

Distributions of Hydrogen Bond Lifetimes in Instantaneous and Inherent Structures of Water

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Dedicated to Prof. Dr. Alfons Geiger on the occasion of his 65th birthday

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Various distribution functions of hydrogen bond lifetimes, used to describe the dynamics of breakage and formation of these bonds are calculated for a molecular dynamics model of water of 3456 molecules at 310 K. Quenched (inherent) structures are derived from instantaneous MD structures. Comparing the distribution functions from I and Q structures allows interpreting their characteristic features. The sharp peak at ~15 fs, which prevails in the most frequently used distributions, is ascribed to short-lived “false” H bonds which results from violations of hydrogen bonding criteria induced by dynamic intermolecular vibrations of molecules. A special type of distribution, proposed earlier [34], contains information not only on dynamics, but on *true*, or *random*, breaking of hydrogen bonds. The distributions reveal four different types of characteristic times which reflect different sides of H bond dynamics.

1. Introduction

The lifetime of hydrogen bonds is a significant feature of the dynamics of H-bonds in liquids. The statistical properties of this characteristic can be described by a variety of functions. Stillinger [1] has proposed to use for this aim the language of correlation functions, which was realized first in a computer simulation of water by Rapaport [2]. Later Tanaka et al. [3] and Geiger et al. [4] introduced different distribution functions of H-bond lifetimes and since then over 30 papers [5–34] have been published devoted to this problem, based on molecular dynamics simulations both of water and other systems with hydrogen bonds [12,

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14] under different thermodynamic conditions. Nevertheless, the general pattern of hydrogen bond breaking rests quite unclear. There are several reasons for this situation. First, different authors used different functions, and it is often impossible to understand just what function was used by a particular author. In order to clarify this question A. Luzar [16] has attempted to find interrelations between different types of distribution functions. We continued her analysis in [34] and introduced a novel type of distribution function (see Sect.1) which, in our opinion, reflects the main peculiarities of the H-bond dynamics at larger timescales.

A serious problem consists in the very concept of hydrogen bond breaking. The present molecular dynamics simulations operate with the total pair interaction potential, without a separate hydrogen bond interaction contribution. A distinction between the existence and non-existence of an H-bond can be made by special criteria (e.g., geometric and/or energetic) which are always of conventional character. Therefore a problem arises how “true” breaks of H-bonds can be distinguished from “false” ones, which result from violation of the H-bond criteria because of intermolecular librational or stretching motions. One approach to this matter was proposed by Rapaport [2], who distinguished ‘continuous’ and ‘intermittent’ distribution functions. Another way is to study the H-bond dynamics in inherent (hidden) structures in which the thermal chaos is quenched (see the review [35]). This idea was used rarely, for example in [6, 9, and 11], where the configurations were averaged over a certain time interval, realizing one type of inherent structures, the so-called V structure. Here we investigate in detail the influence of a transition from the instantaneous to the inherent structure on the dynamics of the H-bond breakage.

Thus, in section 1 we consider various types of distribution functions, describing the dynamics of breakage and formation of hydrogen bonds, and establish interrelations between them. In section 2 a classification of different situations of the existence of hydrogen bonds is given; section 3 contains short information on the computer simulation procedure, and in section 4 the results of the calculation of distribution functions for one water model are presented.

2. Lifetime distribution functions

Various types of distribution functions for the lifetime of hydrogen bonds are systematized in [16]. Here we consider shortly (without derivation of formulae) three of them, which were analyzed in our article [34], where one can find the details.

At first we introduce the lifetime distribution, which measures the probability, that an H-bond, which existed at the moment $t = 0$, will exist all times up to time t , and break at t . This distribution we denote $P_A(t)$ (index “A” means *after*), denoted as $p(t)$ in [16]. Note that the H-bond may have existed here at $t < 0$. A more comprehensive information gives the distribution function of the *total* lifetime of hydrogen bonds, $P_T(t)$, which measures the probability that an

observed H-bond exists for a time t from the moment of its appearance up to the moment of its (first) breaking. There are two variants for the determination of this distribution function. We can count the *number* of H bonds which have a total lifetime t in a trajectory of sufficiently long duration. The fraction of these bonds determines the distribution function $P_{TT}(t)$ that can be named the probability for the total lifetime of an H-bond *along the trajectory*. Alternatively, we can sum up the lifetimes of the H-bonds in a given configuration, which have a total lifetime t (rather than counting the number of such bonds). This gives the probability distribution $P_{TC}(t)$ of the total lifetime of H-bond *in a configuration*. In other words, in the distribution $P_{TT}(t)$ we calculate the number of pairs of molecules which had an un-interrupted H-bond during the time t , whereas in the distribution $P_{TC}(t)$ – the total time, which was taken by such pairs. It is obvious that $P_{TC}(t) \propto t P_{TT}(t)$. Considering that all distributions $P_A(t)$, $P_{TT}(t)$, and $P_{TC}(t)$ are normalized to unit area, we get

$$P_{TC}(t) = tP_{TT}(t) / \langle \tau_{TT} \rangle, \quad (1)$$

where

$$\langle \tau_{TT} \rangle = \int_0^{\infty} tP_{TT}(t) dt \quad (2)$$

or

$$1 / \langle \tau_{TT} \rangle = \int_0^{\infty} \frac{P_{TC}(t)}{t} dt. \quad (2a)$$

The distribution $P_{TT}(t)$ was calculated by many authors, e.g., in [3,4,16]. The distribution $P_{TC}(t)$ was introduced for the first time, as far as we know, by us in [34].

There are some relations between these distributions (see [16, 34]):

$$P_A(t) = \int_t^{\infty} P_{TC}(\tau) \frac{d\tau}{\tau}, \quad (3)$$

$$P_{TC}(t) = -t(dP_A / dt), \quad (4)$$

$$P_A(0) = 1 / \langle \tau_{TT} \rangle \quad (5)$$

$$\frac{1}{\langle \tau_{TT} \rangle} P_{TT}(0) = \frac{P_{TC}(t)}{t} \Big|_{t=0} = \frac{dP_{TC}}{dt} \Big|_{t=0} = -\frac{dP_A}{dt} \Big|_{t=0}. \quad (6)$$

In addition to (2) one can introduce other average time characteristics:

$$\langle \tau_A \rangle = \int_0^{\infty} tP_A(t) dt, \quad (7)$$

$$\langle \tau_0 \rangle = 1 / P_{TT}(0). \quad (8)$$

As regards the average time

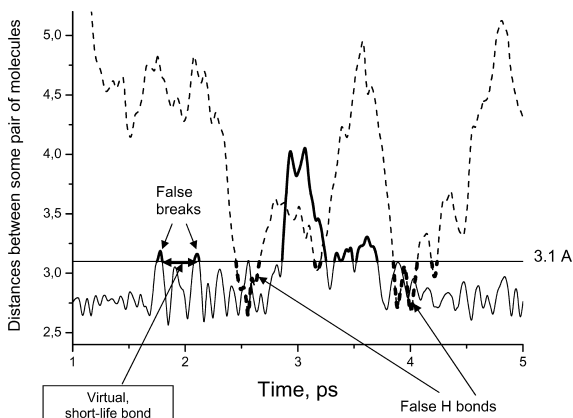


Fig. 1. Typical time dependence of the distance R_{OO} of a molecule B (full line) and a molecule C (dashed line) from molecule A . Heavy lines show trajectory portions that violate the criterion of hydrogen bonding, assumed here as $R_{OO} < 3.1 \text{ \AA}$.

$$\langle \tau_{TC} \rangle = \int_0^{\infty} t P_{TC}(t) dt, \quad (9)$$

it is not a new parameter because

$$\langle \tau_{TC} \rangle = 2 \langle \tau_A \rangle.$$

Hence, we have three independent average time characteristics: $\langle \tau_A \rangle$, $\langle \tau_{TT} \rangle$, and $\langle \tau_0 \rangle$, which reflect different aspects of the dynamics of breaking and reforming of the hydrogen bonds.

3. Definition of hydrogen bonding

In this paper we used a geometric criterion for the existence of an H-bond. Two molecules A and B are considered to be hydrogen bonded if the distance R_{OO} between their oxygen atoms is less than $R_{OO}^* = 3.3 \text{ \AA}$ and the oxygen-hydrogen distance $R(O \dots H)$ is less than $R_{OH}^* = 2.45 \text{ \AA}$. Criteria of such kind, with fixed cutoff values R_{OO}^* and R_{OH}^* give, certainly, an artificial, conventional definition of an H-bond, which does not distinguish different situations in breaking and reforming the H-bonds (Fig. 1). In the course of intermolecular vibrations, the distance R_{OO} may “incidentally”, for 10–20 fs, exceed the cutoff value (see Fig. 1 near $t = 2 \text{ ps}$) without any distortion in the form of vibration. There is no reason to consider such a bond as disrupted. This situation can be called a *spurious* or *false breaking* of the H-bond. Between false breakings there may appear short-lived H-bonds, called by us *virtual* hydrogen bonds.

The second situation is when another molecule C , which had initially no H-bond with molecule A , approaches it incidentally, as a result of diffusive motion,

for a short time to a distance $R_{OO} < R_{OO}^*$ (see bold dashes in Fig. 1 near $t = 2.5$ and 4 ps). This situation can be called *spurious* or *false formation* of an H-bond (or *false H-bond*). The intervals of the existence of such “bonds” $A...C$ are obviously of a shorter time than the duration of the virtual bonds in the first situation.

And, finally, the third situation – the *genuine* or *true breaking* of hydrogen bonds. The H-bond of molecule A with a certain molecule B experiences a *true* breaking if molecules A and B separate for a time noticeably exceeding the time of a single oscillation (although later they may join again). The H bond $A...B$ switches, as a rule, to a new H-bond $A...D$ with some other molecule D . A true breaking of an H-bond (here temporary) is shown in Fig. 1 near $t = 3$ ps.

The two first situations, i.e., false breaking and false bond, relate to the behavior of a fixed pair of H bonded molecules. It is of *dynamical* character, although irregular, as the motion of this pair of molecules $A...B$ is disturbed by thermal fluctuations of the surrounding. By contrast, the true breaking of the bond, i.e. switching the bond $A...B$ over to the bond $A...D$ at a certain moment, is *random*, in the sense that the moment of switching is not controlled by the dynamics of the bond $A...B$ but is the result of complex collective motions of the whole system. In the first approximation the switchover of bonds can be taken as instantaneous, jump-like, which is commonly assumed in theoretical models of water dynamics [36, 37], though the detailed molecular dynamics speaks for “slow jumps” [38].

When the breaking of a hydrogen bond is mentioned, *true breaking* is meant usually. In computer experiments, however, due to the used conditional criteria for the existence of an H-bond, true breaking is inevitably mixed with false breaking and false bonds. We must determine first of all in what way these situations are manifested in different distribution functions of the hydrogen bond lifetime.

True, i.e., random, breaking of hydrogen bonds is comparable to random collisions in gases, and the lifetime distribution of true hydrogen bonding is analogous to the distribution of the free path time. In gas-kinetic theory exclusively the distribution function $P_A(t)$ is considered:

$$P_A(t) = (1/\tau_0)\exp(-t/\tau_0), \quad (10)$$

where τ_0 is the average free path time. Therefore, according to formulae (4) and (1) it follows that in gases

$$P_{TC}(t) = (t/\tau_0^2)\exp(-t/\tau_0), \quad (11)$$

$$P_{TT}(t) = 1/\tau_0 \exp(-t/\tau_0) \quad (12)$$

with $\langle \tau_A \rangle = \langle \tau_{TT} \rangle = 1/2 \langle \tau_{TC} \rangle = \tau_0$. Thus the free path time corresponds to the *total* lifetime of the H-bond, and instantaneous collisions correspond to the breaking of the H-bond for an infinitely small time. The fraction of such infinitely small sections on the trajectory is $P_{TT}(0)$ in terms of the distribution functions we have introduced. On the other hand this is simply the frequency of

collisions $1/\tau_0$. Therefore, $P_{TT}(0) = 1/\tau_0$ in full compliance with (12). The difference of $P_{TT}(0)$ from zero in water is indicative of the presence of *true* breakings of hydrogen bonds that do not result from the violation of the artificial criteria for H-bonds. Then $P_{TT}(0)$ provides a measure for such breakings. On the other hand, the violation of the H-bond criteria as result of intermolecular dynamics leads to $P_{TT}(0) = 0$, because “most bonds form through libration like motion which makes immediate rupture unlikely” [16].

4. Computer simulation details

All distribution functions were calculated on the basis of a molecular dynamics model for water consisting of $N = 3456$ molecules at temperature 310 K and density 1 g/cm^3 . We used the interaction potential of Poltev and Malenkov [39, 21] which is analogous to the well-known three center SPC potential. The time step of the MD simulation was 2 fs. Every 4 fs we specified the ‘configuration’, i.e., a set of all pairs of molecules with an indication whether they form a hydrogen bond or not. These configurations describe the instantaneous structure (I structure) of the model water. Comparing successive configurations back and forth we can determine the time of existence of each H-bond and calculate different distributions of lifetimes. The inherent structures were obtained as follows. Each instantaneous configuration was additionally relaxed by MD during 125 steps of 4 fs duration, the velocities of molecules after each step being set to zero. Such a special case of the inherent structure we named Q (quenched) structure. This procedure does not lead precisely to a local potential minimum, but moves the molecules towards it, minimizing to a certain extent the thermal chaos. The total energy changed from -9.3 in I structures to -11.1 kcal/mol in Q structures. All distributions were averaged over 11 000 configurations.

5. Calculation results and discussion

Among the three H-bond lifetime distributions mentioned above, the distribution $P_{TC}(t)$ has the most complicated form (Fig. 2): it contains three maxima. The distributions $P_A(t)$ and $P_{TT}(t)$, which are calculated by the majority of the authors, look much simpler: $P_A(t)$ decays very quickly (Fig. 3), $P_{TT}(t)$ has only one sharp maximum (Fig. 4). The three maxima in the distribution $P_{TC}(t)$ are situated at roughly 30, 150 and 700 fs (in I structure); the asymptotic behavior of $P_{TC}(t)$ corresponds after about 3 ps to the asymptotic behavior of the distribution $P_A(t)$, which has the exponential form of the gas distribution (10) with $\tau_0 = 1.48$ ps. According to (11), this asymptotic contribution to $P_{TC}(t)$ is a broad hump with its maximum at $t_m = \tau_0$. The advantage of function $P_{TC}(t)$ compared to $P_A(t)$

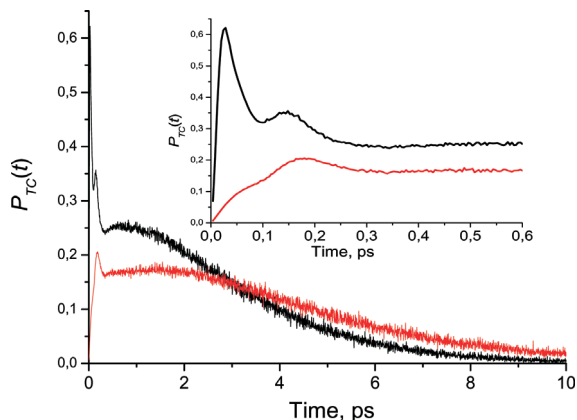


Fig. 2. Distribution $P_{TC}(t)$ for I and Q structures. Inset shows the short time behavior: top – I structure, bottom – Q structure.

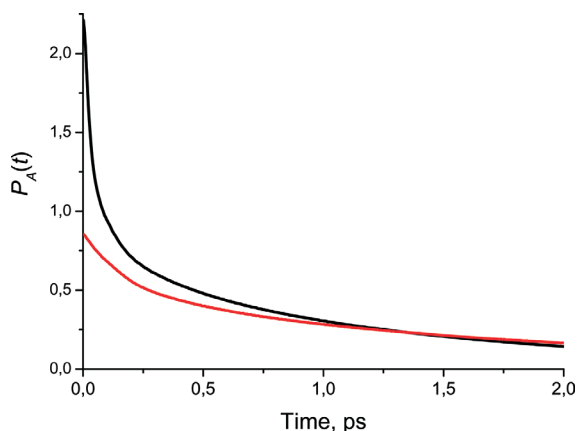


Fig. 3. Distribution $P_A(t)$ for I and Q structures. The curve for the I structure is higher at short times.

and $P_{TT}(t)$ is that it allows observing in detail what occurs on the left of this maximum.

This asymptotic contribution is obviously caused mainly by a true breaking of the H-bonds. By contrast, the first and second maxima in $P_{TC}(t)$ must be related with dynamical effects. We ascribe the first maximum to spurious (or false) H-bonds. Several arguments can be adduced in favor of this interpretation. First, in the Q structures molecules escape the local potential minima very seldom; therefore the number of false H-bonds is diminished strongly, resulting in a drastic decrease of the amplitude of the first maximum (see Fig. 2 and Fig. 5

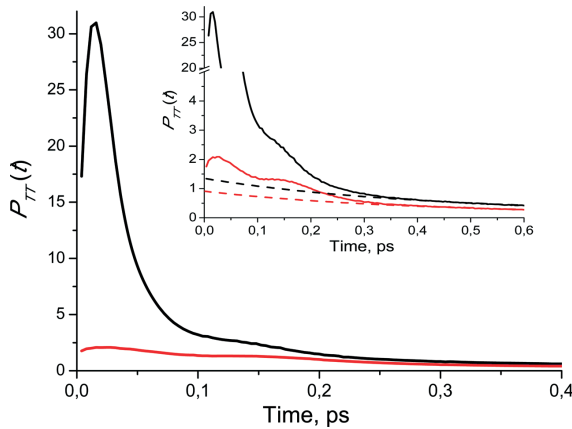


Fig. 4. The function $PTT(t)$ (calculated as $PTC(t)/t$) for I (top) and Q (bottom) structures. Dashed lines in the inset show two gas-like asymptotes: $PTT(t) = 0.367\exp(-t/1.48) + 0.982\exp(-t/0.36)$ for the I structure and $PTT(t) = 0.212\exp(-t/2.05) + 0.699\exp(-t/0.35)$ for the Q structure.

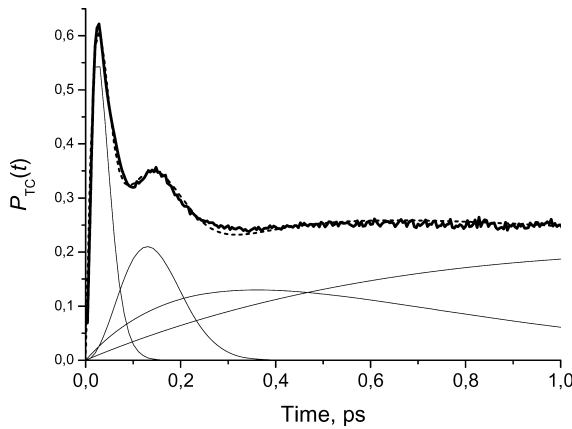


Fig. 5. Distribution $PTC(t)$ for the I structure. Thick line – computer experiment. Dashed line represents fitting by the function $PTC(t) = e[0.56(t/0.025)^{1.25}\exp(-(t/0.025)^{1.25}) + 0.21(t/0.13)^2\exp(-(t/0.13)^2) + 0.13(t/0.36)\exp(-t/0.36) + 0.2(t/1.48)\exp(-t/1.48)]$, thin lines show individual terms of this function. The common factor e is introduced for convenience: the amplitudes give then the values of the maxima of the component terms.

vs. Fig. 6). The second maximum decreases in the Q structure to a lesser extent and it is reasonable to ascribe it to virtual H-bonds between false breaks.

The second argument can be obtained from decomposing the total distribution $P_{TC}(t)$ into components. It is important that the first two maxima can not be fitted to the gas distribution (11), because it would provide much larger widths.

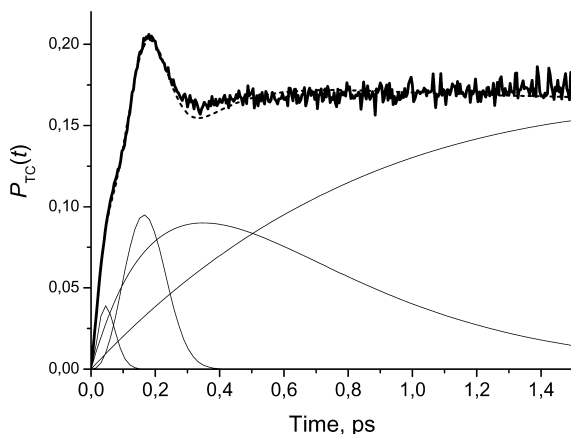


Fig. 6. Distribution $PTC(t)$ for the Q structure. Thick line – computer experiment. Dashed line presents fitting by the function $PTC(t) = e[0.039(t/0.045)^{1.7}\exp(-(t/0.045)^{1.7}) + 0.095(t/0.165)^{2.5}\exp(-(t/0.165)^{2.5}) + 0.09(t/0.35)\exp(-t/0.35) + 0.16(t/2.05)\exp(-t/2.05)]$, thin lines show individual terms of this function.

An appropriate fitting can be reached with narrower distributions. Their form is given in the legends of Figs. 5 and 6. Attention should not be given to the specific forms of the indicated functions, as they have no physical meaning. Their main property is that their derivatives at $t = 0$ are equal to zero. This may be indirect evidence that these maxima do not depict random gas-like breakings of H-bonds, but are of dynamic origin.

In Figs. 5 and 6 it is well seen that to fit the distributions on the left of the maximum at $t = 1.48$ ps (in I structures) and at $t = 2.05$ ps (in Q structures), at least three distributions with three different lifetimes are needed. In addition to two maxima discussed above, it is necessary to introduce the third distribution, which can be represented by the gas like function (11) with a characteristic time of 350–360 fs. Such a form of distributions may correspond to true breaking of hydrogen bonds. The presence of two gas-like components in our approximation does certainly not mean that the model contains hydrogen bonds of two types. It means only that the H-bond lifetime distributions can not be described by a single characteristic time constant.

At the same time, the presence of the far asymptote in the gas-like exponential form (11) is indisputable. This leads to $dP_A(t)/dt \neq 0$ at $t = 0$ and, according to formula (6), to $P_{TT}(0) \neq 0$. The behavior of the distribution $P_A(t)$ at very short times (Fig. 7) confirms very well this result. This fact is very important, because it testifies the existence of true breaks of hydrogen bonds resulting from random (gas like) processes.

Consider now the changes in distributions when passing from I to Q structure. The amplitude of the distribution $P_A(t)$ demonstrates a strong decrease at

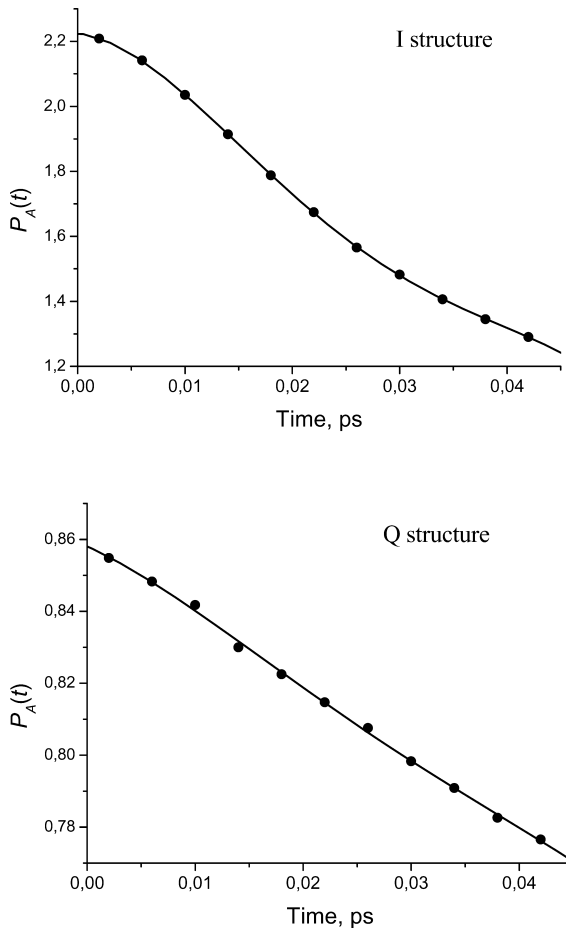


Fig. 7. Distribution $PA(t)$ at very short times. Points – computer experiment. Top – I structure, fitted by $PA(t) = 2.225 - 3.872t + \dots$; bottom – Q structure, fitted by $PA(t) = 0.858 - 1.392t + \dots$

small times (Fig. 3) which corresponds to strong diminution of the first maximum in $P_{TC}(t)$ (Fig. 2). Still more dramatic changes we see in $P_{TT}(t)$ (Fig. 4). The sharp maximum at $t = 14$ fs disappears almost entirely. The insert in Fig. 4 shows that this decrease is caused by elimination of contributions of the false and virtual H-bonds. In the Q structure only contributions of the gas like asymptotes remain effective. Thus, the sharp peak which determines the general view of the distribution $P_{TT}(t)$ of the I structure has nothing to do with *true* breaks of hydrogen bonds.

The characteristic times of the considered distributions are summarized (before any fittings) in the Table. Note that the two possibilities of calculating

Table 1. Characteristic times of the dynamics of hydrogen bond breaking (in fs). τ_{as} – parameter τ_0 in formula (10) for the far asymptote.

	$\langle\tau_A\rangle$	$\langle\tau_{\text{TT}}\rangle$		$\langle\tau_0\rangle$	τ_{as}
		from (5)	from (2a)		
I structure	1238	449	453	575	1480
Q structure	1880	1165	1170	617	2050

$\langle\tau_{\text{TT}}\rangle$, according to equations (2a) and (5), give practically the same results. This is indicative of the consistency of our procedures. In the Table we also give the decay time of the far exponential asymptote τ_{as} which represent the property of the true (or genuine) breaking. Thus, we have four distinct time characteristics of the H-bond dynamics. What do they mean? So far, it is only possible to say that they are related to the involved process of the existence and breaking of hydrogen bonds, in which both dynamics and random breakings are mixed in an intricate way. Four different numbers reflect different aspects of this complicated process. In order to extract information about true breaking of hydrogen bonds special methods are needed which are not yet conclusive (see, e.g., [34]).

6. Conclusions

We have examined different distribution functions of the hydrogen bond lifetime in instantaneous and inherent structures of water. In the so called total lifetimes distribution $P_{\text{TT}}(t)$, averaged over a trajectory, preferred by many authors, only one peak at ~ 15 fs is seen distinctly in the I structure. Substantially more details are revealed by the lifetime distribution averaged by configuration, $P_{\text{TC}}(t)$. The transition to the inherent structure (here Q structure), in which thermal chaos is quenched, made it possible to give a reliable interpretation of the distribution peculiarities. So, the maxima in $P_{\text{TT}}(t)$ and $P_{\text{TC}}(t)$ at about 15 fs must be relate to false H-bonds and the maximum in $P_{\text{TC}}(t)$ at 130 fs to virtual bonds, formed between false breaks. They arise due to short-time violations of the conventional hydrogen bond criteria in the course of dynamic intermolecular vibrations of molecules. These maxima reflect, accordingly, the least interesting moments in the dynamics of H bonds.

Of a much higher interest is the *true breaking* of hydrogen bonds that are not due to intermolecular vibrations, but to “random” switching of the H bond from one molecule to another. The true breaks are correlated with the third maximum of the distribution $P_{\text{TC}}(t)$ at ~ 700 fs and with the asymptotic decay that is well described by the exponential distribution $P_A(t)$ (10) and by a hump-shaped contribution (11) in the distribution $P_{\text{TC}}(t)$. This asymptote is similar to the distribution of the free path times in gases, and instantaneous collisions in the gas phase that interrupt the free flight path are a good model of random, “instantaneous” breaks of the hydrogen bond. The presence of an exponential asymptote proves the existence of random breakings of the H-bond. They also

determine the non-zero value $P_{TT}(0)$, which, according to (12), is the frequency of instantaneous breaks. Unfortunately, the decay time of the asymptote, τ_{as} , can not be considered as a characteristic property of true breaks: this value is strongly dependent on the presence of false H bonds – even in Q structure. Hence, the mean time of true breaks can not be determined until the contributions of true breaks can be separated.

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