MOLECULAR PHYSICS, 1999, VOL. 97, NO. 7, 897–905

Dynamics and hydrogen bonding in liquid ethanol

L. SAIZ[1], J. A. PADRÓ[1]* and E. GUÀRDIA[2]

[1] Departament de Física Fonamental, Universitat de Barcelona, Diagonal 647,
08028 Barcelona, Spain

[2] Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya,
Campus Nord, Mòdul B4-B5, Sor Eulàlia d'Anzizu s/n, 08034 Barcelona, Spain

(*Received 28 September 1998; revised version accepted 31 May 1999*)

Molecular dynamics simulations of liquid ethanol at three temperatures have been carried out. The hydrogen bonding states of ethanol molecules have been characterized by the number of hydrogen bonds in which the molecules participate. It is observed that the mean lifetimes of molecules in each hydrogen bonding state are markedly dependent on the temperature. Moreover, molecules with one hydrogen bond are more stable when they are donors than when they are acceptors. The dependence of the reorientational correlation functions on the hydrogen bonding state of molecules has been studied carefully. The decay of these functions is slower for molecules with higher numbers of hydrogen bonds and also becomes slower as temperature decreases. The relaxation for molecules with only one hydrogen bond is faster for those acting as proton donors than for those acting as proton acceptors. Finally, the results obtained by computer simulation are compared with those from recent measurements of the frequency-dependent dielectric permittivity of liquid ethanol.

1. Introduction

A detailed knowledge of the microscopic properties of liquids such as water and alcohols is indispensable for a deep understanding of many chemical and biological processes. It is well known that properties of these liquids are influenced markedly by the existence of hydrogen bonds among their molecules. Thus, it should be useful to investigate the relationship between hydrogen bonding and molecular behaviour. The direct study of molecular motions in liquids from experiments is rather a difficult task, and computer simulation methods such as molecular dynamics (MD) [1] are used widely to obtain microscopic information. Though based on effective interaction potential models, MD provides detailed pictures of atomic behaviour which are very helpful for the development of new theories and models as well as for the reliable interpretation of the experimental data.

Dielectric properties of polar liquids are strongly related to the characteristics of the reorientational molecular motions. The frequency-dependent dielectric permittivity of water and simple liquid alcohols in the microwave and up to the far-infrared regions has been measured [2, 3]. These experimental data were analysed by fitting the results to a multiple Debye relaxation model. In the case of liquid ethanol, the best fit was obtained by considering an analytical expression with three relaxation times. However, as far as we know, there has been no detailed study of the reorientational motions of different molecules in liquid ethanol. Preliminary results were reported in an MD study of different structural and dynamic properties of this liquid [4]. The main objective of this work is to investigate the molecular reorientations in liquid ethanol at different temperatures. Special attention will be paid to the hydrogen bonds and to their influence on the characteristics of these molecular motions.

2. Computer simulation details

We carried out MD simulations of liquid ethanol at three temperatures ($T = 223$ K, 298 K and 348 K) and the corresponding experimental densities at normal pressure. The thermodynamic states of the systems and technical simulation details were the same employed in [4]. The simulated systems were made up of 125 ethanol molecules in a cubic box with periodic boundary conditions. The integration timestep was of 2.5 fs. Properties were calculated from equilibrium MD runs of 900 ps after equilibration periods of about 50 ps. To check the independence of the results on the length of the simulations, two different MD runs of 900 ps were performed at 298 K.

We adopted the OPLS force field and the molecular model developed by Jorgensen [5]. Hence, each ethanol molecule was represented by four interaction sites corresponding to the methyl (CH_3) and methylene (CH_2)

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* Author for correspondence. e-mail: joan@ffn.ub.es

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groups and the oxygen and hydrogen atoms of the hydroxyl groups. In this model, the hydrogen atoms of the CH_n groups were not considered explicitly following a united atom approach. The bond lengths and the COH and CCO bond angles were kept constant by using the SHAKE method [6]. The only intramolecular motions considered in the simulations were the rotations about the CO bond. Lennard-Jones and Coulomb terms described the interactions between sites. It is worth noting that the CH_3 site has no electric charge. The geometrical parameters of molecules plus the intermolecular and intramolecular potential functions and parameters were those of [5]. Lennard-Jones interactions were truncated at half the box length and the Ewald summation technique [1] was used to handle long range Coulomb interactions. MD simulations using this model allowed us to reproduce acceptably the main trends of the available experimental data on the microscopic behaviour of liquid ethanol [4].

3. Structure and hydrogen bonding

The properties of liquid ethanol are influenced strongly by the intermolecular hydrogen bonds present in the fluid. The adoption of a criterion to decide that one hydrogen bond is established is somewhat arbitrary since the intermolecular energy in the MD simulations is described by a continuous interaction potential. As in previous studies [4, 7], we adopted a geometric definition, i.e., we assumed that a hydrogen bond between two different molecules exists if three conditions are fulfilled [8], namely: 1, the distance between oxygen atoms is smaller than 3.5 Å; 2, the distance between the oxygen atom acting as proton acceptor (termed 'acceptor' oxygen) and the hydrogen of the molecule whose oxygen atom acts as proton donor (termed 'donor' oxygen) is smaller than 2.6 Å; and 3, the $H—O\cdots O$ angle is smaller than 30°. We chose the positions of the first minima of the radial distribution functions as cutoff for the OO and OH distances. Since the positions of the minima do not show significant changes with temperature (see [4], figure 4) we used the same cutoff values for the three temperatures. The third condition is simply a requirement for the hydrogen bond to be linear. Using this geometrical definition, we can identify the hydrogen bonds existing in a given configuration of the system.

The mean number of hydrogen bonds per molecule decreases as T increases (table 1) but it is quite close to two in all cases. This shows that linear winding chains basically constitute the structure of the liquid. Moreover there is rather a high degree of hydrogen bonding even at high temperatures. To gain an insight into the characteristics of hydrogen bonding, we defined the 'hydrogen bonding state' of a molecule according to the number n of hydrogen bonds in which it participates. The resulting averaged percentages of molecules in each hydrogen bonding state are gathered in table 1. The number of non-hydrogen bonded molecules ($n = 0$) increases with T but it is rather low even at 348 K. In all cases, the majority of the molecules are in the $n = 2$ hydrogen bonding state, i.e., molecules located in the middle of a chain. The percentage of molecules with $n = 1$ (located at the end of a chain) is lower than that of molecules with $n = 2$ for all the temperatures studied. When T increases, this difference becomes smaller since there is a decrease of the number of molecules with $n = 2$ whereas the number of molecules with $n = 1$ increases. These findings confirm that the structure of this liquid is dominated by linear winding chains of hydrogen bonded molecules. The chains are made up of a lower number of monomers at higher temperatures [4]. The percentage of molecules in the three-hydrogen bonding state is almost independent of temperature. Molecules with three hydrogen bonds should be associated with ramifications of the linear hydrogen bonded chains. According to these findings the probability of branching is independent of the length of the linear chains. The number of molecules simultaneously participating in more than three hydrogen bonds is negligible for all the temperatures investigated.

Table 1. Percentages of molecules with n hydrogen bonds and mean number n_{HB} of hydrogen bonds per molecule.

	$n = 0$	$n = 1^a$	$n = 2$	$n = 3$	n_{HB}
$T = 223$ K	0.1	4.5 (0.5)	92.0	3.4	1.99
$T = 298$ K	1.3	14.4 (4.4)	78.8	5.5	1.88
$T = 348$ K	4.2	24.5 (9.5)	66.4	4.9	1.72

[a] Values in parentheses are the percentages of single hydrogen bonded acceptor molecules.

In order to analyse in more detail the hydrogen bond characteristics of molecules with $n = 1$, we have determined whether the oxygen of these molecules acts as a proton donor or proton acceptor in the corresponding hydrogen bond (figure 1). We have observed that the number of donor single hydrogen bonded molecules is notoriously higher than that of acceptors (table 1). This difference should be associated with the presence of branching in the chains since in a linear chain without ramifications one of the molecules at the end of the chain is hydrogen bonded as a donor whereas the other molecule at the end of the chain is hydrogen bonded as an acceptor.

4. Hydrogen bonding state autocorrelation functions

We have analysed the survival probability of particles in the different hydrogen bonding states by a method analogous to that proposed by Rapaport [9] to estimate

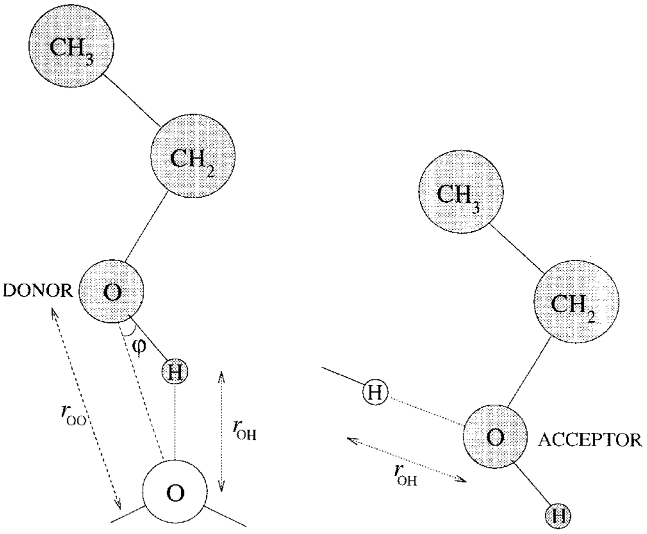

Figure 1. Hydrogen bonded ethanol molecules whose oxygen acts as proton donor (left) and proton acceptor (right).

the lifetime of hydrogen bonds. This procedure has been also used in other MD studies [7, 10] of hydrogen bonded liquids. During the simulations we have determined the stochastic variable $\eta_C^{(n)}(t)$ defined as follows:

$$\eta_C^{(n)}(t) \begin{cases} = 1 & \text{if a molecule which is in the } n \text{ hydrogen bonding state at instant 0 remains in the same state through the interval 0 to } t, \\ = 0 & \text{otherwise.} \end{cases}$$

Thus, for each hydrogen bonding state ($n = 0, 1, 2, 3$), we have calculated the following normalized hydrogen bonding state autocorrelation functions

$$C_C^{(n)}(t) = \frac{\langle \eta^{(n)}(t)\eta^{(n)}(0)\rangle}{\langle \eta^{(n)}(0)\eta^{(n)}(0)\rangle}. \qquad (1)$$

The $C_C^{(n)}(t)$ functions can be associated with the process of making or breaking single hydrogen bonds. The decay of these functions become sharper as T increases (figure 2) which corroborates that the hydrogen bonding states are less stable at higher temperatures. Moreover, the decay of the $C_C^{(n)}(t)$ functions depends on the hydrogen bonding state of the molecules. As the results at 298 K in figure 3 show, for $n = 0$ and $n = 3$ the decays are faster than for $n = 1$ and $n = 2$. This behaviour is consistent with the larger percentage of molecules in the states $n = 1$ and $n = 2$, and it has been observed also at the other two temperatures. It is interesting to point out that the initial decay of $C_C^{(1)}(t)$ is faster than that of $C_C^{(2)}(t)$, whereas for longer times the situation is the opposite and the tail of the former is more persistent than that of the latter. This should be attributed to the different ways followed by molecules with $n = 1$ and $n = 2$ to change their respective hydrogen bonding states, i.e., with a high probability the former will be hydrogen bonded to another molecule whereas the latter will break one of their initial hydrogen bonds. The fast initial decrease followed by a rather slow decay of $C_C^{(1)}(t)$ suggests that the formation of a hydrogen bond may be easy when there is some neighbouring molecule able to be hydrogen bonded but otherwise rather difficult. The more regular decay of $C_C^{(2)}(t)$ indicates that the probability of breaking a hydrogen bond is to a large measure independent of the location of the neighbouring molecules, and therefore almost constant with time.

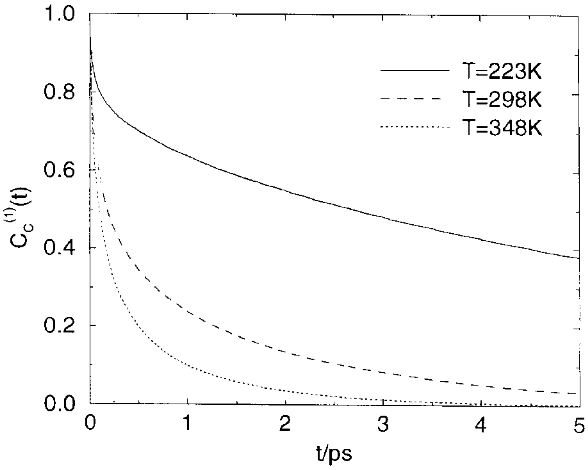

Figure 2. Hydrogen bonding state correlation functions ($C_C^{(n)}(t)$) for molecules in the $n = 1$ state.

In order to estimate the lifetimes $\tau_C^{(n)}$ of the different hydrogen bonding states, the longer time regions of the $C_C^{(n)}(t)$ functions have been fitted to exponential functions

$$C_C^{(n)}(t) \approx \exp(-t/\tau_C^{(n)}). \qquad (2)$$

As may be observed in the logarithmic plots of figure 4, the resulting $C_C^{(n)}(t)$ curves are approximated well by exponential forms. We fitted the $C_C^{(n)}(t)$ values in different time intervals between 0.5 ps and 5 ps and the resulting $\tau_C^{(n)}$ values did not show significant discrepancies. The $\tau_C^{(n)}$ results are gathered in table 2. The changes of $\tau_C^{(n)}$ with T and n are consistent with the decays of the $C_C^{(n)}(t)$ functions commented upon above. So, $t_C^{(1)} > t_C^{(2)}$ despite the initial decay of $C_C^{(1)}(t)$ is clearly than that of $C_C^{(2)}(t)$. The small values of $\tau_C^{(0)}$ and $\tau_C^{(3)}$ in relation to $\tau_C^{(1)}$ and $\tau_C^{(2)}$ reflect the low probability that molecules remain non-hydrogen bonded for large periods of time and the high probability that one of the three hydrogen bonds of molecules in the $n = 3$ state will be broken after a short period of time, respectively. This last finding shows the instability of branching.

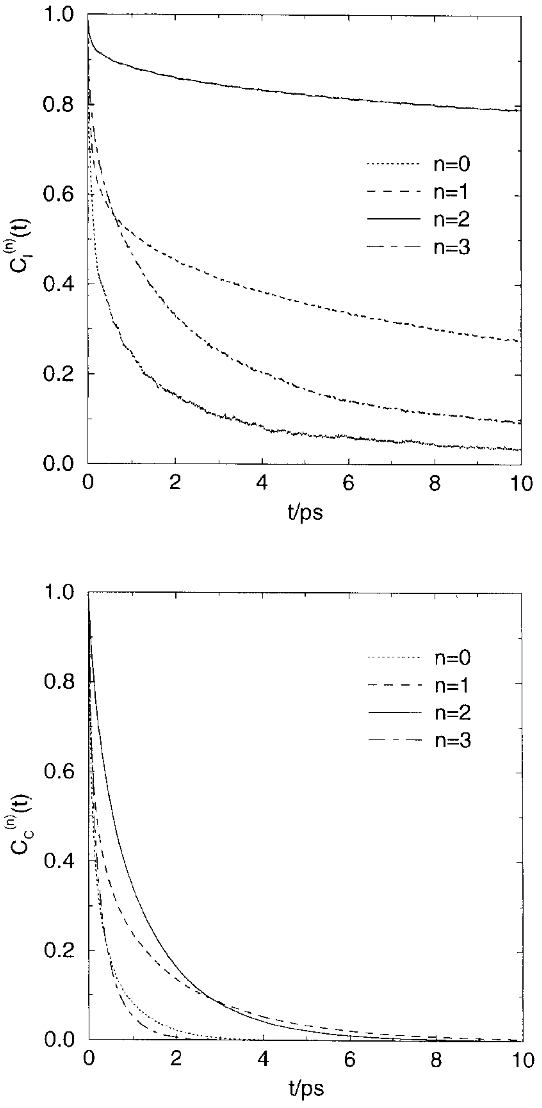

Figure 3. Hydrogen bonding state correlation functions ($C_C^{(n)}(t)$ and $C_1^{(n)}(t)$) at $T = 298$ K.

Earlier MD studies of the hydrogen bond dynamics in liquid alcohols indicated that there is a high probability that broken hydrogen bonds will quickly be reformed [7]. Thus, a great part of the hydrogen bonding state changes will be temporary and molecules will return to their earlier states after short intervals of time. This fact encouraged us to calculate the variable $\eta_l^{(n)}(t)$, defined as follows

$$\eta_l^{(n)}(t) \begin{cases} = 1 & \text{if a molecule that was in the hydrogen bonding state } n \text{ at instant 0 is in the same state at time } t, \text{ independently of whether or not its hydrogen bonding state has changed between 0 and } t, \\ = 0 & \text{otherwise.} \end{cases}$$

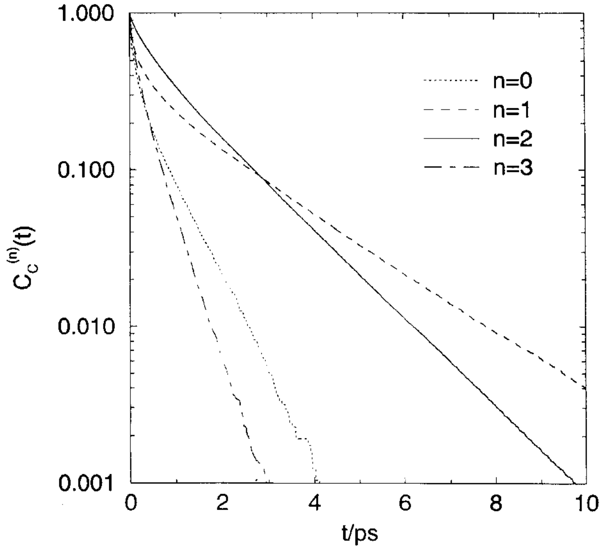

Figure 4. Semilog plots of the hydrogen bonding state correlation functions ($C_C^{(n)}(t)$) at $T = 298$ K.

Table 2. Lifetimes (in ps) of the n hydrogen bonding states.

	$\tau_1^{(0)}$	$\tau_C^{(0)}$	$\tau_1^{(1)a}$	$\tau_C^{(1)a}$	$\tau_1^{(2)}$	$\tau_C^{(2)}$	$\tau_1^{(3)}$	$\tau_C^{(3)}$
$T = 223$ K	3.5	—	42.9 (7.3)	7.3 (0.3)	6.1	5.4	12.7	1.4
$T = 298$ K	2.6	0.7	7.4 (2.3)	1.9 (0.4)	4.1	1.4	3.0	0.5
$T = 348$ K	2.3	0.7	3.3 (1.5)	1.0 (0.3)	2.3	0.8	1.8	0.2

[a] Values in parenthesis correspond to the single hydrogen bonding acceptor states.

The corresponding hydrogen bonding state autocorrelation functions $C_1^{(n)}(t)$ were determined by assuming an equation analogous to (1). Lifetimes $\tau_1^{(n)}$ were computed by fitting the longer time decays of $C_1^{(n)}(t)$ to exponential functions. However, unlike $C_C^{(n)}(t)$, the $C_1^{(n)}(t)$ functions do not tend to zero as $t \to \infty$, but to an equilibrium value. Thus, we have assumed that

$$C_1^{(n)}(t) \approx \exp(-t/\tau_1^{(n)}) + A, \qquad (3)$$

where A is a constant. The resulting $C_1^{(n)}(t)$'s cannot be changed accurately to single exponential functions, and the $\tau_1^{(n)}$ values show a notable dependence on the time interval considered for the fitting. This is consistent with earlier findings for liquid water where it was observed that functions analogous to $C_1^{(n)}(t)$, but for liquid water, also exhibit non-exponential behaviour which is governed mainly by diffusion [11]. For the sake of comparison we have obtained averaged values of $\tau_1^{(n)}$ for each hydrogen bonding state and temperature by considering the same time interval in all cases. The $\tau_1^{(n)}$ values given in table 2 correspond to fittings in a time interval between 1 ps and 5 ps. The $C_1^{(n)}(t)$ functions provide information on the 'survival probability' of hydrogen bonding states overlooking the fast processes of making and breaking single hydrogen bonds. $\tau_1^{(n)}$ are characteristic times for processes that involve a definitive change in the hydrogen bonding state of molecules (a kind of hydrogen bonding lifetime over a rather large timescale). As expected, the decay of $C_1^{(n)}(t)$ is markedly slower than that of $C_C^{(n)}(t)$ for the same hydrogen bonding state (figure 3). Accordingly, the values of $\tau_1^{(n)}$ are higher than the corresponding $\tau_C^{(n)}$ values. However, the qualitative changes of $\tau_1^{(n)}$ with T and n are analogous to those of $\tau_C^{(n)}$. So basically the comments in the earlier discussion on the $C_C^{(n)}(t)$ and $\tau_C^{(n)}$ results can be applied to those for $C_1^{(n)}(t)$ and $\tau_1^{(n)}$. It should be noted that the lifetimes for $n = 1$ are more strongly dependent on T than are those for the other states.

We want to emphasize the significant differences between the results for the single hydrogen bonding states when acceptor and donor molecules are analysed separately. Both $C_C^{(1)}(t)$ and $C_1^{(1)}(t)$ for the acceptors show decays which are notably faster than the corresponding ones for the donors. Moreover, the results at the three temperatures are very close for the former, whereas they show noticeable differences for the latter (figure 5). These findings show that the probability that an acceptor molecule forms a second hydrogen bond is higher than that for a donor molecule. The facility of acceptor molecules to participate in a new hydrogen bond may be attributed to the fact that they have a free hydrogen atom with high mobility that can be hydrogen bonded readily. It should be noted that the results for the donors are almost the same as those for all molecules at $n = 1$ (see figures 2 and 5). For the sake of brevity the lifetimes for the donors have not been included in table 2. The small influence of the acceptors on the total $C_C^{(1)}(t)$ and $C_1^{(1)}(t)$ functions and corresponding lifetimes is due to two factors: on the one hand, the great majority of single hydrogen bonded molecules are donors, and on the other hand, the slower dynamics of the donors are dominant over longer times.

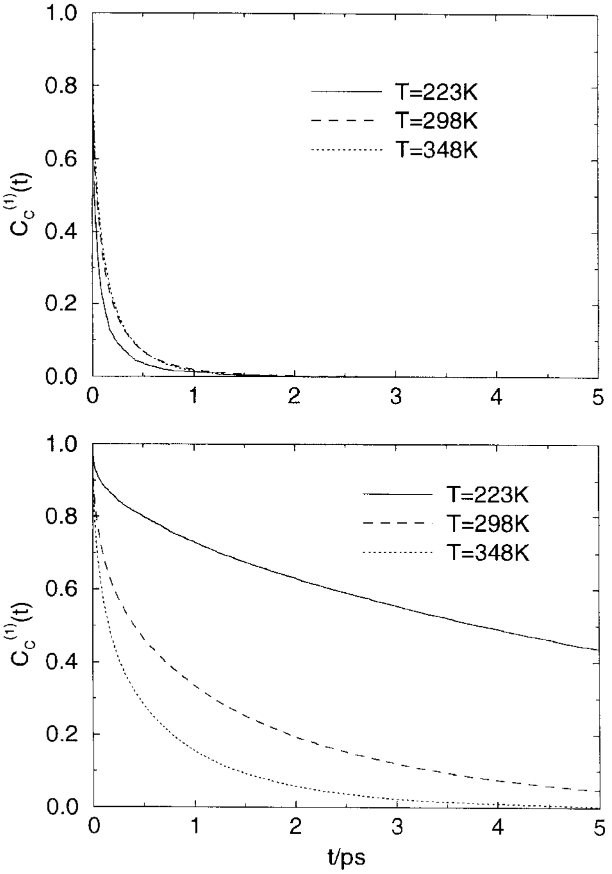

Figure 5. Hydrogen bonding state correlation functions ($C_C^{(n)}(t)$) for molecules participating in a single hydrogen bond as acceptor (upper) and donor (lower).

Table 3. Reorientational times (in ps).

	$^R\tau_P^{(0)}$	$^R\tau_P^{(1)}$	$^R\tau_C^{(1)}$	$^R\tau_P^{(2)}$	$^R\tau_C^{(2)}$	$^R\tau_P^{(3)}$	$^R\tau_C^{(3)}$	$^R\tau$
$T = 223$ K	—	16	13	85	110	53	350	75
$T = 298$ K	6	11	6	22	45	17	35	19.5
$T = 348$ K	6	7	4	9.5	19	9	—	9

5. Reorientational motions

Reorientational motions of the molecular dipole moments have been studied by calculating the time autocorrelation functions $R(t)$

$$R(t) = \langle \hat{\mu}(t) \cdot \hat{\mu}(0) \rangle \tag{4}$$

where $\hat{\mu}(t)$ is a unitary vector along the molecular dipole moment. The averaged $R(t)$ functions for all the molecules of the three systems have been determined during the MD simulations. After the initial decay, the $R(t)$ functions show slow exponential behaviour. A quantitative estimation of the reorientational times has been obtained by fitting the long-term part of the $R(t)$'s to exponential functions

$$R(t) \approx \exp(-t/{}^R\tau). \tag{5}$$

The results in table 3 show that reorientational motions depend significantly on temperature, and the reorientational times (${}^R\tau$) become shorter as T increases.

It is natural to expect that the reorientational motions of a given molecule depend on the number of hydrogen bonds in which it participates. In order to analyse this dependence we have calculated the reorientational time autocorrelation functions corresponding with those molecules that for a given configuration ($t = 0$) are in the same hydrogen bonding state. These functions will

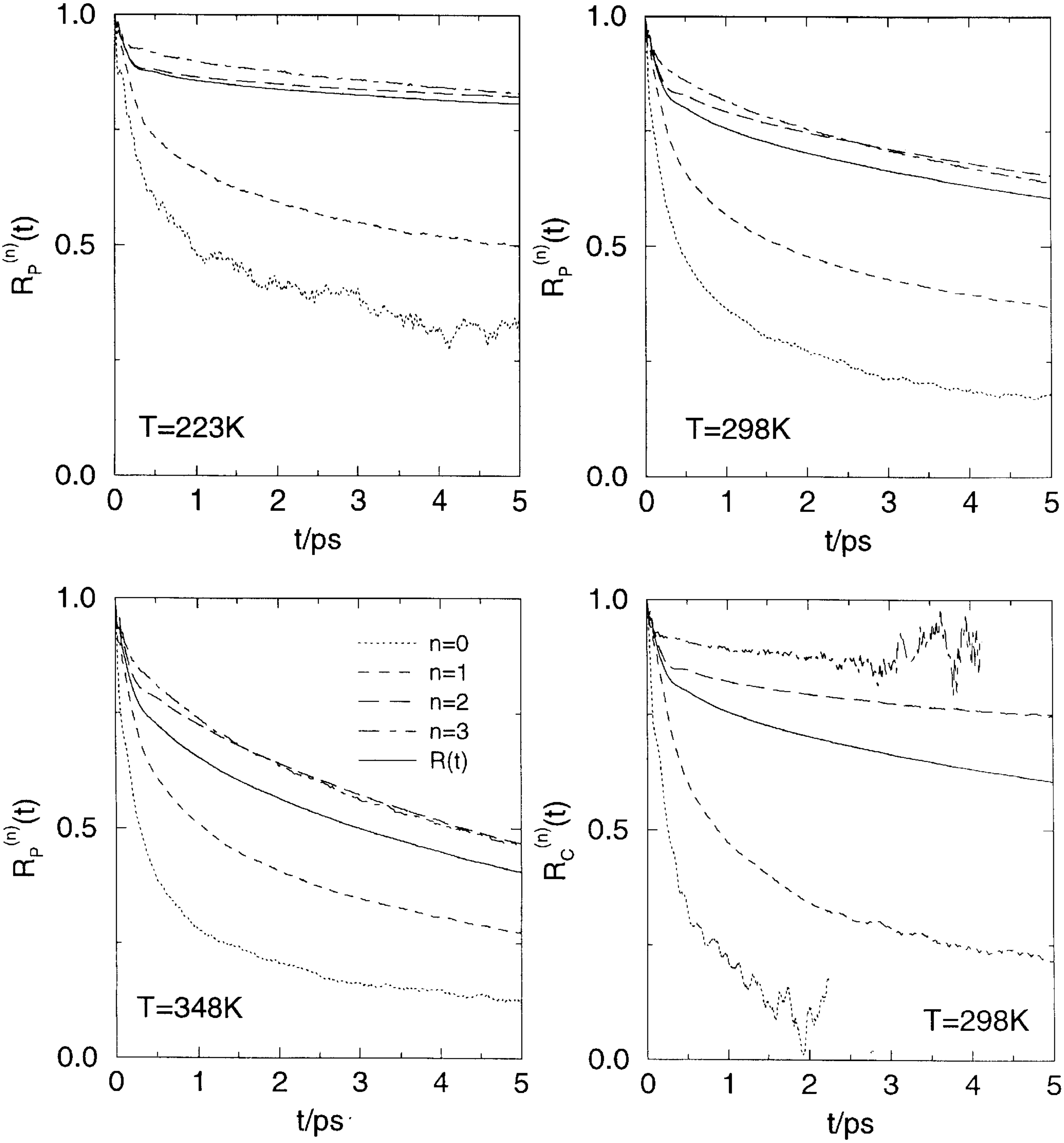

Figure 6. Reorientational correlation functions: $R_P^{(n)}(t)$ at different temperatures and $R_C^{(n)}(t)$ at $T = 298$ K. $R(t)$ are the functions corresponding to all the molecules in the system.

be termed $R_P^{(n)}(t)$ (where $n = 0, 1, 2, 3$). The corresponding correlation times ${}^{R}\tau_P^{(n)}$ have been obtained by fitting the long term part of the $R_P^{(n)}(t)$ functions (after 1ps, approximately) to exponential functions. As with $R(t)$, the $R_P^{(n)}(t)$ functions for each n value decay faster as T increases (see figure 6 and table 3). It should be noted that both $R_P^{(n)}(t)$ and ${}^{R}\tau_P^{(n)}$ at a fixed T change significantly with n. This corroborates that molecular reorientations are strongly dependent on the hydrogen bonding state of a molecule. Nevertheless, it must be pointed out that the $R_P^{(n)}(t)$ functions were determined for all molecules which are in the n hydrogen bonding state at $t = 0$, but frequently this state changes during the time required for the calculation of $R_P^{(n)}(t)$. So often the length of $R_P^{(n)}(t)$ functions is longer than the hydrogen bonding state lifetimes, especially if the $\tau_C^{(n)}$ lifetimes are considered. For this reason we also determined the reorientational correlation functions restricted to the period of time for which the molecules remain in their initial hydrogen bonded state. The resulting functions and corresponding reorientational times will be termed $R_C^{(n)}(t)$ and ${}^{R}\tau_C^{(n)}$, respectively. $R_C^{(n)}(t)$ and ${}^{R}\tau_C^{(n)}$ may be unambiguously associated with a given n hydrogen bonding state but the $R_C^{(n)}(t)$ functions for hydrogen bonding states with low lifetimes only may be calculated for short periods of time, and then the associated reorientational times cannot be determined accurately. The calculation of ${}^{R}\tau_C^{(n)}$ is especially difficult in the case of minority hydrogen bonding states ($n = 0$) and high temperatures. The estimated statistical uncertainties in the ${}^{R}\tau_P^{(n)}$ and ${}^{R}\tau_C^{(n)}$ values reported in table 3 are about 10% and 15%, respectively (in the case of ${}^{R}\tau_C^{(3)}$ about 30%). It should be noted that despite some quantitative discrepancies the $R_C^{(n)}(t)$ functions are similar to the corresponding $R_P^{(n)}(t)$ functions and show the same qualitative dependence on T and n (figures 6, 7 and table 3). This shows that, in general, changes in the hydrogen bonding state of some molecules during the calculation of the $R_P^{(n)}(t)$ functions have only a weak influence on the results, although there are some exceptions, such as the ${}^{R}\tau_P^{(3)}$ results commented upon in the next paragraph.

The decay of the reorientational correlation functions become slower and the reorientational times larger as the number of hydrogen bonds increases (figure 6). However, there is a deviation from this rule (i.e., ${}^{R}\tau_P^{(3)} < {}^{R}\tau_P^{(2)}$) which should be attributed to the fact the ${}^{R}\tau_P^{(3)}$ values are much larger than the lifetimes of molecules in the $n = 3$ state. So frequently the ${}^{R}\tau_P^{(3)}$ reorientational times are calculated for molecules that initially form 3 hydrogen bonds but during a great part of the time required for the calculation of $R_P^{(3)}(t)$ form only 2 hydrogen bonds. This is consistent with the very high values of ${}^{R}\tau_C^{(3)}$. The $R(t)$ and ${}^{R}\tau$ findings corresponding to all the molecules in the system are intermediate between those for $n = 1$ and $n = 2$ but closer to the second (figure 6), which is in accordance with the fact that $n = 2$ is the majority hydrogen bonding state. As could be expected, both the $R_P^{(n)}(t)$ and $R_C^{(n)}(t)$ functions for a given n hydrogen bonding state decay more slowly as T decreases (figure 7).

It is interesting to analyse in detail the behaviour of the $R_C^{(1)}(t)$ functions for very short times (figure 8). After a fast initial inertial decay these functions show an oscillation with a characteristic time of 0.05 ps. This feature is associated with the molecular librations of the COH plane around the CO bond. It is worth noting that the molecular dipole moment of our ethanol molecules is located within the COH plane and its module is constant, i.e., independent of the molecular conformation, since there is no charge placed in the methyl group in the force field used in this work. As observed in figure 8, the characteristics of these librational motions depend on the role that the corresponding molecule plays in the hydrogen bond. Thus, for functions corresponding to molecules whose oxygen acts as a proton donor the

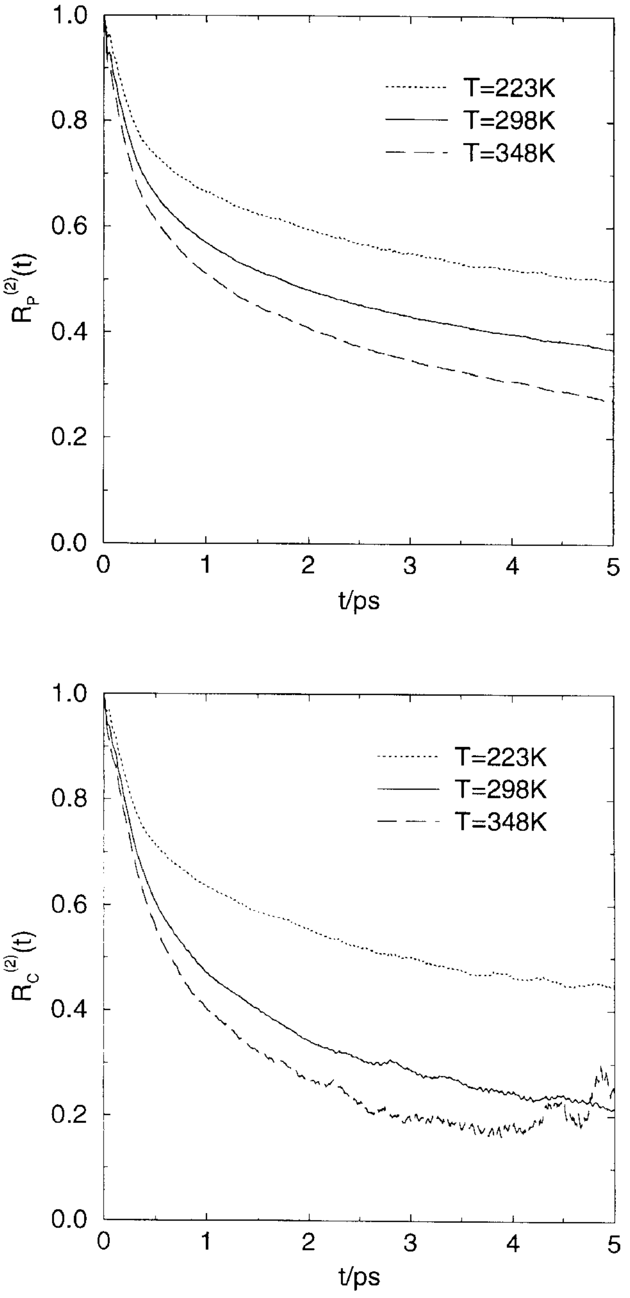

Figure 7. Reorientational correlation functions ($R_P^{(n)}(t)$) for molecules in the $n = 2$ hydrogen bonding state.

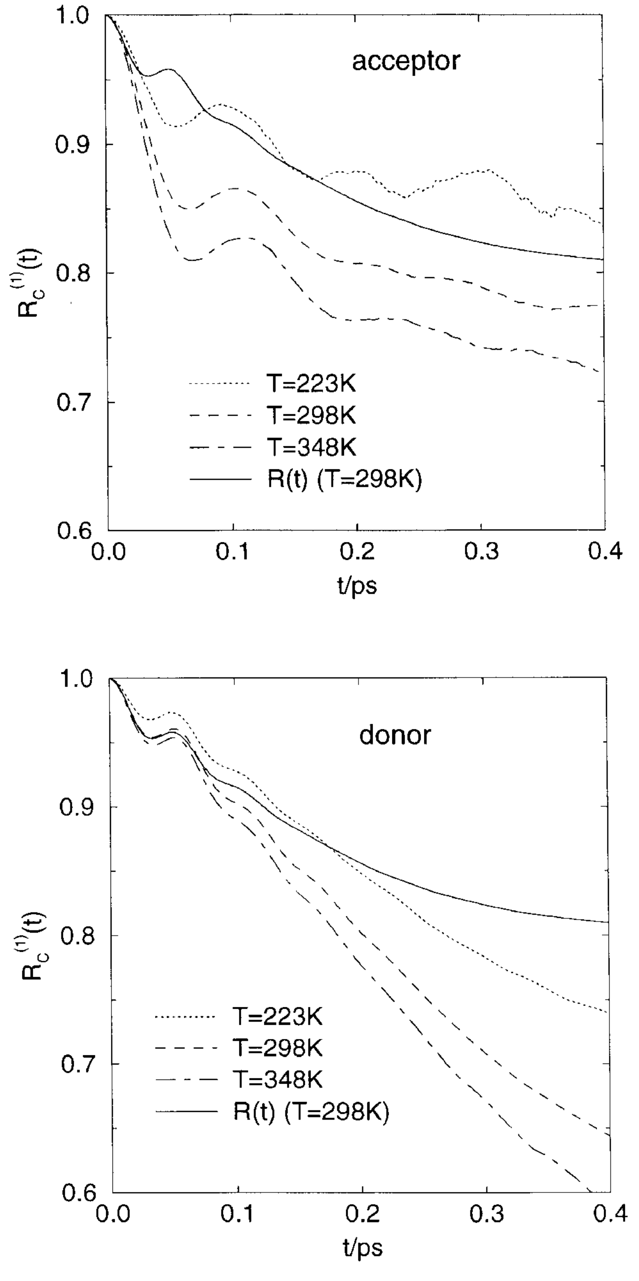

Figure 8. Short time reorientational correlation functions ($R_C^{(n)}(t)$) for molecules participating in a single hydrogen bond as acceptor (upper) and donor (lower). $R(t)$ are the functions for all the molecules in the system.

characteristic time of the oscillation is approximately the same as that for the single hydrogen bonded molecules. However, in the case of molecules whose oxygen acts as proton acceptor the characteristic time of the oscillation is about 0.1 ps (this is also the characteristic time found for molecules not hydrogen bonded). The similarity between the functions corresponding to molecules whose oxygen acts as proton donor and those for all molecules forming a single hydrogen bond is consistent with the fact that the former are a majority. It should be emphasized that the characteristic times of these librational oscillations for both donors and acceptors are independent of the temperature (at least at the interval analysed in this work). Another difference between the $R_C^{(1)}(t)$ functions for molecules whose oxygen acts as proton donor and those for molecules whose oxygen acts as proton acceptor is that the relaxation of the former after the librational oscillation ($t > 0.2$ ps) is faster than that of the latter (figure 8).

6. Conclusion

As was stated in section 1, the frequency-dependent complex permittivity of liquid ethanol at 298 K in the microwave and up to the infrared regions has been measured and the resulting data fitted to a triple Debye model. The relaxation times obtained by Barthel *et al.* [2] were $\tau_1 = 163$ ps, $\tau_2 = 8.97$ ps and $\tau_3 = 1.81$ ps whereas Kindt and Schmuttenmaer [3] obtained significantly faster relaxation times for the second and third Debye processes, $\tau_1 = 161$ ps, $\tau_2 = 3.3$ ps and $\tau = 0.22$ ps. Barthel *et al.* [2] connected τ_3 to the dynamics of hydrogen bonding and suggested that it may be associated with flipping motions of 'free' OH groups between two acceptor sites and/or with the breaking and reforming of a given hydrogen bond in a translational motion. The same authors connected t_2 to the reorientational motions of molecules located at the end of the hydrogen bonded chains. We should like to point out that the order of magnitude of the experimental relaxation times is compatible with our reorientational times. Moreover, recent experimental results at different temperatures [12] have shown that the values of the three relaxation times decrease significantly as T increases, which is consistent with the results in this paper. Nevertheless, MD findings show that there is a continuous distribution of both hydrogen bonding states lifetimes and reorientational times in the system. Then, despite characteristics like the mean reorientational times being markedly dependent on the hydrogen bonding state of the molecule considered, it is difficult to attribute accurate relaxation times to specific molecular processes or to molecules with given characteristics. According to our results the triple Debye model is a rather weak approach to the microscopic behaviour of hydrogen bonded liquids. Therefore more accurate fittings of refined experimental data for the dielectric permitivity at low frequencies (FIR) should be attempted in order to obtain a continuity of relaxation times as suggested by MD findings.

Financial support of DGICYT (Grant No. PB96-0170-C03) and CIRIT (Grant 1997SGR-00149) is gratefully acknowledged.

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