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Molecular-dynamics study of atomic motions in water

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Using a flexible version of a rigid-molecule model of water we have analyzed the velocity autocorrelation functions to investigate the effect of the liquid milieu on the high-frequency internal modes of molecular motion. The calculations have been made at 1 $\mathrm{g\,cm^{-3}}$ and at 250, 325, and 375 K. Good agreement with experimentally determined pair correlations has also been found.

I. INTRODUCTION

Neutron inelastic-scattering experiments with H_2O (water) provide a powerful tool for investigating the dynamics of single protons because of the special manner in which a neutron interacts with a proton. This so-called incoherent inelastic scattering from the protons, denoted by $S_{\mathrm{inc}}(k,\omega)$, is determined by the momentum transfer $\hbar k$ and the energy transfer $\hbar\omega$. It is the Fourier transform of the function $\langle \exp(i\mathbf{k}\cdot\mathbf{d}(t))\rangle$, where $\mathbf{d}(t)$ is the displacement of a typical proton in time t. This function is usually denoted by $F_s(k,t)$.

Molecular-dynamics calculations, by following the trajectory of each proton in an assembly of water molecules at desired density and temperature conditions, can provide information about $F_s(k,t)$.

The motion of a proton obviously participates in three rather different kinds of motions. The center of mass of the molecule diffuses and carries the proton around; this type of motion seems to be similar in all liquids, even water. The molecule, having a rather well-defined structure, can be thought of as librating in the field of its neighbors, especially because of the hydrogen bonds that the molecules form with their immediate neighbors. Finally, the stiff internal forces holding the molecule intact produce high-frequency motions which by themselves are intensely and very thoroughly studied by experimenters using water vapor as their sample; these high-frequency motions in water are the object of the study presented here.

In earlier studies, using rigid molecules, Rahman and Stillinger,[1] studied the density fluctuation in water, i.e., the propagation of sound in the liquid, and later[2] also studied the protonic motion with stong bearing on problems arising from the use of large $\hbar k$ in many existing experiments. For the latter study it is useful to compare the quantity $\omega^2 S_{\mathrm{inc}}(k,\omega)/k^2$ with the spectrum of the velocity autocorrelation of the protons. In the limit of small k, the two functions are identical. The extent to which they differ gives a good indication of how, at not so small k, one encounters a loss of information due to what, in rather imprecise language for a liquid, can be called multiphonon effects.

In this paper we have concentrated on the problem of the high-frequency region of the spectrum which is dominated by internal modes of the molecule. We have found very clear indications of the effect of the liquid surroundings.

In a recent paper, Postma *et al.*[3] have used an ingenious method of investigating these high-frequency band profiles without allowing the molecule to vibrate. They use their rigid-molecule model and at each instant calculate the forces from the neighbors and express these forces in the frame of reference of the particular molecule. This gives them a measure of the degree of distortion the internal force constants would have suffered due to the momentary surroundings of the molecule. This process, when averaged over a sufficiently long run, gives them rather precise band profiles.

The time-correlation method, with flexible molecules, should in principle give the same results. But the degree of averaging necessary seems to be much more demanding as the following results will show.

II. POTENTIAL MODEL

The potential model employed is a modified version of the simple point-charge model (SPC) of Berendsen *et al.*[4] This model, as originally devised, assumes a rigid molecular structure for the water molecule. In the present version, we adopt the same form for the intermolecular interactions, but allow for flexible molecules. The intermolecular interactions consist of a Lennard-Jones potential between oxygens of different molecules and an electrostatic Coulomb potential between the molecules arising from suitable charges on the oxygen and the hydrogens in each molecule. The O-O interaction is taken to be

$$V_{\mathrm{O\text{-}O}} = -\left[\frac{A}{r}\right]^6 + \left[\frac{B}{r}\right]^{12}, \tag{1}$$

$$A = 0.371\,22 \text{ nm } (\mathrm{KJ\,mol^{-1}})^{1/6},$$

$$B = 0.3428 \text{ nm } (\mathrm{KJ\,mol^{-1}})^{1/12}.$$

The electrostatic interaction between the molecules arises from locating charges at the oxygen and the two hydrogen positions in each molecule ($+0.41\,|e|$ at the hydrogens and $-0.82\,|e|$ at the oxygen). Since we use the usual periodic boundary conditions, the standard Ewald summation method is used[5] to sum the long-range Coulomb interactions.

The harmonic intramolecular potential is a quadratic form in Δr_1, Δr_2, and Δr_3:

$$V_{\text{mol}}=\tfrac{1}{2}a[(\Delta r_1)^2+(\Delta r_2)^2]+\tfrac{1}{2}b(\Delta r_3)^2+c(\Delta r_1+\Delta r_2)\Delta r_3+d\Delta r_1\Delta r_2\ , \tag{2}$$

where Δr_1, Δr_2 are the stretch in the O—H bond lengths and Δr_3 is the stretch in the H—H distance. An equivalent form of the potential written in terms of the stretch distances Δr_1, Δr_2 and the change in the angle H-O-H, is

$$V_{\text{mol}}=\tfrac{1}{2}\alpha[(\Delta r_1)^2+(\Delta r_2)^2]+\tfrac{1}{2}\beta(r_{\text{OH}}\Delta\theta)^2+\gamma(r_{\text{OH}}\Delta\theta)(\Delta r_1+\Delta r_2)+\Delta(\Delta r_1\Delta r_2)\ . \tag{3}$$

Definitions of V_{mol} given in Eq. (2) and in Eq. (3) are related via the equations:

$$\begin{aligned}a&=\alpha+\beta\epsilon^2-2\gamma\epsilon\ ,\\ b&=\beta\eta^2\ ,\\ c&=\gamma\eta-\beta\eta\epsilon\ ,\\ d&=\beta\epsilon^2-2\gamma\epsilon+\Delta\ ,\end{aligned} \tag{4}$$

where $\epsilon=\tan(\theta/2)$, $\eta=\sec(\theta/2)$, θ being the H-O-H angle.

For a free water molecule, the three vibrational frequencies consist of a single asymmetric mode and two modes which leave the symmetry of the molecule unchanged.[6] The asymmetric stretch frequency square written in terms of the potential constants in Eq. (3) is given by

$$\omega_{\text{as}}^2=(\alpha-\Delta)[m^{-1}+M^{-1}(1-\cos\theta)]\ , \tag{5}$$

where m and M are, respectively, the masses of the hydrogen and the oxygen. The frequencies of the other two modes are the roots of the quadratic equation in ω^2:

$$\omega^4-B\omega^2+C=0\ ,$$

where

$$\begin{aligned}B&=\beta g-4\gamma\sin(\theta)M^{-1}+(\alpha+\Delta)u\ ,\\ C&=[\beta(\alpha+\Delta)-2\gamma^2][gu-2\sin^2(\theta)M^{-2}]\ ,\\ u&=[m^{-1}+M^{-1}(1+\cos\theta)]\ ,\\ g&=2[m^{-1}+M^{-1}(1-\cos\theta)]\ .\end{aligned} \tag{6}$$

The potential constants in Eq. (3) are taken from Kuchitsu and Morino.[7] Table I lists the potential constants and the three vibrational frequencies for a free water molecule derived from them.

TABLE I. Potential constants and vibrational frequencies for a free water molecule, with $\alpha=8.454$, $\beta=0.761$, $\gamma=0.228$, $\Delta=-0.101$ mdyn/Å, $r_e=1$ Å, and $\theta=109.5°$.

	Model	Experiment (Raman)
Asymmetric stretch	490.69	465.63 meV
Symmetric stretch	474.58	453.34 meV
Symmetric bending	205.17	197.67 meV

Because of the experimentally observed softening of the stretch vibrational band when going from gas to liquid,[8] we have attempted to introduce an anharmonic Morse potential for the O—H stretch vibrational part. For this purpose, the quadratic terms $(\Delta r_1)^2$ and $(\Delta r_2)^2$ in Eq. (2) are replaced by a Morse potential of the form

$$V_{\text{OH}}=D_{\text{OH}}\{1-\exp[-\rho(r-r_e)]\}^2\ , \tag{7a}$$

$$2\rho^2D_{\text{OH}}=\alpha\ . \tag{7b}$$

Equation (7b) ensures the necessary correspondence between Eqs. (7) and (2). The constant D_{OH} is taken as the experimentally determined dissociation energy of the O—H bond.[9]

A system of 100 water molecules in a cubic cell of side 14.41 Å, i.e., at a density of 1 g/cm^3 was studied. Well-equilibrated samples were prepared at the various temperatures at which the study was made. The integration step in time was 6.5×10^{-16} sec, and each run was, on the average, 8000 time steps long. The short-range part of the interaction was cut at a range of 7 Å. A series of simulation runs for the liquid state at 250, 325, and 375 K are reported here. The velocity autocorrelation functions, extending up to $400\Delta t$, and the respective frequency spectra were the main objects of study. The latter were used for comparison with experiment. The pair correlation functions g_{OO}, g_{OH}, and g_{HH} are also reported in the following.

RESULTS

A. Structural results

During all the runs made we calculated the three pair correlations in the system. Figure 1 shows these functions obtained in a run with the Morse potential at 325 K. The $g_{\text{OH}}(r)$ shown in Fig. 1(a) has peaks at distances of 1.035, 1.75, and 3.25 Å between O and H. The first is the O—H bond distance. The 1.75-Å peak is at the distance between an oxygen and a hydrogen along a hydrogen bond. 3.25 Å is the distance from oxygen to a hydrogen of the neighboring hydrogen-bonded molecule.

Figure 1(b) shows $g_{\text{HH}}(r)$ with three peaks at 1.66, 2.28, and 3.8 Å. The 1.66 Å corresponds to the intramolecular H—H distance. The 2.38 Å is the distance between adjacent hydrogen atoms of a well-formed water dimer. Hydrogen atoms opposite to each other in the water dimer are separated by a distance of 3.5 Å.

Figure 1(c) shows $g_{\text{OO}}(r)$ with a peak at 2.8 Å, corresponding to the distance between the oxygen atoms in neighboring water molecules. Apart from this peak, this pair correlation does not show any further structural detail. Comparison of our results with the recent work of Soper[10] shows that our calculated pair correlations are in quantitative agreement with these experimental data.

B. Dynamical results

Our study focuses mainly on two points: (i) studying the effect of anharmonicity in the potential on the vibra-

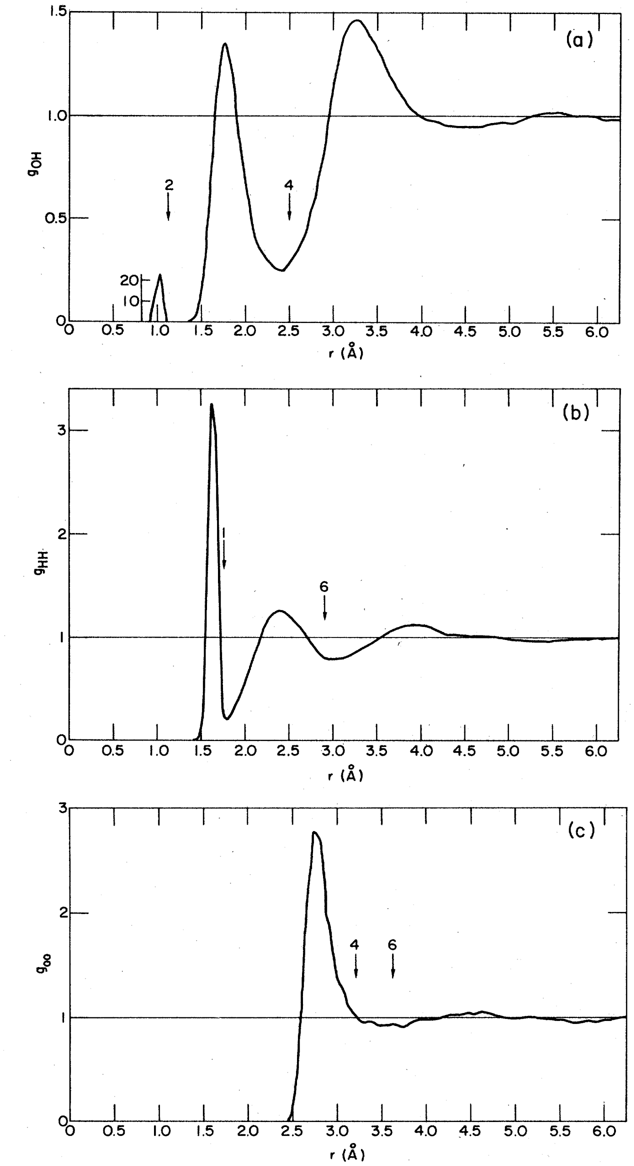

FIG. 1. (a) Pair correlation g_{OH} at 325 K. Prominent peaks are at 1.035 (intramolecular), 1.75, and 3.25 Å. The coordination numbers at two distances are also shown. (b) g_{HH} at 325 K. Peaks are at 1.66 (intramolecular), 2.28, and 3.8 Å. (c) g_{OO} at 325 K. No structure is present except the first-neighbor peak at 2.8 Å.

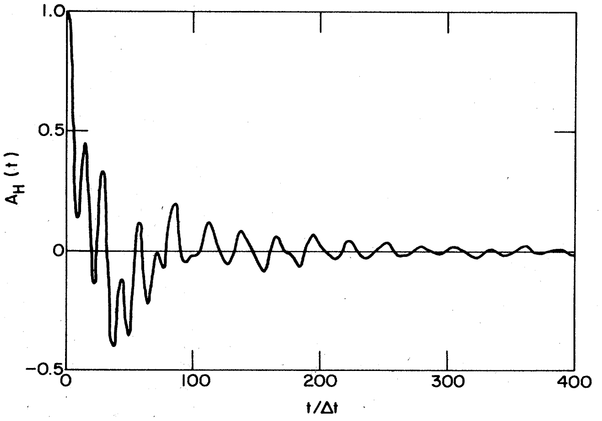

FIG. 2. Velocity autocorrelation function $A_{\mathrm{H}}(t)$ at 325 K using the Morse potential for O—H stretch in each molecule. Δt for simulation was 6.5×10^{-16} sec. $A_{\mathrm{H}}(t)$ has been calculated up to $400\Delta t$.

tional spectra and (ii) monitoring energy shifts in the vibrational bands due to temperature variations. The potential model is written in terms of three stretch distances Δr_1, Δr_2, and Δr_3, as in Eq. (2), the constants being those obtained using Eq. (4). Table II summarizes some of the results of our simulations. These results will be discussed in detail.

The velocity autocorrelation functions of the oxygens and hydrogens are defined as usual by

$$A_\alpha(t)=\langle \mathbf{V}_\alpha(s)\cdot\mathbf{V}_\alpha(s+t)\rangle/\langle \mathbf{V}_\alpha^2(s)\rangle\ , \tag{8}$$

and the power spectrum by

$$\phi_\alpha(\omega)=\int_0^\infty A_\alpha(t)\cos(\omega t)dt\ . \tag{9}$$

As already mentioned, $A_\alpha(t)$ have been calculated up to $t=400\Delta t=2.6\times10^{-13}$ sec.

Figure 2 shows $A_{\mathrm{H}}(t)$ at 325 K. A period of $14\Delta t$ is clearly visible. It corresponds to a frequency of $\sim$450 meV. Figure 3 shows $A_{\mathrm{O}}(t)$ at 325 K. The $14\Delta t$ periodicity is visible; however, it seems clear that a $400\Delta t$ time elapse is not sufficient to describe the slowly varying aspects of the molecular motions.

$\phi_{\mathrm{H}}(\omega)$ at 250 K is shown in Fig. 4; bands which can be characterized as librational, bending, and stretch motions appear in the spectrum as expected. The librational band

TABLE II. Simulation results for harmonic and Morse potentials. Harmonic constants: $a=9.331$, $b=2.283$, $c=-1.469$, $d=0.776$ mdyn/Å. Morse constants: $D=0.708$ mdyn Å, $\rho=2.566$ Å^{-1}, $b=2.283$, $c=-1.469$, $d=0.776$ mdyn/Å.

Potential	T (K)	E_L	E_B	E_S		E_{AS} (meV)
Harmonic	325	67	222.4	476.4		492.0
Morse	250	59.2	228.3	428.2		447.0
Morse	325	55.3	227.0	434.1		451.9
Morse	375	55.3	225.0	436.1		457.8
Supercooled water[a]	258	74	207		418[b]	
	353		207		443[b]	

[a] Reference 8.

[b] Unresolved S and AS peaks.

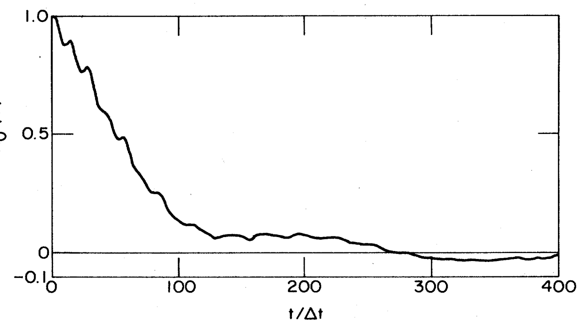

FIG. 3. $A_O(t)$ at 325 K; the other details are as in Fig. 2.

occurs at 59.2 meV; it arises from the electrostatic Coulombic interaction between neighboring molecules. The band due to molecular flexing occurs at 228.3 meV. The stretch O-H band is broken up into an asymmetric stretch at 447.0 meV and a symmetric stretch at 428.2 meV. We thus notice from Fig. 4 the presence of a downshift in the position of the stretch bands by ~44 meV compared to the gas-phase value, and an upshift in the bending band energy by 23 meV compared to the gas-phase value. Considering a similar simulation but with a fully harmonic molecular potential and at 325 K (Table II), one clearly sees that this behavior of the bending band is present just as in the anharmonic case. However, with the fully harmonic potential the stretch bands maintain the same energy as in the gas. This suggests that the upshift in the bending-band energy is primarily due to the liquid surroundings. On the other hand, the downshift in the stretching-band energy is attributed to a combined effect of the anharmonicity of the potential and the liquid surroundings. In the next section, we will account quantitatively for the shift in the band energies from the case of a gas to that of a liquid. The formation of hydrogen bonds in the liquid state must affect the nature of the molecular vibrations. The variation of the hydrogen bond from its well-formed linear character as in ice to the absence of such bonds in the gas implies obviously that in the liquid there will be a dependence on temperature of the degree to which well-formed bonds are present.

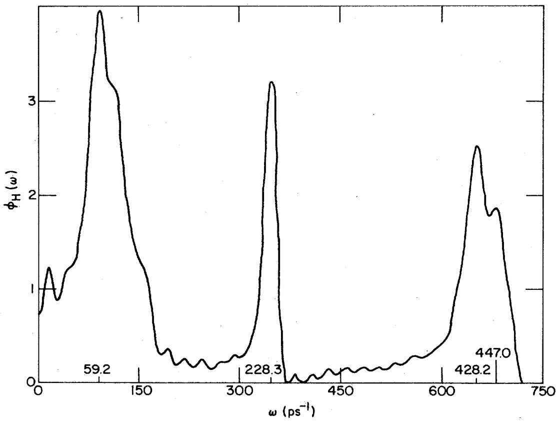

FIG. 4. $\phi_H(\omega)$, the spectrum of $A_H(t)$ at 250 K, with the Morse intramolecular potential. The values of the frequency at the peak positions are also given in meV.

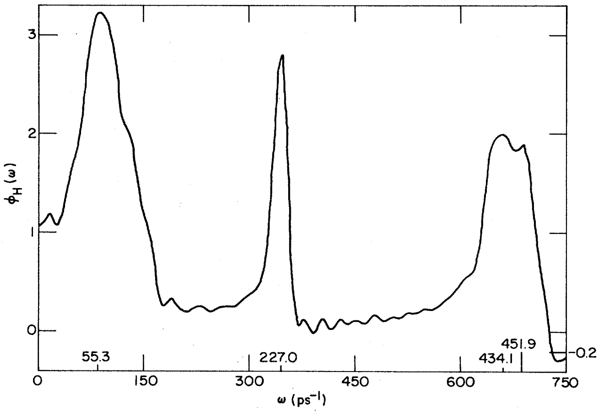

FIG. 5. $\phi_H(\omega)$ at 325 K; otherwise as in Fig. 4.

Figure 5 shows the results at 325 K, all other conditions being those at 250 K. Stretch-mode hardening by 6 meV with this increase in temperature, associated with a softening of the librational band energy by 4 meV, is clearly seen when compared to Fig. 4. The same trends continue to persist with a further increase in temperature to 375 K as seen in Fig. 6.

In the model used here, the hydrogen bond is a consequence of attractive intermolecular Coulombic interactions. The alignment of atoms in the presence of well-formed hydrogen bonds at low temperatures therefore will increase the effect of these intermolecular forces on the intermolecular vibrations. One can roughly describe the hydrogen bonds as being tight at low temperature, loose at high temperature. This must lead to the effect on the librational band as in Figs. 4—6. Recent neutron inelastic-scattering experiments from water[8] confirm the abovementioned effect on the librational band energy.

The oxygen spectrum at 325 K is shown in Fig. 7. Since oxygen is heavier than the hydrogens and hence much closer to the center of mass of the molecule, the in-

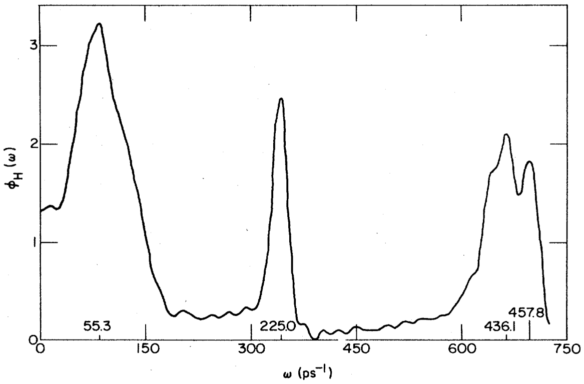

FIG. 6. $\phi_H(\omega)$ at 375 K; otherwise as in Fig. 4.

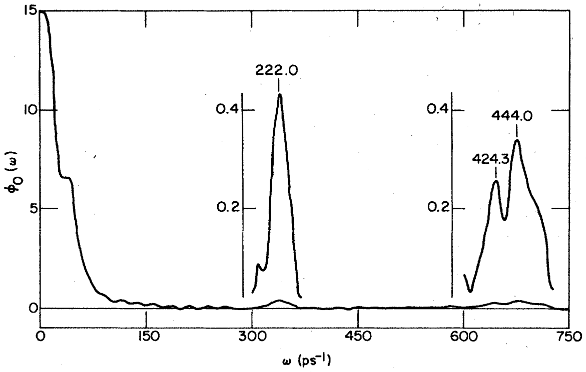

FIG. 7. $\phi_O(\omega)$ at 325 K; otherwise as in Fig. 4. For clarity the intramolecular regions of the spectrum have been expanded in scale.

tramolecular dynamics is manifested in the motion of the oxygen to a much lesser extent than the overall diffusive "long" time scale motion of the molecule. To study the low-frequency part of the spectrum in detail requires that the velocity autocorrelation function be extended beyond the time for which it has been calculated during the calculations presented here. Note that the normalization of $A_\alpha(t)$ in Eq. (8) gives $\phi_\alpha(0)=DM_\alpha/k_BT$.

In Fig. 7 the stretch and bending bands occur at slightly lower energies than the values at which they have occurred in the hydrogen spectrum (5 to 10 meV). This is perhaps due to the fact that the oxygen participates simultaneously in the formation of more than one hydrogen bond and hence the intermolecular effects are slightly more pronounced. We do not know of any systematic experimental investigation of the differences between the spectra obtained from the correlated properties of $\mathbf{V}_0(t)$ as against those of $\mathbf{V}_H(t)$, i.e., between $A_O(t)$ and $A_H(t)$ of Eq. (8).

IV. EFFECT OF THE LIQUID ENVIRONMENT ON VIBRATIONAL FREQUENCIES

(a) In the calculation being reported here, we have noted that in water there is a small but unambiguous *increase* in the average O—H distance in a molecule; this average distance is not 1 Å (see Table I), but increases to 1.02 Å. Its dependence on temperature is not very marked (1.017 Å at 375 K and 1.019 Å at 250 K). Potential V_{OH} given in Eq. (7) implies that the constant α of Eq. (3) *decreases* to 0.85 of its original value; obviously this "bond weakening" will manifest itself in the dynamics of the various atoms.

(b) The alignment of an O—H bond with the oxygen of the neighboring molecule, namely the O—H · · · O hydrogen bond configuration, further softens the O—H bond dynamics. In the SPC model, the hydrogen bond arises out of Coulomb interactions and in a perfectly formed hydrogen bond at an O—H distance of 2.8 Å, there is a contribution of -0.266 mdyn/Å to the constant α of Eq. (3). Obviously the full effect of the perfectly formed hydrogen bond cannot be present in water. However, as already seen in Fig. 1 the $g_{OH}(r)$ has a clear peak at 1.75 Å and $g_{OO}(r)$ at 2.8 Å; the hydrogen bond formation should thus produce an effective stretch force constant different from the value appropriate for an isolated molecule.

(c) The formation of hydrogen bonds also implies certain preferred H—H distances between hydrogens of different molecules. Figure 1(b) shows a peak at 2.28 Å in $g_{HH}(r)$. Again assuming perfect hydrogen bond formation and a tetrahedral arrangement of hydrogens around an oxygen (2 at 1 Å and 2 at 1.8 Å), the SPC model gives a $+0.0289$ mdyn/Å contribution, to the stretch constant α of Eq. (3) and $+0.0322$ mdyn/Å to the constant β, i.e., to the bending force constant, which has a value 0.761 mdyn/Å in the isolated molecule. Table III summarizes the various effects mentioned above.

V. RECENT NEUTRON INELASTIC SCATTERING DATA AND COMPARISON WITH CALCULATIONS

In a recent study, Chen *et al.*[8] have analyzed the incoherent neutron scattering from water over a wide temperature range, from the supercooled region to the "hot" water region. Figure 8 shows the spectrum at $-15\,^\circ$C. The data was taken at a scattering angle of 8°.

We note that in the region of the 420-meV energy transfer, the two stretch modes do not get resolved. This is due to the experimental resolution of about 16 meV in this region of energy transfer. One can hope that in the future this deficiency will be rectified.

We shall now make a few comparisons between Figs. 4 and 8, i.e., the calculation at 250 K and the experiment at $-15\,^\circ$C.

(a) The librational band occurs at 74 meV in Fig. 8 and at 59.3 meV in Fig. 4. This indicates that the SPC model is "simpler" than, for example, the four-point-charge (ST2) model, but still gives the same librational frequency band,[2] but in both models, this band is lower than the experimental value[8] as seen in Fig. 8.

TABLE III. Modification in vibration frequencies due to inclusion of effects (a), (b), and (c) (Sec. IV).

	E_B	E_S	E_{AS} (meV)	Remarks
H [no (a), (b), and (c) effects]	205.17	474.58	490.69	One harmonic molecule (Table I)
V_{OH} plus (a) effect	205.33	439.14	454.93	O—H bond elongation in V_{OH} in Eq. (7)
V_{OH} plus (a) and (b) effects	205.43	430.79	446.6	O—H · · · O in SPC model
V_{OH} plus (a), (b), and (c) effects	209.5	431.8	446.6	H—H effect in SPC model
250 K	228.3	429	446.8	Simulation
375 K	225.4	436.9	458.6	Simulation

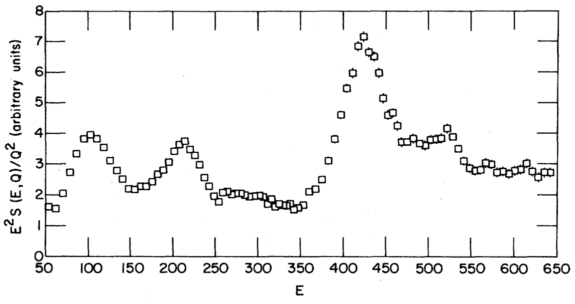

FIG. 8. Neutron inelastic scattering expressed as $\omega^2 S_{\text{inc}}(k,\omega)/k^2$ taken at $-15\,^{\circ}\mathrm{C}$ (supercooled water) at 8° angle of scattering (for details see Ref. 8). $E=\hbar\omega$ shown in meV.

than the experimental value[8] as seen in Fig. 8.

(b) The bending vibration of the molecule occurs at 207 meV in Fig. 8 and 228 meV in Fig. 4. We believe that a proper description of anharmonicity in the $\Delta\theta$-dependent part of Eq. (3) describing molecular vibrations is needed for a better description of this part of the spectrum. The sharpness of the calculated peak at 228 meV in Fig. 4 is also an indication of the lack of intrinsic anharmonicity for coordinate $\Delta\theta$ in the potential for molecular vibration.

(c) The center of the band in Fig. 8 at 418 meV is lower than the value $\sim$440 meV in Fig. 4; this is despite the anharmonicity introduced into the appropriate part of the potential function.

Despite the usual shortcomings of molecular-dynamics calculations, and one can easily make the usual list, it appears to us from the results reported here that the vibrational potential function for the H_2O molecules in water vapor gets modified in the liquid state to a degree such that in a quantitative comparison with liquid-state data one cannot achieve agreement beyond a 10—15% level. However, for the region of frequency below 80 meV, various models need to be investigated for their meritorious performance or otherwise in describing the dynamics in the liquid state.

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