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# Hydrogen bonded clusters in the liquid phase: I. Analysis of the velocity correlation function of water triplets

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Received 26 June 1998, in final form 11 August 1998

**Abstract.** We present an analysis of hydrogen bonded triplet clusters of water in terms of velocity projections on locally defined molecular coordinates. This makes it possible to perform an approximate normal mode analysis and to establish the relative motions of hydrogen bonded molecules. We find that the interpretation of the velocity autocorrelation function (VACF) of water in terms of stretching and bending motions of hydrogen bonded neighbours is an oversimplification due to cooperative effects in the hydrogen bonded network. Especially, for the peak at  $\omega = 10 \text{ ps}^{-1}$  we find that it is not only due to O–O–O bending motions in hydrogen bonded groups but also to librational motions of the whole cluster.

## 1. Introduction

As is well known water molecules in the bulk phase have preferentially four hydrogen bonded neighbours forming tetrahedral clusters. At ambient conditions the coordination number of the molecules, and in particular the hydrogen bonded coordination, is a fluctuating variable. Nevertheless it has been shown that water is a percolating system [1] in the sense that one can find closed paths in the system over hydrogen bonded pairs. This may be understood as a manifestation of a short range structural ordering which on a long length scale becomes distorted but not completely broken. This internal structure which is stabilized by the hydrogen bonds will be mirrored in the dynamical properties of the liquid. Indeed, an analysis of the collective  $k$ -dependent current correlation functions gives strong evidence that water behaves on a molecular length scale more like a solid than a liquid [2]. At a wavenumber of  $\approx 1 \text{ \AA}^{-1}$  the sound velocity shows a strong dispersion [3] and approaches nearly the value of  $c_\infty(k)$ , which is a measure of the instantaneous response of a medium [4]. For the same wavenumber it was found by computer simulations [5] that in the correlation function of the longitudinal and transverse currents a nearly dispersionless low frequency peak ( $\omega \approx 10 \text{ ps}^{-1}$ ) appears.

A natural question arises: what kind of collective motions are supported by the liquid? In an ideal situation one may consider a tetrahedral arrangement, including five water molecules with symmetry  $C_{2v}$  (as was suggested in [6] and [7]). In this completely hydrogen bonded arrangement one may evaluate, within a specific model, the normal modes and assign them to different frequencies of observed spectra. Within this approach the low frequency part of measured Raman spectra was assigned to bending vibrations ( $\omega \approx 10 \text{ ps}^{-1}$ ) and stretching

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vibrations ( $\omega \approx 45 \text{ ps}^{-1}$ ) of associated molecules. The bending motion has been invoked to explain the appearance of a peak at about  $10 \text{ ps}^{-1}$  in the longitudinal current correlation spectrum [3, 8, 9]. The problem with this approach is that it considers an isolated cluster with no interactions with its surroundings. Whether this provides a good approximate description of the spectra actually depends on the extent of the nearest neighbour structural ordering and the distribution of hydrogen bond energies over water clusters.

The present report intends to answer the question of how well the dynamics of hydrogen bonded clusters can be defined. To this aim we analyse the motions of hydrogen bonded triplets in terms of the correlation functions of velocity projections on local molecular coordinate systems. This procedure allows to distinguish different types of *normal vibration*. An advantage of this approach is to include the full information on the second and higher neighbour shells, which will give rise to a modification of the normal mode spectrum of the cluster with respect to its *isolated counterpart*.

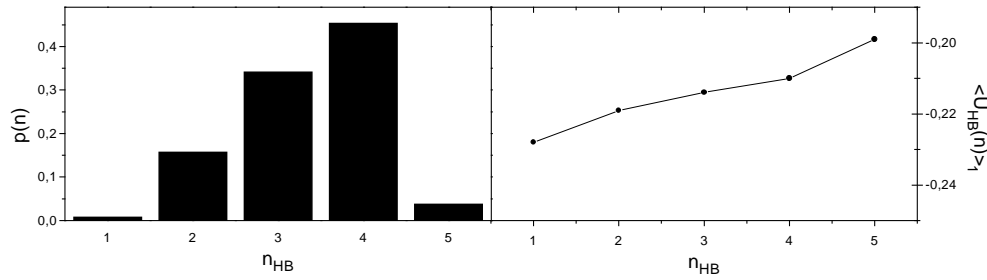
The present report is organized as follows: we first describe the procedure of how to *identify* a hydrogen bonded cluster in the bulk phase. Then we present the method of analysis which was used for the description of the motions. Finally we present the results.

## 2. Method

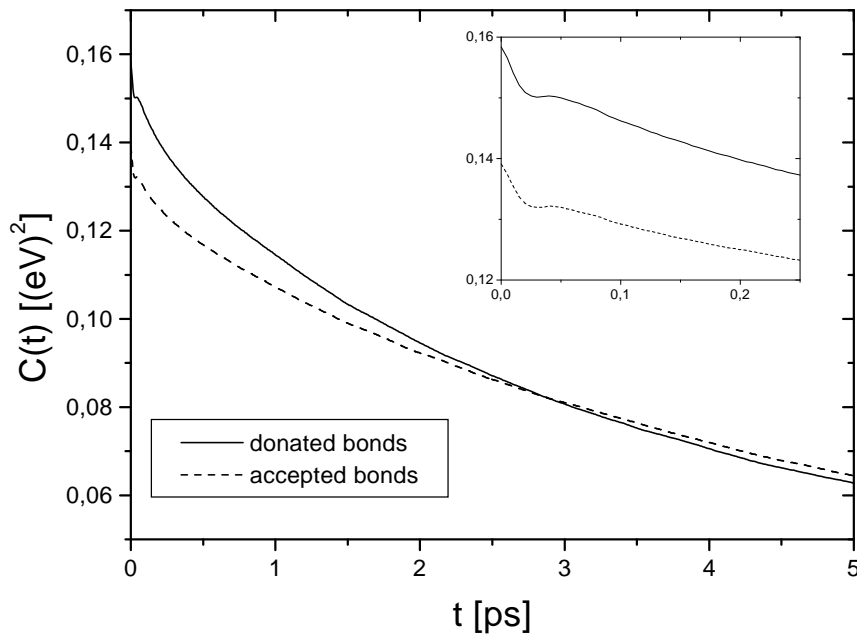
In order to analyse the dynamics of hydrogen bonded clusters in the bulk phase at ambient conditions we have performed a molecular dynamics simulation of the SPC/E water model [10]. The system contained 500 molecules treated with periodic boundary conditions and a tapered reaction field method was applied to take long range interactions of the molecules into account [11]. The system temperature was  $\langle T \rangle = 300 \text{ K}$  and the mass density was  $\rho = 0.998 \text{ g cm}^{-3}$ . For the analysis of the velocities we used a trajectory length of 30 ps.

Since the SPC/E water model has a Lennard-Jones interaction centre on the oxygen and fixed partial charges on each site which give rise to a Coulomb interaction, there are no *extra potential functions* which would characterize a hydrogen bonded configuration [12] (this also implies that in such a type of simulation the hydrogen bond configuration obeys the electrostatic superposition theorem). For that reason one has to apply a certain criterion, which allows one to call a configuration hydrogen bonded or not. In this report we use a hybrid description of geometrical and energetical characterization. In the following a pair of molecules is called hydrogen bonded when *all* of the following criteria are satisfied: (i) the angle between the connecting lines of the intramolecular O–H sites and the intermolecular O–O sites is less than  $35^\circ$ , (ii) the distance between neighbour O–O sites is less than  $3.5 \text{ \AA}$  and (iii) the interaction energy between neighbour water molecules is less than  $-0.1 \text{ eV}$ . The probability,  $p(n)$ , for a molecule to have  $n$  hydrogen bonded neighbours is shown in figure 1 for this type of criterion (left figure). Also shown is the average hydrogen bond energy per bond,  $\langle U_{HB}(n) \rangle_1$ , (right figure), as a function of  $n$ , from where it is seen that the specific hydrogen bond energy is weakened for an increasing  $n$ . To obtain a more complete picture of different configurations, we distinguished *donated triplets* when the central molecule donates two bonds and *accepted triplets* when the central molecule accepts two bonds. The combination of these two kinds of *triplet* is representative of a tetrahedral arrangement which is likely to be the most common disposition of molecules in the bulk.

In order to calculate a time correlation function it is important that the triplets are stable for a long enough time. To ensure this we have calculated the evolution of the relative distance of neighbour molecules and the total cluster energy as a function of time. From this analysis we find that after a time of 1–2 ps still about 40% of the triplets fulfill our criteria. The lifetime of a triplet configuration may also be estimated from the



**Figure 1.** Probability,  $p(n)$ , for one molecule to have  $n$  hydrogen bonded neighbours (left) and hydrogen bond energy per bond,  $\langle U_{HB} \rangle_1$ , as a function of  $n$  (right).



**Figure 2.** Energy autocorrelation function,  $C_U(t)$ , for the donated and accepted cluster configurations. The inset shows the short time correlation behaviour.

energy autocorrelation function of a hydrogen bonded cluster,  $C_U = \langle U^{tr}(t)U^{tr}(0) \rangle$ , where  $U^{tr} = \sum_{i<j} U_{ij}$  and  $U_{ij}$  is the pair energy of two molecules in the cluster. At long times the molecules will diffuse out of the cluster and consequently  $C_U$  will decrease to zero. In figure 2 the correlation functions  $C_U$  are shown for the donated and accepted configurations; the slow decay indicates that the clusters are stable for a long enough time to perform a correlation function analysis of the triplet motions. It is interesting to note that, although the donated configurations are bound more strongly initially, the lifetime of this type of cluster is somewhat shorter than for the accepted configuration. Also note that the long time decay of  $C_U$  is nonexponential. This finding is in line with a study of hydrogen bond dynamics in water performed in [13] and [14], where, within a diffusion model of hydrogen bonded pairs, this feature could be described reasonably. Also note that the short time dynamics (see the inset) is different due to making and breaking of hydrogen bonds which is not diffusion controlled.

For the calculation of the time correlation function of a certain type of triplet vibration  $\Xi$  (see below)

$$C_{\Xi}(t) = \frac{1}{N_{tr}} \frac{1}{N_{\tau}} \sum_{i=1}^{N_{tr}} \sum_{j=1}^{N_{\tau}} u_{i,\Xi}(t + \tau_j) u_{i,\Xi}(\tau_j) \quad (1)$$

we identified at a certain time step,  $t_0$ , separately all donated (d) and accepted (a) triplets in the system,  $N_{tr}^{(d)}(t_0)$  and  $N_{tr}^{(a)}(t_0)$ . Then we monitored the motions of these triplets for a time interval  $\Delta t = 0.75$  ps ( $\Delta t = N_{\tau} \delta t$ , where  $N_{\tau}$  is the number of subsequent configurations and  $\delta t$  the time interval between two of them) and filled a velocity autocorrelation vector for each triplet separately. At  $t = t_0 + \Delta t$  all those triplets were discarded which were not hydrogen bonded any longer and an average of the velocity correlation functions was performed for  $N_{tr}^{(i)} = N_{tr}^{(i)}(t_0 + \Delta t)$  ( $i = a, d$ ). This procedure does not exclude that the triplets were meanwhile, within the interval  $[t_0, t_0 + \Delta t]$ , not hydrogen bonded (this implies a recombination), but it guarantees that unstable triplets are not taken into account for the velocity correlation function. In our calculations we have found a probability  $p$  for one molecule to be involved in a donated or accepted configuration of  $p = 0.7$  and  $p = 0.6$  respectively. After a time  $\Delta t$ , 27% of the donated and 37% of the accepted triplet configurations had to be discarded for further analysis.

In order to distinguish the different motions of the clusters we have performed an approximate normal mode analysis [15]. Within this approximation we do not analyse the eigenfrequencies by diagonalizing the dynamical matrix (instantaneous normal mode analysis), but we assume that we know the normal coordinates. From that point of view the approach is somehow complementary to an instantaneous normal mode analysis. In so doing the com velocity of the cluster as a whole

$$\mathbf{v}_{cm}^{tr} = \frac{1}{3} \sum_{i=1}^3 \mathbf{v}_i \quad (2)$$

was subtracted from the com velocities,  $\mathbf{v}_i$ , of the single molecules. The velocities in the cluster com frame were then projected on local coordinate systems  $(\xi, \eta, \zeta)_i$ , where the index  $i$  refers to the molecules in the cluster, i.e.

$$u_{i,\Xi_i} = (\mathbf{v}_i - \mathbf{v}_{cm}^{tr}) \Xi_i \quad \Xi_i = \xi_i, \eta_i, \zeta_i. \quad (3)$$

The local coordinate systems were constructed in the following way: the  $\xi$ -axis is defined in the direction from the cluster com to the com of molecule  $i$ , the  $\zeta$ -axis is perpendicular to the plane defined by the three com positions of the cluster molecules and  $\eta = \zeta \times \xi$  in order to define a right-handed local coordinate system. We now define the following scalar quantities

$$V_1 = \frac{1}{\sqrt{3}} \sum_{i=1}^3 u_{i,\xi} \quad (4)$$

$$V_2 = \frac{1}{\sqrt{3}} (u_{1,\eta} - u_{2,\xi} + u_{3,\xi}) \quad (5)$$

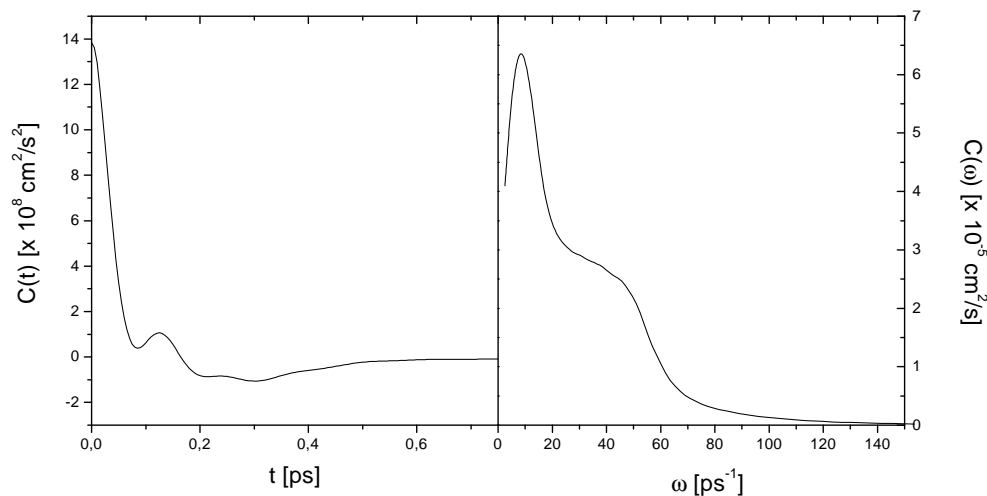
$$V_3 = \frac{1}{\sqrt{3}} (u_{1,\xi} + u_{2,\eta} - u_{3,\eta}) \quad (6)$$

$$R_x = \frac{1}{\sqrt{3}} \sum_{i=1}^3 u_{i,\eta} \quad (7)$$

$$R_y = \frac{1}{\sqrt{3}} (u_{1,\zeta} - u_{2,\zeta} - u_{3,\zeta}) \quad (8)$$

$$R_z = \frac{1}{\sqrt{2}}(u_{2,\zeta} - u_{3,\zeta}). \quad (9)$$

The numerical factors in equations (4)–(9) were introduced in order to make the correlation functions comparable with the molecular VACF (cf figure 3). From the definition of the local axis and from the fact that the triplet com is at rest, it is clear that a correlation function of the quantities in equations (4)–(9) characterizes the symmetric stretching ( $V_1$ ), asymmetric stretching ( $V_2$ ), the bending motion ( $V_3$ ) and three librational motions which are defined in the cluster frame. The expression for the correlation function contains both self- (of the form  $\langle u_{i,\Xi_i}(t) u_{i,\Xi_i}(0) \rangle$ ) and cross contributions (of the form  $\langle u_{i,\Xi_i}(t) u_{j,\Xi_j}(0) \rangle$ ), the latter of which gives especially information on the collective character of the molecular motions.

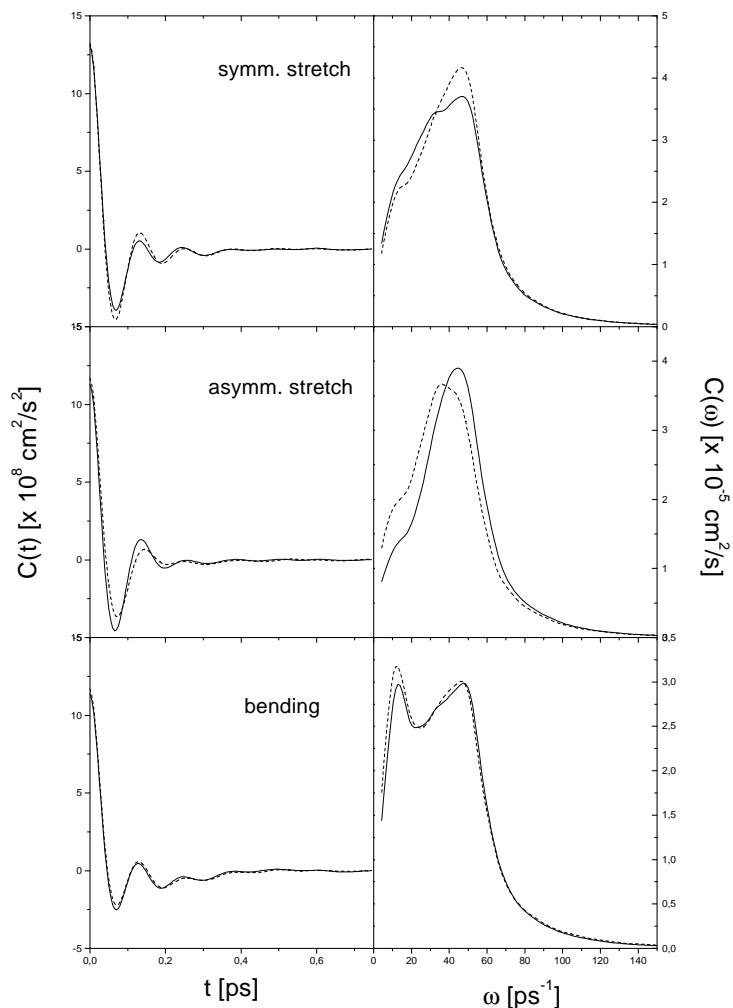


**Figure 3.** Velocity autocorrelation function and its spectrum of SPC/E water at ambient conditions.

### 3. Results and discussion

In figures 4 and 5 the results for the time correlation functions and the relative spectra of the *internal* vibrations and the three librational motions are shown. The symmetric and asymmetric stretching motions show similar damped oscillatory time behaviour where evidently the oscillations are around zero. The major differences appear in the frequency spectra,  $C(\omega)$ . It is seen that the symmetric stretch has a peak at  $\approx 45 \text{ ps}^{-1}$  but has also strong contributions at smaller frequencies. It is not possible to describe the symmetric stretch by a single contribution (like a damped harmonic oscillator). This is somewhat different for the asymmetric stretch. Although it seems not to be possible to parametrize the line shape by a single mode it is evident that the contribution in the high frequency region is the dominating one. At small frequencies ( $\omega \approx 10 \text{ ps}^{-1}$ ) a little shoulder is observed.

A somewhat different result is obtained for the bending motion. First one observes a different time correlation function, which is not oscillating around zero. Nevertheless, also here a similar fast oscillatory process is observed as for the stretching vibrations. In

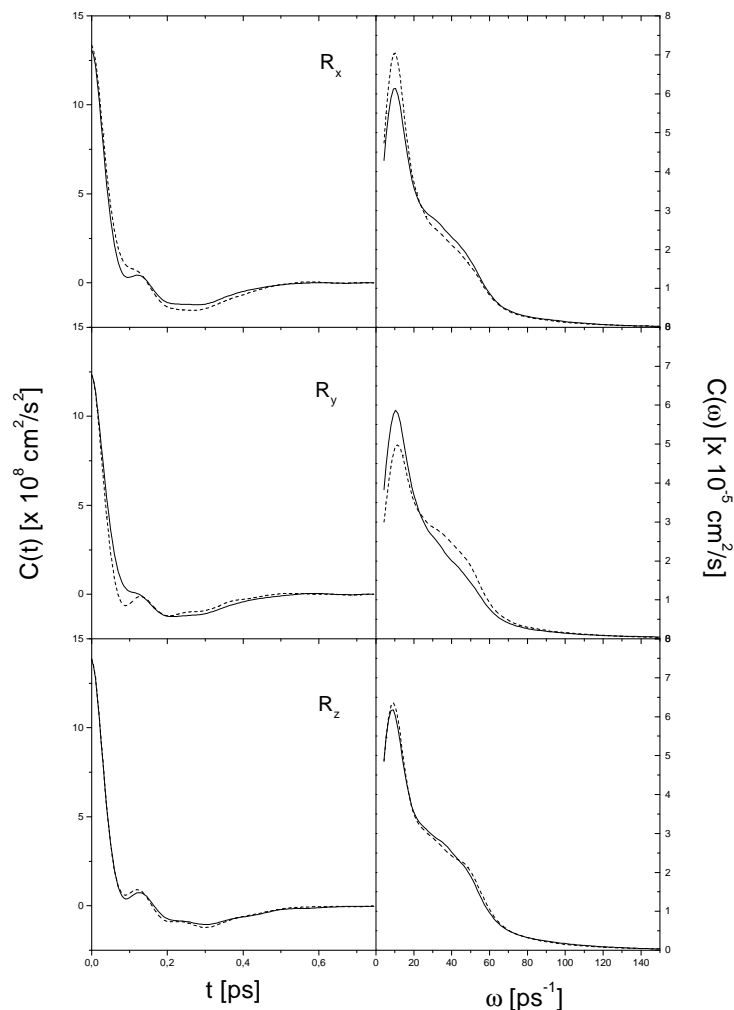


**Figure 4.** Velocity correlation functions and their spectra for the internal vibrations of hydrogen bonded triplet configurations. Distinguished are the donated (solid line) and accepted (dashed line) configurations.

the frequency domain the picture now is clearly different from the stretching motions. Two contributions of nearly the same magnitude are observed, the first one in the small frequency range at  $\omega \approx 10 \text{ ps}^{-1}$ , and the second one in the higher frequency range at  $\omega \approx 50 \text{ ps}^{-1}$ .

The time behaviour of the VACF for the donated and accepted triplets looks qualitatively very similar. Different dynamical features are more clearly shown in the relative spectra, mostly for the asymmetric stretch where a shift of the peak to lower frequencies is present for accepted triplets.

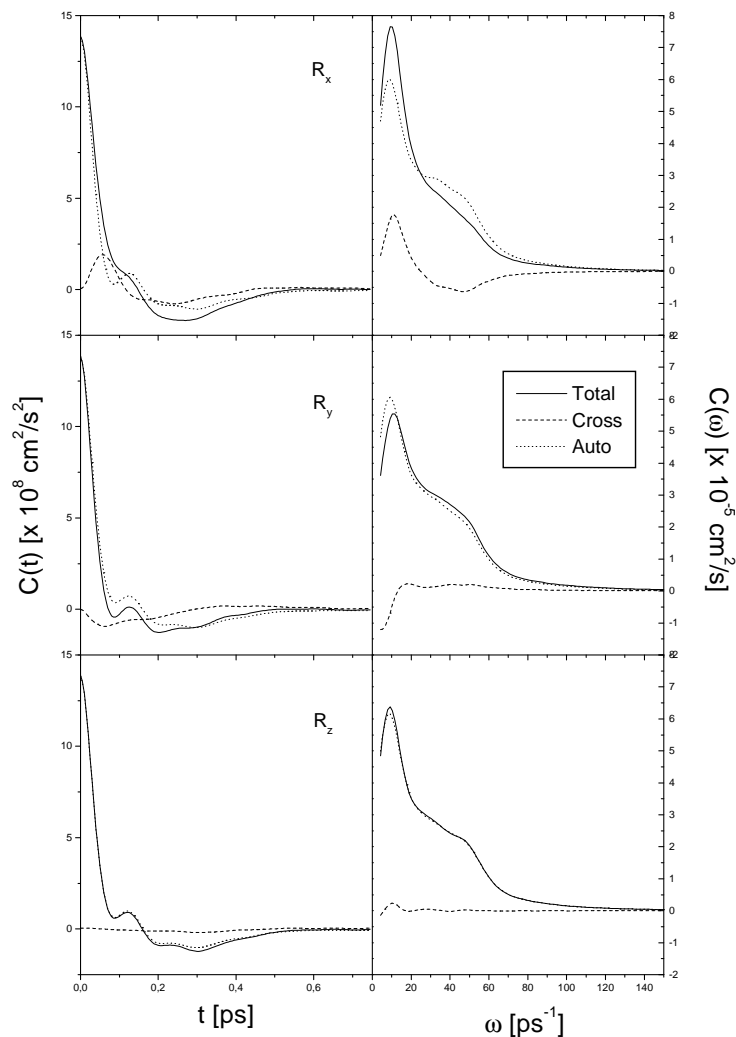
An opposite picture is observed for the librational motions (figure 5). Here, qualitatively a similar result is obtained for all three types of librational motion. A strong contribution to the spectrum is observed in the small frequency region, where a definite peak is located at  $\omega \approx 10 \text{ ps}^{-1}$ . In the higher frequency region a shoulder is observed, thus indicating a second, broad contribution. The shape of the librational spectra resembles very much the



**Figure 5.** Velocity correlation functions and their spectra for the librational motions of hydrogen bonded triplet configurations (line symbols as in figure 4).

one of the VACF (cf figure 3). The librational motion analysis indicates that the cluster as a whole performs a *rotational* diffusion which can be compared with the single molecule diffusion process (this, of course, may be only strictly defined for a hypothetical cluster, which would be stable in the limit  $t \rightarrow \infty$ ). The time correlation function behaviour (and that of the corresponding spectra) is very similar to what one finds for the single molecule velocity correlation function. In order to study the cooperativity of the molecules in the cluster we have studied separately the cross-correlation functions of velocity projections of different cluster members. For this purpose we have studied the correlation functions in the laboratory axis frame. This leads to more decisive conclusions since in the moving frame the cross-correlations still contain contributions from the com motions of the cluster molecules ( $\langle u_{\Xi}(t) u_{\Xi}(0) \rangle = \langle (\mathbf{v}(t) - \mathbf{v}_{cm}^{tr}(t))_{\Xi} (\mathbf{v}(0) - \mathbf{v}_{cm}^{tr}(0))_{\Xi} \rangle$ ). In figure 6 the total, cross- and autocorrelation functions of the donated triplets are shown. As compared with figure 5 the total functions for  $R_x$  and  $R_y$  are somewhat changed in the zero time value





**Figure 6.** Velocity correlation functions and their spectra for the librational motions of donated triplet configurations, analysed in the laboratory frame. Distinguished are the total (solid line), cross (dashed line) and autocorrelations (dotted line).

and in the overall shape due to the motion of the cluster com. An exception is obtained for  $R_z$  which is nearly not affected by the transformation which means that there is nearly no motion of the cluster com perpendicular to its plane. Concerning the cross-correlation functions between the cluster molecules it appears that they give significant contributions to the total librational spectrum in the cluster plane ( $R_x$ ). This is less pronounced for  $R_y$  and nearly negligible for  $R_z$ . This suggests that a large part of the diffusive motion of single molecules which are bound in a hydrogen bonded triplet cluster (this is the main portion of all molecules in the system) may be described by the *rotational* diffusion of the cluster as a whole [16]. This may even give rise to the speculation that the activation barrier for diffusive motions is not fully determined by the breaking of single hydrogen bonds but it is partly due to rearrangements of whole molecular groups.

The librational motions indicate that the different directions, probed by the projection analysis, are not equivalent. As a matter of fact, since the molecules of the tagged cluster participate in hydrogen bonds with other molecules, the cluster is not surrounded by an effective, average-like structure, but it is embedded in a potential energy landscape which is strongly anisotropic. Eventually the clusters here analysed are bound to form a percolating network. Therefore the clusters will have a *normal mode spectrum*, which is influenced by the motions of the molecules in the neighbouring clusters. Thus, calculating the bending motions of the cluster one will also find contributions from stretching vibrations which are due to the interaction with the molecules surrounding the cluster. The superposition of different contributions to the normal mode spectra thus reflects the topology of the hydrogen bond network structure.

We note that the above results depend somehow on our choice of the definition of a hydrogen bond. This, however, affects only the width of the peaks in the spectra and presumably not their position. Suppose we applied a weaker criterion for the definition of the hydrogen bond. In that case the peaks would be broadened due to very weakly bonded configurations. On the other hand, a stricter criterion would only consider the most stable clusters. These, however, will not be representative for the system, since they are rare. Our choice of the hydrogen bond definition thus leads to a compromise between good statistics and good resolution.

It would be interesting to compare our findings with *ab initio* calculations for free trimers [17–19] or spectroscopic measurements in the gas phase [20]. Experimentally [21] a vibration–rotation–tunnelling band was found for  $(\text{D}_2\text{O})_3$  at  $89.6 \text{ cm}^{-1}$  ( $16.8 \text{ ps}^{-1}$ ). In [17] results from *ab initio* calculations were reported where the lowest intermolecular *harmonic* frequencies of  $101 \text{ cm}^{-1}$  ( $18.93 \text{ ps}^{-1}$ ) and  $158 \text{ cm}^{-1}$  ( $29.63 \text{ ps}^{-1}$ ) were found (depending on the applied method). However, one has to take into account that the minimum energy ring structure of a trimer looks very different with respect to the triplet configurations discussed in the present report so that a direct comparison would be misleading. In addition, what is missing in the free trimer are the librational spectra due to the missing restoring forces acting on the whole cluster.

In conclusion we may note that the interpretation of the VACF of water is not easily reduced to the assignment of normal vibrational modes of the molecule with its hydrogen bonded neighbours. This type of interpretation, which seems natural at a first glance, becomes difficult (if not meaningless) due to the fact that the molecules may be members of different cluster configurations at the same time and have a more complicated normal coordinate geometry than suggested by an isolated cluster. The present analysis clearly shows that the contribution at  $\approx 10 \text{ ps}^{-1}$  in the VACF spectra is not only due to the bending vibrations but it comes predominantly from the librational motion of the trimer cluster. This suggests that earlier assignments of the low frequency peak in the VACF as well as in the longitudinal and transversal current spectra were indeed oversimplified. From our analysis one may, furthermore, speculate about the nature of the low frequency peak in the collective current spectra, found in [5], [8] and [22]. This peak appears at a wavenumber  $k^* \approx 1 \text{ \AA}^{-1}$  which corresponds to a spatial scale  $l^* = 2\pi/k^* \approx 6 \text{ \AA}$ . This spatial scale may be considered as characteristic for the trimers, discussed in the present report (the distance between the *end molecules* is of order  $l^*$ ) which means that the feature in the collective spectra may be mainly explained by the *localized modes* discussed above.

We note that our present analysis may be easily extended to larger hydrogen bonded clusters. A natural choice would be to study the tetrahedrally arranged pentamer. However, with increasing size of the clusters the computational time for the analysis will increase considerably to obtain sufficient statistics. A more detailed analysis may be performed by a

full normal mode (or instantaneous normal mode) analysis. This will be necessary to reveal a more detailed picture of motions of water molecules in the hydrogen bond network. Work in this direction is in progress.

### Acknowledgments

GS is grateful for discussions about the dynamics analysis with Ph A Bopp. He is also grateful for partial financial support from the Istituto Nazionale per la Fisica della Materia (INFN) during his stay in Trento.

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