

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/244355562>

Dynamics of the hydrogen bond network in liquid water

ARTICLE *in* JOURNAL OF MOLECULAR LIQUIDS · MAY 2002

Impact Factor: 2.52 · DOI: 10.1016/S0167-7322(01)00320-8

CITATIONS

18

READS

4

2 AUTHORS:



Godehard Sutmann

Forschungszentrum Jülich

89 PUBLICATIONS 988 CITATIONS

SEE PROFILE



Renzo Vallauri

Università degli Studi di Trento

129 PUBLICATIONS 2,111

CITATIONS

SEE PROFILE

Dynamics of the hydrogen bond network in liquid water

G. Sutmann ^{a,1} and R. Vallauri ^{b,2}

^a Central Institute for Applied Mathematics (ZAM) and John von Neumann Institute for Computing (NIC), Research Centre Jülich, D-52425 Jülich, Germany

^b Istituto Nazionale per la Fisica della Materia and Università degli Studi di Trento, Dipartimento di Fisica, I-38050 Povo (Trento), Italy

Dedicated to Professor M. D. Zeidler in honour of his 65th birthday.

The dynamics of the hydrogen bonded network in liquid water is studied by means of molecular dynamics simulations for the SPC/E water model at different thermodynamic conditions. The *n*-folded hydrogen bond coordination of single molecules and the life time of such configurations is studied by correlation functions. A special focus is put on the dynamics of associated trimers. A velocity projection technique is applied to study the trimer dynamics and to interpret the corresponding velocity-autocorrelation function of single molecules.

© 2002 Elsevier Science B.V. All rights reserved.

1. INTRODUCTION

Hydrogen bonds strongly determine the structure and dynamics of water. As is well known from experimental [1, 2] and computer simulation [3, 4] results, water is arranged in a tetrahedral structure, i.e. each molecule has ideally four nearest neighbors, two of which can get two donated bonds and the other two can accept a bond from a tagged molecule. Due to the possibility of accepting and donating bonds, water forms a hydrogen bonded network structure which lies above the percolation threshold [5]. In a realistic situation the coordination number of a molecule is slightly larger than four, indicating that the network is not formed of ideal tetrahedra. This is due to temperature fluctuations and a dynamical reordering of water molecules, thereby leading to a making and breaking of the hydrogen bonded structure. Studying the single molecule dynamics in an experiment or in a computer simulation one therefore could expect that the collective nature of the hydrogen bond network would be reflected in the molecular motion.

A first attempt to interpret the results from Raman light scattering in such a collective picture was done by Walrafen [6], who assigned features observed in the spectra as symmetric and asymmetric stretching vibrations of associated molecules as well as bending vibrations of three hydrogen bonded molecules. This assumption was tested in a computer simulation study [7] where an approximate normal mode analysis was performed which could discriminate different types of motions in associated water clusters found in

¹e-mail: g.sutmann@fz-juelich.de

²e-mail: vallauri@science.unitn.it

the bulk. It was found that the internal cluster vibrations can be associated with the observed features in the spectrum of the velocity autocorrelation function. In addition it was found that rotational motions of water trimers also contribute to the low frequency part in the spectrum.

The present paper is focused on two aspects of hydrogen bond dynamics. In a first part the average coordination of the molecules is characterized due to a certain criterion for a hydrogen bond. Starting from this static picture the lifetime of a given coordination in terms of dynamical correlation functions is studied. In a second part focus is put on the dynamics of associated trimer molecules in terms of velocity projections. Two different reference frames for the projection technique are compared and it is shown that cluster internal normal modes can be identified. All quantities are calculated for a broad range of temperatures, ranging from the supercooled regime at $T = 210\text{ K}$ up to $T = 450\text{ K}$.

2. MOLECULAR DYNAMICS SIMULATION

Extensive molecular dynamics simulations were performed for a set of thermodynamic state points for the SPC/E model of water [8]. The number of molecules was $N = 256$ and the temperature was varied in the interval from 210 K to 450 K with an incremental temperature step of $\delta T = 15\text{ K}$, i.e. resulting in 17 different state points. The simulations were carried out in the microcanonical ensemble at constant mass density, $\rho = 0.998\text{ g/cm}^3$, for all temperatures. The equilibration of the systems was done in a step wise fashion. After equilibration of a system at a high temperature, the configuration was used as a starting point for a system at lower temperature which was reached by applying a weak-coupling thermostat [9]. Equilibration at a constant temperature was done for $\approx 100\text{ ps}$ at high temperature and several 100 ps at low temperature, after which trajectories were used for statistical averaging. The long range interactions were taken into account via a tapered reaction field method [10] and usual periodic boundary conditions were applied.

3. RADIAL DISTRIBUTION FUNCTIONS

In order to get an impression of the time averaged coordination of two water molecules and their sites, respectively, one may analyse the radial pair-correlation function, $g(r)$. In Fig. 1 this function is shown for the distribution of the relative center-of-mass (g_{com}) separation of water molecules. Also shown is $g_{OH}(r)$, which reflects at short distances the appearance of a hydrogen bond between molecules. Due to the constant density of all configurations, the peak positions of $g(r)$ at all temperatures remain almost the same at short distances. However the height and the width of the peaks changes strongly from low to high temperatures, which reflects the fact of a temperature variation in mobility and coupling between water molecules. At small temperature ($T = 210\text{ K}$), in the supercooled regime, water becomes very viscous and diffusion occurs on time scales ≈ 100 times longer than in the high temperature region ($T = 450\text{ K}$). This fact is reflected in the fact that $g(r)$ takes very small values after the first coordination peak in $g_{com}(r)$.

The appearance of nonvanishing oscillations at larger distances reflects the appearance of long range correlations in the low temperature regime. Increasing the temperature

reduces these features and at $T = 450\text{ K}$ all long range correlations vanish. After the first peak at $r \approx 2.8\text{ \AA}$ water seems to be a structureless medium at this temperature. This trend is also observed in the function $g_{OH}(r)$. At low temperature the hydrogen bond peak is very pronounced and it decreases in height with temperature. As is seen in the inset of Fig. 1, the distance dependent coordination number $n(r)$, which is defined as

$$n(r) = 4\pi\rho \int_0^r dr' r'^2 g(r') \quad (1)$$

takes the same value $n(r = 2.5\text{ \AA}) = 2$ and $n(r = 3.2\text{ \AA}) \approx 4$ for g_{OH} and g_{com} respectively, reflecting the fact that a water molecule can accept two hydrogen bonds and that it has four neighboring water molecules as neighbors in a tetrahedral arrangement (inspection shows that this number is slightly larger than four due to the appearance of interstitial water molecules [4]).

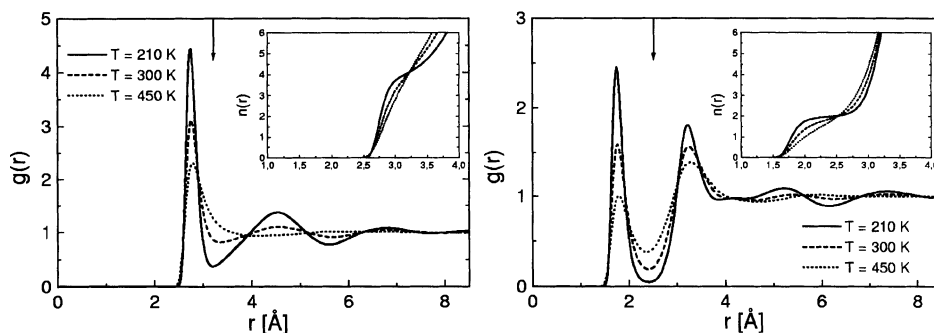


Figure 1: The radial pair-distribution function $g(r)$ for three selected temperatures. The inset shows the distance dependent coordination number $n(r)$. The arrow in the figure indicates the position where $n(r)$ takes approximately the same value for all temperatures. Left: the molecular center-of-mass distribution. Right: the oxygen-hydrogen site-site-distribution, indicating the hydrogen bond coordination at small distances.

4. HYDROGEN BOND DYNAMICS

In order to characterize the dynamics of hydrogen bonded molecules one first has to define a criterion for the appearance of a hydrogen bond. We have tested several criteria and have chosen one which reflects those properties which are commonly believed to be realized in real water. Since it is known from experiment that water has a coordination number of slightly more than four and that the most probable geometric configuration is a tetrahedral arrangement, it is understood that a criterion for the hydrogen bond should give a considerable number of molecules which have four hydrogen bonds: two donated ones and two accepted ones. We have chosen a combined geometrical-energetical criterion:

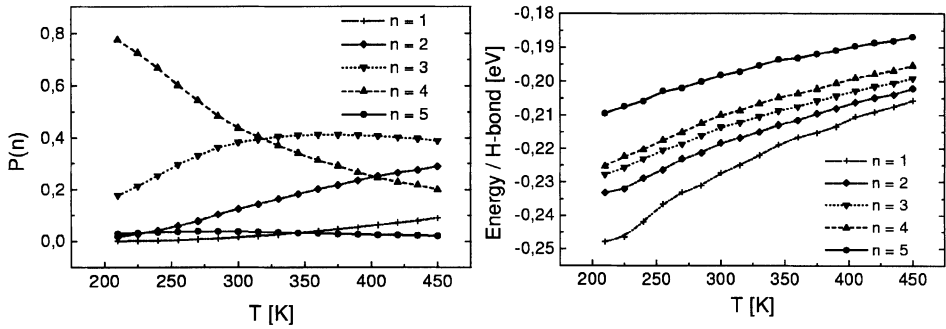


Figure 2: Left: The distribution $P(n)$ as a function of temperature, where $P(n)$ gives the probability to find molecules with n hydrogen-bonded neighbors. For all temperatures there is a non-vanishing but negligible probability to have zero or six hydrogen bonded neighbors. Right: The hydrogen bond energy per bond in n -folded clusters as function of temperature.

a configuration of two water molecules is called to be hydrogen bonded if (i) the mutual interaction energy is less than -0.1 eV, (ii) the oxygen-oxygen distance is less than 3.5 Å and (iii) the angle O-H...O is smaller than 35° .

In Fig.2 the probability is shown for a broad range of temperatures to find a molecule with zero up to five hydrogen bonds. According to the criterion it is apparent that at low temperatures almost 80% of the molecules have four H-bonds. The rest portion of molecules is mainly engaged in three bonds. It is, however, also found that about 5% of the molecules have five bonds. Increasing the temperature while keeping the density fixed the picture is changed. At $T = 300$ K the number of molecules with only two or three bonds is increased to $\approx 50\%$ showing that H-bonds are broken. However, the number of five-coordinated molecules remains almost the same as in the low temperature regime. At $T = 450$ K the molecules become less bonded, indicating a melting of the network. Especially the number of five-coordinated molecules becomes negligible. Inspection of the data shows that in the temperature range under study maxima exist for the coordination numbers $n = 3$ and $n = 5$ at $T = 365$ K and $T = 270$ K respectively. It may be extrapolated that for each coordination number a maximum exists where the ones for $n = 1$ and $n = 2$ are located at higher temperatures. Furthermore one may expect the maxima for $n = 4$ and $n = 0$ at $T \ll 200$ K and $T \gg 450$ K respectively.

In the lower temperature regime the appearance of a fifth molecule may be interpreted as a distortion of the hydrogen bonded network, which is not an ideally formed tetrahedral structure. This distortion may be quantitatively studied by calculating the hydrogen bond energies per bond (cf. Fig.2). Starting from the one-coordinated molecules it is apparent that in this case the lowest energy per bond is realized for all temperatures. Adding another molecule decreases of course the total energy of the complex but increases the energy per bond. Since the molecules which are bonded to a tagged one do not, in general, attract each other it can be understood that the molecules must find a compromise between attraction to the central molecule and repulsion and this compromise costs some

extra energy. This effect becomes most pronounced for the five-coordinated molecules. Adding a fifth molecule to a tetrahedral arrangement means to create some extra space for this molecule which will distort the other bonded molecules from their preferential orientation.

Up to now we have considered only a static picture of the hydrogen bonds. It is, however, clear that the hydrogen bonded network is a highly dynamic object. Since molecules obey translational and rotational diffusion, there are always processes of making and breaking hydrogen bonds. The question therefore arises about the lifetime of a hydrogen bond or, more generally, the lifetime of an n -coordinated hydrogen bonded cluster. In order to shed some light on this question we first define a dynamic variable h_n which, at time $t = 0$, takes the value 1 for a hydrogen bonded coordination of a tagged molecule and n other molecules. If, at $t > 0$, the molecule is bonded *only* to these n molecules, $h_n = 1$, otherwise $h_n = 0$. Therefore, $\langle h_n \rangle / N$, gives the probability for a molecule to be n -coordinated. In order to investigate the lifetime, we calculate the normalized time correlation functions

$$C_n(t) = \frac{\langle h_n(t)h_n(0) \rangle}{\langle h_n^2 \rangle} \quad (2)$$

which are displayed in Fig.3 for three selected temperatures. If one defines roughly the lifetime, τ_n , of a hydrogen bonded complex as the time where $C_n(t) = 0.5$, it is found that at all temperatures the lifetimes of the four-coordinated complexes are the longest ones. Although at high temperature the probability for having four-coordinated molecules is relatively small, the lifetime is nevertheless longer than for other coordinations, i.e. the lifetime is not directly correlated with the probability of the appearance.

According to the criterion for τ one finds a very strong dependence on the temperature. While at small temperatures $\tau_4 > 5$ ps, we find $\tau_4(T = 300 \text{ K}) \approx 0.2$ ps and $\tau_4(T = 450 \text{ K}) \approx 0.02$ ps. For $T = 300 \text{ K}$ the time compares well with other computer simulation studies [11]. Most obvious at high temperature it is found, however, that the long time decay behavior becomes different. Here the one coordinated complexes have the smallest decay, followed by two-, three-, four- and five-coordinated ones. In this time region the dynamics is mainly diffusion controlled. From the simulation data it seems that in this time regime the probability for a cluster to dissociate is inversely proportional to the number of cluster constituents. At $T = 450 \text{ K}$ the cross-over between the two time regimes occurs after ≈ 0.6 ps. At $T = 300 \text{ K}$ a similar behavior seems to occur. If one extrapolates to longer times the correlation functions for the one- to four-coordinated complexes will cross each other.

As is apparent from C_n at high temperature, the hydrogen bonded network is very weak and undergoes fast motions of reordering. On the other hand at low temperature the network is very stable. Fast dynamics is only observed for the cases of small coordinated molecules, which means that if a molecule has only one or two H-bonds there is a very high probability to increase the number of bonds in a short time. A feature, which is clearly seen in the logarithmic plots is the non-exponential decay of C_n . At short times there is even a non-monotonic behavior in several cases (cf. right column Fig.3), which is a signature of an oscillating process of making and breaking hydrogen bonds. These short time dynamics are certainly quite sensitive to the definition of the hydrogen bond. In a

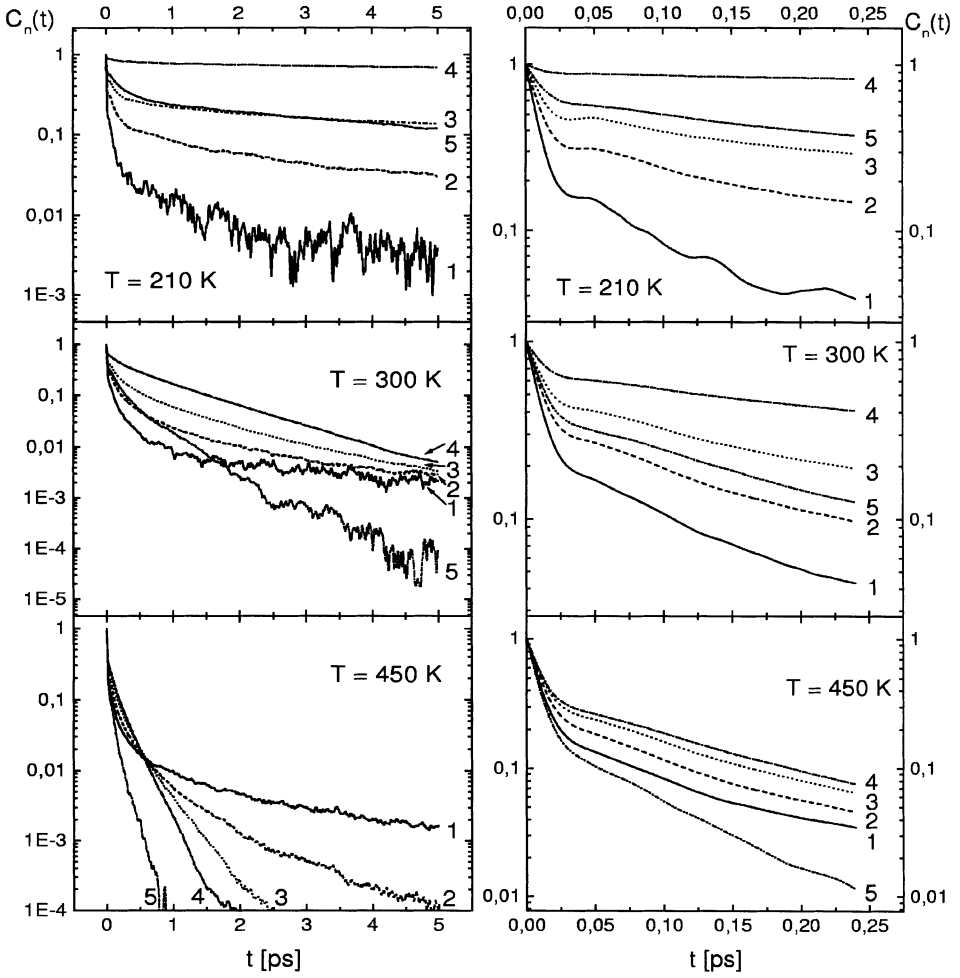


Figure 3: Logarithm of the time correlation function $C_n(t)$ of hydrogen bonded n -coordinated complexes at three different temperatures in the long (left) and short time regime (right): $n = 1$ (solid line), $n = 2$ (dashed line), $n = 3$ (dotted line), $n = 4$ (dash-dotted line), $n = 5$ (dash-dot-dotted line).

study where coordination numbers were not distinguished [11] a model was proposed on the basis of molecular pair interdiffusion and different rate constants for the making and breaking process of bonds. It could be clearly demonstrated that this model describes the correct decay characteristics of the dynamical correlation function, i.e. it leads to a non-exponential decay. One therefore could be inspired to extend the model towards an accurate description of n -coordinated complexes. This is, however, beyond the aim of the present investigation.

5. CLUSTER DYNAMICS

From the subsequent analysis it is apparent that clusters of associated molecules form and that at low and room temperatures the lifetime for a certain portion of them may be more than 1 ps . In Ref.[6] an interpretation of the velocity autocorrelation function (VACF, see Fig.4) was given in terms of molecular motions, arising from normal mode vibrations of a tetrahedral arrangement of molecules. It was argued that the low frequency peak at $\approx 10\text{ ps}^{-1}$ in the spectrum of the VACF originates from bending motions of three associated water molecules, while the shoulder at $\approx 40\text{ ps}^{-1}$ is due to stretching motions of the hydrogen bond between two molecules. This assumption may be tested using a velocity projection technique [7] or an instantaneous normal mode procedure [12]. Here we use the projection technique which is briefly described. For technical details the reader is referred to the Appendix of the present paper and to Ref.[7].

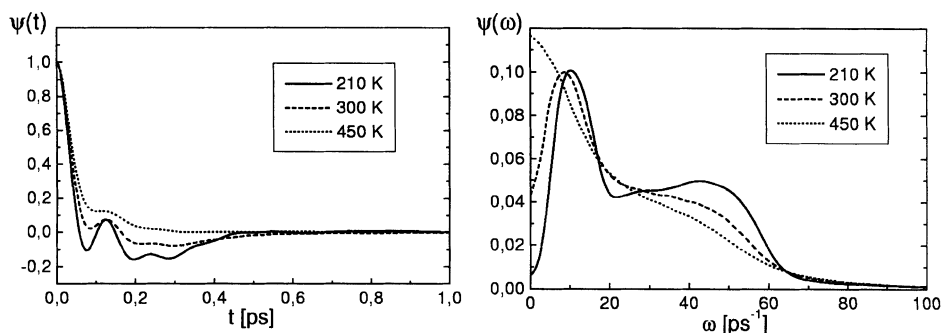


Figure 4: The normalized center-of-mass velocity autocorrelation function ψ in the time and frequency domain at three temperatures. Two distinct line shape contributions are present at $\omega \approx 10\text{ ps}^{-1}$ and $\omega \approx 40\text{ ps}^{-1}$.

One may consider a water molecule from two viewpoints. On the one hand it may donate two hydrogen bonds to neighbored molecules, on the other hand it may accept two bonds. If one considers these cases separately, one may study a donated and an accepted trimer configuration of molecules. In a next step one may assume that these three molecules perform vibrations which may be analysed within a picture of normal modes. In analogy

to an isolated water molecule one may consider such a trimer as a loosely bounded supermolecule for which one can calculate the normal modes in analogy to a single water molecule. In Ref.[13] a procedure, based on a velocity projection technique, was introduced to analyse the internal vibrations of a water molecule. This technique may be extended to the case where all three sites of a molecule have the same mass. In so doing one defines a local coordinate system on each trimer molecule i of the cluster (c.f. Fig.6 in the Appendix), where the one axis ξ_i points from the center-of-mass (com) of the trimer to the com of the molecule. A next axis, ζ_i , is perpendicular to the cluster plane. Finally the axis $\eta_i = \zeta_i \times \xi_i$ is constructed. In order to analyse the internal cluster motions the reduced velocity $\mathbf{u}_i = \mathbf{v}_i - \mathbf{v}_{cm}^{tr}$ is calculated. Projecting this velocity on different combinations of local axis (ξ_i, η_i, ζ_i) and calculating correlation functions of these projections gives information about symmetric and asymmetric stretching, bending and trimer rotational motions (see Appendix).

The description given so far refers to trimers. Since it is known that the preferred configuration is a tetrahedral arrangement, i.e. a pentameric cluster of molecules, it would be interesting to analyse the whole normal mode spectrum of a pentamer. The number of normal modes in this case is increased to nine, where some of them are degenerated. Since for a pentamer the projection technique is not that transparent as it is in the case of trimers one may assume the following. In a pentamer the central molecule (the one which accepts and donates bonds, indicated as molecule 1) is located very close to the com of the cluster. Constructing a local coordinate system on each cluster molecule in the same way as it was described before would mean that the ξ -axes points from the central molecule along the hydrogen bond to the neighbor molecule. The other axis are then constructed analogously as before. Assuming that molecules taking part in donated and accepted bonds are not strongly correlated with each other, one may calculate the normal modes for accepted and donated trimers separately. Considering the central molecule fixed in space requires now to calculate the reduced velocity as $\mathbf{u}_i = \mathbf{v}_i - \mathbf{v}_1$.

The two different cases will be referred to as projections in the com-frame (c-frame) and central-molecule-frame (m-frame), respectively. We will discuss both cases in the following. We will restrict ourselves to the discussion of donated trimers. Our calculations have shown that results of donated and accepted trimers are not identical within statistical accuracy, but they agree qualitatively with each other and a separate discussion leads to no further insight.

In Fig.5 the spectra of the normalized projected velocity trimer correlation functions are shown in the c-frame (left) and m-frame (right) at three temperatures. Let us start with a discussion of the c-frame. As a first observation one can state that all vibrational modes exhibit contributions at $\omega \approx 40\text{ps}^{-1}$, thus showing that the VACF in this frequency range gets contributions from all three motions.

For the case of the bending motion there is clear evidence for a low frequency vibration which coincides with the one in the spectrum of the VACF. On the other hand there are also small contributions at low frequency in the symmetric and asymmetric stretching. Due to this mixture of frequency contributions one might argue that the choice of the reference coordinate system could be inadequate. A comparison with the m-frame results shows that at least the low frequency peaks in the stretching motions disappear and that the low frequency peak in the bending motion is more pronounced. Nevertheless, there is

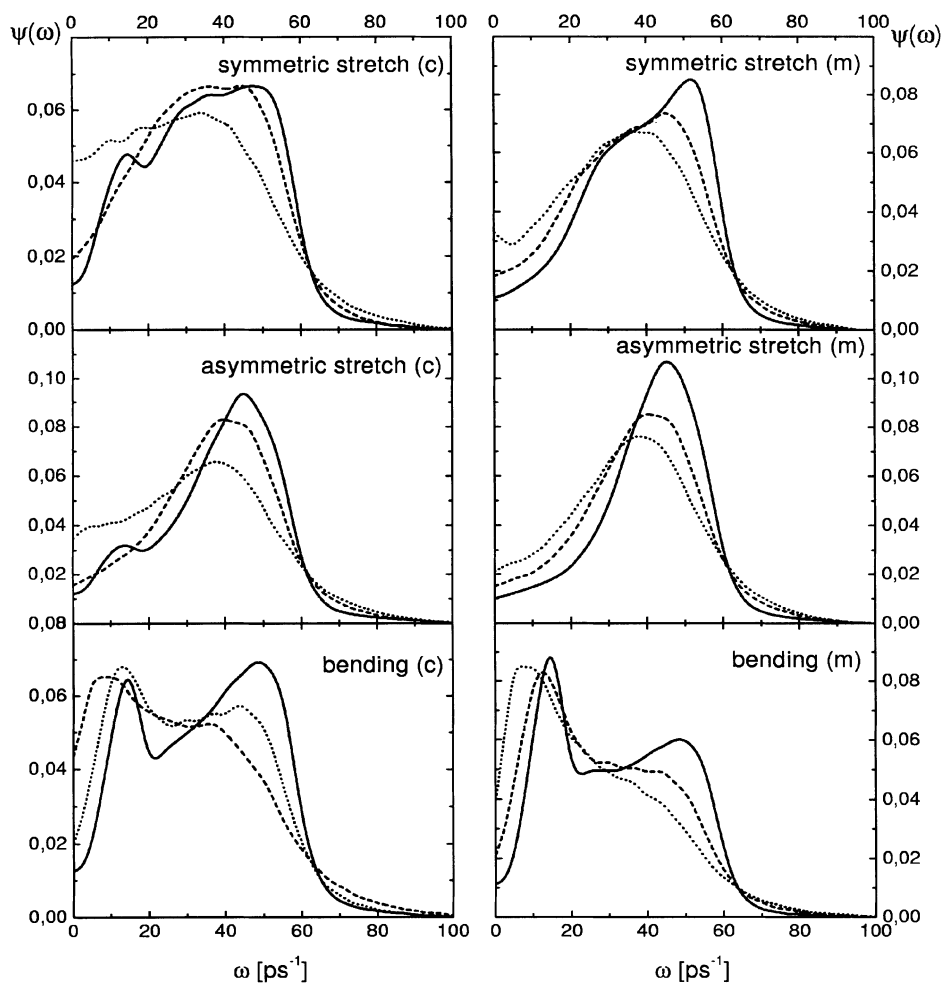


Figure 5: Spectra of the normalized internal vibrational trimer motions at three different temperatures for the donated configurations, obtained by velocity projections on molecular axis. The spectra for accepted configurations look similar. Left: projections in the center-of-mass frame. Right: projections in the central-molecule frame.

still a strong contribution at higher frequencies in the bending. This reflects the fact that molecules are associated, especially at low temperature, to a whole network of hydrogen bonds, i.e. the velocity, projected along the axis describing bending motions in the trimer, contains also contributions from stretching motions with molecules outside the trimer.

The symmetric stretching motion shows in the c-frame a rather broad distribution in contrast with the asymmetric stretching which shows a quite well defined peak at $\omega \approx 40ps^{-1}$. From results in the m-frame it seems to be evident that the symmetric stretch gets two different contributions. At the lowest temperature there is one at $\omega \approx 50ps^{-1}$ and another at $\omega \approx 40ps^{-1}$. The higher frequency contribution shows a clear temperature dependence while the position of the second one seems to be independent of temperature. A fitting procedure of the line shape reveals that the low frequency contribution is located at $\omega_1 \approx 35ps^{-1}$ where the width increases from $\Delta\omega_1 \approx 30ps^{-1}$ at low temperature to $\Delta\omega_1 \approx 41ps^{-1}$ at high temperature. The high frequency part is located at $\omega_2 \approx 52ps^{-1}$ at low T and merges into the low frequency one at high temperature. As was shown in Fig.2 the energy of the hydrogen bond decreases with increasing temperature. This implies also a decreasing force constant between associated molecules, i.e. a decreasing stretching frequency, which is observed for the higher frequency peak. Thus, the origin of the temperature independent contribution of the symmetric stretch remains to be clarified.

Acknowledgements

This project was supported in part by the german-italian Vigoni program of the German Academic Exchange Service (DAAD) and the Conferenza Permanente dei Rettori delle Università Italiane (CRUI).

APPENDIX

Cluster velocity projections

In this appendix we describe the different velocity projection techniques referred to in the text. We first define two reduced velocities, the one, $u_{i,\Xi_i}^{(c)}$ in the center-of-mass (com) frame of the hydrogen bonded cluster and the other $u_{i,\Xi_i}^{(m)}$ in a central molecule frame, where the central molecule is the one which donates or accepts the bonds. In this way we write

$$u_{i,\Xi_i}^{(c)} = (\mathbf{v}_i - \mathbf{v}_{cm}^{tr})\Xi_i^{(c)} \quad (1)$$

$$u_{i,\Xi_i}^{(m)} = (\mathbf{v}_i - \mathbf{v}_1)\Xi_i^{(m)} \quad (2)$$

where

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

and $\Xi_i^{(\alpha)} = (\xi_i^{(\alpha)}, \eta_i^{(\alpha)}, \zeta_i^{(\alpha)})$ are vectors, defined as unit vectors in a local coordinate system for each molecule in the cluster (see Fig.6). In the case of the c-frame ($\alpha = c$), ξ_i points

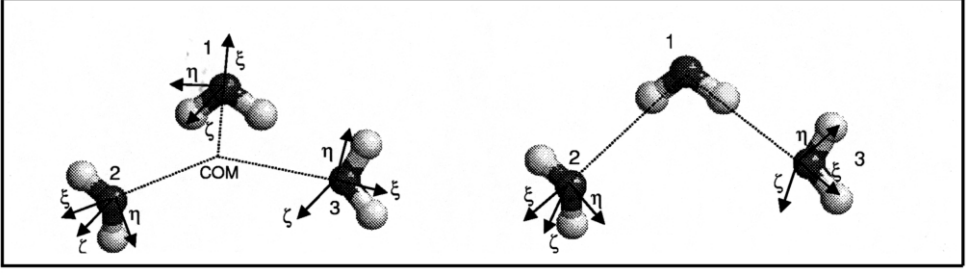


Figure 6: Illustration of the two different reference frames used in the velocity projection technique. Left: c-frame. Right: m-frame.

from the com of the cluster to the molecule, labeled with i . The vector ζ_i is perpendicular to the plane, defined by the three molecules. Finally, η_i is defined as $\eta_i = \zeta_i \times \xi_i$. In the case of the m-frame the definition for ξ_i is that it points from molecule 1 to molecule i and η_i and ζ_i are defined in line with the definition before.

We then define the following projections of the reduced velocities for the com frame

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

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

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

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

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

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

In a similar way we define the projections on the central molecule frame

$$V_1^{(m)} = \frac{1}{\sqrt{2}} \sum_{i=2}^3 u_{i,\xi}^{(m)} \quad (10)$$

$$V_2^{(m)} = \frac{1}{\sqrt{2}} (-u_{2,\xi}^{(m)} + u_{3,\xi}^{(m)}) \quad (11)$$

$$V_3^{(m)} = \frac{1}{\sqrt{2}} (u_{2,\eta}^{(m)} - u_{3,\eta}^{(m)}) \quad (12)$$

$$R_x^{(m)} = \frac{1}{\sqrt{2}} \sum_{i=2}^3 u_{i,\eta}^{(m)} \quad (13)$$

$$R_y^{(m)} = \frac{1}{\sqrt{2}} (-u_{2,\zeta}^{(m)} - u_{3,\zeta}^{(m)}) \quad (14)$$

$$R_z^{(m)} = \frac{1}{\sqrt{2}}(u_{2,\zeta}^{(m)} - u_{3,\zeta}^{(m)}) \quad (15)$$

Inspection shows that approximately $V_1^{(\alpha)}$ describes the motion of symmetric stretching, $V_2^{(\alpha)}$ an asymmetric stretching and $V_3^{(\alpha)}$ a bending mode, while $R_x^{(\alpha)}, R_y^{(\alpha)}, R_z^{(\alpha)}$ describe rotational motions of the whole cluster. Calculating the correlation functions

$$C^{(\alpha)}(t) = \langle\langle Z^{(\alpha)}(t)Z^{(\alpha)}(0) \rangle\rangle \quad (16)$$

then gives information about the approximate normal mode vibrations of the clusters in the c- and m-frame respectively ($\alpha = c, m$). Here, $Z^{(\alpha)} = V_1, V_2, V_3, R_x, R_y, R_z$ and we have used the notation $\langle\langle \dots \rangle\rangle$ for the combined averaging process over time and the number of trimers found in the liquid.

References

- [1] A. K. Soper, J. Chem. Phys., 101 (1994) 6888.
- [2] A. K. Soper, F. Bruni, and M. A. Ricci, J. Chem. Phys., 106 (1997) 247.
- [3] A. Rahman and F. H. Stillinger, J. Chem. Phys., 55 (1971) 3336.
- [4] P. G. Kusalik and I. M. Svishchev. Science, 265 (1994) 1219.
- [5] A. Geiger, F. H. Stillinger, and A. Rahman. J. Chem. Phys., 70 (1979) 4185.
- [6] G. E. Walrafen. J. Chem. Phys., 40 (1964) 3249.
- [7] G. Sutmann and R. Vallauri. J. Phys.: Condens. Matter, 10 (1998) 9231.
- [8] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma. J. Phys. Chem., 91 (1987) 6269.
- [9] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak. J. Chem. Phys., 81 (1984) 3684.
- [10] O. Steinhauser. Molec. Phys., 45 (1982) 335.
- [11] A. Luzar and D. Chandler. Nature, 379 (1996) 55.
- [12] G. Garberoglio and R. Vallauri. Phys. Rev. Lett., 84 (2000) 4878.
- [13] Ph. A. Bopp. Chem. Phys., 106 (1986) 205.