

Hydrogen Bonding in Supercritical Water. 1. Experimental Results

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The upper temperature limit for the existence of hydrogen bonding in supercritical water is discussed with respect to the recent statement by Postorino et al.⁸ about hydrogen bonds disappearing at 673 K. This paper demonstrates, on the contrary, that hydrogen bonds in supercritical water can be observed experimentally at least up to 800 K using both spectroscopic and diffraction techniques, yet it may be predicted that hydrogen bonding persists to even higher temperatures. An attempt has been made to estimate quantitatively the temperature dependence of the degree of hydrogen bonding.

I. Introduction

Unusual and in many aspects enigmatic properties of water are known to be the result of hydrogen bonding between water molecules. The importance of this fact cannot be overestimated. Life on Earth in its present form is possible due to this remarkable phenomenon. We must admit, however, that despite a great deal of experimental and theoretical work, we are still far from a complete understanding of the nature of hydrogen bonding. This is especially true regarding the behavior of water at high temperatures and pressures.

The lack of data on the character of hydrogen bonding in water at high temperatures and pressures hinders our understanding of the structure and properties of supercritical water. This fundamental problem is closely associated with many important practical applications, ranging from geological, biological, and environmental sciences to power and chemical engineering.^{2–5} That is why any new spectroscopic or diffraction data obtained at high temperatures and pressures meet a great interest.^{6–8}

Among many points that ought to be clarified, the significant question is to what temperatures the hydrogen bonds in water can exist. The answer to this question has varied over time, but as more knowledge on the subject was gained, the temperature limit for hydrogen bonding in water was predicted to be higher. At first, hydrogen bonds were believed not to exist above 400–420 K. Then, Murchi and Eyring⁹ had suggested, using the approach of significant structures, that slightly above 523 K the hydrogen bonds disappear and water consists of freely rotating monomers. Later on, Luck,¹⁰ studying the IR absorption in liquid water, extended the limit for hydrogen bonding at least up to the critical temperature ($T_c = 647$ K). A subsequent series of high-temperature spectroscopic experiments^{11–15} has shown that the upper bound for hydrogen bonds in water had not been found even at temperatures as high as 823 K.¹⁴ Moreover, X-ray scattering studies of liquid and supercritical water^{16–18} revealed a non-negligible probability even for tetrahedral configurations of the hydrogen-bonded molecules to exist at 773 K.

Against such a background, the results of the recent high-temperature neutron diffraction study by Postorino et al.⁸ seem quite unexpected. Having made measurements for three pressure–temperature thermodynamic states, they observed a complete vanishing of the peak at ~ 2 Å in the pair correlation functions $g_{OH}(r)$ at a temperature of 673 K and a pressure of

80 MPa. The peak corresponds to the separation between the oxygen and hydrogen atoms of the two nearest water molecules involved in a hydrogen bond. The authors used this observation as direct evidence for almost all hydrogen bonds being broken at a temperature that is only slightly above the critical point. The argument is, indeed, very strong. It is, however, not at all obvious that the peak of $g_{OH}(r)$ at ~ 2 Å can be considered as the only experimental criterion for the existence of hydrogen bonding in supercritical water. Moreover, recent computer simulations^{23,24} have shown that this criterion alone is a very inadequate measure of the degree of hydrogen bonding because of the angle-averaged nature of the $g_{OH}(r)$ correlation function. To get a better picture of hydrogen bonding, this criterion should be complemented by angular²³ or energetic²⁴ constraints.

The subject of the present paper is a discussion of results obtained with some other experimental methods. In general, the authors believe that none of the existing methods used to prove the fact of weak hydrogen bonding, taken independently of the others, can give an unambiguous answer to this very complicated problem. The answer obviously strongly depends on the definition of a hydrogen bond, an old problem still unsolved. The difficulty only deepens as we notice that two different terminologies are used to describe the behavior of hydrogen bonds. We can use, for example, the words “intact” and “broken” to characterize the state of hydrogen bonds. We can even speak of the “mole fraction” of the hydrogen-bonded molecules or the number of broken bonds. On the other hand, remembering that only at extremely low densities may one neglect the charge transfer interaction affecting the electron configurations of the nearest molecules, we prefer terms such as “weakening” or “strengthening” of hydrogen bonding. Both terminologies are valid, but neither of them is adequate. Unfortunately, authors using these different terminologies often cannot understand each other, and this circumstance seems to be the main reason for the hot discussion of the principal model of the water structure (“continuum” or “mixture”?) that has lasted for many years.¹⁹

In this paper the temperature dependence of a quantity χ will be discussed. It may with equal success be considered as *the mole fraction of hydrogen bonds* or as *the overall degree of hydrogen bonding in water*. With such an approach we shall try to smooth conflicting viewpoints. Our reasoning is mainly based on the experimental data on IR absorption and X-ray scattering in supercritical water obtained at the laboratory of the authors during a period of more than two decades. The data were carefully revised and processed anew using more

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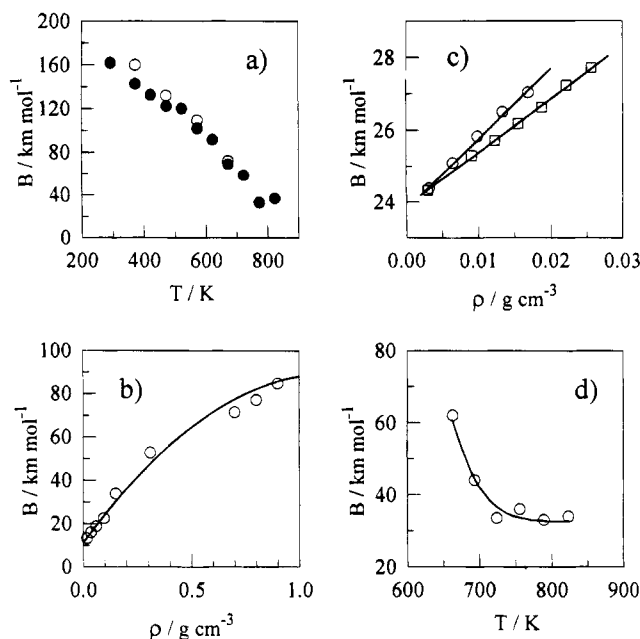


Figure 1. (a) Temperature dependence of the integral intensity for the valence bands of HDO. Open circles are the reduced data from ref 11 for ν_{OD} HDO. Filled circles represent our data for ν_{OH} HDO. (b) Density dependence of the integral intensity (ref 11, reduced) for ν_{OD} HDO at a constant temperature of 673 K. (c) Density dependence of the integral intensity in the valence bands region for the low-density water vapor. Circles are experimental data for the isotherm 673 K and squares, for 723 K. (d) Temperature dependence of the integral intensity of ν_{OH} HDO at a constant density of $\rho = 0.21 \text{ g cm}^{-3}$.

powerful computer techniques available today. Some experimental data of other authors, in particular the very accurate data of Franck and Roth¹¹ on the behavior of OD vibration of HDO, are also included for consideration. We intentionally restrict our discussion to experimental data obtained by direct measurements. A detailed analysis of hydrogen bonding in supercritical water based on the results of recent Monte Carlo and molecular dynamics computer simulations^{20–24} will be the subject of a separate paper.

In the present work we shall try not only to establish that hydrogen bonds can exist at temperatures of up to 670–700 K but also to derive the temperature dependence of χ for supercritical water, using both spectroscopic and diffraction data. Detailed descriptions of experimental techniques used to obtain the data have been given elsewhere.^{14,25–27} We shall frequently refer to the work of Postorino et al.,⁸ taking it as a suitable target and an occasion to set forth our own views on the subject.

II. IR Spectroscopy Data

Involvement of a water molecule in a hydrogen bond with a neighboring molecule strongly affects the OH valence vibration. It is well-known that the corresponding spectral band undergoes a red shift and both its intensity and width increase.^{19,28} The integral intensity of the valence band B is an especially sensitive indicator for hydrogen bonding. While the possible band shift, occurring at the transition from low-density water vapor to ice-Ih, constitutes about 10% of the band frequency for vapor, the integral intensity increases by a factor of 20–30. Figure 1a demonstrates the temperature dependence of B ($B = \int_{\nu_1}^{\nu_2} \epsilon(\nu) d\nu$, where ν is the wavenumber and $\epsilon(\nu)$ is the molar (decadic) absorption coefficient) for ν_{OH} HDO at a constant pressure of 50 MPa.

When water is in a high-density fluid state, the effect of pressure on the integral intensity is much weaker than that of

temperature. This makes possible a comparison of our data on ν_{OH} obtained at a constant pressure of 50 MPa with the data of Franck and Roth¹¹ on the behavior of the ν_{OD} of HDO obtained in the density range $0.9\text{--}1 \text{ g cm}^{-3}$. The theoretical value for the isotopic ratio $B_{\nu_{OH}}/B_{\nu_{OD}}$ is known to be ~ 1.83 . The experimental ratio is, however, close to 1.88.²⁹ Multiplying the data from ref 11 by this factor, we can combine the temperature dependencies of intensity for both ν_{OH} and ν_{OD} bands on a single plot.

As Figure 1a shows, the integral intensity decreases roughly from 160 to 30 kmol^{-1} in the temperature range from 293 to 823 K. The very fact that B continues to decrease at temperatures higher than 673 K indicates that hydrogen bonding in supercritical water at these temperatures still takes place. One can see that the value of $B \approx 30 \text{ kmol}^{-1}$ even at 823 K is far from the integral intensity for an isolated water molecule. The latter can be estimated by an extrapolation to zero density of the data of Franck and Roth¹¹ for the isotherm 673 K, shown in Figure 1b. The resulting value of $\sim 11.3 \text{ kmol}^{-1}$ is fairly close to many other estimates for the low-density water vapor, for example, of Vetrov and Yuhnevich¹² (11.7 kmol^{-1}), Lowder³⁰ (9.6 kmol^{-1}), Iogansen and Brown³¹ (9.5 kmol^{-1}), and other authors.

As may be seen in Figure 1a, $B_{\nu_{OH}} \approx 70 \text{ kmol}^{-1}$ at 673 K. This value exceeds the integral intensity for nonbonded molecules by a factor of 7. This is obvious evidence in support of a rather high degree of hydrogen bonding at this temperature. Even at 823 K and 50 MPa the integral intensity of the valence band is several times higher than that for nonbonded molecules.

Postorino et al.⁸ would be partially right, asserting that hydrogen bonds practically disappear at 673 K, if only they considered very low densities. However, they worked in the range of rather high densities ($0.66 < \rho < 1.0 \text{ g cm}^{-3}$). The density dependence of B at a constant temperature of 673 K shown in Figure 1b (from the data of Franck and Roth¹¹) can be explained only by the increasing number of hydrogen bonds or (using another terminology) by the strengthening of hydrogen bonding.

On the other hand, it is very difficult to indicate a range of densities in which hydrogen bonds do not exist. The data for the integral intensity of the $(\nu_1 + \nu_3)$ H_2O band along two isotherms of 673 and 723 K, shown in Figure 1c, make apparent the fact that hydrogen bonding takes place at any density other than 0. The linear dependencies have been used to obtain the enthalpy of dimerization for water molecules.³²

Other evidence in support of hydrogen bonding in supercritical water is produced by measurements of the integral intensity for ν_{OH} H_2O along the isochore of 0.21 g cm^{-3} (Figure 1d), which is about 2/3 of the critical density. As may be seen, the integral intensity continually decreases as the temperature rises, but it does not reach the value of $\sim 10 \text{ kmol}^{-1}$ (an average value from a number of references^{11,12,30,31}) characteristic for nonbonded water molecules. At 673 K B is still equal to $\sim 50 \text{ kmol}^{-1}$.

Thus, the data on the intensity of IR absorption evidently show that the degree of hydrogen bonding in the near-critical region can hardly be considered negligible. The inference made by Postorino et al.⁸ rests on the analysis of geometric characteristics of the structure of supercritical water. In the next section a similar methodology is used that, however, gives rise to a different conclusion.

III. Temperature Dependence of the Shortest Intermolecular Separation

Let us consider now the most meaningful region of the molecular pair correlation functions of water, presented in Figure

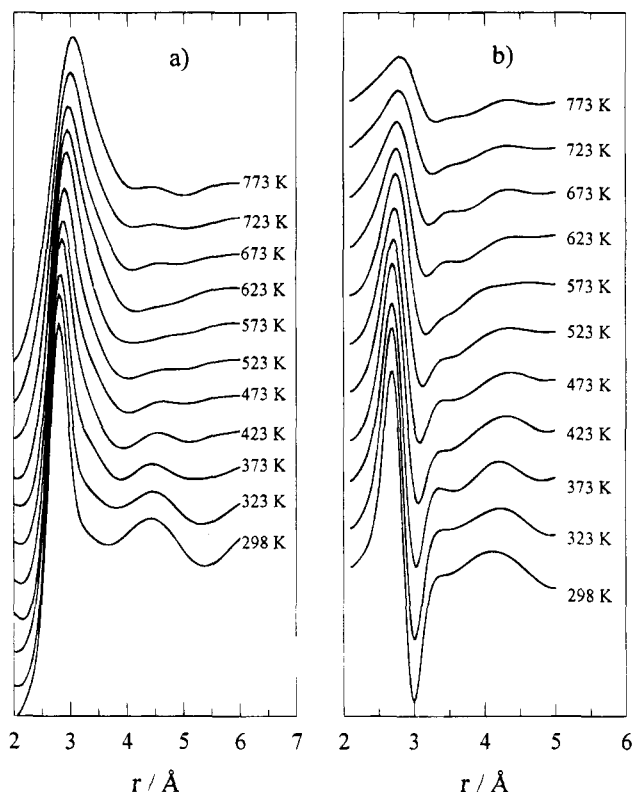


Figure 2. (a) Molecular pair correlation functions of liquid and supercritical water at a constant pressure of 100 MPa. (b) First derivatives of these functions.

2a. The functions were obtained in a wide temperature range from 298 up to 773 K at a constant pressure of 100 MPa,¹⁸ using the energy-dispersive X-ray diffraction technique. The first peak of the function, centered at ~ 2.8 Å, corresponds to the distribution of shortest intermolecular (oxygen–oxygen) separations. The position of the peak gives strong evidence for the nearest molecules to be involved in hydrogen bonding. In principle, if the average distance between two water molecules is less than 3.6 Å (the sum of the van der Waals' radii), a hydrogen bond between them should always be suspected. Figure 3a demonstrates the temperature dependence of the position of the first peak. The dependence is almost linear, and the peak position changes from 2.805 Å at 298 K to 3.04 Å at 773 K (2.97 Å at 673 K). This means that, even at the highest temperature achieved in the experiments, the peak position is still in the range of distances characteristic for the hydrogen-bonded molecular pairs.

The distance between nearest nonbonded molecules in water cannot be shorter than that in liquid Ne, which is isoelectronic with H₂O. In liquid Ne at 35.5 K, the shortest separation is equal to 3.11 Å,³³ and it can only increase with temperature. This value is significantly larger than O–O separations in water even at the highest temperature presently discussed. In an attempt to make the comparison more quantitative, we can use the well-known fact that liquid neon can be quite accurately described by the Lennard-Jones interaction potential.³⁴ Filled symbols in Figure 3b show the temperature dependence of the $g_m(r)$ maximum in liquid and supercritical neon at the same reduced temperatures and densities (i.e., normalized to the critical values of density and temperature) as those of our X-ray measurements for water. These points were calculated using the analytical representation of the radial distribution function for the Lennard-Jones fluid proposed by Goldman.³⁵ Open symbols in Figure 3b show the same data as in Figure 3a but normalized to the critical temperature of water and assuming

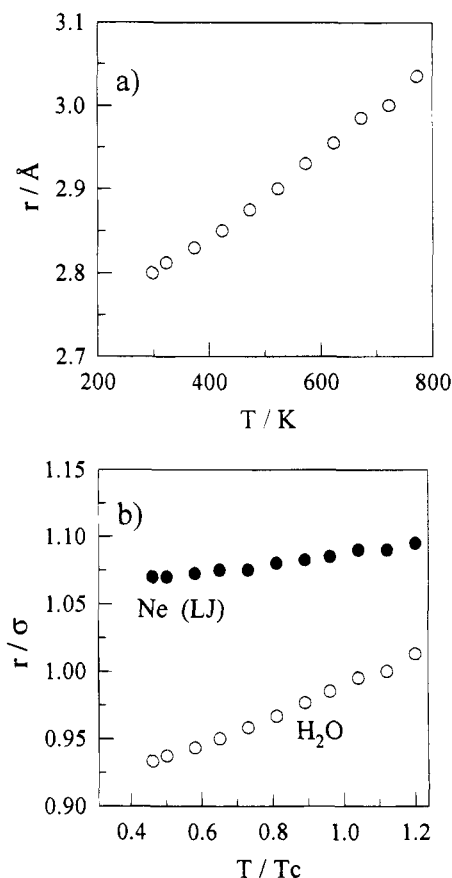


Figure 3. (a) Temperature dependence of the shortest intermolecular separation in liquid and supercritical water. (b) Temperature dependence of the shortest intermolecular separation in liquid and supercritical neon (filled symbols) and water (open symbols) at the same reduced temperatures and densities. See text for details.

the Lennard-Jones parameter σ for water to be equal to 3.15 Å, which is close to the values most commonly used in numerous models of water–water interactions.³⁶

The difference between these two curves clearly demonstrates the profound effect of hydrogen bonding on the shortening of nearest intermolecular separations in water in comparison to those in a simple liquid. Even if we assume $\sigma_{\text{H}_2\text{O}} = \sigma_{\text{Ne}} = 2.8$ Å, which can obviously be considered the lowest limit possible, the values for water would asymptotically approach those for neon only at the highest supercritical temperature in Figure 3b. Thus, the first peak of $g_m(r)$ of water in our experiments corresponds to the hydrogen-bonded molecules in the whole temperature range studied. One can guess, looking at Figure 2, that the number of such hydrogen-bonded pairs is not at all negligible, even at 773 K.

IV. Temperature Dependence of the Degree of Hydrogen Bonding in Supercritical Water

In the preceding sections we have arrived at the conclusion that hydrogen bonding in supercritical water does not disappear even at so a high temperature as 800 K. Yet, this inference is of little value if it is not supported by quantitative estimates. We shall attempt now to make these estimates using both diffraction and spectroscopic data.

Let us go back to Figure 2a, where the molecular pair correlation functions $g_m(r)$ (practically they coincide with the $g_{\text{OO}}(r)$ functions) in the region of the first and the second coordination spheres are shown. Consider first the intriguing behavior of the second peak at ~ 4.5 Å that is characteristic for tetrahedral nearest ordering of water molecules (the distance

between the vertices of the tetrahedron). As hydrogen bonding weakens, the number of molecules participating in the formation of tetrahedral configurations decreases. As may be seen, the peak practically disappears at a temperature of 623 K. Yet, with the further temperature rise the peak not only reappears but seems to escalate noticeably. An explanation for this phenomenon in terms of preferential structure fluctuations has been given elsewhere.^{18,27} The behavior of the peak correlates with the growing fluctuations of the thermodynamic quantities induced by large fluctuations of the structure. Then, short-lived tetrahedral arrangements become possible along with the less bonded structural elements and freely rotating monomers. This fact produces one more piece of evidence of the possibility for hydrogen bonds to exist in supercritical water.

An important feature of the pair correlation functions shown in Figure 2a is an excess of correlation at distances between the first and the second coordination spheres. It is distinctly visible as a shoulder on the right side of the first peak at ~ 3.2 – 3.3 Å. The shoulder is less conspicuous at temperatures higher than 473 K, but inflection points on the right slope of the first peak may still be recognized. The first derivatives of the functions $g_m(r)$, presented in Figure 2b, demonstrate that the feature under question occurs in the whole temperature range studied. If there were only two distributions, centered at ~ 2.8 and ~ 4.5 Å and typical for the tetrahedral nearest environment, no such features could be observed. So, one can suppose that one more distribution may be distinguished within the first coordination sphere that corresponds to the second nearest neighbors, either nonbonded or weakly bonded. The existence of such neighboring molecules is especially obvious when studying the pressure effect on the water structure.^{27,37} At high pressures a distinct peak can be observed instead of a shoulder.

The actuality of the shoulder and inflection points in the contour of the first peak allows us to apply a fitting procedure to calculate contributions of bonded and (tentatively) nonbonded molecules in the nearest environment. The function $4\pi r \rho_0 g_m(r)$ in the region from 2 to 4.5 Å can be represented as a sum of three Gaussians:

$$4\pi r \rho_0 g_m(r) = \sum_{i=1}^3 \frac{\alpha_i}{\sqrt{4\pi\gamma_i}} \exp\left[-\frac{(r-r_i)^2}{4\gamma_i}\right] \quad (4.1)$$

where r_i is the center of i th distribution, α_i is the area under the i th Gaussian, and γ_i relates to the half-width Γ_i of the i th Gaussian as $\Gamma_i = 4\sqrt{\gamma_i \log 2}$. Two distributions ($i = 1, 2$) describe, respectively, the first peak of $g_m(r)$ and the shoulder, while the third one ($i = 3$) imitates a background contributed by the second and following coordination spheres. Assuming that the second nearest neighbors also belong to the first coordination sphere, the first coordination number N is equal to $\alpha_1 r_1 + \alpha_2 r_2$. Then, the parameter χ (see above) may be found as $\chi = \alpha_1 r_1 / N$. The procedure cannot give a single solution, but due to the well-distinguished inflection points in the region of overlap, the least squares fitting procedure gives good results, as may be seen in Figure 4. These results are practically the same as in our previous work,¹⁸ although the data were processed with a better fitting algorithm.

It is important to note that the groups of the water molecules, involved in two different types of nearest ordering, are most likely *separated in space* and arise as a result of structure fluctuations.^{27,37} Otherwise, there would be not much sense in the deconvolution picture, in particular obtained at 773 K, at so great an overlapping of components. If one accepts such a point of view, the behavior of the first two components in Figure 4 appears to be quite logical.

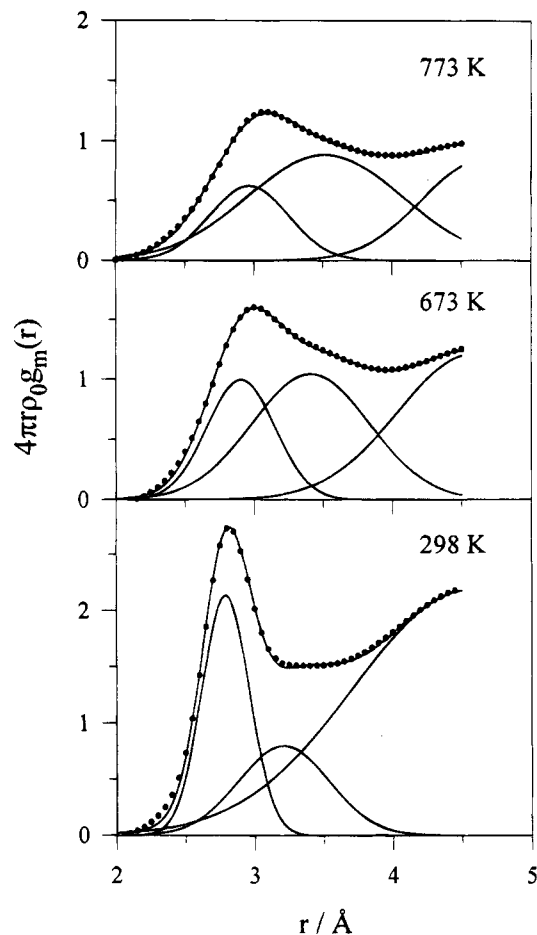


Figure 4. Examples of the fitting procedure. Dots are the experimental data at a constant pressure of 1000 bar; solid lines correspond to three Gaussians and their sum (see text).

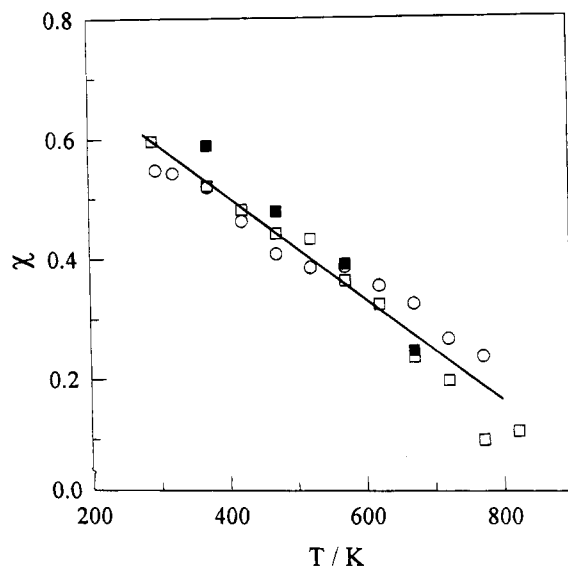


Figure 5. Temperature dependence of the quantity χ derived from the X-ray data (open circles), IR absorption by ν_{OH} HDO (open squares), and IR absorption by ν_{OD} HDO¹¹ (filled squares).

The temperature dependence of χ is presented in Figure 5 (open circles). In the range from 298 up to 773 K the temperature dependence of χ is roughly linear. At 298 K the value of χ is ≈ 0.55 . This means that the degree of hydrogen bonding in liquid water is roughly half of that in ice, in which χ must be equal to 1. At a temperature of 673 K, which Postorino et al. consider as a limit for the existence of hydrogen

bonding, χ is about 0.3. Even at 773 K the value of χ is still higher than 0.2.

The temperature dependence of χ can also be roughly estimated using the IR absorption data shown in Figure 1a. Our measurements have given the value of the integral intensity of 269 km mol^{-1} (262 km mol^{-1} in ref 26) for ν_{OH} HDO in ice-Ih near the melting point. Taking a value of B equal to 265 km mol^{-1} at $\chi = 1$ and $B = 10 \text{ km mol}^{-1}$ at $\chi = 0$ (see section II), we can calculate χ simply as $\chi = (B_T - 10)/255$, where B_T is the integral intensity at temperature T . An assumption underlying this expression may be treated in two ways, depending on the language used to describe the phenomenon of hydrogen bonding. In terms of "broken" bonds it means that B of a single OH group involved in the hydrogen bond is a constant, and the decrease of the integral intensity with temperature is due to the decrease of the number of hydrogen bonds with increasing temperature.³⁸ If, on the other hand, the decrease in the intensity is explained by certain "weakening" of hydrogen bonds, then the expression implies a linear dependence of B on the strength of hydrogen bonding. Both of these assumptions are not, of course, quite correct. Still, it is interesting to estimate the temperature behavior of the parameter χ even with such a rude approach, leaving wide margins for possible errors.

The results of our estimates are shown in Figure 5 (filled and open squares). One can see that temperature dependencies of χ , found by two quite different experimental techniques, agree fairly well within the limits of the experimental errors. The array of the experimental points in Figure 5 may be approximated with the linear equation

$$\chi = (-8.68 \times 10^{-4})T + 0.851 \quad (4.2)$$

which, as we believe, describes the behavior of χ in the temperature range 280–800 K and at densities of $0.7\text{--}1.1 \text{ g cm}^{-3}$ with the accuracy of ± 0.1 . The density range here is chosen rather tentatively in order to exclude the density dependence of χ , which, of course, is stronger for a low-density fluid and, certainly, ought to be taken into consideration for more precise estimates.

It is not clear at which temperatures χ is to be equal to 0. Extrapolation of eq 4.2 to $\chi = 0$ gives a temperature of about 1000 K, but, most likely, the value of χ should approach 0 asymptotically, similar to the trend observed at isochoric heating (Figure 1d). Thus, it will not be surprising if weak hydrogen bonding is revealed at higher temperatures.

V. Conclusions

In conclusion, we would like to note that hydrogen bonds in liquid water, even at ambient conditions, should be considered as weak ones, regarding the broad range of energies that is characteristic for this phenomenon. At high temperatures, as the specific interaction gets attenuated to a high degree, the choice of criteria for establishing the fact of hydrogen bonding in a fluid becomes very difficult. It may be anticipated that in this case such an important feature of a hydrogen bond as the strong orientational correlation should be gradually lost. It makes unreliable the use of such purely geometric criteria of hydrogen bonding as interatomic separations involving oxygen and hydrogen atoms. The approach embracing the whole set of all known indications of hydrogen bonding seems to be more reasonable. Yet, maybe even more important is to deal with a large enough series of experimental data obtained at a constant thermodynamic parameter (temperature, pressure, or density). Such data are much easier to analyze and interpret.

We would also like to note that there exists sufficient evidence of hydrogen bonding in supercritical water obtained by computer simulations. A detailed analysis of the simulated data will be the subject of a separate paper.

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- (38) Such an assumption is rather legitimate if the low-density vapor is considered, in which only the simple reaction of dimerization takes place.³²