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# Structural Correlations in Liquid Water: A New Interpretation of IR Spectroscopy

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We present a new and alternative interpretation of the structure of the IR vibrational mode ( $\nu(\text{OH})$  band) of pure water. The re-interpretation is based on the influence of the cooperative hydrogen bonding arising from a network of hydrogen bonds in the liquid. The  $\nu(\text{OH})$  band has six components that are dominated by differences in their O–H bond lengths but deviate from thermodynamically average values due to interactions with the hydrogen bond network. The physical origin of the structure in the  $\nu(\text{OH})$  band is directly related to the O–H bond length, and variations in this bond length are caused by the influence of the surrounding hydrogen-bonded network of water molecules.

Liquid water has been the focus of many experimental and theoretical calculations. The unique physical, chemical, and structural properties of liquid water have long been attributed to hydrogen bonding (HB).<sup>1</sup> Most of the structural models of liquid water fall into either a continuum of geometries and energies or a mixture of discrete species, with neither being sufficient to fully explain the broad physical properties of water. However, there is both experimental and theoretical evidence that it is the three-dimensional spatial network of hydrogen bonds that gives water its unique physical properties.<sup>2–8</sup> This view is often taken from the interpretation that, because HBs are formed and broken at subpicosecond time scales, HB rearrangement occurs quickly and the interconnected network is well-defined a majority of the time,<sup>7–9</sup> even under supercritical conditions.<sup>10</sup>

There are numerous experimental techniques used to investigate the structural properties of liquid water, with neutron scattering, X-ray diffraction (XRD), and spectroscopic techniques preferred because of their ability to give either static (pair correlation functions) or dynamic structural information. Currently, there is not a consensus regarding the interpretation of X-ray absorption and photoelectron spectra, but it is clear that a single water molecule is hydrogen bonded to at least two (2-coordinated) and at most four (4-coordinated) water molecules.<sup>11–13</sup> However, beyond this first coordination shell, it is unclear what the extended coordination structure is like. In addition, although Raman spectroscopy has also been used to investigate structural correlations,<sup>4,5,14,15</sup> there is an additional complexity as this technique involves electronic transitions to a virtual state of the molecular spectrum. Infrared (IR) absorption spectroscopy is particularly well-suited for examining the structural correlations in liquid water as it directly probes the interactions of the oscillators and couples to the ground state of the molecules.<sup>16</sup> However, there is debate as to how the local structure relates to the IR vibrational spectroscopy. Thus, to understand water's unique properties, it is important to develop

a framework for describing the HB network of liquid water and its relation to IR spectra.

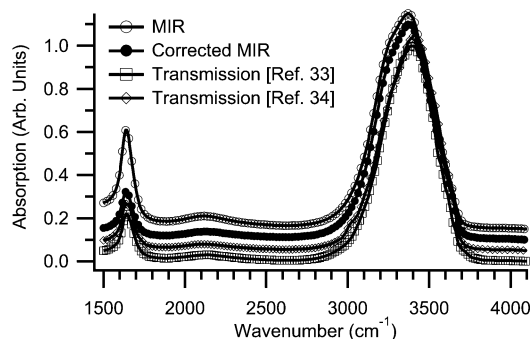
The complex structure of the stretching mode ( $\nu(\text{OH})$ ) is believed to be related to the structure of water,<sup>1,9,17–20</sup> and although this mode is strictly probing vibrations along the O–H bond, the influence of neighboring HBs alter the intramolecular O–H bond and thus the dipole moment and vibrational spectra.<sup>3,20–24</sup> Thus, the structure of the  $\nu(\text{OH})$  band can provide information about the HB network and how it is modified by defects. Here, we propose a new interpretation of the  $\nu(\text{OH})$  band of water that is based on cooperative hydrogen bonding,<sup>23</sup> a two-state physical model of liquid water,<sup>25</sup> and an ensemble system that is driven to thermodynamic equilibrium.

Water is a strong absorber in the 2800–3700  $\text{cm}^{-1}$  region, which can make transmission IR absorption experiments unreliable due to saturation effects from long path lengths. Total internal reflection (TIR) spectroscopy (or attenuated total reflection (ATR) spectroscopy), on the other hand, is very effective in obtaining information about molecular interactions in aqueous solutions.<sup>26–32</sup>

IR spectra were obtained using a BOMEM FT-A2000 MB Fourier transform infrared (FTIR) spectrometer. The signal was detected with a liquid  $\text{N}_2$  cooled HgCdTe (MCT) detector. Liquid samples (200  $\mu\text{L}$ ) were contained in a Teflon cell equipped with a Si(001) crystal prism in a TIR configuration. The prisms were  $0.5 \times 10 \times 30$  mm with  $45^\circ$  bevels on the 10 mm sides resulting in approximately 26 internal reflections. Each spectrum is averaged over 400 scans with a resolution of 2 or 4  $\text{cm}^{-1}$ . Spectra were collected under a dry nitrogen flow to remove residual water vapor and  $\text{CO}_2$  from the spectrometer. All measurements used semiconductor-grade distilled water ( $\rho > 18 \text{ M}\Omega\cdot\text{cm}$ ) and were taken at  $25^\circ\text{C}$ .

Although TIR reduces the effective penetration depth and eliminates saturation effects, the intensity of low-wavenumber absorptions is affected due to the wavelength dependence on the penetration depth.<sup>26</sup> To quantitatively analyze the structure of the vibrational modes, as well as have a direct comparison to transmission experiments, TIR data must be corrected by dividing the intensity by  $\lambda$  (Figure 1).<sup>26</sup> The wavelength-

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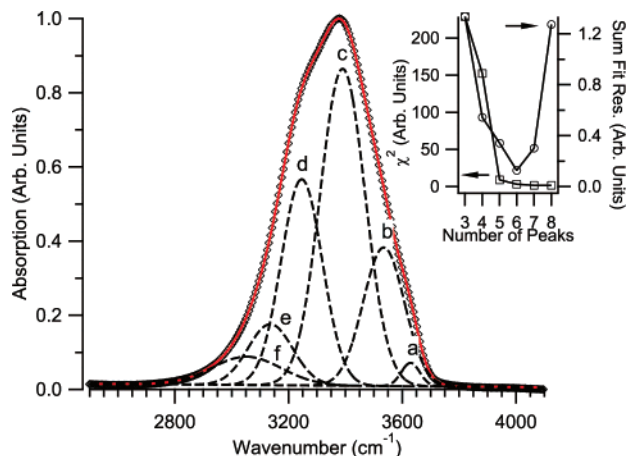


**Figure 1.** Vibrational spectra of pure H<sub>2</sub>O showing the stretching band (3000–3700 cm<sup>−1</sup>), scissor (~1650 cm<sup>−1</sup>), and the scissor and libration overtone (~2100 cm<sup>−1</sup>). Raw TIR data (○), corrected TIR data (●), and transmission data (□, ◇) from refs 33 and 34, respectively. Curves are offset relative to each other by 0.05 units for clarity.

corrected spectrum (●) is in excellent agreement with previously published transmission experiments (□ and ◇)<sup>33,34</sup> with only small deviations on either side of the main OH vibration peak (curves offset for clarity). These small deviations could be due to dispersion in the index of refraction, as discussed in ref 26; specifically, when the incident angle is much greater than the critical angle, this leads to small distortions in the absorption band compared to transmission measurements. However, it is also recognized that the dispersion in refractive index is not taken into account when simple transmission spectra are recorded.<sup>26</sup> In addition, recent work by others have shown that “anomalous dispersion” does not influence the chemical analysis of water solution ATR spectra and has not affected the previous study of the hydrogen-bonding structure of water in ionic solutions.<sup>29,30,32,35</sup> Thus, we do not consider the “anomalous dispersion” to significantly deter from broader conclusions regarding the chemical analysis of water solutions.

To understand more clearly how defects modify the hydrogen bond network, and thus the OH stretching band of water, it is necessary to deconvolute the spectrum and assign the vibrational components physical and molecular origins. Previous work on the deconvolution and assignment of the Raman and IR  $\nu(\text{OH})$  band has claimed that the structure comes from the formation and breaking of donor and acceptor type hydrogen bonds,<sup>36</sup> the type of hydrogen bond,<sup>5</sup> number of HBs,<sup>15</sup> or the bond bending angles.<sup>37</sup> Although each description has been strongly argued, the structure within the  $\nu(\text{OH})$  band must contain at least all of these characteristics. In other words, liquid water is a system of an ensemble of states that tend to thermodynamic equilibrium and give rise to the structure seen in the  $\nu(\text{OH})$  band. Thus, a more appropriate description cannot be limited to considering a single origin leading to the structure of the  $\nu(\text{OH})$  band but must include multiple effects.

Our new interpretation of the  $\nu(\text{OH})$  band is based on cooperative hydrogen-bonding resulting from the thermodynamic equilibrium ensemble of states. Ohno et al. parametrized the effect of cooperative hydrogen bonding using a single value ( $M_{\text{OH}} = -d' + a' + d'' - a''$ ), an integer ranging from −2 to +4, with +4 describing stronger cooperativity of the hydrogen bonds.<sup>23</sup> Here,  $d$  and  $a$  denote the number of proton “donors” and “acceptors” for the initial proton donor (single prime) and acceptor (double prime) pair. This value describes the extent of local hydrogen bonding for water molecules and was introduced as a magnitude for the OH frequency shift due to the hydrogen-bonding patterns. This value can also be considered as a “structure factor” or “bond ordering” parameter to characterize the locally networked water molecules and can thus be used to quantify the ensemble structural correlations of pure



**Figure 2.** Deconvolution of the OH stretching band. Corrected TIR data (◇); band components (dashed lines, a–f, corresponding to free,  $M_{\text{OH}} = 0$  and 1, 2, 3, 3', and 4, respectively; total fitted curve (red). Inset: plot of  $\chi^2$  and sum of fit residual vs number of Gaussian peaks showing a minimum sum of the fit residual using six components.

water and how their respective contributions might be modified by defects in the liquid (i.e., ions or molecules).

The idea of a “structure factor” for water is supported by the two-state physical model recently put forth by Tanaka.<sup>25</sup> In this model, the free energy of the system contains additional terms that depend on a bond order parameter,  $S$ , that is related to well-defined locally favored structures (short-range order). As the system (liquid water) tends to thermodynamic equilibrium, the molecular structures associated with each component ( $M_{\text{OH}}$  value) are the locally favored ensemble structures. Thus, we anticipate a direct relationship between the  $M_{\text{OH}}$  value and the bond order parameter in Tanaka’s two-state model.

We have used this description as a basis for assigning the components of the  $\nu(\text{OH})$  band using six Gaussian peaks (Figure 2). Both Lorentzian<sup>38–40</sup> and Gaussian<sup>5,15,37</sup> line shapes have been used to fit OH vibrational spectra, with Lorentzians used to describe frequency components that arise from individual vibrational states and Gaussians describing thermally broadened states. In the present work, we use Gaussians for deconvolution because the components contributing to the  $\nu(\text{OH})$  band consist of groupings of individual vibrational states that, due to the distribution of bonding environments in the liquid, are described by a Gaussian profile. Lorentzian line shapes were also unable to adequately characterize the  $\nu(\text{OH})$  envelope this way and consistently had larger fit residuals than Gaussian line shapes.

The  $\nu(\text{OH})$  band was deconvoluted using standard algorithms based on minimizing  $\chi^2$ , with all fit parameters having a 95% confidence interval. Currently, there is ambiguity as to the number of components, with up to five or six vibrational bands possible,<sup>4,5,14,37</sup> all of which are limited to a single type of contribution, discussed previously. We monitored both  $\chi^2$  and the sum of the fit residual as a function of the number of components (Figure 2 inset). As the inset shows,  $\chi^2$  monotonically decreases with the increasing number of components. However, the sum of the fit residual has a clear minimum at six components, indicating that the sum of the deviations of the total fit from the data contain the least amount of errors compared to the other fits. This suggests that an optimal fit to the  $\nu(\text{OH})$  band requires at most six Gaussian components. The deconvolution and assignments do not include discussions of Fermi resonance contributions, as our interpretation is similar to that of Whalley and Sceats et al.: it is primarily the intermolecular coupling that determines the spectral response of water.<sup>18,41</sup>

**TABLE 1:  $\nu(\text{OH})$  Band Assignments, Local Molecular Environments, and Peak Positions ( $\text{cm}^{-1}$ ) for Pure Water**

component	$M_{\text{OH}}$ value	% of $\nu(\text{OH})$ band	min no. of $\text{H}_2\text{O}$ molec	no. of HBs	this work	ref 23 <sup>a,b</sup>	ref 31	ref 32
a	free	1.2	1–2	0–1	3629	3685	3633	3620
b	$M_{\text{OH}} = 0$ and 1	17.3	3–7	2–6	3535	3512	3524	3540
c	$M_{\text{OH}} = 2$	42.1	4, 6, 8	3, 5, 7	3390	3386	3364	3420
d/e	$M_{\text{OH}} = 3/3'$	25.5/8.3	5, 7	4, 6	3246/3134	3223/3124	3260/–	3230/–
f	$M_{\text{OH}} = 4$	5.6	6	5	3045	2987	–	–

<sup>a</sup> Estimated from the tabulated values contained in the online supporting information for ref 23. <sup>b</sup> Calculated using GAUSSIAN 03 and a B3LYP/6-311++G(d,p) exchange functional.

The  $\nu(\text{OH})$  band components, bond ordering, and corresponding local molecular environment are summarized in Table 1. Peaks a–f have been assigned the following bond ordering parameters ( $M_{\text{OH}}$  values): a, free; b, 0 and 1; c, 2; d, 3; e, 3'; f, 4. Larger values indicate an increase in hydrogen bond cooperativity. Peak a is termed a free-like (monomer-like) vibration, as this component is comparable to the experimental and theoretical values for a free O–H vibration,<sup>16,23,39,42,43</sup> although red-shifted (discussed later). However, the position of peak a is close to that measured ( $3680\text{ cm}^{-1}$ ) for water at vapor/liquid and hydrophobic-solid/liquid interfaces<sup>44,45</sup> and could therefore have contributions from water at the solid(Si prism)/liquid interface. In addition, previous work has shown a similar frequency of the OH stretch at  $3695\text{ cm}^{-1}$  for ice or water surfaces,<sup>46,47</sup> supporting the interpretation that the band centered at  $3629\text{ cm}^{-1}$  is associated with free-like OH stretching. Unfortunately, the ATR technique cannot probe interactions as a function of depth and thus is currently not able to distinguish any free-like vibrations from those which might be due to surface interactions.

Components b–d contribute  $\sim 85\%$  to the total signal, and e and f contribute  $\sim 14\%$ , indicating that the majority of water molecules have a local hydrogen-bonded network which includes 3–7  $\text{H}_2\text{O}$  molecules. Recent theoretical calculations indicate a maximum in the HB energy for 5–6  $\text{H}_2\text{O}$  molecules due to cooperative enhancement of the HB network,<sup>48</sup> indicating components b–d are dominated by water ensembles in a hydrogen-bonded network of 5–6  $\text{H}_2\text{O}$  molecules. Note that a local grouping of water molecules can have multiple  $M_{\text{OH}}$  values.

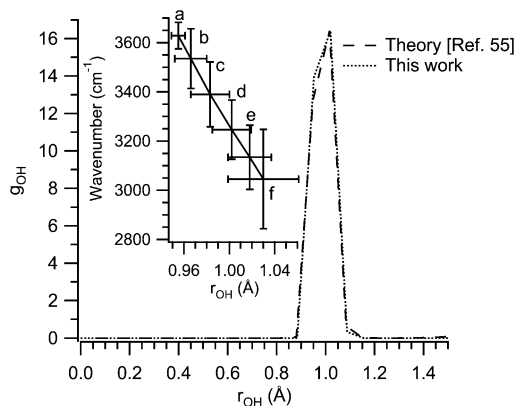
The bond ordering values of  $M_{\text{OH}} = -2, -1$ , and 0, corresponding to 4 (3), 3 (2), and 2 (1) molecules (HBs), respectively, are energetically unfavorable local arrangements of molecules in liquid water.<sup>49</sup> Thus, they are not expected to contribute to the distribution of the highest probable local environments that lead to the structure of the  $\nu(\text{OH})$  band. Due to the similarity in configuration space between  $M_{\text{OH}} 0$  and 1 bonding environments, it is not possible to separate the b component as two distinct contributions. It is possible the splitting of  $M_{\text{OH}} = 3$  bond ordering results from different dipole moments of the five- and seven-member water network, as has been reported previously for water clusters.<sup>50</sup>

Table 1 also summarizes the peak positions from this work, the calculations of Ohno et al., and experimental values reported by Fischer et al. and Wei et al. There is very good agreement of peak positions a–d and previously published experimental results.<sup>31,32</sup> It is also interesting to note that the peak positions presented here are in good agreement with those measured on small solid water clusters by Buck et al., namely that the vibrational frequency for  $n = 2, 3, 4$ , and 5 water clusters contribute to the spectrum at  $3600, 3532, 3416$ , and  $3360\text{ cm}^{-1}$ , respectively.<sup>39</sup> Additionally, they found that larger solid clusters ( $n = 6–10$ ) have OH-stretching contributions in the  $3500–3600$  and  $3050–3150\text{ cm}^{-1}$  regions, with the 6 and 7 molecular clusters having additional contributions between these ex-

tents,<sup>39,51</sup> supporting the interpretation presented here. Specifically, the local structuring in liquid water exhibits distinct groupings of frequencies that ultimately contribute to the envelope of the  $\nu(\text{OH})$  band. In addition, peaks e and f agree well with the calculations of Ohno et al.<sup>23</sup> There are many sources for errors in theoretical calculations including the choice of basis set, corrections for basis set superposition errors, harmonic or anharmonic approximations, and any scaling applied to calculated vibrational values. All of these can contribute to the overall error in calculations and might be the source(s) of the small discrepancy between the experimental values presented here and previous theoretical results.

The inset of Figure 3 shows the dependence of the peak position *vs* O–H bond length, with corresponding standard deviations. The values were calculated by transforming the frequency and full-width half-maximum values of the  $\nu(\text{OH})$  band components using Badger's rule.<sup>52</sup> The components follow a nearly linear relationship between the red shift of the frequency and an increase in the O–H bond length in this wavelength region (i.e., Badger's rule is approximately linear in this region).

With an increase in O–H bond length, Badger's rule predicts an associated red shift in the components of the  $\nu(\text{OH})$  band, as seen in the inset. We interpret that this red shift is caused by the influence of the surrounding hydrogen bond network (when O–H bonds lengthen and become weaker, hydrogen bonds shorten and become stronger, causing a red shift in energies), similar to that previously reported for small clusters.<sup>19,20,53</sup> An analogous HB network interpretation was recently used in analyzing the O1s core photoelectron spectra, leading to similar results of red-shifted energies resulting from the interaction of the HB network.<sup>13</sup> For example, taking accepted values for the O–H...H distance to be approximately  $2.78\text{ \AA}$ ,<sup>54,55</sup> we find stronger HB are formed for O...H distances  $\leq 1.8\text{ \AA}$  (transition around peaks c and d), consistent with values from refs 11 and 13.



**Figure 3.**  $g_{\text{O-H}}$  computed pair correlation function (dashed) compared to that calculated from the peak positions of the fits to the IR data (dotted). Inset: main peak positions versus O–H bond length as calculated using Badger's rule and corresponding standard deviations.



The physical origin to the structure in the stretching band comes from the range of O–H distances in liquid water, which are directly influenced by the extended HB network. Figure 3 compares the first O–H peak in the  $g_{\text{O-H}}$  pair correlation function (dashed) calculated using Car–Parrinello molecular dynamics (CPMD) simulations<sup>55</sup> and that calculated by transforming the vibrational components into distances, with each converted component weighted according to its contribution to the  $\nu(\text{OH})$  band. As can be seen, the agreement between values derived from experiments (dotted line) and CPMD simulations (dashed line) is rather good. The striking agreement clearly shows that the features of the  $\nu(\text{OH})$  band arise from both the O–H bond distance as well as the local extent of hydrogen bonding and interactions with the hydrogen-bonded network in the liquid.

In summary, we presented a new and alternative interpretation of the structure of the IR vibrational mode of pure water. The interpretation is based on the cooperative hydrogen bonding arising from a network of HBs in the liquid. This cooperativity can be expressed using a simple “bond ordering” parameter detailed by Ohno et al. and is supported by a recent two-state physical model of water developed by Tanaka that incorporates an “order parameter” ( $S$ ) that characterizes locally favored structures. Our six-component deconvolution is directly related to the  $M_{\text{OH}}$  values of Ohno et al., as can be seen in Table 1. In addition, we have shown that the physical origin of the structure in the  $\nu(\text{OH})$  band is directly related to the O–H bond length (Figure 3) and number of hydrogen bonds (Figure 2 and Table 1), and that variations in this bond length are caused by the influence of the surrounding hydrogen-bonded network of water molecules. Thus, our interpretation incorporates not only the O–H bond length and the number of hydrogen bonds but also the bond angles and type of hydrogen bonds.

We believe this interpretation and deconvolution can be applied to IR experiments of aqueous solutions provided the defect density is relatively low and the defects do not absorb IR in the same region as water. We also consider there to be a strong correlation between the  $M_{\text{OH}}$  bond order and the dipole moments (vibrational frequency) of liquid water “clusters”, similar to that reported in previous experiments and calculations<sup>21,22,24,50</sup> and are currently performing *ab initio* CPMD calculations on liquid water to thoroughly explore this correlation.

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