CHEMICAL PHYSICS LETTERS

Local structural effects on low-frequency vibrational spectrum of liquid water: The instantaneous-normal-mode analysis

K.H. Tsai, Ten-Ming Wu *

Institute of Physics, National Chiao-Tung University, 1001 Ta-Hsueh Road, HsinChu 300, Taiwan

Abstract

Currently, the designations for the low-frequency vibrational spectrum of liquid water are still diversified. In this Letter, using the instantaneous normal mode (INM) formalism for subensembles, we have examined the effects of local structure on the low-frequency INM spectrum of liquid water. The classified subensembles of water molecules are characterized by either the geometry of Voronoi polyhedron or the H-bond configuration. With these subensembles, the translational contribution to the INM spectrum is investigated. Providing insights into the local structural dependence of the vibrations between H-bonded water molecules, our results are consistent with the conventional designations for the Raman spectrum of liquid water.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

The low-frequency vibrational spectrum of liquid water was observed a long time ago by several experimental techniques, including far infrared, Raman spectroscopies and incoherent neutron scattering [1]. Generally, two broad bands around 60 and 180 cm^{-1} are confirmed by these experiments [2,3]. However, the designations for the two bands from a microscopic point of view are still a subject in dispute, especially for the band around 60 cm^{-1}. Walrafen et al. [4] attributed the 60 cm^{-1} band to the bending mode of a triplet cluster, which is composed of a central water molecule and its two H-bonded neighbors, and the 180 cm^{-1} band to the stretching mode between two water molecules connected by a H-bond; the bending and stretching modes are actually associated with the molecular motions perpendicular and parallel to a H-bond, respectively. From another point of view, the two bands are also considered as arising from the restricted translations, with each water molecule hindered by the local structure formed by its neighbors [5,6]. Recently, by comparing the power

spectra of velocity autocorrelation functions of molecules in liquids with and without H-bonds, Padro and Marti [7] gave a different interpretation for the 60 cm^{-1} band, although they agreed the Walrafen's designation for the 180 cm^{-1} band. In their interpretation, the 60 cm^{-1} band is not necessarily associated with the H-bonds, but mainly resulted from frustrated translations hindered by the local structure around each molecule, and should be a general result due to the cage effect occurring in all kinds of dense liquids. Later, De Santis et al. [8] commented that, due to the hindrance of a cage formed by the four H-bonded neighbors of a water molecule, the 60 and 180 cm^{-1} bands, with their intensities crucially determined by the H-bonds, are contributed by the transverse and longitudinal dynamics of nearest neighboring oxygen pairs, respectively; however, the transverse dynamics is not necessarily described by the O...O...O bending motion. Supposing that the structural cage in a Lennard–Jones (LJ) liquid plays a similar role as the H-bonded cage in liquid water, they also concluded that both of the two bands observed for liquid water are expected to occur in the melting and supercooled liquids of argon but with different intensity ratio.

Developed in the past decade, the instantaneous-normal-mode (INM) formalism has been an established

---

* Corresponding author. Fax: +886 03 5720728.
  E-mail address: tmw@faculty.nctu.edu.tw (T.-M. Wu).

theory to describe microscopically the collective dynamics in condensed systems by the normal modes of the Hessian matrices evaluated for the system configurations [9,10]. In terms of the INM formalism, the intermolecular spectra of many liquids, including liquid water, have been analyzed and interpreted [11–19]. One advantage of the formalism is to assess the molecular contributions to the INM density of states (DOS) by using different projection operators, which are defined by the INM eigenvector components selected for specific molecules or molecular degrees of freedom [20,21]. One recent example is given by Vallauri and co-workers [18], who used the projection operators defined for the H-bonded triplet clusters to show that for liquid water the INMs with real frequencies less than 130 cm^{-1} are dominated by the bending motions of the triplet clusters, with a maximum at 70 cm^{-1}, whereas the INMs with real frequencies in the range from 185 to 240 cm^{-1} are by the stretching motions of the triplets.

In order to examine the local structural effects on the molecular motions in liquid water, we classify all molecules in the simulated liquid water into different subensembles, according to either the asphericity of the Voronoi polyhedron (VP) constructed for oxygens [22] or the H-bonded configuration of a water molecule, which is defined as the numbers of the H-bonds donated and accepted by the molecule [23]. By using the INM approach with the projection operators defined for the subensembles of water molecules and comparing the averaged contribution of different subensembles to the rotational INM spectrum, the local structural effects on the orientational motions in liquid water have been investigated recently [24]. In this Letter, we will do the similar analyses for the molecular contributions to the translational INM spectrum, with attention to the local structural effects on the INMs of real frequencies around 60 and 180 cm^{-1}.

With the details given in [24], the normalized translational INM DOS of a subensemble L in a system is defined as

$$D_T^L(\omega) = \frac{1}{3N_L} \left\langle \sum_{\alpha=1}^{6N} \delta(\omega - \omega_\alpha) P_{\alpha T}^L \right\rangle, \qquad (1)$$

where N_L is the average number of molecules in the subensemble and N is the total number in the system. $P_{\alpha T}^L$ is the translational projection operator of INM α due to the molecules of the subensemble L, and can be explicitly given as

$$P_{\alpha T}^L = \sum_{j=1}^{N} \sum_{\mu=1}^{3} U_{\alpha,j\mu}^2 \Theta_j(L), \qquad (2)$$

where $U_{\alpha,j\mu}$ is the three-dimensional eigenvector of INM α for molecule j, with μ labeling the Cartesian coordinates of the center of mass. $\Theta_j(L) = 1$ if molecule j belongs to the subensemble L and zero otherwise. Defined in this way, $D_T^L(\omega)$ is the averaged contribution of a molecule in the subensemble L to the normalized translational INM spectrum $D_T(\omega)$ of the system. In terms of the averaged number fraction of molecule for each subensemble, given by

$\chi_L = N_L/N$, we have the sum rule $D_T(\omega) = \sum_L \chi_L D_T^L(\omega)$, where all classified subensembles are summed.

The Letter is organized as the following: The effects due to the geometry of local structure are given in Section 2 and the effects due to the H-bonds are in Section 3. We give our conclusions in Section 4.

2. Geometric effects of local structure

We have simulated 256 SPC/E water molecules at density $\rho = 1.0 \text{ g cm}^{-3}$ and temperature $T = 300 \text{ K}$ [25]; the details of the simulation are given in [24]. After equilibrium, 1500 configurations were generated. With these configurations, we have performed the VP analysis for oxygens [22,26,27]. The geometry of each VP is characterized by two parameters: the volume V and the asphericity $\eta = A^3/36\pi V^2$ of the polyhedron, where A is its total surface area. For a sphere, $\eta = 1$. As η increases, the geometry of the polyhedron becomes more aspherical. We classified the molecules of each configuration into four subensembles, named as asphericity group (AG) I–IV, with increasing η value. For the four AGs, the averaged number fractions of molecule, the oxygen–oxygen radial distribution functions $g_{oo}(r)$ and the length distributions of the H-bonds attaching to each molecule have been presented in [24]. For AG IV, the $g_{oo}(r)$ distribution has a sharp first peak and nearly 70% molecules have four H-bonds; this suggests that the local structures of the molecules in AG IV are mostly in the H-bonded tetrahedral arrangement. For AG I, the $g_{oo}(r)$ distribution, unlike those of the other three AGs, has a plateau region, rather than a sharp maximum, in the first shell, and most molecules (about 30%) have only two H-bonds, with one donated and one accepted, which indicates that the molecules in AG I are weakly connected in H-bonds with their neighbors. Generally, the H-bond lengths of a molecule tend to be shorter as the asphericity of its Voronoi polyhedron increases.

Similarly, according to the Voronoi volume, we also divided the molecules of each configuration into four different subensembles, named as volume group (VG) I–IV, with increasing the value of V. For the four VGs, the averaged number fractions are given in Table 1 and their $g_{oo}(r)$ distributions are shown in Fig. 1a. Due to a strong compression from the neighbors, the $g_{oo}(r)$ of VG I has a sharp first maximum, indicating a compact structure in the first shell. However, unlike those of the four AGs, the distinctions among the four $g_{oo}(r)$ distributions shown in Fig. 1a diminish fast at distances right beyond the first minimum. This manifests that the structures beyond the first shell of a molecule have a stronger correlation with the shape, rather than the volume, of the VP of the molecule. Shown in Fig. 1b, the H-bond lengths of a molecule tend to be longer as the Voronoi volume increases; the trend is reverse to the case by increasing the asphericity.

To examine whether the subensembles of the AGs and the VGs are correlated or not, we have calculated the conditional probability χ_{ML} to find a molecule in the suben-
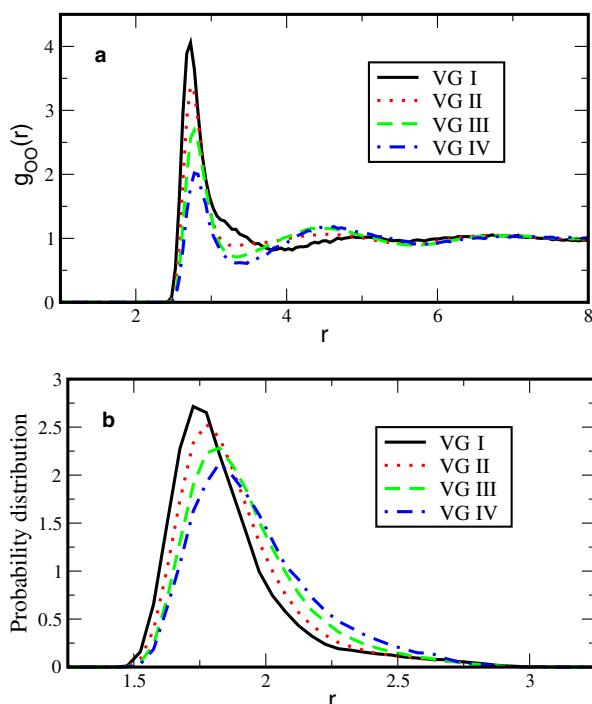
Fig. 1. The oxygen–oxygen radial distribution function (a) and the H-bond length distribution (b) of molecules in a volume group. Each distribution in (b) is normalized. The density of liquid water is 1.0 g cm^{-3} and the temperature 300 K. The unit of distance r is in Å.

semble of AG M for the molecules which belong to the subensemble of VG L. The results of χ_{ML} for the simulated liquid water are given in Table 1. The data show that the order of magnitude of χ_{ML} is roughly independent of the VG which the molecules belong to, except that for finding the molecules in AG IV χ_{ML} for VG IV is one order larger than that for VG I. Thus, the two kinds of local structural subensembles are weakly correlated. This is consistent with the conclusion given in [26]: For liquid water at room temperature, the shape of a VP is almost independent of its volume. Therefore, the asphericity and the volume of a VP can be considered as two independent parameters to

Table 1
Averaged number fraction χ_L of each volume group and the conditional probability $\chi_{ML} = N_{ML}/N_L$ to find a molecule in asphericity group M for those in volume group L, where both L and M can be I, II, III, and IV

	VG I	VG II	VG III	VG IV
$\widetilde{V} = V/V_{ave}$	∼0.84	0.84–1.0	1.0–1.24	1.24∼
χ_L	0.039	0.510	0.419	0.032
$\tilde{\chi}_{ML}$				
AG I	0.010	0.011	0.021	0.043
AG II	0.765	0.685	0.652	0.602
AG III	0.223	0.296	0.306	0.287
AG IV	0.002	0.008	0.021	0.067

N_L is the averaged number of molecules in volume group L and N_{ML} is that of the molecules which belong to both volume group L and asphericity group M. $\widetilde{V}$ is the Voronoi volume V scaled by the averaged molecular volume of liquid water. The ranges of the four asphericity groups are given in [24].

characterize the local structure of a molecule in liquid water.

The INM DOS of SPC/E liquid water and the contributions due to the translational and rotational molecular motions have been presented in [24]. The shape of the real-frequency INM spectrum looks similar as the Raman spectrum [28,29]. The frequency range of the translational contribution covers from 650 cm^{-1} in the real branch to 250 cm^{-1} in the imaginary branch. Roughly above 300 cm^{-1} in the real branch, the translational and rotational contributions are strongly overlapped, indicating that the translational and rotational motions at these frequencies are significantly coupled together. Using Eq. (1), we have calculated $D_T^L(\omega)$ for the subensembles of AGs and VGs, and the results are shown in Fig. 2. For the AG I and the VG IV, the overall shape of $D_T^L(\omega)$ is similar as the INM spectrum of a LJ atomic liquid, which has a triangular shape in each branch and a monotonically decaying long tail in the real branch [9]. A common feature for the local structures of the AG I and the VG IV is that the H-bonds attaching to the molecules in these subensembles are generally weak in strength due to their longer bond lengths, so that the translational motions of these molecules in liquid water behave more like the atomic motions in a LJ liquid. As the asphericity increases or the Voronoi volume decreases, the real-frequency spectrum shape of $D_T^L(\omega)$ deviates from the triangular shape with a hump growing in the frequency region above 150 cm^{-1}. According to the spectrum variation of $D_T^L(\omega)$ with V or η, one
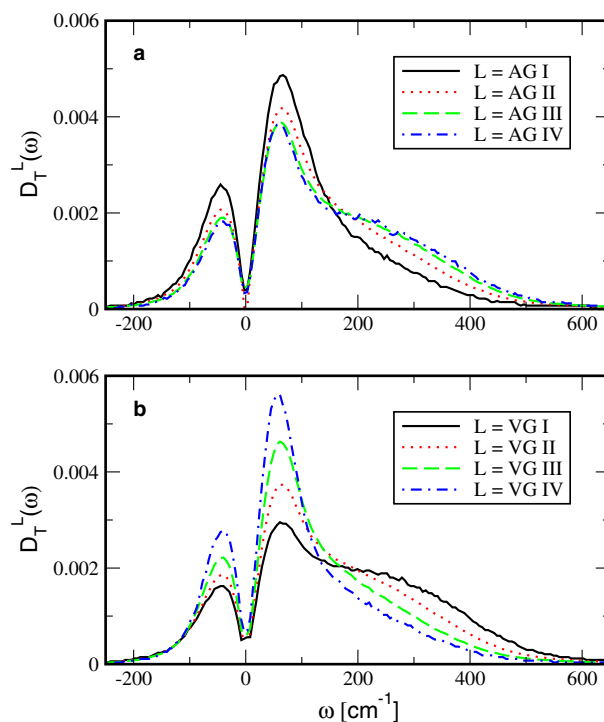

Fig. 2. Geometric effects of local structure on the translational INM DOS of a subensemble. The subensembles are either the asphericity groups (a) or volume groups (b).

can divide the real-frequency branch into two regions: At frequencies less than 150 cm^{-1}, $D_T^L(\omega)$ generally increases with either increasing V or decreasing η; at frequencies above 150 cm^{-1}, the variation of $D_T^L(\omega)$ with V or η is reversed. The low- and high-frequency regions generally correspond to the INMs dominated by the O...O...O bending modes and the O...O stretching modes of the H-bonded triplet clusters in liquid water, respectively [18].

In the low-frequency region, the translational INM DOS has a peak located around 65 cm^{-1}. As shown in Fig. 2, the peak position is insensitive to the geometry of the VP, by changing either its asphericity or its volume, but the peak value is indeed affected by the geometry, gently by its asphericity and strongly by its volume. That is, the larger the Voronoi volume of a molecule, the more significant the contribution due to the translational motion of the molecule to the 65 cm^{-1} peak. These results disagree with the picture of the cage effect, in which the oscillation frequency of a molecule inside a cage formed by its neighbors is expected to vary with the local volume of the molecule (the smaller the local volume is, the larger the oscillation frequency). Thus, based upon the results obtained by the INM analysis so far, a possible explanation for the local-volume effect on the 65 cm^{-1} peak is that a larger local volume occupied by the central molecule of a triplet would favor the O...O...O bending motion; on the contrary, a smaller local volume would restrict, or even 'freeze', the bending motion.

In the high-frequency region, the increase of $D_T^L(\omega)$ with either increasing η or decreasing V can be interpreted by the stretch of a H-bond. For a molecule with smaller local volume or larger asphericity, the H-bonds attaching to the molecule is generally short in bond length and strong in bond strength, so the stretching motions of these H-bonds are active and, therefore, contribute more to $D_T^L(\omega)$.

3. The H-bond effects

In an elementary picture, the formation of a H-bond in liquid water is resulted from the Coulomb interaction between the partially positive charge q_H of a H atom, covalently bound to the O atom of a molecule, and the partially negative charge q_O of a neighboring O atom of another molecule. As the H atom lies between the two O atoms, the electrostatic interactions cause the two water molecules bound together with a lower energy. So, a H-bond is highly directional. As before, we consider two water molecules to be connected with a H-bond as the energy between them is less than −12 kJ mol^{-1} [24].

In this section, we examine the effects of H-bonds on the INMs in the two frequency regions given in the last section. We first investigate whether the low-frequency INMs contributed to the translational spectrum $D_T(\omega)$ are related to the H-bonds in liquid water. In the SPC/E model [25], the potential between two water molecules is made up of two parts: the pairwise additive site–site Coulomb potentials between the point charges at the H

and O coordinates with $q_H = 0.4238q$ and $q_O = -0.8476q$, where q is the charge of a proton, and a LJ potential between the two O atoms. To investigate the electrostatic effect, we calculated $D_T(\omega)$ for a fictitious system with its structure the same as that of the simulated SPC/E liquid water but having reduced partial charges $q_H' = \gamma q_H$ and $q_O' = \gamma q_O$ on the H and O atoms, respectively. Here, γ is a parameter between one and zero. As $\gamma = 1$, the system is exactly the SPC/E model; as $\gamma = 0$, there are no electrostatic interactions but the LJ interactions between water molecules. With the same criterion for a H-bond, we find that the number of H-bonds in this fictitious system decreases dramatically by reducing the value of γ from one. The fraction of molecules having four H-bonds is over 40% at $\gamma = 1$ but only about 5% at $\gamma = 0.75$, and almost vanishes at $\gamma = 0.5$. Meanwhile, the fraction of molecules without H-bonds is almost vanished at $\gamma = 1$ but increases to 50% at $\gamma = 0.75$, and almost hundred percent at $\gamma = 0.5$. The $D_T(\omega)$ calculated for this system are shown in Fig. 3 for several γ values. It is found that as γ is reduced from one to half, the peak value at 65 cm^{-1} in the real branch drops dramatically but the spectrum has only a small change at real frequencies above 200 cm^{-1}. For the situation of the fictitious system without H-bonds, $D_T(\omega)$ does not change much as γ is reduced from half to zero. This investigation gives a strong support that the 65 cm^{-1} peak in $D_T(\omega)$ is partially associated with the H-bonds.

In the following, the molecular nature of the INMs contributed to the translational motions in liquid water is examined. Shown in Fig. 4 is the dependence of $D_T^L(\omega)$ on n, the number of H-bonds attaching to a molecule. Clearly, there are two main effects on $D_T^L(\omega)$ as n is varied from 1 to 4. First, the position of the low-frequency peak in the real branch increases about 10 cm^{-1}, but the peak value is not significantly changed. Based on the interpretation that the translational INMs in the low-frequency region are dominated by the bending modes of triplet clusters, the shift of the peak position implies that the force constant
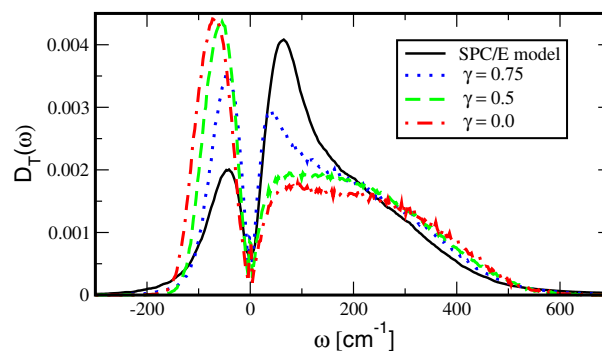

Fig. 3. $D_T(\omega)$ calculated for the SPC/E liquid water and some fictitious systems with the same configurations. The solid line is for the SPC/E model. The dotted, dashed and dot-dashed lines are for the fictitious system with the same LJ interactions in the SPC/E model but the charges of the O and H atoms reduced by a common factor γ.
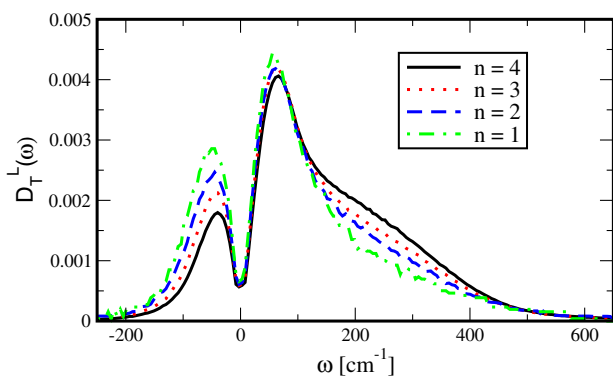
Fig. 4. The normalized translational INM DOS for subensembles of molecules having totally n H-bonds.

of the bending mode increases with the number of the H-bonds attaching to the central molecule of a triplet. The shifting amount of this peak position with n is roughly in the same order of the decrease in the peak position of the $60\ cm^{-1}$ band in the Raman spectrum observed experimentally by increasing temperature [3]. Here, we should make a
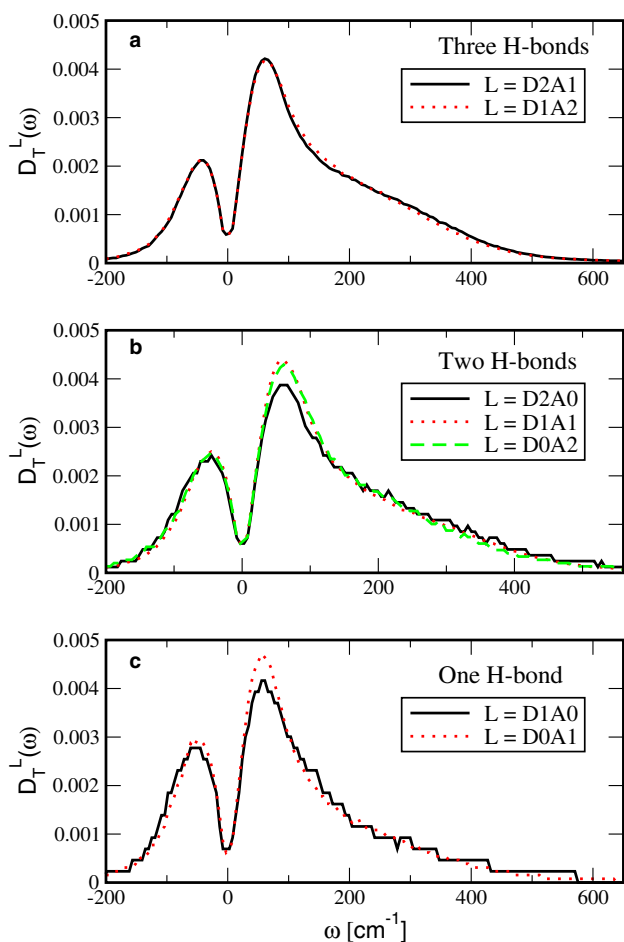

Fig. 5. The same as Fig. 4, but for subensembles classified by the H-bond configurations. The three panels from top to bottom are for molecules having totally three, two and one H-bonds.

notice that the variation of the peak in $D_T^L(\omega)$ with n is obtained by averaging different subensembles of water molecules at one temperature, but the temperature variation observed in the Raman experiment is the average of all molecules in liquid water at different temperatures. Since the averaged number of H-bonds per molecule in liquid water generally decreases with increasing temperature [30], we think that the pictures of the two different approaches are consistent due to the same physical origin and, therefore, the results of the two variations are qualitatively agree with each other. Secondly, as n increases from one to four, a hump grows in $D_T^L(\omega)$ in the frequency region above $150\ cm^{-1}$, with a maximum rate at $220\ cm^{-1}$. The strong dependence of the growing hump on n is consistent with attributing the predominant INMs in this frequency region to the stretch of the H-bonds between a molecule and its neighbors.

To distinguish the roles of the donated and accepted H-bonds of a molecule on its translational motion, we have calculated $D_T^L(\omega)$ for the subensembles of different H-bond configurations, denoted as DlAm for molecules having l donated and m accepted H-bonds with l and m being 0, 1 and 2. From the results given in Fig. 5, we find that the donated and accepted H-bonds have an almost indistinguishable effect on $D_T^L(\omega)$ and, therefore, play an equivalent role on the translational motions in liquid water. This is different from the fact that the donated H-bonds play a dominated role on the short-time orientational motions [24]. Thus, we conclude that the bending and stretching motions between a molecule and its neighbors only depend on the total number of the H-bonds attaching to the molecule, but it does not matter whether the H-bonds are donated or accepted.

4. Conclusion

Using the INM projection approach, we have investigated the effects of local structure on the real-INM spectrum of liquid water; the shape of the spectrum is similar as its Raman spectrum. In this Letter, we pay attention to the INMs with real frequencies below $300\ cm^{-1}$, where the translational motions are dominated. By reducing the charges of the O and H atoms in the examined model, we find that the INMs in this frequency range are indeed partially associated with the H-bonds in liquid water.

To investigate the molecular nature of the INMs, we have classified the simulated water molecules into subensembles by either the geometry of local structure or the H-bond configurations. Due to the opposite variation of the spectrum with the local structures examined, we naturally divide the INM spectrum of liquid water into two regions; the division is roughly at $150\ cm^{-1}$. The two regions generally correspond to the two bands observed in the Raman experiment. The translational contribution has a peak around $60\ cm^{-1}$; the position of the peak is influenced by n, the number of H-bonds attaching to a molecule and its intensity by the geometry of local structures,

especially the local volume. On the other hand, as n increases from one to four, a hump grows above 150 cm^{-1}. Physically, our results are consistent with the interpretation of the observed Raman spectrum as the bending motions of water triplets for the 60 cm^{-1} band and the H-bond stretching for the 180 cm^{-1} band. According to our results, the force constant of the bending motion of a triplet increases with the number of the H-bonds attaching to the central molecule of the triplet. We also suggest that a smaller local volume of the central molecule of a triplet would restrict or freeze the bending motion of the triplet and, therefore, cause the intensity of the 60 cm^{-1} band reduced. This conclusion is consistent with the temperature variation of the 60 cm^{-1} band observed in the Raman spectrum.

Acknowledgements

References

[1] I. Ohmine, S. Saito, Acc. Chem. Res. 32 (1999) 741.
[2] J.B. Hasted, S.K. Husain, F.A.M. Frescura, J.R. Birch, Chem. Phys. Lett. 118 (1985) 622.
[3] G.E. Walrafen, M.R. Fisher, M.S. Hokmabadi, W.H. Yang, J. Chem. Phys. 85 (1986) 6970.
[4] G.E. Walrafen, Y.C. Chu, G.J. Piermarini, J. Phys. Chem. 100 (1996) 10363.
[5] K. Mizoguchi, Y. Hori, Y. Tominaga, J. Chem. Phys. 97 (1992) 1961.
[6] K. Winkler, J. Lindner, P. Vohringer, Phys. Chem. Chem. Phys. 4 (2002) 2144.
[7] J.A. Padro, J. Marti, J. Chem. Phys. 118 (2003) 452.
[8] A. De Santis, A. Erocli, D. Rocca, J. Chem. Phys. 120 (2004) 1657.
[9] R.M. Stratt, Acc. Chem. Res. 28 (1995) 201.
[10] T. Keyes, J. Phys. Chem. A 101 (1997) 2921.
[11] M. Cho, G.R. Fleming, S. Saito, I. Ohmine, R.M. Stratt, J. Chem. Phys. 100 (1994) 6672.
[12] J.T. Kindt, C.A. Schmuttenmaer, J. Chem. Phys. 106 (1997) 4389.
[13] P. Moore, B. Space, J. Chem. Phys. 107 (1997) 5635.
[14] S. Saito, I. Ohmino, J. Chem. Phys. 108 (1998) 240.
[15] R.L. Murry, J.T. Fourkas, T. Keyes, J. Chem. Phys. 109 (1998) 2814.
[16] H. Ahlborn, X.D. Ji, B. Space, P.B. Moore, J. Chem. Phys. 111 (1999) 10622.
[17] H. Ahlborn, B. Space, P.B. Moore, J. Chem. Phys. 112 (2000) 8083.
[18] G. Garberoglio, R. Vallauri, G. Sutmann, J. Chem. Phys. 117 (2002) 3278.
[19] S. Ryu, R.M. Stratt, J. Phys. Chem. B 108 (2004) 6782.
[20] M. Buchner, B.M. Ladanyi, R.M. Stratt, J. Chem. Phys. 97 (1992) 8522.
[21] M.C.C. Ribeiro, M. Wilson, P.A. Madden, J. Chem. Phys. 108 (1998) 9072.
[22] Y.L. Yeh, C.Y. Mou, J. Phys. Chem. B 103 (1999) 3699.
[23] S. Myneni et al., J. Phys: Conden. Matter 14 (2002) L213.
[24] S.L. Chang, T.M. Wu, C.Y. Mou, J. Chem. Phys. 121 (2004) 3605.
[25] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, J. Phys. Chem. 91 (1987) 6269.
[26] G. Ruocco, M. Sampoli, R. Vallauri, J. Chem. Phys. 96 (1992) 6167.
[27] R. Ruocco, M. Sampoli, A. Torcini, R. Vallauri, J. Chem. Phys. 99 (1993) 8095.
[28] E.W. Castner Jr., Y.J. Chang, Y.C. Chu, G.E. Walrafen, J. Chem. Phys. 102 (1995) 653.
[29] D.M. Carey, G.M. Korenowski, J. Chem. Phys. 108 (1998) 2669.
[30] G. Sutmann, R. Vallauri, J. Mol. Liq. 98–99 (2002) 213.