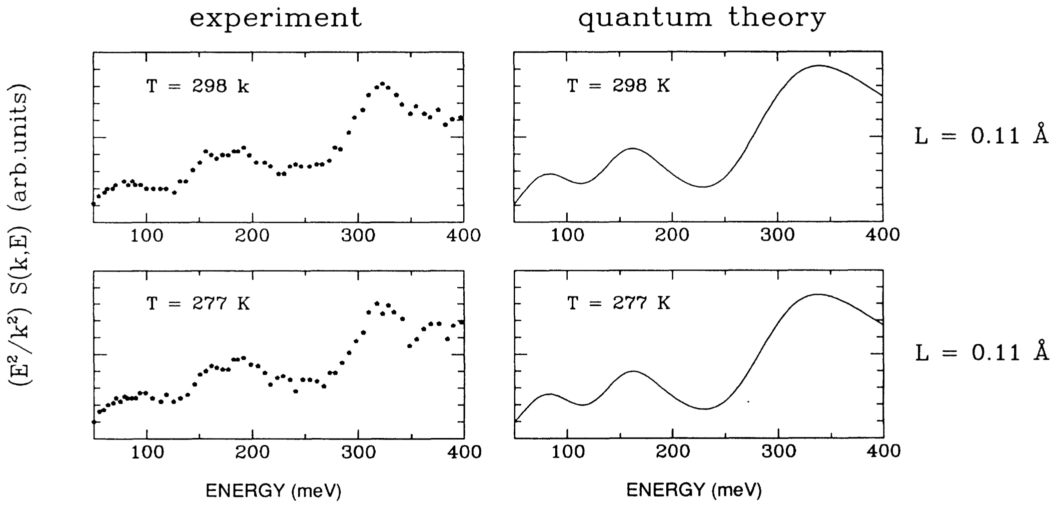

FIG. 2. Quantum-mechanical reconstruction of the k-dependent deuteron density of states $G_S(\mathbf{k}, E)$ for heavy water (D_2O) and its comparison with the experiment. These spectra are averaged over an angular range between 4° and 20°. Other indications are the same as in Fig. 1.

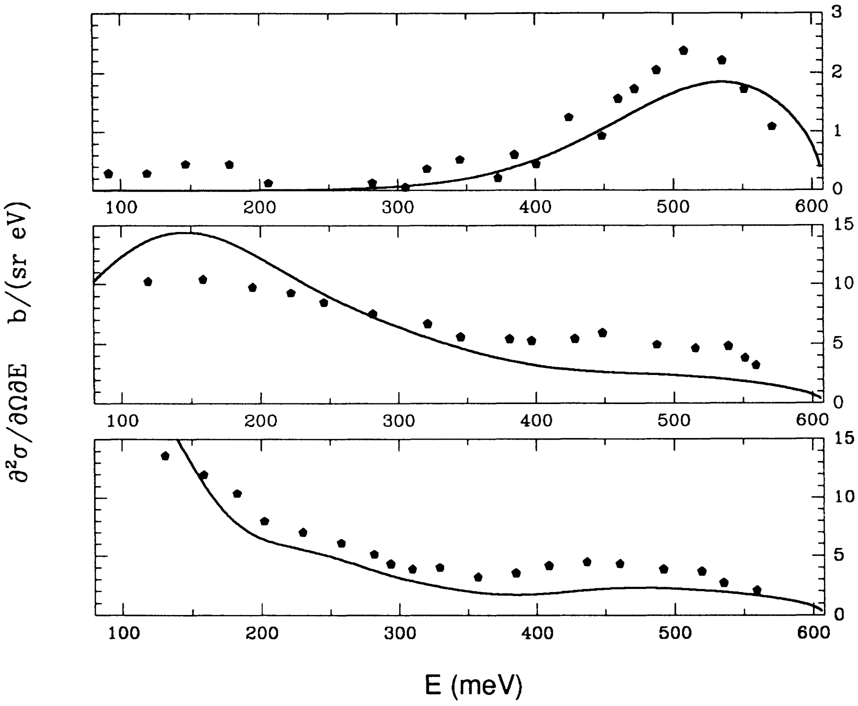

FIG. 3. Quantum-mechanical reconstruction of the incoherent inelastic-scattering cross section for liquid water (H_2O) at 299 K (——) and its comparison with Harling's experimental data [5] (●). The energy of the incident neutrons is equal to 608 meV and $\theta = 125.5°$, 45°, and 30° (from top to bottom).

$$S_l(\mathbf{k}) = I_l(\mathbf{k},0) = \frac{1}{1+e^{-\beta\hbar\omega_0}}\left(\frac{k^2L^2}{3}\right) \times \exp\left[-\frac{1}{3}k^2\left(L^2+\sum_{\nu'}L_{\nu'}^2\right)\right], \tag{24a}$$

$$S_\nu(\mathbf{k}) = I_\nu(\mathbf{k},0) = \left(\frac{k^2L_\nu^2}{3}\right)\exp\left[-\frac{1}{3}k^2\left(L^2+\sum_{\nu'}L_{\nu'}^2\right)\right], \tag{24b}$$

$$S_{\nu\pm l}(\mathbf{k}) = I_{\nu\pm l}(\mathbf{k},0) = \frac{1}{1+e^{\mp\beta\hbar\omega_0}}\left(\frac{k^2L^2}{3}\right)\left(\frac{k^2L_\nu^2}{3}\right) \times \exp\left[-\frac{1}{3}k^2\left(L^2+\sum_{\nu'}L_{\nu'}^2\right)\right]. \tag{24c}$$

They depend, essentially, on the proton amplitudes L and L_ν. As L is larger than are the L_ν (Table II), the librational bands are prominent in neutron-scattering spectra, a feature which is not observed in Raman spectra. Note that the values of L obtained here correspond to those of a tridimensional harmonic oscillator of frequency ω_0: librations thus appear as harmonic oscillations on the time scales of the present neutron-scattering experiment.

(iii) The band profiles are different in the two spectra. In a Raman spectrum of water, only one band-shaping mechanism operates, the vibrational relaxation due to dephasing of molecular vibrations by the intermolecular noise [32]. In the neutron spectra of Chen *et al.*, two band-shaping mechanisms are in action. One of them is the vibrational relaxation, described in Eqs. (21) and (22) by the exponential $\exp\left(-\frac{1}{2}\langle\Delta\omega_\nu^2\rangle_c t^2\right)$. The second

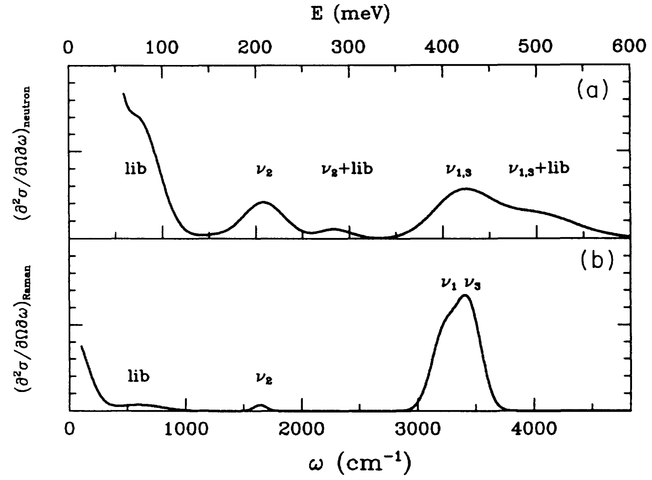

FIG. 4. Comparison of the neutron- and light-scattering spectra of liquid water. (a) The theoretically determined neutron-scattering cross section $(\partial^2\sigma/\partial\Omega\partial E)_{\rm inc}$ is plotted against the transfer energy E for $\theta = 8°$. In (b) the experimental Raman cross section $(\partial^2\sigma/\partial\Omega\partial\omega)_R$ is plotted against the transfer wave number $\tilde{\omega}$ at $\theta = 90°$. The energy of the incident neutrons is equal to 0.8 eV, and that of the incident photons to 2.7 eV. The intensity scales are chosen arbitrarily.

mechanism is the Doppler broadening, due to the motion of the water molecules during the scattering process; it is described by the factor $\exp\left[-k^2/6\left(\langle V^2\rangle - \omega_0^2 L^2\right)t^2\right]$ in Eqs. (20)–(22). The effects of these two band-shaping mechanisms on the half-width of the fundamentals are comparable. For example, the contribution of the vibrational relaxation to the half-width of each stretching band is of the order of 30 meV, whereas the Doppler broadening provides about 50 meV at $k = 6.5$ Å^{-1}. One concludes that the bands are intrinsically broader in a neutron- than in a light-scattering spectrum.

The last question is whether classical mechanics is suitable for the study of inelastic-neutron-scattering by water. The answer to this question is required to decide whether the standard molecular-dynamics simulations are applicable to this problem. By repeating the treatment of Secs. III A and III B but considering the internal vibrations as classical, one obtains a completely classical theory, in which vibrational amplitudes L_ν are reduced by a factor of $(2/\beta\hbar\,\langle\omega_\nu\rangle)^{1/2}$ whereas the amplitude L of the librational mode is more or less correctly reproduced. The integrated intensity of the 200-meV band is thus reduced by a factor of the order of 5, and that of the bands at 400 and 430 meV by a factor close to 10. The integrated intensity of the whole 50–600-meV region decreases to about half of its value. The spectral distribution changes dramatically, deviates from the experiment, but approaches that calculated by molecular dynamics (Fig. 5). These results are in agreement with the observation reported in Ref. [7] that the combination band at 525 meV is absent from the simulated spectra. On the contrary, even a crude, but quantum-mechanical, one-dimensional model assuming a breaking of the H bond and a simultaneous excitation of the OH vibration predicts correctly the ratio of the stretching and the satellite peak intensities [16, 17]. One concludes that classical mechanics is not appropriate for the present problem and molecular-dynamics simulations cannot be employed in the standard way. On the contrary, Eqs. (6) and (7) are well adapted to this technique.

C. Discussion

The most important contribution of the neutron-scattering experiments employing the spallation sources concerns the librational motion of H_2O. Figures 4(a) and 4(b) illustrate this point in a spectacular way. However, to observe the librational band in optimum conditions, the scattering vector **k** must be chosen to satisfy the relation $1/k \sim L$; this condition can never be satisfied in optical spectra where $1/k \gg L$. It is then possible to use the inelastic neutron scattering to measure the amplitude of librational motions in the H-bond network in water, or study its rupture by molecular motions and related problems. More generally, inelastic-neutron-scattering spectroscopy will certainly prove useful in analyzing rapid, nondiffusive modes of translational-rotational motions of molecules in the liquid phase.

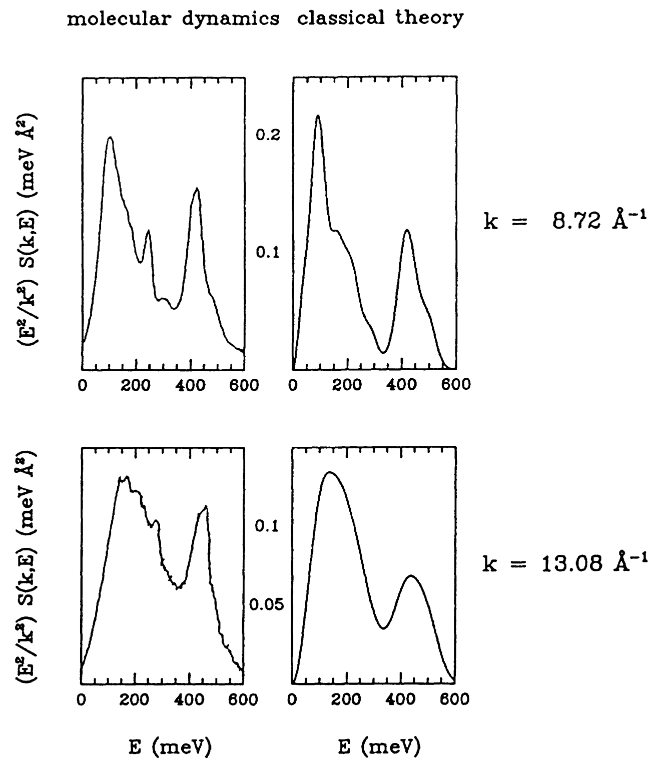

FIG. 5. Classical reconstruction of the incoherent, inelastic-neutron-scattering spectra of water and their comparison with molecular-dynamics data of Refs. [7, 15]. The conversion of the present theory into a classical form is straightforward.

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