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Quantum Cluster Equilibrium Theory Applied in Hydrogen Bond Number Studies of Water. 2. Icebergs in a Two-Dimensional Water Continuum?

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Abstract: With the aid of the quantum cluster equilibrium method, we calculate thermodynamic properties for a new water cluster set containing 2-fold and additional tetrahedrally hydrogen-bonded water molecules on the basis of accurate correlated electronic structure calculations. The addition of clusters with 4-fold coordinated water molecules leads to an improved thermodynamical description of the liquid phase in comparison to experimental values. The comparison of the obtained isobars from the pure 2-fold cluster set with the mixed cluster set shows improved results for the mixed set. Furthermore, the results of the liquid-phase entropy calculation compare excellently with experiment if the mixed cluster set is applied. The calculated populations allow us to determine hydrogen bond numbers, resulting in a temperature-dependent average hydrogen bond number. We observe a decreasing average hydrogen bond number of 2.77 at 274 K to 2.26 at 373 K and a dominance of 75% 2-fold hydrogen-bonded water molecules at room temperature for the mixed cluster set.

1. Introduction

For many decades scientists have been trying to reveal the complicated structure of liquid water to understand why it is such an important solvent. Already in 1892 Wilhelm Conrad Röntgen characterized the constitution of liquid water as an aggregate of two types of water; the first type of molecules he denoted as ice molecules.[1] Furthermore, he explained that both types of molecules are needed to predict the point of maximum density at 4 °C by the two opposing processes during cooling. These are on one hand a dilatation and on the other hand the common thermal contraction of liquids. According to that, the first type of molecules will change into the second type of molecules by heating the liquid and vice versa. Most later publications on the matter of liquid water highlight the need of tetrahedrally coordinated molecules for the occurrence of the point of maximum density as well. However, since the challenging paper of Wernet et al.,[2] the coordination number of water molecules in the liquid phase again has become a topic of heated debate

in the literature. For example, Ball opens his essay on water with the following sentence: "No one really understands water."[3] Although the textbook opinion of the coordination number of water dissolved in itself was three to four, Wernet et al. found in their study indications for a coordination number of mainly two.[2] The authors applied X-ray absorption spectroscopy (which is sensitive to local hydrogen bond patterns) next to density functional theory calculations.[2] The emerging picture was a two-state pattern of the water hydrogen bond, namely, a "random soup" (hydrogen-bonded chains or rings) with "tiny icebergs" (tetrahedrally coordinated water).[3] Many papers on this subject (the number at the end of the year 2008 is approximately 270) followed, and we mention here only a selection. One of the critical papers was published by Head-Gordon and Johnson.[4] The authors carried out X-ray scattering experiments and inferred from those that asymmetry is inconsistent with their data, indicating fluctuations in the local molecular water environment.[4] An asymmetric water charge model for the site−site potential was investigated by Soper.[5] Soper found that neither the asymmetric model is correct nor the symmetric model is incorrect, but that X-ray and neutron diffraction data on

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water are rather insensitive to these details.[5] This was also discussed by Lee and Tuckerman. They concluded that overstructuring found in radial distribution functions (RDFs) calculated from *first-principles* simulations does not necessarily imply more rigid hydrogen bonds. Furthermore, the authors gave a warning toward deriving local structures of water from averaged quantities such as the RDFs.[6,7]

A remarkably outstanding paper describing a study in which traditional molecular dynamics simulations were applied in modified water was published recently.[8] Chatterjee, Debenedetti, Stillinger (who simulated, together with Rahman, water for the first time[9]), and Lynden-Bell investigated the effects of a water model that induces a 2-fold hydrogen bond only.[8] This was carried out in line with the previously studied idea to change the molecular dynamics potential parameters of Bergman and Lynden-Bell.[10] It was shown that a tetrahedrally coordinated hydrogen bond network is necessary to reproduce the water density anomaly. Head-Gordon and Rick also showed that classical molecular dynamics simulations lead to an erroneous description of the liquid phase of water, if a water model with an environment of two hydrogen bonds only is applied.[11] The origin of the density maximum in water was recently studied by Deeney and O'Leary.[12] The authors accounted for the density maximum in terms of opposing action of two independent physical processes,[12] one of these processes being a classical expansion/contraction effect and the other being identified as quantum zero-point-energy fluctuations. These effects counterbalance each other, resulting in a density maximum.[12]

The observations of ref 6 are in line with the finding of Ludwig, who could also show that only the tetrahedrally coordinated water structures are able to reproduce the density maximum of water.[13] On the basis of Hartree–Fock and density functional theory in the framework of the quantum cluster equilibrium (QCE) method, Ludwig discussed the importance of the tetrahedrally coordinated water versus a twice hydrogen-bonded water molecule. By inclusion of a tetrakaidecahedral $(H_2O)_{24}$ cluster, a triple point could be determined. Furthermore, Ludwig could show that the three-dimensional water clusters $(H_2O)_{13}$, $(H_2O)_{15}$, and $(H_2O)_{17}$ including tetrahedrally coordinated water molecules are necessary to mimic liquid-phase properties.[13] The voluminous water clusters are consistent with the oxygen–oxygen pair correlation function from X-ray diffraction experiments, and these clusters are able to reproduce the main features of the OH stretch region in the IR spectrum.[13]

In the present study we apply the quantum cluster equilibrium method to investigate hydrogen bond patterns in liquid water. We focus on the discussion of populations along the liquid temperature range, i.e., from 274 to 373 K.

This paper is structured as follows. First, a short methodological introduction to the QCE method as well as the calculation of the hydrogen bond numbers is given. Second, we compare the isobars of two cluster sets containing either 2-fold or 2-, 3-, and 4-fold hydrogen-bonded clusters. Next, cluster populations are considered. Thereafter, we show the improved results of the entropy calculations with rising temperature. Finally, we analyze the calculated temperature-

dependent hydrogen bond numbers. The paper ends with the Discussion and Conclusion.

2. Methodology

The QCE theory and the computational details are described in the accompanying article (10.1021/ct800310a).[14] In the QCE approach modulated partition functions from static quantum chemical calculations are applied to obtain polynomials which are solved in a self-consistent fashion. The resulting populations are used to obtain bulk partition functions, and from those it is possible to calculate bulk thermodynamic properties.[15–17] To evaluate the importance of distinct cluster structures, we show monomer-normalized populations in this study as introduced in the previous paper (10.1021/ct800310a).

Cluster populations within our QCE program[18] usually refer to the total number of clusters. This number varies within a QCE calculation. If mainly large clusters are populated, more monomers are bound within these large clusters. Because the amount of monomers is fixed in the QCE calculation, there are fewer monomers to form the other clusters. This implies a reduction of the total number of clusters; i.e., if the total number of clusters decreases, the percentage population of each individual cluster increases. This is not useful when insight into the physical nature of a phase point is desired. For this purpose it is better to analyze populations which are related to the monomer reference system. Given that the total number of monomers is equal to 1 mol for all phase points, the percentage now provides an estimate of how many monomers of the total 1 mol are bound in a particular cluster and thereby reflects the physical composition of the phase point.

Furthermore, we analyze the average hydrogen bond number at each phase point as described in the following. For each cluster j and temperature the QCE calculation provides the *intercluster* interaction in terms of the mean field energy E_j^{inter}, depending on the cluster size and the calculated volume as well as the selected a_{mf} value:

$$E_j^{\text{inter}} = -i_j a_{\text{mf}} V^{-1} \qquad (1)$$

This energy needs to be correlated to a hydrogen bond number (n^{hb}). Therefore, it will be divided by the cluster-specific intracluster interaction energy per hydrogen bond E_j^{hb}, the latter being obtained, e.g., by a natural bond orbital (NBO) analysis, leading to

$$n_{\text{inter},j}^{\text{hb}} = \frac{E_j^{\text{inter}}}{E_j^{\text{hb}}}, \quad \text{with} \quad E_j^{\text{hb}} = \frac{\Delta E_j^{\text{intra}}}{n_j^{\text{hb}}} \qquad (2)$$

Alternatively, the mean field energy could be divided by an average binding energy per hydrogen bond E^{hb} given for each cluster set, similar to the energy criterion for hydrogen bonds in molecular dynamics simulations:

$$n_{\text{inter}}^{\text{hb}} = \frac{E_j^{\text{inter}}}{E^{\text{hb}}} \qquad (3)$$
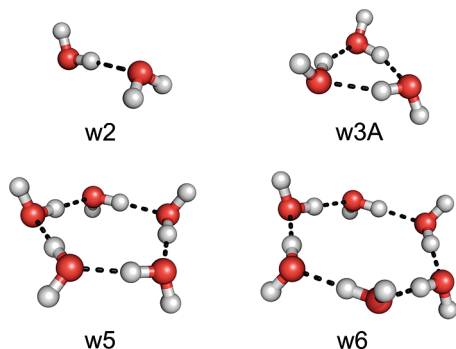
Figure 1. Ball-and-stick model of the 2-fold water cluster set (abbreviated as the **2_opt** set) as introduced in the previous paper (10.1021/ct800310a).[14]

The calculation of these additional hydrogen bonds arising from the mean field interaction ($n_{\text{inter}}^{\text{hb}}$) of a specific cluster has to be repeated for each cluster of the particular set. To derive the global average number of hydrogen bonds in the system, these cluster-specific additional hydrogen bonds have to be weighted by the monomer-normalized population of each cluster N_j, with $\sum_{j=1}^{\eta} N_j = 1$ and η being the total number of clusters. After the calculation of all hydrogen bonds and the weighting by their respective populations, they are added to yield the global average hydrogen bond number, leading to the final equation

$$\langle n^{\text{hb}} \rangle = \sum_{j=1}^{\eta} (n_{\text{inter},j}^{\text{hb}} + n_j^{\text{hb}}) N_j \tag{4}$$

It should be noted here that the above sketched scheme is not from first principles, because (a) an empiric parameter (a_{mf}) enters our model and (b) we distribute this energy not unequivocally. The optimized cluster sets employed in the present study are taken from the previous paper (10.1021/ct800310a).[14] In the present work we only show MP2/TZVPP electronic structure data. The **2−4_opt** set denotes the optimal cluster set containing clusters with tetrahedrally coordinated water molecules (see Figure 2), whereas the **2_opt** set only contains clusters with 2-fold hydrogen-bonded water molecules; see Figure 1.

The applied QCE parameters are listed in Table 1. A detailed discussion can be found in the accompanying paper (10.1021/ct800310a).[14]

3. Results

3.1. Comparing the Pure 2-Fold Water Set (2_opt) to the Mixed Set (2−4_opt). In the former paper (10.1021/ct800310a) we found an improvement with respect to the accuracy as well as a reduction of the mean field parameter a_{mf} especially at low temperature if tetrahedrally coordinated water molecules were included in the QCE calculations.[14] To further discuss this point, we show the resulting isobars in Figure 3.

We observe a definite improvement of the isobar due to the inclusion of additional spiro clusters. The slope of the experimental curve is reproduced better, and the previously discussed larger deviation at lower temperature is also reduced. This result clearly points at the importance of
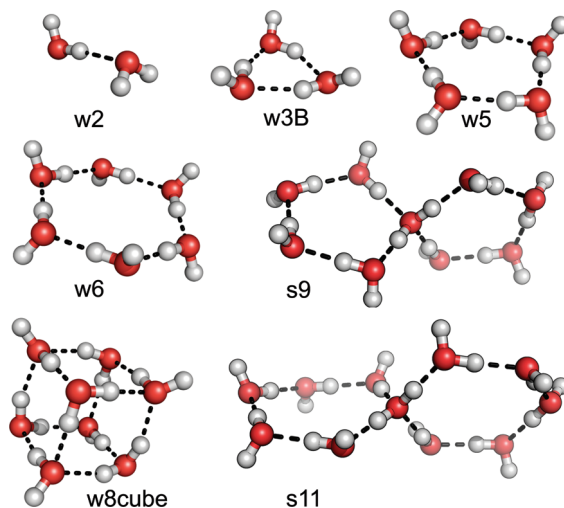

Figure 2. Ball-and-stick model of the cluster set containing tetrahedrally coordinated water molecules (abbreviated as the **2−4_opt** set) as introduced in the accompanying paper (10.1021/ct800310a).[14]

Table 1. QCE Parameters for the Sets without Spiro Clusters (**2/3** and **2_opt**) and with the Spiro Clusters (**2−4_opt**) at the Temperature Range from 274 to 373 K[a]

| set	$\|\Delta V\|$	a_{mf}	b_{xv}
2/3	311.80	0.162	1.107
2_opt	167.57	0.136	1.088
2_opt pair	405.63	0.343	1.068
2−4_opt	137.07	0.130	1.105
2−4_opt pair	420.18	0.351	1.071

[a] $\|\Delta V\|$ (μL) gives the accuracy of the corresponding isobar, i.e., the root mean square deviation from the experimental values.
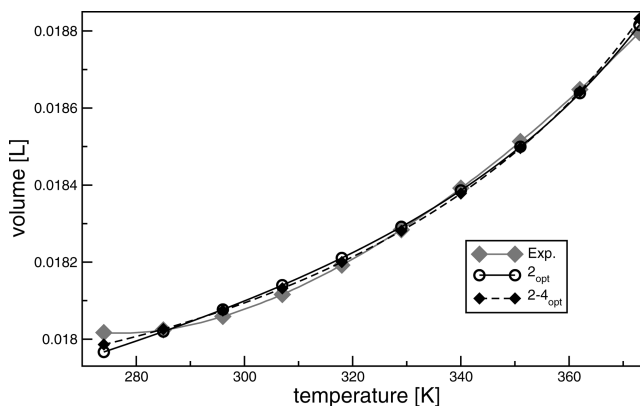
Figure 3. Calculated isobars for the **2_opt** (solid line and circles) and the **2−4_opt** (dashed line and tilted squares) cluster sets at the temperature range from 274 to 373 K with fitted parameters.

tetrahedrally coordinated water, which has to be applied in the calculation of the partition functions at low temperatures. It is noteworthy to remark that this result cannot be achieved by selecting the QCE parameters accordingly. Only the explicit treatment of the tetrahedrally coordinated water leads to improved results, which is a strong point in favor for the applicability of the QCE method and which shows that the QCE is sensitive to structural motifs of the condensed phase.

3.2. Populations of Clusters in the Bulk. According to QCE methodology, cluster populations are obtained at
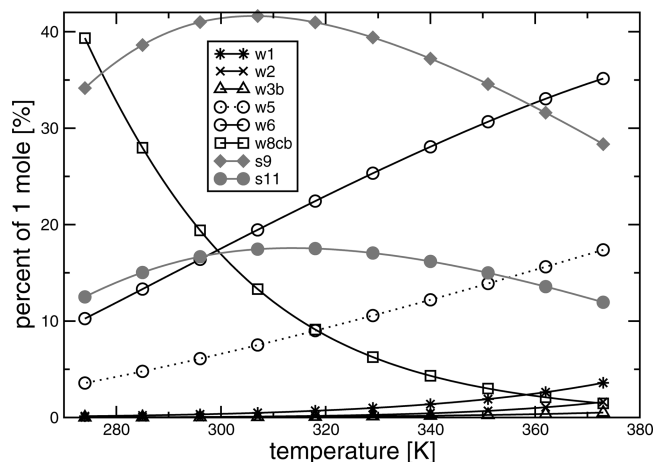
Figure 4. Monomer-normalized populations for the liquid-phase temperature range for the optimal $2-4_{opt}$ set.

Figure 5. Entropy as calculated according to ref 17. The reference point for the calculations and the experimental data is set to $S^{(273.16K)} = 0$.

every phase point of a QCE calculation, thereby providing insight into the composition of the bulk. This constitutes a link between isolated clusters obtained from static quantum chemical calculations and the bulk, as mentioned in the Introduction of the accompanying paper (10.1021/ct800310a).[14] In Figure 4 we depict the monomer-normalized populations; these populations show to what extent a particular cluster is populated with respect to the constant total monomer number of 1 mol.

There are three regions in which different clusters are mainly populated. At very low temperature the cagelike **w8cube** cluster shows a population of 40%, between 280 K and approximately 360 K the **s9** spiro cluster plays the important role with a maximum population of approximately 42% at 306 K, and at high temperature (>362 K) the **w6** cluster is most highly populated with 35%. While the populations of all clusters with only 2-fold coordination grow with increasing temperature, the spiro clusters show each a maximum. These maxima are approximately at 310 K for **s9** as well as for the **s11** cluster. The cagelike **w8cube** cluster, which seems to be an important motif of the low-temperature region, decreases much faster than the ring clusters increase. Thus, the QCE model predicts a significant temperature dependence of the liquid-phase coordination pattern, which has also been observed in recent experiments.

The importance of the investigated temperature is also emphasized in the paper of Head-Gordon and Johnson.[4] With the aid of temperature-dependent experiments, the authors draw the conclusion of a mainly tetrahedrally coordinated water structure. These conclusions are based on three temperature measurements, i.e., at 1 °C (274 K), 25 °C (298 K), and 77 °C (360 K). As can be seen from Figure 4, **s9** shows a maximum at approximately 306 K and the ring structures are just starting to show a growing population. Thus, the QCE results imply that the complete picture might be more complicated and that a simple linear temperature dependence might not apply. According to these QCE calculations, it would seem to be helpful to add more temperature-dependent measurements, for example, at 283 K (10 °C) and at 320 K (47 °C). The temperature-dependent behavior was also observed by Chatterjee et al. in the temperature-dependent spatial distribution functions plot for
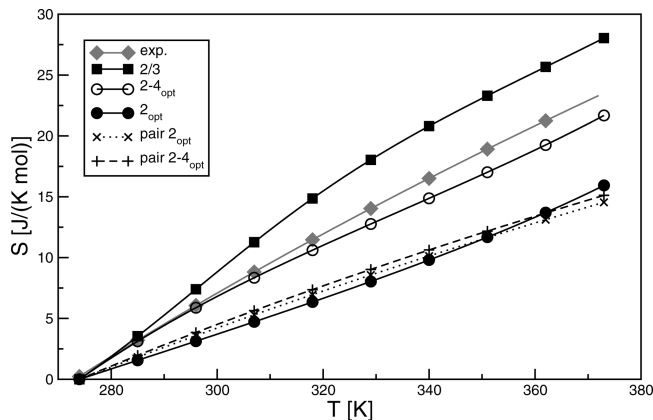
their modified model with a water H−O−H angle of 90° and 100°. These two models acquire a waterlike (tetrahedral) structure upon cooling.[8]

3.3. Entropy. One of the strong points of the QCE method is the possibility to calculate different thermodynamic quantities once the partition functions are known. Please note that once the QCE parameters are set they are not changed anymore; i.e., the outcome of the calculations does not depend on the selection procedure of the QCE parameters, but on how well the model-inherent approximations work for the particular properties. In a previous study we employed QCE calculations to derive entropies of the liquid phase as well as the liquid−vapor phase transition.[17] The neglect of cooperativity led to large errors in the obtained entropy values. In contrast, a correct treatment of the intracluster many-body interaction yielded liquid-phase entropies and phase transition entropies in very good agreement with the experimental reference.[17]

In Figure 5 we show the entropy plotted against temperature for our different sets. As can be observed, the original **2/3** set lies above the experimental values; i.e., the slope of the curve is too large. All other methods underestimate the experimental reference. To obtain a closer agreement with experiment, tetrahedrally coordinated water molecules are necessary as reflected in the excellent agreement of the $2-4_{opt}$ entropies with the experimental values; see Figure 5, black curve with open circles. To facilitate the relevance of the $2-4_{opt}$ cluster set, it should be mentioned that the vaporization entropy $\Delta_{vap}S$ (not depicted), calculated with this set, also shows a more accurate value of 109.42 J/(K mol) (exp.: 109.06 J/(K mol)).[19] Applying 2-fold hydrogen-bonded clusters alone leads to entropies as inaccurate as the ones depending on pair energies only; see Figure 5, black curve with closed circles and dashed and dotted curves. This indicates that from the entropical point of view the 2_{opt} cluster set and the sets applying the pair energies underestimate the entropy.

3.4. Hydrogen Bond Numbers. In the last section, we showed monomer-normalized populations for calculations with the $2-4_{opt}$ set. However, the mean field QCE parameter prevents us from giving a quantitative statement of the average hydrogen bond for water molecules that could be
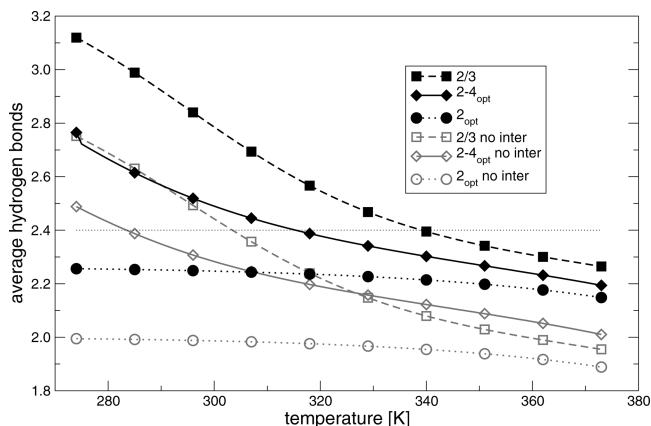
Figure 6. Average number of hydrogen bonds at different phase points with intercluster interaction recalculated as described in section 2.

expected from our calculations, since the number of hydrogen bonds accounted for by the mean field energy is only accessible in an indirect way (see section 2). While in the 2_{opt} clusters the maximum average hydrogen bond number that occurs is 2, the average number is 3.0 for the **w8cube** cluster and 2.22 for the **s9** cluster in the $2-4_{opt}$ set. To estimate the number of hydrogen bonds according to section 2, we have to evaluate the mean field energy in terms of the average hydrogen bond energy per cluster. The procedure to obtain the total average hydrogen bond number at different phase points is described in section 2.

In Figure 6 the average hydrogen bond numbers are depicted against temperature. We observe that for all sets these numbers decrease with increasing temperature; i.e., none of the sets provides hydrogen bond numbers that behave identically at every phase point, thus showing the temperature dependency of the hydrogen bond number as discussed in the earlier section. Considering the average hydrogen bonds in Figure 6, we find a monotonically decreasing behavior. This monotonical behavior could not be deduced directly from the populations. The QCE-predicted hydrogen bond numbers for set $2-4_{opt}$, set **2/3**, and set 2_{opt} do not reflect the picture of a mainly tetrahedrally hydrogen-bonded water. Furthermore, it is apparent from Figure 6 that the mean field term corrects the intercluster interaction in different ways. At lower temperature a higher hydrogen bond amount is added in all sets. This is the reason why the uncorrected curves ($n_{inter}^{hb} = 0$) at higher temperature (gray curves in Figure 6) show an order different from that of the curves including n_{inter}^{hb} from the intercluster interactions. In general, the curves are a little bit more spread out at low temperature than at high temperature. At high temperature (373 K) the curves including n_{inter}^{hb} exhibit values between 2.14 (2_{opt}) and 2.26 ($2-4_{opt}$), which indicates a high probability for 2-fold hydrogen-bonded water molecules at this phase point (87–93%) in the calculated cluster phase.

The maximum hydrogen bond number (3.12) is obtained for the **2/3** set at lowest temperature (274 K). At the same temperature the value for the 2_{opt} set amounts to 2.26 and for the $2-4_{opt}$ set to 2.77. At this stage it is necessary to keep in mind that the isobars and entropies were most accurate for the $2-4_{opt}$ set; i.e., the obtained data from this

set should be taken as the most reliable results. This reasoning is based on the assumption that the most accurate thermodynamics also yield the most precise structural information. The hydrogen bond numbers indicate (if we neglect the fact that 3-fold hydrogen bonding occurs) 38% tetrahedrally coordinated water molecules and 62% 2-fold hydrogen bonds for the $2-4_{opt}$ set, 13% tetrahedrally coordinated water and 87% 2-fold hydrogen-bonded water molecules for the 2_{opt} set, and 56% tetrahedrally coordinated water molecules and 44% 2-fold hydrogen bonds for the **2/3** set at 274 K. A ratio of 80% tetrahedrally to 20% 2-fold coordinated water would be represented by a hydrogen bond number of 3.6. This clearly shows that our results are to a greater extent in accordance with the findings of Wernet et al.;[2] i.e., we obtain the closest agreement to the experimental thermodynamics (e.g., see Figure 3 in section 3.1 and Figure 5 in section 4) with mainly 2-fold coordinated water molecules (75% at 298 K with the $2-4_{opt}$ set). It should be noted here that these numbers are based on the approximate evaluation of the mean field energy (see section 2) and thus should be taken as semiquantitative. In traditional molecular dynamics simulations values from 3.1 to 3.3 hydrogen bonds at room temperature are discussed.[11] The hydrogen bond number of 2.4 could be attributed to a ratio of 80% 2-fold hydrogen bonds to 20% tetrahedrally coordinated water molecules (see the dotted horizontal line in Figure 6) with the hypothetical assumption of these two possibilities only. From approximately 315 K the total hydrogen bond number of the $2-4_{opt}$ set drops below 2.4; see the dotted line in Figure 6. However, the limited size of the clusters present in the $2-4_{opt}$ set makes it difficult to realize a distribution of 80% 4-fold to 20% 2-fold coordination at all, because in these medium-sized clusters the number of 2-fold coordinated molecules will always be larger than the number of 4-fold coordinated molecules due to surface effects. Nevertheless, these QCE results demonstrate that the coordination number distribution present in the $2-4_{opt}$ set is consistent with experimental thermodynamics, at least concerning densities and entropies.

Applying the binding energy criterion of the dimer as mentioned earlier in section 2 (not depicted) instead of the cluster-specific binding energy for a hydrogen bond results in a 4.9% higher hydrogen bond number for the $2-4_{opt}$ set, while the **2/3** set shows a difference of 5.9% and the 2_{opt} set shows the largest difference with an increase of 6.2%.

If we compare the curves from the cooperative energies with those of the pair energies (not depicted), we find that the pair curves of both sets obviously exhibit much lower coordination numbers. For the uncorrected case ($n_{inter}^{hb} = 0$) both sets exhibit an n^{hb} of below 1, while the corrected sets show a hydrogen bond number increased to an amount of more than 1, $\langle n^{hb} \rangle$.

4. Discussion

To clarify several indistinct issues, it seems to be important to recapitulate different aspects of theoretical investigations, and additionally we want to reconsider some structural aspects of liquid water.

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(1) Water has a coordination number (as opposed to the hydrogen bond number examined in the present study) that is given by the number of surrounding water molecules or the first integrated X-ray oxygen−oxygen radial distribution function $g_{oo}(r)$ peak. As Soper explains, the question of this coordination number is distinct from that concerning the number of hydrogen bonds.[5] Some scientists infer that water molecules mainly contain two hydrogen bonds, and some believe that water largely shows a tetrahedral hydrogen bond pattern in the liquid phase.[3]

(2) From the theoretical perspective the water structure was mainly investigated by traditional molecular dynamics (MD) simulations.[8,20] These methods include a model-inherent dynamical description and large samples (Soper used 1800 water molecules[5]). Nevertheless, the methods are mostly applied with fixed charges (even if these are distributed asymmetrically) and with the pairwise additivity approximation as well as the neglect of nuclear quantum effects.[21] Many suggestions for polarizable water models appeared in the literature.[22] The quality of parametrization varies from system to system and from quantity to quantity, raising the question of transferability.[23] Despite these problems, it is possible to reproduce such important quantities as the density maximum with traditional MD simulations.[8]

(3) First-principles simulations, for instance, in the framework of Car−Parrinello[24] molecular dynamics simulations, circumvent the approximation of traditional molecular dynamics simulations. However, within these methods it is only possible to treat a small sample (∼1000 molecules; see ref 25) with a short simulation time (<100 ps scale). Due to large computational costs, the calculations are mainly carried out with density functional theory (neglecting dispersion) and relatively small basis sets. Hybrid functionals[26] and correction schemes for dispersion[27−29] were successfully tested. A very valuable discussion of different effects is given by Lee and Tuckerman.[7] One of the major advantages of first-principles simulations is that the electronic structure can be analyzed on the fly.[30] For example, it is possible to calculate local dipole moments[31,32] or charges[33,34] in the liquid phase.

(4) Despite the fact that only a few clusters in relation to MD simulations are applied within the QCE model, the cluster-inherent parameters as geometries and frequencies depend on accurate electronic structure models. Furthermore, the QCE method employs no effective potentials in the description of intermolecular interactions contrary to traditional molecular dynamics simulations, which makes it more sensitive to questions of hydrogen-bonding patterns. While it is difficult to employ an unambiguous criterion for hydrogen bonding in traditional molecular dynamics simulations, a less crude analysis of the clusters calculated with accurate electronic structure methods gives rise to the question of how many "hydrogen bonds" are inherent in a specific cluster. From those clusters further calculations such as the calculation of the populations or isobars were carried out, finally leading to the prediction of a hydrogen bond number in the temperature range of the liquid phase of water, still on the basis of the accurate electronic structure calculations. The QCE model is not able to describe the dynamics of hydrogen bond formation and

breaking, but nonetheless, a strong point of the model is that temperature-dependent properties, e.g., the $\langle n^{hb} \rangle$ or the population of a distinct motif, of the investigated systems can be shown easily. Moreover, the QCE model can be used as a tool to trace deviations from the experiment due to certain characteristics such as geometries or electronic structure methods.

5. Conclusion

The extended water cluster set ($\mathbf{2-4_{opt}}$), containing tetrahedrally hydrogen-bonded clusters, leads to an enhanced description of the liquid phase of water in the frame of the QCE theory. This result shows once more that the 4-fold coordination is necessary to obtain an accurate description of liquid water, e.g., in the case of the improved results in liquid-phase entropies. The analysis of the hydrogen bond patterns within our model clearly shows that, although the tetrahedrally coordinated water molecules have to be included in the cluster set to obtain an accurate physical behavior, the calculated cluster phase exhibits an average hydrogen bond number below 3 at room temperature. Furthermore, the application of the dimer hydrogen bond interaction energy alone as a criterion for hydrogen bonding leads to an erroneous because overstructured picture of the liquid phase. It might be inferred that traditional MD compensates the too low hydrogen bond energy of approximately 20 kJ/mol with an overstructuring (too many tetrahedrally coordinated water molecules) of the hydrogen bond network. Considering the averaged cooperative interaction energies of the higher populated clusters which dominate the QCE cluster phase, a much higher value (between 28 and 31 kJ/mol) is obtained. Thus, at equal total energy in the system the higher energy per hydrogen bond leads to a sparser hydrogen-bonded water network. This issue together with the poor performance of pairwise additive interaction energies applied in QCE calculations reconfirms the importance of cooperative effects in liquid water.[15]

Wernet et al. reinvestigated a conventional wisdom of water coordination with their set of experiments.[2] One of the benefits or side effects of these experiments lies in the improvement of other experiments, models and methods. At present no method or theory can claim to describe all features of water correctly. Therefore, the QCE is a helpful and necessary tool toward understanding this important task. It certainly provides us also with a link between isolated clusters and the condensed phase.

To gain additional insight into the local structure of liquid water, further studies in the frame of the QCE theory and thus on the basis of accurate electronic structure methods are necessary. Moreover, it is still a mandatory task to understand how the water molecules interact with each other on the molecular level.

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