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Computer simulation study of inelastic neutron scattering from liquid water

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A computer simulation study is presented to examine the incoherent inelastic neutron scattering from liquid water. A mixed quantum-classical method is employed: the quantum-mechanical vibrational degrees of freedom are treated analytically, whereas the rotational-translational degrees of freedom are studied by a classical molecular-dynamics simulation. The spectral effects of vibrational relaxation mechanisms are explicitly accounted for. The results are in good agreement with experiments. The limitations of a purely classical description are discussed.

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I. INTRODUCTION

A considerable effort has been recently devoted to study the incoherent, inelastic scattering of neutrons from liquid water by employing spallation sources of epithermal neutrons [1–3]. Neutron spectra obtained by using them [4,5] have a much more intense signal than those measured by conventional techniques [6]. Analytical theories [7–13] as well as molecular-dynamics (MD) methods [5,14–16] have been used to interpret the ancient and new experimental data. For a review describing the present state of the art in this field, see Ref. [17].

The computer simulation studies began with the work of Stillinger and Rahman [14], and Toukan and Rahman [15]. In these papers, the proton velocity autocorrelation function was calculated; this function determines the neutron scattering spectra for vanishingly small momentum transfers. Later, Bansil *et al.* [16] and Toukan *et al.* [5] carried out a molecular-dynamics calculation of the k-dependent proton density of states $G_S(\boldsymbol{k},t)$; different, not necessarily small, values of k were considered. However, all the previously mentioned simulations of the proton dynamics are classical and question arises whether, or not, classical mechanics can be applied to this problem. The answer comes from the observation that the intensity of the classically calculated spectra in the hydrogen stretching region is smaller than the experimental intensities by an order of magnitude. This negative result entirely conforms to a general rule of statistical mechanics: quantum mechanics must be used whenever $\beta\hbar\omega \gg 1$, where $\hbar\omega$ is a representative energy of the process under investigation. The fact that quantum and classical harmonic oscillators exhibit some similarities does not alter this general rule.

A similar problem was encountered by authors simulating infrared and Raman spectra of liquid water and ice. However, their approach was to disentangle the vibrational degrees, which are quantum mechanical, from the remaining degrees of freedom, which are classical. In their papers, Rice *et al.* [18–20] introduced the random network model assuming a continuous, distorted system of hydrogen bonds throughout the liquid phase. Inserted in this time-averaged structure, the molecules execute quantum-mechanical internal vibrations. Classical molecular-dynamics simulations were employed to determine the external configurations. Later, Reimers and Watts [21] described a similar calculation, but using the Monte Carlo rather than the molecular-dynamics method. Finally, Postma, Berendsen, and Straatsma [22] performed a molecular-dynamics simulation to determine the forces perturbing the internal vibrations; spectral band shapes were deduced from the distribution of forces. All these simulations considered rigid molecules.

We report here a study of incoherent, inelastic neutron spectra of water, similar to that of Refs. [10,11] and having many features in common with the papers [18–22] on infrared and Raman spectra mentioned above. The vibrational and rotational-translational degrees of freedom are treated separately; the fact that vibrational motions are much faster than any other motion of the system, and have low amplitudes, makes this separation practicable. The quantum-mechanical problem can be solved analytically, and one is then left with a problem concerning a classical system of rigid water molecules. The latter can be treated either analytically, or by molecular-dynamics simulation. The former of these routes was explored earlier [11]. Here, we describe a calculation that corresponds to the second one. For a preliminary account, see Ref. [13].

II. BASIC THEORY

A. Description of the model

The following model is used to study the present problem. (i) The internal vibrations of a water molecule are described by the normal coordinates n_α, $\alpha = 1, 2, 3$, and are governed by the quantum-mechanical Hamiltonian:

$$\begin{aligned} H(\boldsymbol{n},t) &= \left[\frac{1}{2}\sum_{\alpha}(p_{\alpha}^{2}+\lambda_{\alpha}n_{\alpha}^{2})+\frac{1}{6}\sum_{\alpha,\beta,\gamma}\lambda_{\alpha\beta\gamma}n_{\alpha}n_{\beta}n_{\gamma}+\cdots\right] \\ &\quad+\left[\sum_{\alpha}V_{\alpha}(t)n_{\alpha}+\frac{1}{2}\sum_{\alpha,\beta}V_{\alpha\beta}(t)n_{\alpha}n_{\beta}+\frac{1}{6}\sum_{\alpha,\beta,\gamma}V_{\alpha\beta\gamma}(t)n_{\alpha}n_{\beta}n_{\gamma}+\cdots\right] \\ &= H^{(0)}(\boldsymbol{n}) \;+\; H^{(1)}(\boldsymbol{n},t)\,. \end{aligned} \tag{1}$$

Here $\lambda_{\alpha}=\omega_{\alpha}^{2}$ where ω_{α} is the αth normal frequency, $\boldsymbol{n}=\{n_1,n_2,n_3\}$, $V(\boldsymbol{n},t)$ is the interaction potential acting on a tagged water molecule, $V_{\alpha}=\partial V/\partial n_{\alpha}$, $V_{\alpha\beta}=\partial^{2}V/\partial n_{\alpha}\partial n_{\beta}$, etc. .... (ii) The molecules execute classical rotations and translations. (iii) The correlations between vibrations and translations rotations are neglected. These assumptions are discussed in Ref. [11].

B. Description of the scattering process

Since the scattering from the oxygen nuclei is negligible compared to that from hydrogen nuclei, the incoherent scattering cross section of a sample containing N water molecules can be written [23]

$$\left(\frac{\partial^{2}\sigma}{\partial\Omega\partial E}\right)_{\mathrm{inc}}=\frac{1}{2\pi\hbar}\frac{k_s}{k_i}2Na_{\mathrm{inc}}^{2}\times\int_{-\infty}^{+\infty}dt\exp\left(-iEt/\hbar\right)I(\boldsymbol{k},t)\;, \tag{2a}$$

$$I(\boldsymbol{k},t)=\left\langle e^{-i\boldsymbol{k}\cdot\boldsymbol{r}(0)}\cdot e^{i\boldsymbol{k}\cdot\boldsymbol{r}(t)}\right\rangle_{\mathrm{av}}\;. \tag{2b}$$

In these equations, a_{inc} designates the incoherent proton scattering length, $\boldsymbol{k}_i$ and $\boldsymbol{k}_s$ the wave vectors of the incident and scattered neutrons, respectively, and $\boldsymbol{k}=\boldsymbol{k}_i-\boldsymbol{k}_s$. Moreover, $I(\boldsymbol{k},t)$ is the intermediate scattering function, $\boldsymbol{r}$ is the Heisenberg position operator for an arbitrarily chosen proton in an arbitrarily chosen water molecule whereas $\langle\,\rangle_{\mathrm{av}}$ indicates the full equilibrium average. The calculation of the spectrum then reduces to that of the intermediate scattering function $I(\boldsymbol{k},t)$.

C. The intermediate scattering function

The problem is to extend the Zemach-Glauber theory [24,25] from gases to liquids and from harmonic to anharmonic potentials. This can be done by proceeding as follows: (i) The averaging operation $\langle\,\rangle_{\mathrm{av}}$ in Eq. (2b) is executed separately for vibrations and for rotations-translations. Considering the semiclassical nature of the present theory, the former is represented by a trace operation, and the latter by an angle bracket $\langle\,\rangle$. The vibrational density matrix ρ_0 is built on the wave functions of the nonperturbed anharmonic Hamiltonian $H^{(0)}(\boldsymbol{n})$. (ii) At room temperatures, only the vibrational ground state is populated. Then, writing $\boldsymbol{r}=\boldsymbol{R}+\sum_{\alpha=1}^{3}\boldsymbol{\rho}_{\alpha}$, where $\boldsymbol{R}$ indicates the equilibrium position of one of the two protons of the tagged molecule and $\boldsymbol{\rho}_{\alpha}$ its displacement in the normal mode α, one finds

$$I(\boldsymbol{k},t)=\left\langle e^{-i\boldsymbol{k}\cdot[\boldsymbol{R}(0)-\boldsymbol{R}(t)]}\left[\exp\left(-i\boldsymbol{k}\cdot\sum_{\alpha=1}^{3}\boldsymbol{\rho}_{\alpha}(0)\right)\times\exp\left(i\boldsymbol{k}\cdot\sum_{\beta=1}^{3}\boldsymbol{\rho}_{\beta}(t)\right)\right]_{000,000}\right\rangle. \tag{3}$$

The set of quantum numbers $(0,0,0)$ designates the ground state of the anharmonic Hamiltonian $H^{(0)}(\boldsymbol{n})$ and $\boldsymbol{\rho}_{\alpha}=\boldsymbol{l}_{\alpha}n_{\alpha}$, where $\boldsymbol{l}_{\alpha}$ designates the direction of the proton motion in the normal mode α. (iii) The theory is further simplified by the fact that all vibrational energy levels, with the exception of the two hydrogen stretching levels, are widely spaced as compared with k_BT. The latter two belong to different irreducible representations of the point group of the water molecule which precludes their mixing through $V(\boldsymbol{n},t)$. The adiabatic approximation can thus be safely used when treating Eq. (3), which can be rewritten as follows [11]:

$$\begin{aligned} I(\boldsymbol{k},t) &= \left\langle e^{-i\boldsymbol{k}\cdot[\boldsymbol{R}(0)-\boldsymbol{R}(t)]}\left[e^{-i\boldsymbol{k}\cdot\sum_{\alpha=1}^{3}\boldsymbol{l}_{\alpha}(0)n_{\alpha}}\right]_{000,000}\left[e^{i\boldsymbol{k}\cdot\sum_{\beta=1}^{3}\boldsymbol{l}_{\beta}(t)n_{\beta}}\right]_{000,000}\right\rangle \\ &\quad+\left\langle e^{-i\boldsymbol{k}\cdot[\boldsymbol{R}(0)-\boldsymbol{R}(t)]}\left[e^{-i\boldsymbol{k}\cdot\sum_{\alpha=1}^{3}\boldsymbol{l}_{\alpha}(0)n_{\alpha}}\right]_{000,100}\left[e^{i\boldsymbol{k}\cdot\sum_{\alpha=1}^{3}\boldsymbol{l}_{\alpha}(t)n_{\alpha}}\right]_{100,000}\right\rangle \\ &\quad+\left\langle e^{-i\boldsymbol{k}\cdot[\boldsymbol{R}(0)-\boldsymbol{R}(t)]}\left[e^{-i\boldsymbol{k}\cdot\sum_{\alpha=1}^{3}\boldsymbol{l}_{\alpha}(0)n_{\alpha}}\right]_{000,010}\left[e^{i\boldsymbol{k}\cdot\sum_{\alpha=1}^{3}\boldsymbol{l}_{\alpha}(t)n_{\alpha}}\right]_{010,000}\right\rangle \\ &\quad+\left\langle e^{-i\boldsymbol{k}\cdot[\boldsymbol{R}(0)-\boldsymbol{R}(t)]}\left[e^{-i\boldsymbol{k}\cdot\sum_{\alpha=1}^{3}\boldsymbol{l}_{\alpha}(0)n_{\alpha}}\right]_{000,001}\left[e^{i\boldsymbol{k}\cdot\sum_{\alpha=1}^{3}\boldsymbol{l}_{\alpha}(t)n_{\alpha}}\right]_{001,000}\right\rangle \\ &\quad+(\text{higher-order terms}), \end{aligned} \tag{4}$$

where the sets (1,0,0), (0,1,0), and (0,0,1) denote the singly-excited states of $H^{(0)}(\boldsymbol{n})$. (iv) The full anharmonic wave functions are only employed to calculate the vibrational phase factors $\left\langle \exp\left(i\int_0^t dt'\omega_\alpha(t')\right)\right\rangle$, appearing when the matrix elements are evaluated. In turn, the amplitude factors are determined by replacing the full anharmonic wave functions by their harmonic counterparts. Approximations of this nature are of current use, and should not produce significative errors. Then, designating by $I_Q(\boldsymbol{k},t)$ the intermediate scattering function appropriate to the low-energy spectrum, and by $I_\alpha(\boldsymbol{k},t)$ that associated with the fundamental α, the following formulas may be found:

$$I_Q(\boldsymbol{k},t) = \left\langle e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}(0)-\boldsymbol{R}(t))} \prod_{\beta=1}^{3} \exp\left\{ -\frac{1}{2}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\beta(0)\right]^2 -\frac{1}{2}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\beta(t)\right]^2 \right\} \right\rangle , \tag{5a}$$

$$\begin{aligned} I_\alpha(\boldsymbol{k},t) = {} & \left\langle e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}(0)-\boldsymbol{R}(t))} \left[\boldsymbol{k}\cdot\boldsymbol{L}_\alpha(0)\right]\left[\boldsymbol{k}\cdot\boldsymbol{L}_\alpha(t)\right] \right. \\ & \times \left. \prod_{\beta=1}^{3} \exp\left\{ -\frac{1}{2}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\beta(0)\right]^2 -\frac{1}{2}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\beta(t)\right]^2 \right\} \right\rangle \\ & \times \left\langle \exp\left(i\int_0^t dt'\omega_\alpha(t') \right) \right\rangle , \end{aligned} \tag{5b}$$

$$\begin{aligned} \omega_\alpha(t) &= \omega_\alpha^{(0)} + \frac{1}{2\omega_\alpha^{(0)}} \left(V_{\alpha\alpha}(t) - \sum_{\beta=1}^{3} \frac{\lambda_{\alpha\alpha\beta}}{\omega_\alpha^{(0)}} V_\beta(t) \right) \\ &= \omega_\alpha^{(0)} + \Delta\omega_\alpha(t) , \end{aligned} \tag{6}$$

where $\boldsymbol{L}_\alpha(t) = \boldsymbol{l}_\alpha(t)\,[n_\alpha]_{01}$ and $\Delta\omega_\alpha(t)$ are the proton amplitude and the interaction-induced frequency shift of the normal mode α, respectively. Similar expressions may be derived for overtone and combination bands.

The principal merit of Eqs. (5,6) is that vibrational and rotational-translational degrees of freedom have been disentangled from each other. The intermediate scattering functions $I_Q(\boldsymbol{k},t)$, $I_\alpha(\boldsymbol{k},t)$ can thus be calculated by performing a classical molecular-dynamics simulation of a system of N rigid water molecules. This simulation will be described in Sec. III, whereas the semiclassical corrections, which turn out to be necessary, will be analyzed in Sec. IV.

III. MOLECULAR-DYNAMICS SIMULATION

A. Basic data

The simulation box contained 256 rigid water molecules and periodic boundary conditions were imposed. The long-range electrostatic interactions were taken into account by calculating the Ewald sum. The equations of motion were integrated with the help of leap frog algorithms. Typical runs were of 10–20 ps after equilibration with a time step of 0.5 fs. The thermodynamic point considered here corresponds to T=300 K and ρ = 1 g cm^{-3}.

B. Potentials

The potential employed in the simulation was the pair-additive extended-simple-point-charge (SPCE) potential of Berendsen *et al.* [26]. It is written as a sum of terms describing Lennard-Jones interactions between oxygen nuclei and Coulombic interactions between point charges placed on all the atoms. Although not introduced explicitly, the polarization is accounted for implicitly by an appropriate choice of charges. The potential U_{12} of a given pair of water molecules can then be written:

$$U_{12} = 4\epsilon\left[\left(\frac{\sigma}{R_{12}}\right)^{12} - \left(\frac{\sigma}{R_{12}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\sum_{s,t}\frac{q_{1s}q_{2t}}{r_{1s2t}} , \tag{7}$$

where R_{12} denotes the distance between the two oxygen nuclei and r_{1s2t} that between the point charges q_{1s}, q_{2t} located on the oxygen and hydrogen nuclei. The complete potential U is then obtained by summing over all possible pairs of water molecules which can be formed in a sample containing N of them, $U = \sum_{i<j} U_{ij}$, and the interaction potential V acting on a tagged molecule, say 1, is the sum of all pair interactions involving molecule 1, $V = \sum_{j\neq 1} U_{1j}$. Despite its simplicity, the SPCE potential reproduces correctly the H bond network as well as many dynamic properties of liquid water.

C. Normal coordinates

The water molecule belongs to the point group C_{2v}. There are three normal modes. The mode n_1 corresponds to the totally symmetric irreducible representation A_1 of this group and describes the symmetric hydrogen stretching motions; the mode n_2 corresponds to the same irreducible representation and describes the HOH bending motions; and the mode n_3 belongs to the irreducible representation B_1 and represents the antisymmetric hydrogen stretching vibrations [27]. These definitions are of current use in spectroscopy.

The normal coordinates n_1, n_2, n_3 were assumed proportional to the symmetry coordinates $S_1 = (r_1+r_2)/\sqrt{2}$, $S_2 = \alpha$, $S_3 = (r_1 - r_2)/\sqrt{2}$, where r_1 and r_2 indicate the variation of the length of the two OH bonds, and α designates the variation of the angle between them [27]. This can be done without any significative loss of accuracy. In fact, the normal modes n_1 and n_2 are separated by as much as 200 meV and are virtually decoupled; the Fermi resonance that involves the first overtone of the mode n_2 is not considered here. In turn, n_3 is the only vibration of its symmetry class. Eventually, the normal coordinates can be written:

$$n_1 = \left\{2\left[\mu_{\rm H} + 2\mu_{\rm O}\cos^2(\theta/2)\right]\right\}^{-1/2}(r_1 + r_2) \ ,$$
$$n_2 = \left\{\sqrt{2}d\left[\mu_{\rm H} + 2\mu_{\rm O}\sin^2(\theta/2)\right]\right\}^{-1/2}\alpha \ ,$$
$$n_3 = \left\{2\left[\mu_{\rm H} + 2\mu_{\rm O}\sin^2(\theta/2)\right]\right\}^{-1/2}(r_1 - r_2) \ , \qquad (8)$$

where $\mu_{\rm O}$, $\mu_{\rm H}$ are inverse masses of the hydrogen and oxygen nuclei, respectively, d the OH equilibrium bond length and θ the equilibrium HOH angle. The harmonic and anharmonic force constants of the free H_2O molecule are given in Table I [28].

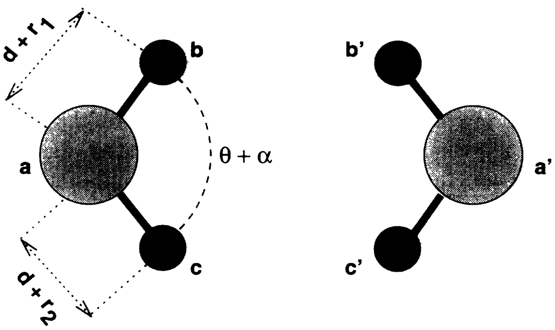

FIG. 1. Choice of displacement coordinates for a pair of water molecules.

D. Derivation of intermolecular potentials

Once the potential V as well as the normal coordinates n_α have been defined, the derivatives $V_\alpha(t)$ and $V_{\alpha\alpha}(t)$ entering into Eq. (6) for $\Delta\omega_\alpha(t)$ can be calculated. Here the methodology is relatively new and some comments are useful. (i) The SPCE potential was designed to describe a system of rigid water molecules and offers no guarantee when applied to nonrigid molecules; nonetheless, for lack of more refined models, it was used here. The same remark applies to the fully classical simulations of Refs. [16,17]. The parameters ϵ, σ, $q_{\rm O}$, $q_{\rm H}$ were considered independent of the internal coordinates. (ii) There is an ambiguity in the definition of the vibrational displacement coordinates r_1, r_2, α. For example, the H_1OH_2 angle variation α can be generated either by displacing proton H_1 alone, proton H_2 alone, or both of them. This ambiguity is lifted by imposing the Eckart conditions [27]

$$\sum_i m_i \boldsymbol{\rho}_i = \mathbf{0} \ , \quad \sum_i m_i\left(\mathbf{r}_i^e \times \boldsymbol{\rho}_i\right) = \mathbf{0} \ , \qquad (9)$$

where m_i indicates the mass of the nucleus i, $\mathbf{r}_i^e$ its equilibrium position and $\boldsymbol{\rho}_i$ its displacement. Equation (9) simply indicates the fact that internal vibrations do not constitute translations or rotations. No similar restriction exists in a molecular-dynamics simulation in which all degrees of freedom are considered. They appear in the present calculation as a consequence of the separate study of the vibrational and the rotational-translational motions.

The present choice of displacement coordinates is illustrated in Fig. 1 where the coordinates r_1, r_2, and α are defined. To simplify the calculations, violations of the Eckart conditions due to the finite mass of the oxygen nuclei were tolerated. As indicated, the increment r_1 was realized by shifting only the nucleus b of the molecule M in direction ab; a similar procedure applies to r_2. In turn, α was defined by a symmetric shift of the nuclei b and c in directions perpendicular to ab and ac, respectively. Derivations of $V(t)$ with respect to the normal coordinates n_α were thus reduced to derivations with respect to the cartesian coordinates of the protons. The analytical expressions obtained in this way are reproduced in the Appendix and may then be computed.

TABLE I. The harmonic and cubic forces constants (in meV) of the potential function of the free H_2O molecule defined in terms of dimensionless normal coordinates [28].

K_{11}	474.9	K_{133}	-114.21
K_{22}	204.3	K_{211}	4.91
K_{33}	488.5	K_{222}	-7.67
K_{111}	-39.58	K_{233}	18.25
K_{122}	31.65		

E. Details of calculation

The vibrational phase factors $\left\langle \exp\left(i\int_0^t dt'\Delta\omega_\alpha(t')\right)\right\rangle$, $\alpha = 1,2,3$, were calculated in the following way. The molecular-dynamics run containing $\mathcal{N}$ time steps of length Δt, was split into a set of ν shorter runs containing $\mathcal{N}_1$ time steps each, $\mathcal{N} = \nu\mathcal{N}_1$. The integral $\int_0^t dt'\Delta\omega_\alpha(t')$ was evaluated on each short run and the real and imaginary parts of the exponential were averaged over its ν realizations. Next, the calculation was repeated for another value of time t. In practice, these calculations were grouped into a single, long molecular-dynamics run with a time step of 0.1 fs. Proceeding in this way, it was possible to calculate the above vibrational phase factors with good statistics.

Calculation of the amplitude factors of Eqs. (5a) and (5b) shows no particularity. However, since experimental spectra were recorded at constant scattering angle, the scattering wave vector $\mathbf{k}$ varies with the transfer energy E. The amplitude factors were thus calculated for many values of $\mathbf{k}$, of the order of 25. The relation between $\mathbf{k}$ and E for a scattering angle of 8° is given in Fig. 2.

F. Semiclassical corrections

Although the translational and rotational motions of molecules in liquid water are predominantly classical, their quantum characteristics cannot be fully neglected when studying inelastic neutron spectra of water. A number of analytical theories have been published to introduce the necessary corrections [11,12,29–31]; unfor-

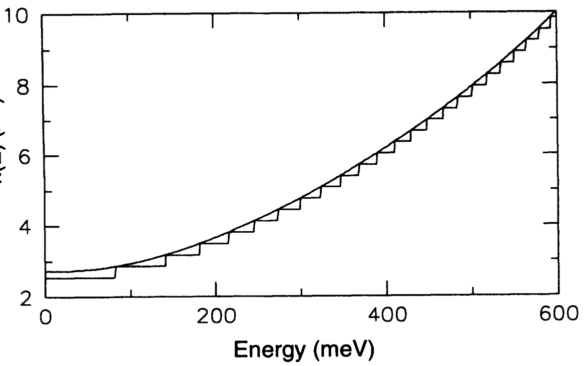

FIG. 2. Magnitude of the wave vector k as a function of the energy E for a neutron scattering experiment. The incident neutron energy is equal to 800 meV and the scattering angle to 8°. The steps indicate the different values of k at which $I(\boldsymbol{k},t)$ was calculated by MD simulation.

tunately, they cannot easily be built into a molecular-dynamics simulation. This is even more true for the present theory which is semiclassical in essence. One must avoid double counting and only introduce semiclassical corrections in factors entirely governed by the translational-rotational dynamics. This was done for the two correlation functions,

$$\left\langle e^{-i\boldsymbol{k}\cdot[\boldsymbol{R}(0)-\boldsymbol{R}(t)]}\prod_{\beta=1}^{3}\exp\left\{-\frac{1}{2}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\beta(0)\right]^2 -\frac{1}{2}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\beta(t)\right]^2\right\}\right\rangle , \tag{10a}$$

$$\left\langle e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}(0)-\boldsymbol{R}(t))}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\alpha(0)\right]\left[\boldsymbol{k}\cdot\boldsymbol{L}_\alpha(t)\right] \times\prod_{\beta=1}^{3}\exp\left\{-\frac{1}{2}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\beta(0)\right]^2-\frac{1}{2}\left[\boldsymbol{k}\cdot\boldsymbol{L}_\beta(t)\right]^2\right\}\right\rangle \tag{10b}$$

appearing in Eqs. (5a) and (5b); the following procedure was employed. (i) The well known relation $G_{\mathrm{as}}(\omega) = 2(1+e^{-\beta\hbar\omega})^{-1}G_{\mathrm{sym}}(\omega)$ was introduced between the Fourier transforms of the asymmetric and symmetrized correlation functions

$$\begin{aligned} G_{\mathrm{as}}(t) &= \langle A^*(0)A(t)\rangle \ , \\ G_{\mathrm{sym}}(t) &= \frac{1}{2}\,\langle [A^*(0)A(t)+A^*(t)A(0)]\rangle \ , \end{aligned} \tag{11}$$

where $A = \exp(i\boldsymbol{k}\cdot\boldsymbol{R})\prod_\beta \exp(-[\boldsymbol{k}\cdot\boldsymbol{L}_\beta]^2/2)$ or $\boldsymbol{k}\cdot\boldsymbol{L}_\alpha\exp(i\boldsymbol{k}\cdot\boldsymbol{R})\prod_\beta\exp(-[\boldsymbol{k}\cdot\boldsymbol{L}_\beta]^2/2)$.

(ii) Next, the expression for $G_{\mathrm{sym}}(t)$ was replaced by its classical analog. This is justified since, contrary to $G_{\mathrm{as}}(t)$, the function $G_{\mathrm{sym}}(t)$ is even and real as are classical autocorrelation functions. In practice, the above procedure amounts to introducing the detailed balance factor $2(1+e^{-\beta\hbar\omega})^{-1}$; no expansion in powers of $\hbar$ was required.

Unfortunately, no simple and systematic way was found to incorporate the correction describing the recoil effect in the present molecular-dynamics simulation. This was only possible by employing various ad hoc arguments; none of them was retained. However, the spectral effect of nuclear recoil is non-negligible in the hydrogen stretching region [11,12]. Its absence is a weakness of the present theory.

IV. RESULTS AND DISCUSSION

The following results have been reached by the present theory: (i) The proton density of states $G_S(\boldsymbol{k},t) = E^2S_S(\boldsymbol{k},t)/k^2$ was calculated first. In order to make the comparison theory experiment more meaningful, the theoretical spectra were convoluted with an experimental function taken from Ref. [5]. The agreement is only moderate; as discussed earlier, quantum characteristics of molecular translations and rotations are not entirely negligible. (ii) The comparison between theory and experiment becomes satisfactory if semiclassical corrections are introduced (Fig. 3). The agreement is equally good for the self-structure factor $S_S(\boldsymbol{k},E)$ (Fig. 4). One can see from this figure that the discrepancy between the calculated and the experimental spectra at energies below 180 meV is mainly due to the central peak, which anyhow is not well resolved experimentally. (iii) Analytical and simulated proton self-structure factors $S_S(\boldsymbol{k},E)$ are also in very good agreement (Fig. 5). (iv) Proton densities of states $G_S(\boldsymbol{k},E)$, calculated by the present simulation, strongly differ from those produced by fully classical simulations [5,16]. At high-energy transfers, the difference attains an order of magnitude, as expected (Fig. 6). (v) Two band shaping mechanisms are operating, the Doppler and the vibrational broadening. As a consequence, the bandwidths $\Delta E_{1/2}$ are neither proportional to k nor independent of it at small k's. Unfortunately,

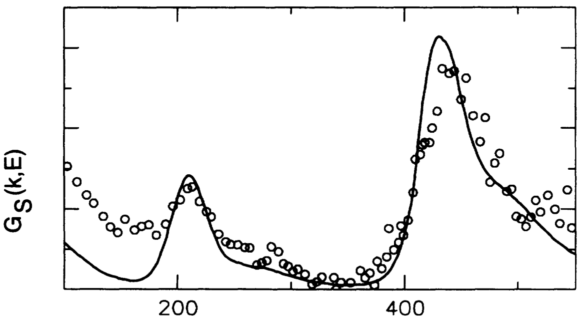

FIG. 3. The proton density of states $G_S(\boldsymbol{k},t)$ calculated by MD simulation including the semiclassical corrections (——), and measured experimentally (o o o) [5]. The scattering angle is equal to 8°.

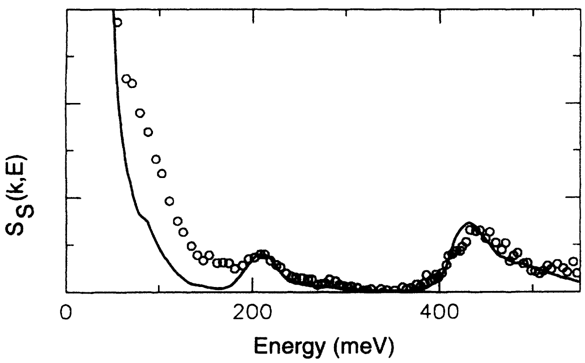

FIG. 4. The self-structure factor $S_S(\mathbf{k},E)$ calculated by MD simulation including the semiclassical corrections (——), and measured experimentally (o o o) [5]. The scattering angle is equal to 8°.

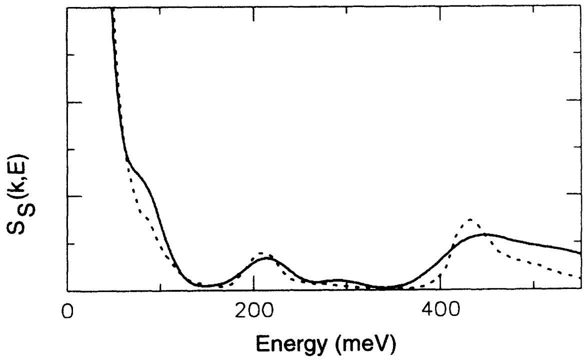

FIG. 5. The self-structure factor $S_S(\mathbf{k},E)$ calculated analytically (——) [11], and by MD simulation including the semiclassical corrections (– – –). The scattering angle is equal to 8°.

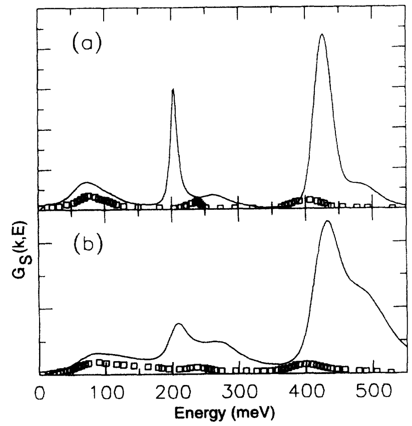

FIG. 6. The proton densities of states $G_S(\mathbf{k},E)$ calculated by the present semiclassical (——) and by a fully classical MD simulation (□ □ □) [11]. The wave vector k is constant and its modulus is equal to 4.4 Å^{-1} (a) and 8.6–8.7 Å^{-1} (b).

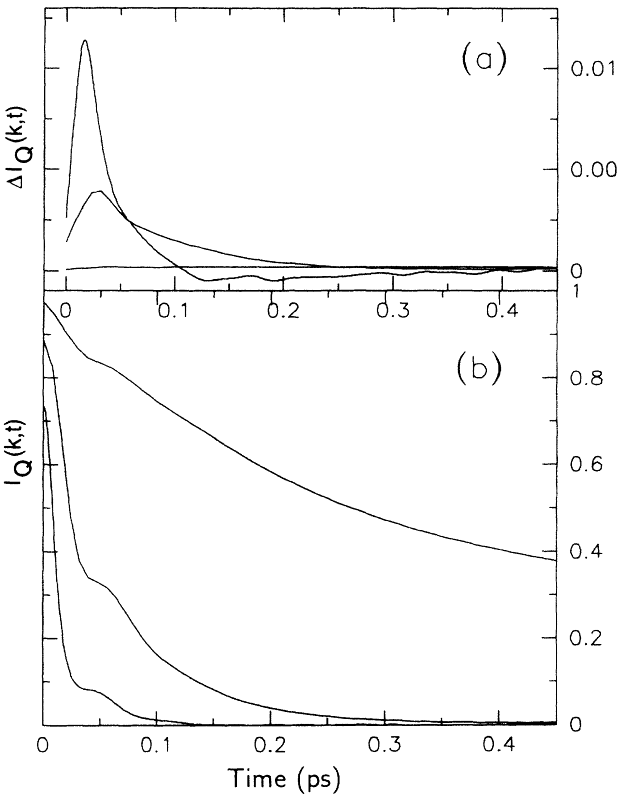

FIG. 7. Difference $\Delta I_Q(k,t)$ between $I_Q(k,t)$ calculated by employing the full Eq. (5a) and by averaging the factors $\exp[-i\mathbf{k}\cdot(\mathbf{R}(0)-\mathbf{R}(t))]$ and $\prod_\beta \exp\{-[\mathbf{k}\cdot\mathbf{L}_\beta(0)]^2/2 -[\mathbf{k}\cdot\mathbf{L}_\beta(t)]^2/2\}$ separately. The curves correspond to three different values of k comprised between 2.226 and 10.176 Å^{-1} (a). The exact function $I_Q(k,t)$ is plotted for comparison (b).

the OH bending band is the only one lending itself to this sort of analysis; all other bands are composite. It should also be pointed out that the effects of the finite instrumental resolution must be eliminated before studying this problem. Their presence would invalidate the conclusions completely. (vi) All basic assumptions of the analytical theory of Ref. [11] were carefully checked by the present numerical calculation. For example, separate averaging of the factor $\prod_{\alpha=1}^{3}\exp\{-\frac{1}{2}[\mathbf{k}\cdot\mathbf{L}_\alpha(0)]^2-\frac{1}{2}[\mathbf{k}\cdot\mathbf{L}_\alpha(t)]^2\}$ in the expression (5a) for $I_Q(\mathbf{k},t)$ leaves no detectable trace on the numerical result for this quantity (Fig. 7). This is also true for other assumptions employed therein [32].

It results from the above study that the inelastic scattering from water is generated by mechanisms which are of quantum-mechanical nature. They cannot be simulated by a purely classical molecular-dynamics method. Quantum-mechanical simulations, similar to those proposed by Car and Parrinello, could be considered, but they are not easy to realize in practice. In any case, the mixed quantum-classical method described here has been shown sufficient in the present context.

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APPENDIX: DERIVATIVES OF THE PAIR POTENTIAL U_{1J} WITH RESPECT TO INTERNAL COORDINATES OF H$_2$O

Calculation of the derivatives of the interaction potential between the tagged molecule 1 and an arbitrary molecule j requires some elementary algebra. It leads to the following expressions for the first derivatives

$$
\begin{aligned}
\left[\frac{\partial U_{1j}}{\partial r_1}\right]_{\mathbf{0}} &= E_0 d\left[\frac{2\mathbf{R}_{a'b}}{R^3_{a'b}}-\frac{\mathbf{R}_{b'b}}{R^3_{b'b}}-\frac{\mathbf{R}_{c'b}}{R^3_{c'b}}\right]\cdot\mathbf{e}_{\parallel 1}\,,\\
\left[\frac{\partial U_{1j}}{d\,\partial\theta}\right]_{\mathbf{0}} &= \frac{E_0 d}{2}\left[\frac{2\mathbf{R}_{a'b}}{R^3_{a'b}}-\frac{\mathbf{R}_{b'b}}{R^3_{b'b}}-\frac{\mathbf{R}_{c'b}}{R^3_{c'b}}\right]\cdot\mathbf{e}_{\perp 1}\\
&\quad+\frac{E_0 d}{2}\left[\frac{2\mathbf{R}_{a'c}}{R^3_{a'c}}-\frac{\mathbf{R}_{b'c}}{R^3_{b'c}}-\frac{\mathbf{R}_{c'c}}{R^3_{c'c}}\right]\cdot\mathbf{e}_{\perp 2}\,,\\
\left[\frac{\partial U_{1j}}{\partial r_2}\right]_{\mathbf{0}} &= E_0 d\left[\frac{2\mathbf{R}_{a'c}}{R^3_{a'c}}-\frac{\mathbf{R}_{b'c}}{R^3_{b'c}}-\frac{\mathbf{R}_{c'c}}{R^3_{c'c}}\right]\cdot\mathbf{e}_{\parallel 2}, \qquad \text{(A1)}
\end{aligned}
$$

and the second derivatives

$$
\begin{aligned}
\left[\frac{\partial^2 U_{1j}}{\partial r_1^2}\right]_{\mathbf{0}} &= E_0\left\{\frac{2d}{R^3_{a'b}}\left[1-3\frac{(\mathbf{R}_{a'b}\cdot\mathbf{e}_{\parallel 1})^2}{R^2_{a'b}}\right]-\frac{d}{R^3_{b'b}}\left[1-3\frac{(\mathbf{R}_{b'b}\cdot\mathbf{e}_{\parallel 1})^2}{R^2_{b'b}}\right]-\frac{d}{R^3_{c'b}}\left[1-3\frac{(\mathbf{R}_{c'b}\cdot\mathbf{e}_{\parallel 1})^2}{R^2_{c'b}}\right]\right\}\,,\\
\left[\frac{\partial^2 U_{1j}}{d^2\partial\theta^2}\right]_{\mathbf{0}} &= \frac{E_0}{4}\left\{\frac{2d}{R^3_{a'b}}\left[1-3\frac{(\mathbf{R}_{a'b}\cdot\mathbf{e}_{\perp 1})^2}{R^2_{a'b}}\right]-\frac{d}{R^3_{b'b}}\left[1-3\frac{(\mathbf{R}_{b'b}\cdot\mathbf{e}_{\perp 1})^2}{R^2_{b'b}}\right]-\frac{d}{R^3_{c'b}}\left[1-3\frac{(\mathbf{R}_{c'b}\cdot\mathbf{e}_{\perp 1})^2}{R^2_{c'b}}\right]\right\}\\
&\quad+\frac{E_0}{4}\left\{\frac{2d}{R^3_{a'c}}\left[1-3\frac{(\mathbf{R}_{a'c}\cdot\mathbf{e}_{\perp 2})^2}{R^2_{a'c}}\right]-\frac{d}{R^3_{b'c}}\left[1-3\frac{(\mathbf{R}_{b'c}\cdot\mathbf{e}_{\perp 2})^2}{R^2_{b'c}}\right]-\frac{d}{R^3_{c'c}}\left[1-3\frac{(\mathbf{R}_{c'c}\cdot\mathbf{e}_{\perp 2})^2}{R^2_{c'c}}\right]\right\}\\
&\quad-\frac{E_0}{4}\left[\frac{2\mathbf{R}_{a'b}}{R^3_{a'b}}-\frac{\mathbf{R}_{b'b}}{R^3_{b'b}}-\frac{\mathbf{R}_{c'b}}{R^3_{c'b}}\right]\cdot\mathbf{e}_{\parallel 1}-\frac{E_0}{4}\left[\frac{2\mathbf{R}_{a'c}}{R^3_{a'c}}-\frac{\mathbf{R}_{b'c}}{R^3_{b'c}}-\frac{\mathbf{R}_{c'c}}{R^3_{c'c}}\right]\cdot\mathbf{e}_{\parallel 2}\,,\\
\left[\frac{\partial^2 U_{1j}}{\partial r_2^2}\right]_{\mathbf{0}} &= E_0\left\{\frac{2d}{R^3_{a'c}}\left[1-3\frac{(\mathbf{R}_{a'c}\cdot\mathbf{e}_{\parallel 2})^2}{R^2_{a'c}}\right]-\frac{d}{R^3_{b'c}}\left[1-3\frac{(\mathbf{R}_{b'c}\cdot\mathbf{e}_{\parallel 2})^2}{R^2_{b'c}}\right]-\frac{d}{R^3_{c'c}}\left[1-3\frac{(\mathbf{R}_{c'c}\cdot\mathbf{e}_{\parallel 2})^2}{R^2_{c'c}}\right]\right\}\,. \qquad \text{(A2)}
\end{aligned}
$$

The notations are the same as in Fig. 1; the index **0** denotes the condition $r_1 = r_2 = \alpha = 0$, $E_0 = q^2/4\pi\epsilon_0 d$, and $\mathbf{e}_{\parallel 1}$, $\mathbf{e}_{\parallel 2}$, $\mathbf{e}_{\perp 1}$ represent the unit vectors along (ab), (ac), and perpendicular to (ab), respectively.

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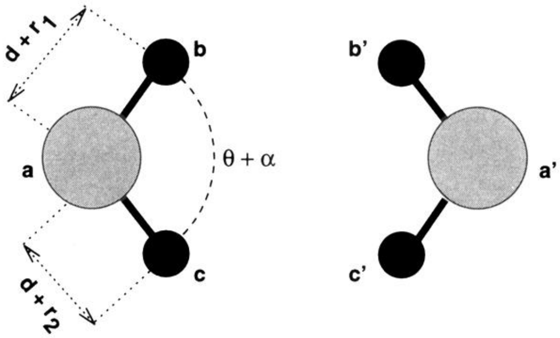

FIG. 1. Choice of displacement coordinates for a pair of water molecules.