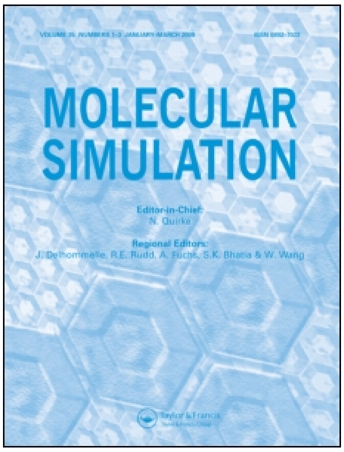

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Computer Simulation of Molecular Motions in Liquids: Infrared Spectra of Water and Heavy Water

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To cite this Article Martí, J. , Padró, J. A. and Guardia, E.(1993) 'Computer Simulation of Molecular Motions in Liquids: Infrared Spectra of Water and Heavy Water', Molecular Simulation, 11: 6, 321 — 336
To link to this Article: DOI: 10.1080/08927029308022517
URL: http://dx.doi.org/10.1080/08927029308022517

Molecular Simulation, 1993, Vol. 11, pp. 321-336
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COMPUTER SIMULATION OF MOLECULAR MOTIONS IN LIQUIDS: INFRARED SPECTRA OF WATER AND HEAVY WATER

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(Received April 1993, accepted April 1993)

The infrared spectra of liquid water and heavy water are calculated from molecular dynamics simulations using different spectroscopic properties. A flexible simple point charged (SPC) molecular model is assumed. The near, mid and far infrared spectra calculated from simulations are compared with experimental data. Special attention is paid to the relationship between the frequency bands of spectra and the nature of the microscopic motions. The usefulness of molecular dynamics simulation for interpreting the spectroscopic measurements is discussed.

KEY WORDS: Molecular dynamics simulation, molecular motions, infrared spectra, liquid water and heavy water

1 INTRODUCTION

Experimental information on the dynamic properties of liquids is ordinarily obtained by spectroscopic techniques such as infrared, Raman, nuclear magnetic resonance or neutron scattering. However, spectroscopic properties may also be determined from molecular dynamics (MD) simulations [1, 2]. MD has been largely applied to the study of microscopic properties of liquids. When suitable interaction potential models are employed, realistic and detailed pictures of atomic and molecular motions emerge from MD simulations. This information is very helpful for a better understanding of the relationship between experimental results and microscopic physical processes. Despite it is a classical approximation, MD may be very useful for the analysis of spectroscopic measurements which interpretation is usually based on approximate arguments. Moreover, MD calculations of the spectra can be used for testing both theoretical approximations [2, 3] and the interaction potentials used in the MD simulations [3-6].

Water is perhaps the most important liquid in Nature since it plays a decisive role in life processes. Despite tremendous interest and a great deal of work devoted to the study of water, its microscopic behaviour as well as the relation between the microscopic and macroscopic properties are not yet well understood. The peculiar characteristics of liquid water are strongly related to its quasi-tetrahedral structure due to the tridimensional network of H-bonds between the water molecules [7]. One of the most powerful techniques to study the properties of H-bonded liquids at the molecular level is the infrared (IR) spectroscopy [8]. As a consequence of the large absorption coefficient of water and heavy water, the number of experimental studies is rather scarce and precise measurements of the mid-IR spectra have not been possible until the recent development of the ATR method [9].

The IR spectra of liquid water and heavy water have not been extensively studied by MD simulation. Many MD studies assume rigid models for water molecules. These simulations are more eficient than those using flexible models because they permit larger integration time steps. However MD simulations with rigid models only can provide direct information about the low frequency motions (far-IR spectra) [10]. MD calculations of intramolecular motions at higher frequencies (mid-IR spectra) have been usually based on the determination of the Fourier transform (FT) of the velocity autocorrelation function of the hydrogen atoms [4–6, 11, 12] and very few MD studies have been carried out using other spectroscopic properties [13–15]. To our knowledge, the near IR spectra of water and the full IR spectra of heavy water have not been calculated from MD simulations.

The first objective of this paper is to discuss the characteristics and advantages of different procedures for the calculation of the IR spectra of molecular liquids from MD simulations. Our second aim is to show that MD simulation is a helpful tool for establishing a rigorous relationship between the different frequency bands of the spectra and the specific microscopic motions. In general, this relationship cannot be rigorously deduced by other methods and the interpretation of spectroscopic measurements in liquids is ordinarily based on analogies with the spectra of monomers or gas phases. In order to illustrate these points we have calculated the IR spectra of liquid water at room temperature for different regions (far, mid and near IR spectra). Finally, the reliability of the atomic and molecular motions of H_2O and D_2O resulting from MD simulations using the flexible SPC model of Toukan and Raman [4] has been checked by comparing the simulation results with the experimental IR spectra.

2 METHODS FOR THE CALCULATION OF THE IR SPECTRA

The IR spectra ($\hat{S}_P(\omega)$) are calculated as the FT of the time dependent correlation function ($C_P(t)$) of a spectroscopic property ($P(t)$)

$$\hat{S}_P(\omega) = \int_0^\infty C_P(t) \cos \omega t \, \mathrm{d}t \tag{1}$$

where $C_P(t) = \langle P(t) \cdot P(0) \rangle$. Differences in the methods for calculating the IR spectra from MD are related with the choice of different $P(t)$ properties. In this study we have considered four methods.

2.1 *Method A*

Experimental light absorption spectra are directly related with the FT of the total electric dipole moment ($\vec{M}(t)$) autocorrelation functions [16]. However, $\vec{M}(t)$

cannot be easily obtained from MD simulations because it is a collective property which calculation requires very long MD runs of large systems. A frequent way to obviate the calculation of $\vec{M}(t)$ is to assume that the influence of the intermolecular cross-correlations on the spectra is negligible [1, 10]. Then, the dipolar moment of single molecules is taken as the spectroscopic property $(C_\mu(t) \equiv \langle \vec{\mu}(t)\cdot\vec{\mu}(0)\rangle)$ and the corresponding IR spectrum is $\hat{S}_\mu(\omega)$. However, as will be shown in Section 3 for water, the decay of $C_\mu(t)$ is in general very slow and the corresponding FT cannot be accurately calculated. Moreover, $\hat{S}_\mu(\omega)$, as well as the experimental measurements, supplies the distribution of frequencies in the considered system but does not provide information about the origin of the different contributions to the spectra.

Since changes in the total electric dipole moment are due to microscopic motions, kinematic properties such as the atomic displacements or velocities may be taken as IR spectroscopic properties. In particular, intramolecular motions are clearly related with changes in the molecular dipole moments [15]. The consideration of different kinematic properties as $P(t)$'s is the basis of the following methods.

2.2 *Method B*

The IR spectroscopic properties most frequently used in MD simulation studies are the atomic velocities $\vec{v}(t)$. Then, the IR spectra $(\hat{S}_v(\omega))$ are the FT of the velocity autocorrelation functions $(C_v(t))$. In the case of water [4–6, 11, 12], two atomic spectra may be considered, i.e. $\hat{S}_v^{O}(\omega)$ and $\hat{S}_v^{H}(\omega)$. This method allows us to obtain separately the distribution of frequencies corresponding to the motions of Hydrogen and Oxygen but the contributions to the spectra of the different kinds of inter or intra-molecular motions cannot be distinguished.

2.3 *Method C*

A procedure which allows us to find the distribution of frequencies associated with a given motion is to consider as spectroscopic property a combination of atomic coordinates (displacements or velocities) directly related to such specific motion. So, for example, in the case of water we have studied the relative motions of each hydrogen (H_1) with respect to both the oxygen (O) and the other hydrogen (H_2) of the same molecule. To this end, we have defined two spectroscopic properties

$$P_\delta^{OH}(t) = \delta\vec{r}_{OH_1}(t) = \vec{r}_{H_1}(t) - \vec{r}_{O}(t) - \vec{r}^{\,eq}_{OH_1}(t) \tag{2}$$

$$P_\delta^{HH}(t) = \delta\vec{r}_{H_1H_2}(t) = \vec{r}_{H_1}(t) - \vec{r}_{H_2}(t) - \vec{r}^{\,eq}_{H_1H_2}(t) \tag{3}$$

where $\vec{r}^{\,eq}_{OH_1}(t)$ and $\vec{r}^{\,eq}_{H_1H_2}(t)$ are the time-averaged interatomic values. Then, $\hat{S}_\delta^{OH}(\omega)$ and $\hat{S}_\delta^{HH}(\omega)$ are the spectra associated with the OH and HH motions, respectively. The spectroscopic property defined by equation (2) was also used by Bansil *et al.* [15] for the calculation of the vibrational spectrum of water.

2.4 *Method D*

Vibrational molecular motions are commonly analysed in terms of the normal modes. Vibrations of an isolated water molecule are described as the superposition of two stretching (symmetric and asymmetric) and one bending mode which frequencies may be approximately calculated by classical normal coordinate analysis. Although the same treatment cannot be straightforwardly applied to liquids, it is habitual to describe the intramolecular motions of liquid water as a combination of stretching (symmetric and asymmetric) and bending modes (see for example reference [7]).

Symmetric and asymmetric stretching motions of water are more complex than the simple relative coordinates defined in Equation (2) and (3). Moreover, the frequency bands for the two stretching modes show an important overlap. Then, it is useful to generalize the method C by choosing a $P(t)$-set which approximate the essential features of the normal coordinate motions. Following this idea Bopp [13] proposed a simple procedure for the analysis of normal vibrational modes in liquid water. This method is based on the decomposition of the instantaneous velocities of the H atoms relative to the center of mass of the molecule ($\vec{u}_i(t)$) into components parallel and perpendicular to the molecular plane

$$\vec{u}_i(t) = \vec{u}_i^{\parallel}(t) + \vec{u}_i^{\perp}(t); \quad i = 1,2 \tag{4}$$

where i refers to the hydrogen atom of a molecule and $\vec{u}_i^{\perp}(t) = u_i^{\perp}(t)\vec{\eta}(t)$ (See Figure 1). Moreover, $\vec{u}_i^{\parallel}(t)$ is decomposed into components parallel ($\vec{B}_i(t) = B_i(t)\vec{e}_i(t)$) and perpendicular ($\vec{A}_i(t) = A_i(t)\vec{f}_i(t)$) to the OH directions. Then, three combinations of the resulting velocity components are defined and taken as spectroscopic properties

$$Q_1(t) = B_1(t) + B_2(t); \; Q_2(t) = A_1(t) + A_2(t); \; Q_3(t) = B_1(t) - B_2(t) \tag{5}$$

$Q_1(t)$ and $Q_3(t)$ are combinations of atomic motions along the OH directions and they approximately describe the symmetric and asymmetric stretching modes, respectively. $Q_2(t)$ is a combination of velocities which are perpendicular to OH and it corresponds to the bending mode.

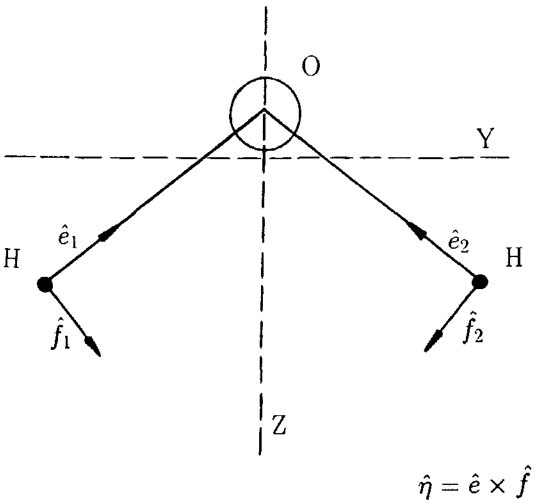

Figure 1 Unitary vectors and rotation axes used in method D.

Although rotations are defined for rigid bodies, it is also usual to describe the rotational motions of flexible molecules as a combination of rotations around characteristic molecular axes. Rotations involve in general the motion of several atoms and, in the case of water, the frequency bands for rotations around different axes cannot be easily distinguished in the total spectra because they are notoriously overlapped. The procedure proposed for molecular vibrations was extended to rotations by Pálinkás *et al.* [14]. The spectroscopic properties are

$$R_x(t) = A_1(t) - A_2(t);\ R_y(t) = \vec{u}_1^{\perp}(t) + \vec{u}_2^{\perp}(t);\ R_z(t) = \vec{u}_1^{\perp}(t) - \vec{u}_2^{\perp}(t) \tag{6}$$

where the x-axis is perpendicular to the instantaneous plane of molecule and $R_y(t)$ and $R_z(t)$ are associated with the rotations around axes in the molecular plane (z is along the dipole moment) (see Figure 1).

3 MD CALCULATION OF THE IR SPECTRA OF WATER

3.1 *Computer simulations*

Liquid water at $T = 298\,K$ and $\rho = 1\ \mathrm{g/cm^3}$ was simulated by MD. The flexible simple point charge (SPC) model of water proposed by Toukan and Rahman [4] was assumed. In this model intramolecular forces are described by a Morse potential for OH and a harmonic potential for HH. We considered a system of 216 molecules with the usual periodic boundary conditions. The Ewald method was used for the computation of the long-range coulombian interactions. A leapfrog Verlet integration algorithm with coupling to a thermal bath [17] was employed. The integration time-step was of 0.5 fs. In order to achieve quickly the desired temperature for the different degrees of freedom the equilibration of translational and intramolecular motions was performed separately [18].

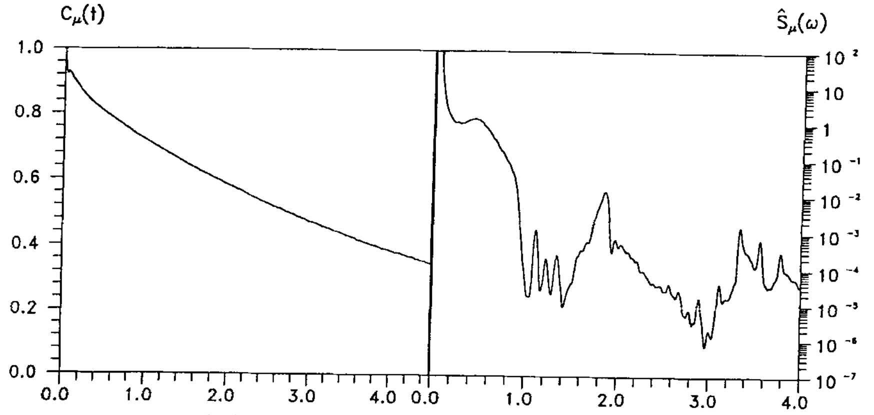

Figure 2 Normalized molecular dipole moment autocorrelation function and its spectrum (in arbitrary units).

3.2 *Method A*

As may be observed in Figure 2, $C_\mu(t)$ shows a very slow decay which is nearly exponential. For reducing the spurious influence of the sharp $C_\mu(t)$-cutoff on the FT, a Hanning window [19] was used. The initial glitch of $C_\mu(t)$, which may be attributed to the short time librational motions of a molecule in the cage of its close neighbours [10], may be easily seen but contributions of faster motions to $C_\mu(t)$ cannot be distinguished. Then, $\hat{S}_\mu(\omega)$ for mid and high frequencies is very small, so that a logaritmic scale has been used for representing $\hat{S}_\mu(\omega)$ in Figure 2. Although $\hat{S}_\mu(\omega)$ is very noisy we can observe peaks around 500, 1900 and 3500 cm^{-1} which can be associated to the rotational and vibrational molecular motions. These results corroborate that the IR spectrum is contained in $C_\mu(t)$ but $\vec{\mu}(t)$ is a "bad" spectroscopic property for MD simulation studies.

3.3 *Method B*

The decays of $C_v^H(t)$ and $C_v^O(t)$ (Figure 3) are markedly faster than the decay of $C_\mu(t)$. Then, the corresponding FT's ($\hat{S}_v^H(\omega)$ and $\hat{S}_v^O(\omega)$) may be more accurately calculated than those in method A. According to the difference of masses of H and O, the high frequency vibrational motions are more clearly reflected in $C_v^H(t)$ and $\hat{S}_v^H(\omega)$ than in $C_v^O(t)$ and $\hat{S}_v^O(\omega)$.

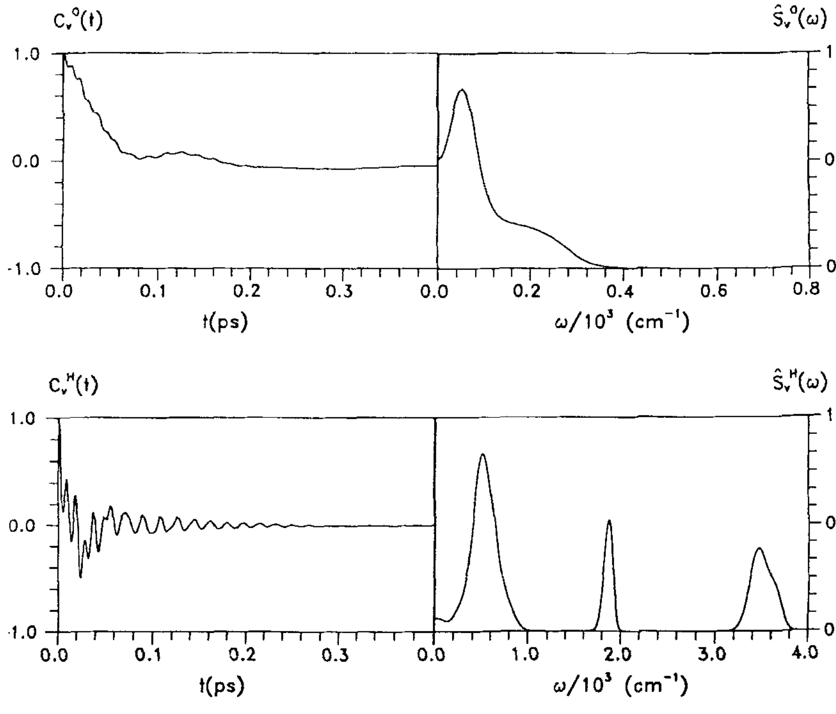

Figure 3 Normalized Oxygen (top) and Hydrogen (bottom) velocity autocorrelation functions and their spectra (in arbitrary units).

Table 1 MD Simulation spectra of water and heavy water (cm^{-1}) (frequencies are in cm^{-1}).

Spectroscopic properties	*Water*	*Heavy water*	*Origin*
ν_O	50	45	O-O-O Flexing?
ν_O	≅ 180	≅ 170	O-H ... O Stretch.?
ν_H; $R_X + R_Y + R_Z$	505	355	Rotation
R_X	505	350	Axis-X Rota.
R_Y	705	490	Axis-Y Rota.
R_Z	485	335	Axis-Z Rota.
ν_H; δr_{HH}; Q_2	1860	1355	Bending
ν_H; δr_{OH}; $Q_1 + Q_3$	3460	2475	Stretching
Q_1	3410	2465	Sym. Stretch.
Q_3	3585	2640	Asym. Stretch.
ν_H	5370	3995	Bend. + Stretch.
ν_H	6830	5020	2 x Stretch.

Table 2 Comparison of MD results with IR experimental data (frequencies are in cm^{-1}).

Microscopic Motions		*MD Results*	*Experimental IR values(*)*
Intermolecular motions	(H_2O)	50 ≅ 180	50 [22] 170 [20]
Rotations	(H_2O)	505	570 [20]
Vibrations	(H_2O)	1860 3460	1645 [9] 3400 [9]
	(D_2O)	1355 2475	1210 [9] 2495 [9]
Overtones	(H_2O)	6830	≅6900 [21]

(*) maxima of imaginary dielectric constant $\varepsilon''(\omega)$.

$\hat{S}^H_v(\omega)$ shows three maxima at 505, 1860 and 3460 cm^{-1} (Table 1) which may be associated with the rotation, bending and stretching motions, respectively [7]. Similar results were obtained by Toukan and Rahman [4] at other temperatures. Our findings are in quite good accordance with the experimental measurements [9, 20] (See Table 2). The agreement for the rotation and stretching peaks is very good, although it should be pointed out that in the case of rotation the band is very broad, so that the position of the maximum is not well defined. The bigger discrepancy for bending (about 200 cm^{-1}) may be attributed to shortcomings of the potential model used in our simulations.

When a logaritmic scale is used, two $\hat{S}^H_v(\omega)$ maxima in the near IR (overtones) region may be observed (Figure 4). The position of the former is for a frequency (5370 cm^{-1}) which is about the sum of those for bending and stretching. The

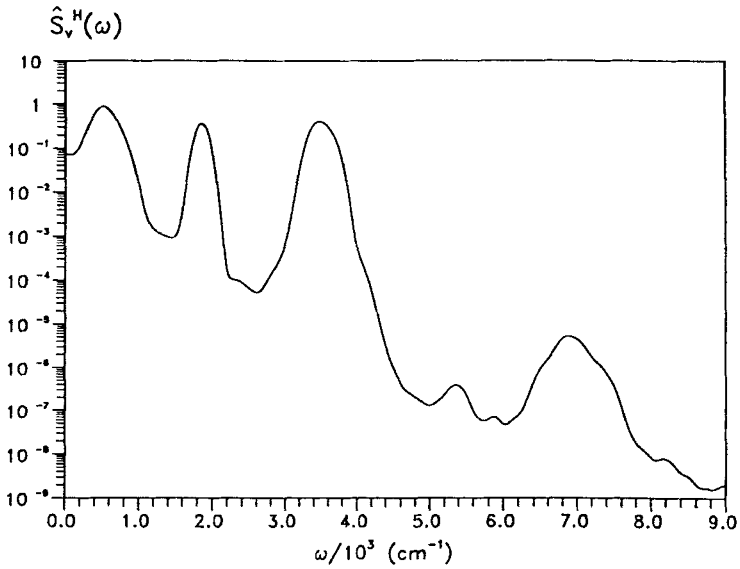

Figure 4 Spectrum of the hydrogen velocity autocorrelation function (in arbitrary units).

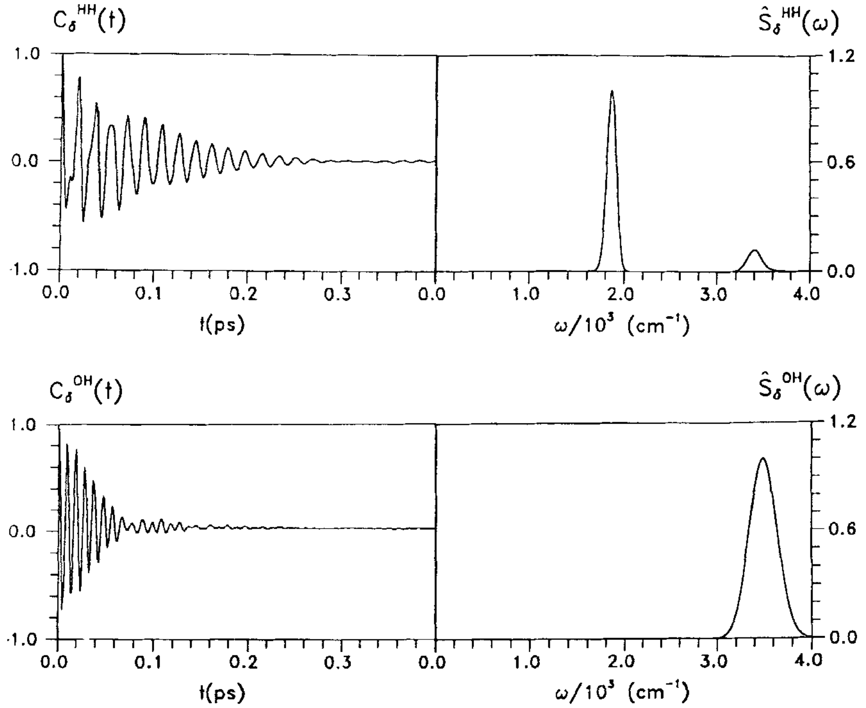

Figure 5 Normalized autocorrelation functions of $\delta\vec{r}_{H_1H_2}(t)$ and $\delta\vec{r}_{OH_1}(t)$ displacements and the corresponding spectra (in arbitrary units).

second is located at a frequency (6830 cm^{-1}) which is about two times the stretching frequency and was also observed in the near IR experimental measurements [21].

$\hat{S}_v^{O}(\omega)$ shows a peak at 50 cm^{-1} and a shoulder in the vicinity of 180 cm^{-1} (Figure 3) which are consistent with the far-IR measurements [20, 22] (Table 2). Frequency bands centered near 50-60 cm^{-1} and 170 cm^{-1} were also found by Raman spectroscopy [23, 24]. These low frequency bands are attributed to intermolecular motions. The band close to 50 cm^{-1} has been associated with the O-O-O flexing [25] and the one around 180 cm^{-1} with the O-H...O stretching [24].

3.4 *Method C*

$C_\delta^{OH}(t)$ and $C_\delta^{HH}(t)$ show a fast decay and a marked oscilatory behaviour (Figure 5) which is consistent with the existence of high frequency intramolecular vibrations in the OH and HH directions. As expected, the maximum of $\hat{S}_\delta^{OH}(\omega)$ corresponds to the stretching frequency whereas $\hat{S}_\delta^{HH}(\omega)$ shows a high peak at the bending position (Figure 5). Since bending motions of H are perpendicular to the OH-bond and not along the HH direction [7], $\hat{S}_\delta^{HH}(\omega)$ also shows a noticeable maximum for the stretching frequencies. One of the advantages of Method C is that it allows us to find the distribution of frequencies corresponding to a given relative motion. A detailed study of the relationship between the far IR spectra and the intermolecular motions in liquid water is in progress.

3.5 *Method D*

The results shown in Figures 6, 7 and Table 1 corroborate that method D allows us to obtain separately the symmetric and asymmetric contributions to the stretching spectra as well as the contributions of rotations around the X, Y and Z axes to the librational spectra. Moreover, the correspondence between the different frequencies and motions can be unambigously established. Like for an isolated water molecule [7] the frequency corresponding to the asymmetric stretching peak is higher than that for the symmetric (Figures 6 and 8). The frequency bands for the X and Z rotations are almost completely overlapped whereas the Y rotation is shifted toward higher frequencies (see Figures 7 and 9). As expected, the time correlation functions for the stretching properties show oscillations which are more marked than those for rotations (Figures 6 and 7).

Unfortunately, these findings cannot be easily tested with experimental results since the decomposition of the measured spectra cannot be accurately performed. Although this decomposition is necessary for a complete interpretation of the spectroscopic measurements, this is a difficult problem which is ordinarily solved by fitting a sum of Gaussian functions to the experimental data [24]. In the case of water rotations, Walrafen [24] obtained Gaussian components in the Raman spectra centered near 425, 550 and 740 cm^{-1} whereas Moskovits and Michaelian [23] found librational components centered at approximately 470, 570 and 760 cm^{-1}. Our MD findings are consistent with these two sets of experimental data (Table 1).

Method D not only provides information about the frequency bands and peaks corresponding to the different motions but also about their relative contribution to the spectra. This has been verified by calculating the total spectra ($\hat{S}_Q^{\text{stretch}}(\omega)$, $\hat{S}_R^{\text{rota}}(\omega)$), which are simply defined as the sum of the partial spectra

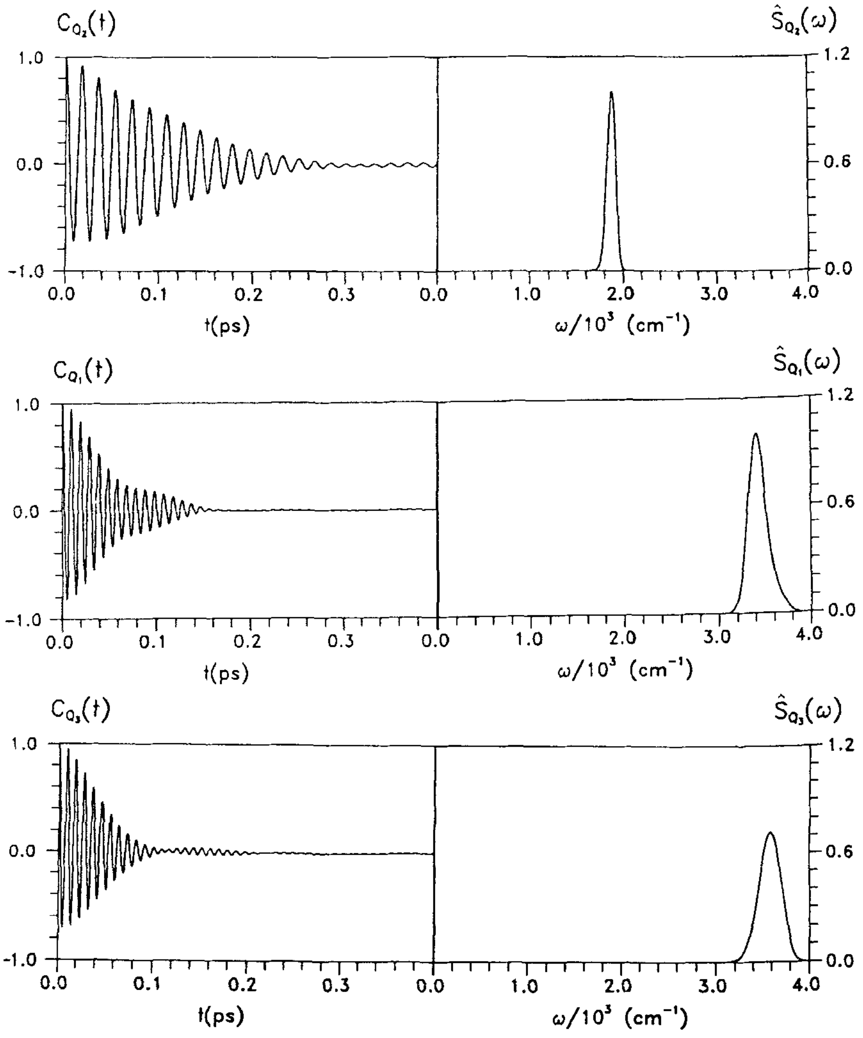

Figure 6 Normalized autocorrelation functions of the approximate normal vibrational coordinates $Q_2(t)$, $Q_1(t)$ and $Q_3(t)$ (from top to bottom) and the corresponding spectra (in arbitrary units).

$$\hat{S}_Q^{\text{stretch}}(\omega) = \hat{S}_{Q_1}(\omega) + \hat{S}_{Q_3}(\omega) \tag{7}$$

$$\hat{S}_R^{\text{rota}}(\omega) = \hat{S}_{R_x}(\omega) + \hat{S}_{R_y}(\omega) + \hat{S}_{R_z}(\omega) \tag{8}$$

As may be observed in Figures 8 and 9, the results obtained using these expressions are in good accordance with those calculated by method B. This corroborates that this procedure may be useful for a reliable decomposition of the spectra.

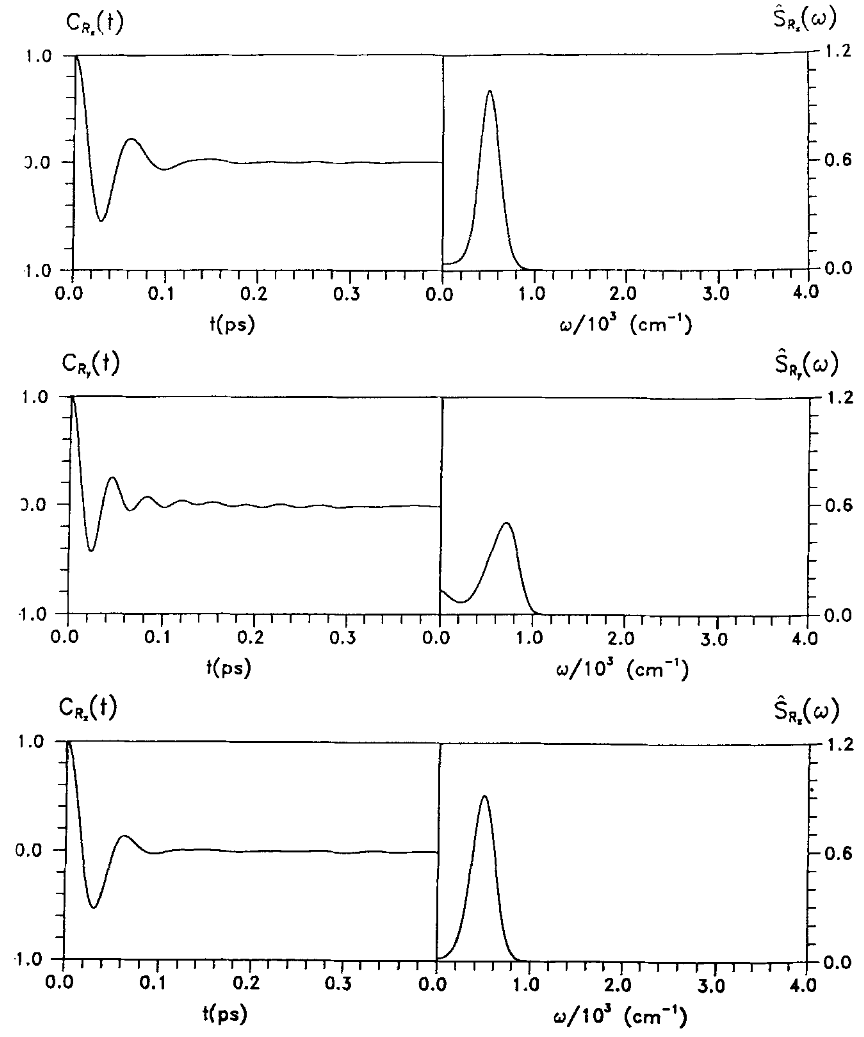

Figure 7 Normalized autocorrelation functions of the approximate rotational coordinates $R_x(t)$, $R_y(t)$ and $R_z(t)$ (from top to bottom) and the corresponding spectra (in arbitrary units).

4 MD CALCULATION OF THE IR SPECTRA OF HEAVY WATER

MD simulations of liquid D_2O at $T = 298\,K$ and $\rho = 1\,g/cm^3$ were carried out. The same SPC interaction potential used for water was employed in these MD simulations. Other computation details are also the same than those for water (Section 3.1).

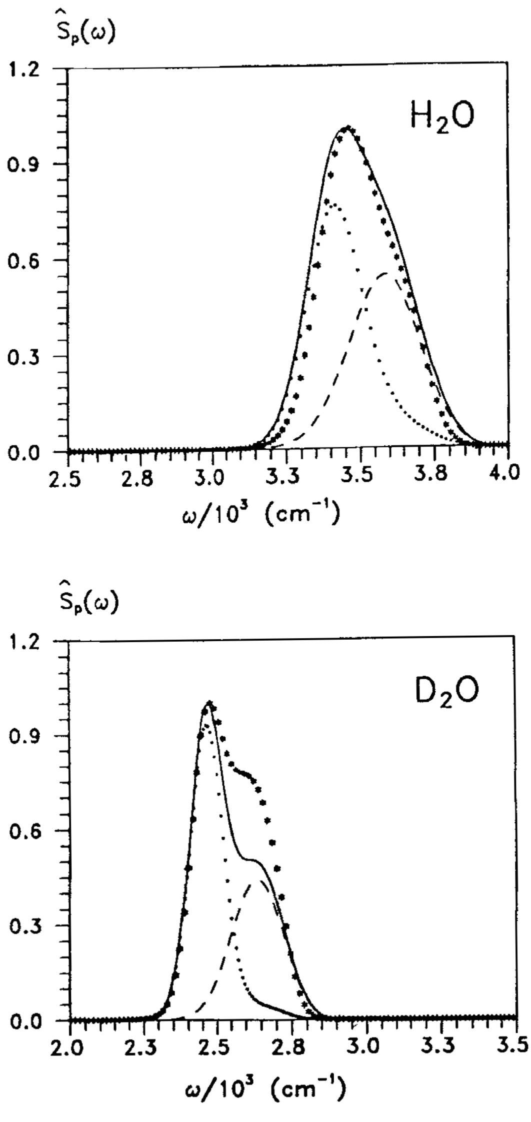

Figure 8 Vibrational (stretching) spectra of water (top) and heavy water (bottom). (——) $\hat{S}_Q^{stretch}(\omega)$; (.....) $\hat{S}_{Q_1}(\omega)$; (----) $\hat{S}_{Q_3}(\omega)$; (****) $\hat{S}_v^H(\omega)$ or $\hat{S}_v^D(\omega)$. The units have been chosen so that the height of both $\hat{S}_Q^{stretch}(\omega)$ and $\hat{S}_v^H(\omega)$ or $\hat{S}_v^D(\omega)$ maxima are equal to 1.

Methods B, C and D were applied to the calculation of the IR spectra (Figures 8–10). The qualitative shape of $\hat{S}_v^D(\omega)$ (Figure 10) is very similar to that for water (Figure 4) but the peaks are shifted towards lower frequencies (Table 1). This result is consistent with the bigger mass of deuterium. As for water, the position of the stretching peak is in good agreement with the experimental IR results [9] but there are greater discrepancies for bending (Table 2). Two overtones with maxima

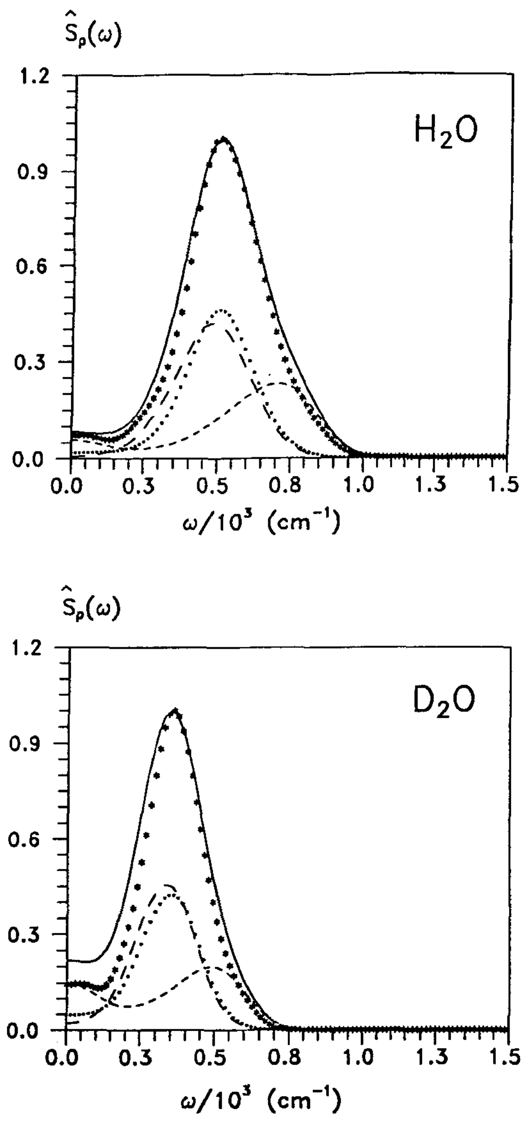

Figure 9 Rotational spectra of water (top) and heavy water (bottom). (——) $\hat{S}_Q^{\text{rota}}(\omega)$; (.....) $\hat{S}_{R_x}(\omega)$; (-----) $\hat{S}_{R_y}(\omega)$; (– – – –) $\hat{S}_{R_z}(\omega)$; (****) $\hat{S}_v^H(\omega)$ or $\hat{S}_v^D(\omega)$. The units have been chosen so that the height of both $\hat{S}_Q^{\text{rota}}(\omega)$ and $\hat{S}_v^H(\omega)$ or $\hat{S}_v^D(\omega)$ maxima are equal to 1.

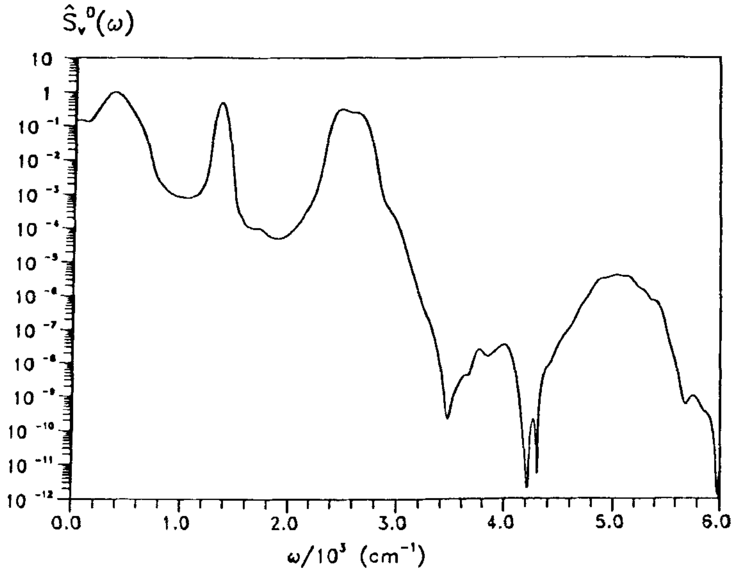

Figure 10 Spectrum of the deuterium velocity autocorrelation function (in arbitrary units).

centered at frequencies near the sum of those for bending and stretching and two times that for stretching are also shown by $\hat{S}_v^D(\omega)$. $\hat{S}_v^O(\omega)$ shows a peak and a shoulder at frequencies slightly lower than those for H_2O (Table 1). However, this shift, which was not observed in the Raman spectra [24], is very small and cannot be accurately determined (specially in the case of the shoulder).

The differences in the height of symmetric and asymmetric stretching distributions are greater than in the case of water and the two stretchings may be observed in the total spectra (Figure 8b). As for H_2O, the overlap between the X and Z rotations is almost complete and the frequencies corresponding to the Y rotation are higher (Figure 9b). Our results are consistent with the libration bands found in Raman spectra (centered at 350, 425 and 570 cm^{-1}) [23].

5 CONCLUDING REMARKS

Although a rigorous study of the microscopic properties related to light atoms like H would require a quantum-mechanical treatment, the results presented in this paper indicate that studies based on classical mechanics may also be very useful. MD simulations assuming suitable potential models provide us with a realistic classical picture of different microscopic motions such as intramolecular vibrations, molecular rotations, intermolecular vibrations and translations. The bands of the spectra corresponding to the different kind of motions can be unambigously identified by choosing as a spectroscopic property a coordinate (atomic displacements or velocities or combinations) associated with a given motion. Moreover when different bands are overlapped they may be separated and their relative contribution analysed. This information is very helpful in obtaining a reliable interpretation of the spectroscopic results.

The flexible SPC potential of Toukan and Raman [4] produces an overall agreement between the MD calculations and the experimental measurements of the near, mid and far IR spectra of liquid water. The only discrepancies correspond to the position of the peak for bending. This disagreement may be corrected by using a more refined potential model, but it should be remembered that we are using a classical approximation and recent studies have shown that quantum corrections may be quantitatively important [25]. Nevertheless, we think that a qualitative agreement between MD simulations and experimental results may be enough for obtaining realistic and interesting information on the characteristics of atomic and molecular motions in "complex" liquids like water. It should be remembered that the usual interpretations of spectroscopic experimental data requires hypotheses and approximations which, in general, are not adequately justified and can introduce bigger errors than the MD calculations.

Acknowledgements

This work has been supported by the "Centre de Supercomputació de Catalunya" under a CESCA grant. Financial support of DGICYT, project PB90-0613-CO3 is also acknowledged

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