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Temperature, pressure, and isotope effects on the structure and properties of liquid water: A lattice approach

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We present a lattice model to describe the effect of isotopic replacement, temperature, and pressure changes on the formation of hydrogen bonds in liquid water. The approach builds upon a previously established generalized lattice theory for hydrogen bonded liquids [B. A. Veytsman, J. Phys. Chem. **94**, 8499 (1990)], accounts for the binding order of $1/2$ in water-water association complexes, and introduces the pressure dependence of the degree of hydrogen bonding (that arises due to differences between the molar volumes of bonded and free water) by considering the number of effective binding sites to be a function of pressure. The predictions are validated using experimental data on the temperature and pressure dependence of the static dielectric constant of liquid water. The model is found to correctly reproduce the experimentally observed decrease of the dielectric constant with increasing temperature without any adjustable parameters and by assuming values for the enthalpy and entropy of hydrogen bond formation as they are determined from the respective experiments. The pressure dependence of the dielectric constant of water is quantitatively predicted up to pressures of 2 kbars and exhibits qualitative agreement at higher pressures. Furthermore, the model suggests a—temperature dependent—decrease of hydrogen bond formation at high pressures. The sensitive dependence of the structure of water on temperature and pressure that is described by the model rationalizes the different solubilization characteristics that have been observed in aqueous systems upon change of temperature and pressure conditions. The simplicity of the presented lattice model might render the approach attractive for designing optimized processing conditions in water-based solutions or the simulation of more complex multicomponent systems. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2804418]

I. INTRODUCTION

The structure of liquid water, its response to changes in the environmental conditions, and the implications of structural changes on the solubilization characteristics have been subject of intense research for many decades.[1–45] Under ambient conditions, it was first described by Bernal and Fowler as a tetrahedral network of water molecules with local order.[1] Since then the development of models that appropriately account for the distinctive structural features of liquid water and their implications on its "anomalous" thermodynamic properties—such as its density maximum at 4 °C at atmospheric pressure, its density decrease upon crystallization, its increasing specific heat at lower temperatures, or its minimum in isothermal compressibility—is an active field of research.[2–20] In general, the particular properties of water are attributed to hydrogen bond (H-bond) formation, i.e., the existence of strong (much larger than the thermal energy k_BT) directed interactions between water molecules.[21–26] The complexity associated with directed interactions has rendered the theoretical understanding of water a challenging task since it violates many of the assumptions that are fundamental to liquid state theories.

Given the enormous relevance of water-based solutions in nature and technology, the development of predictive models that are capable of being extended to more complex solution scenarios to estimate the changes in the solvation properties of water as a function of temperature and pressure is important. For instance, recently we demonstrated that the structure of polymers in electrolyte solutions is intimately linked to the solvent's dielectric constant and capacity of hydrogen bonding. We found that under nonhydrogen bonding conditions the coordination of ions to polymer chains is observed, representing a "precursor state" of the respective polymer/salt crystal structure in the solid state that has shown to exhibit high ionic conductivity at room temperature.[46–48] Predictive models that capture the effect of

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external parameters (such as temperature and pressure) on hydrogen bond and structure formation are of interest since they could facilitate the identification of processing conditions, in which water exhibits properties that are preferential to particular structure formation processes. In this context, the application of mean-field lattice theories to describe fluid mixtures with hydrogen bonding is particularly interesting. While the approach disregards the characteristics of a hydrogen bonded network or cluster formation, it has been shown that identical conclusions are derived as compared to more complex nonlattice theories.[49–51] The success of lattice models—despite the simplifications underlying the approach—has been related to the time scale of water-water exchange reactions that occur on the order of picoseconds to microseconds, thus justifying the replacement of the "discrete cluster" by mean-field lattice models for the description of properties that relate to much longer time scales.[21] The versatility of lattice models to predict the phase behavior of complex solution scenarios was demonstrated recently in the study of reentrant phase behavior of hydrogen bonded fluid mixtures and polymer solutions.[50–61] The use of lattice models to describe the structure formation of associating liquids was first discussed by Walker and Vause.[52,53] Veytsman demonstrated that lattice models based on a Flory-type mean-field approximation result in identical equations than nonlattice "discrete cluster models" and provided an adequate approach to formulate free-energy relations for hydrogen bonded liquids.[49] Suresh *et al.* applied this approach to derive an expression for the structure factor of hydrogen bonded fluids based on the Kirkwood-Fröhlich theory that facilitated deduction of thermodynamic parameters of hydrogen bond formation from measurements of the dielectric constant of water.[62–64] Recently, the Flory-type model was extended in order to describe the structure of aqueous polymer solutions.[61] While this work clearly demonstrated the versatility of lattice models to describe the phase behavior of aqueous polymer solutions, thermodynamic parameters for hydrogen bond formation different to the experimental values needed to be assumed. This is unsatisfactory since, for example, the entropy of hydrogen bond formation is related to the geometry of the association and the values obtained with the fitting procedures sometimes correspond to rather unphysical binding situations.

In this paper, we demonstrate that the consideration of the binding order of $1/2$ for H-bond formation facilitates the correct prediction of available experimental data on the temperature dependence of the degree of hydrogen bonding and dielectric constant without any adjustable parameter. By extending the approach with a phenomenological description of the effective number of binding sites, the model furthermore reproduces experimental data on the pressure dependence of the dielectric constant of liquid water. It thus presents a theoretically founded and more predictive alternative to the semi-empirical Tait equation[65,66] that is currently often used by experimentalists.

The structure of the paper is as follows. First, based on Veytsman original work[49] we present a lattice model to predict the degree of association of a fluid containing $2N_w$ acceptor and $2N_w$ donor sites, with N_w being the total number
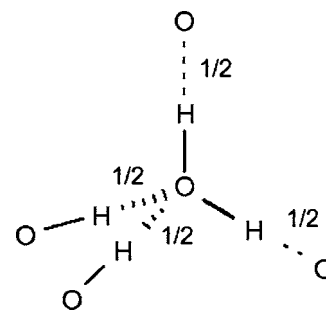
SCHEME 1. Illustration of the tetrahedral binding geometry of associated water-water molecules in which each oxygen atom is hydrogen bonded to four other oxygen atoms through an O–H–O bridge. Thermal disruption causes a more disordered arrangement. The binding order per H bond is $1/2$ due to the symmetry of the bond formation, i.e., two hydrogen bonds are formed per water molecules.

of molecules in the system, as a function of temperature. We then apply Kirkwood-Fröhlich theory combined with the structure factor introduced by Suresh *et al.* in order to validate our model based on experimental measurements of the temperature dependence of the water dielectric constant. We discuss the implications of isotopic replacement on hydrogen bond formation that is significant when deuterated solvents are being used instead of normal water (e.g., in neutron scattering or nuclear resonance spectroscopy), and we demonstrate that differences in hydrogen bonding between the respective isotopic isomers can be balanced by temperature shifts. In the last part of the paper we discuss an extension of the model to capture the pressure dependence of the degree of hydrogen bonding and validate the predictions against existing experimental data on the pressure dependence of the dielectric constant of liquid water. The analysis will suggest a sensitive dependence of the degree of H bonding on the applied pressure with almost complete loss of H-bond formation at pressures above 20 kbars at 40 °C.

II. THEORETICAL FORMALISM, RESULTS, AND DISCUSSION

A. Hydrogen-bond formation under zero pressure condition

1. Temperature effect on hydrogen bond formation

In water, donor and acceptor sites are arranged in tetrahedral symmetry, giving rise to a typical binding situation as depicted in Scheme 1. Hydrogen bonds in liquids have been described by Kohler as cohesive forces with a lifetime ranging from 10^{-11} to 10^{-5} s. It has been argued that this characteristic lifetime determines the time necessary to describe the stationary state of a molecule but has no influence on the exchange possibilities. Thus, the combinatorial entropy of a system in the presence of H bonds can be calculated in the same way as in the absence of H bonds.[21] In thermal equilibrium, liquid water is thus assumed to be constituted of a mixture of two states, i.e., bonded and free water molecules. The system can then be represented as being divided in N_w equal lattice sites, where N_w is the number of water molecules. The volume of a lattice site is v_0 (equal to the volume of a water molecule). The specifications of the water molecules in hydrogen bond formation will be captured via the
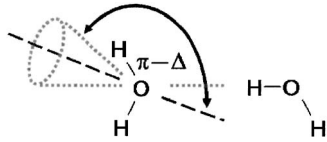
SCHEME 2. Illustration of the characteristic space angle Δ_S describing the permissible angular spread in the actual binding configuration (dotted line) around the ideal tetrahedral configuration (dashed line) to retain stability of the hydrogen bond.

characteristic energetic and entropic change upon H-bond formation. Each water molecule has two H-donor sites and two H-acceptor sites. A donor site of a water molecule can form a H bond with an acceptor site of another water molecule if the sites are located in the adjacent cells. Thus the total number of proton donors and proton acceptors for H-bond formations is $g=2N_w$, respectively. Let n_b and n_0 be the number of H-bonded and free sites. The relationship between these numbers is given via the volume of the system V, where $V=N_w v_0 = v_0 g/2 = v_0(n_0+n_b v_b/v_0)$ with v_b being the volume per water-water H bond (note that $g=2n_0+n_b$ where v_b equals to one-half the volume of a lattice unit). One should compute the free energy due to the hydrogen bonding interactions βF ($\beta=1/k_B T$ with k_B being the Boltzmann constant and T the absolute temperature) at a given n_b and minimize it with respect to n_b. In the mean-field approximation, βF is given as[49,61,62]

$$\beta F = -\frac{v_0}{V}\ln Z, \qquad (2.1a)$$

where the partition function Z reads

$$Z = P_{\text{comb}} p_r^{n_b} e^{n_b \beta \Delta E_{\text{HB}}}, \qquad (2.1b)$$

ΔE_{HB} is the energetic gain for H-bond formation between water molecules. The combinatorial factor P_{comb} describes the number of ways to distribute n_b H bonds between the donor and acceptor sites (i.e., the number of ways that the g donor sites and g acceptor sites can form n_b H bonds). p_r is the probability that the donor and acceptor sites can be found in the vicinity of each other for formation of the corresponding H bonds. p_r can be defined as $p_r=(v_b/V)=v_b/(N_w v_0)$ $=v_b/(v_0 g/2)$.[61] One can define the entropic loss associated with the formation of one bond as $\Delta S_{\text{HB}}^{\text{dis}}/k_B=-\ln(2v_b/v_0)$

(Ref. [67]) and the entropic parameter for a single bond formation as $-\lambda_0=e^{-\Delta S_{\text{HB}}^{\text{dis}}/k_B}$. In the context of the lattice model, $\Delta S_{\text{HB}}^{\text{dis}}$ corresponds to the disorientational entropy associated with the local alignment of proton donors and acceptors and the corresponding loss of rotational degrees of freedom. Its explicit relation to the lattice parameters has been described by Flory,[68] Matsuyama and Tanaka,[69] and Bekiranov et al.[70] An alternative—but physically equivalent—interpretation has been proposed by Walker and Vause[52,53] and Dormidontova[61] that relates $\Delta S_{\text{HB}}^{\text{dis}}$ to the decrease in orientational entropy upon hydrogen bond formation due to the particular molecular orientation. The local change of entropy upon hydrogen bond formation is related to the characteristic space angle Δ_S for bond formation (the definition of Δ_S is illustrated in Scheme 2) that denotes the maximum angular spread about the ideal molecular orientation that still allows for bond formation via $\Delta S_{\text{HB}}^{\text{dis}}/k_B=-\ln((1-\cos \Delta_S)/2)$.[61] Since Δ_S is determined by the electronic structure of the water molecule, it can be considered to be approximately temperature and pressure independent. Typically, H bonds have a low angular spread, i.e., hydrogen bonds are only stable within a narrow angular range about Δ_S.[52,53] Note that this interpretation of $\Delta S_{\text{HB}}^{\text{dis}}$ has the advantage of limiting permissible values to physically realistic bonding conditions and it sets bounds to the use of the disorientational entropy as fitting parameter to experimental data. $\Delta S_{\text{HB}}^{\text{dis}}$ has been determined by several authors using IR absorption spectroscopy or x-ray scattering (see Table I).[71–78]

Using combinatorial considerations (note that $C_{2n_0}^g C_{n_b}^g$ $=C_{n_b}^g C_{n_b}^g = C_{2n_0}^g C_{2n_0}^g$, where C_x^g is the number of ways to select x out of g) one can write

$$P_{\text{comb}} = n_b! C_{n_b}^g C_{n_b}^g = \frac{g!}{(g-n_b)!}\frac{g!}{(g-n_b)! n_b!}$$

$$= \frac{g!}{(g-n_b)!}C_{n_b}^g. \qquad (2.2)$$

Using Eqs. (2.1a), (2.1b), and (2.2), the free energy of the system becomes

TABLE I. Summary of literature values on the energy and entropy of hydrogen bond formation used in this work (values are given per mol of H bonds).

	Ref. 76 H_2O	Ref. 29 H_2O	Refs. 74 and 78 H_2O	Refs. 29 and 78 H_2O	Refs. 71 and 72 HDO	Ref. 29 D_2O
ΔE_{HB} (kcal/mol)	2.8	3.57	4.5	3.57	3.69	3.81
$\Delta E_{\text{HB}}/k_B$ (K)	$\sim$1408	$\sim$1796	$\sim$2264	$\sim$1796	$\sim$1856	$\sim$1917
$\Delta E_{\text{HB}}/k_B T$ at $T=298$ K	4.73	6.03	7.6	6.03	6.23	6.43
$\Delta S_{\text{HB}}^{\text{dis}}$ (cal/deg mol)	9.5	11.0	7.4	7.4	7.2	7.0
$\Delta S_{\text{HB}}^{\text{dis}}/k_B$	4.78	5.53	3.72	3.72	3.62	3.52
$\lambda_0=e^{-\Delta S_{\text{HB}}^{\text{dis}}/k_B}$	8.4×10^{-3}	3.95×10^{-3}	2.42×10^{-2}	2.42×10^{-2}	2.67×10^{-2}	2.96×10^{-2}
$\Delta_s\equiv$Arccos $(1-2\lambda_0)$	$\sim$0.05π $\sim$11°	0.04π $\sim$7°	0.0995π $\sim$18°	0.0995π $\sim$18°	0.105π $\sim$19°	0.11π $\sim$19°

$$\beta F = g\frac{v_0}{V}\left\{\varphi_0\ln(\varphi_0) + \varphi_b\beta\Delta F_b - \frac{1}{g}\Delta S_{\text{comb}}/k_B\right\} \quad (2.3a)$$

or

$$\beta F = g\frac{v_0}{V}\{2\varphi_0\ln(\varphi_0) + \varphi_b\ln(\varphi_b) + \varphi_b\beta\Delta F_b\}$$

$$\equiv g\frac{v_0}{V}\{2(1-p)\ln(1-p) + p\ln(p) + p\beta\Delta F_b\}, \quad (2.3b)$$

with $-(1/g)\Delta S_{\text{comb}}/k_B = -(1/g)\ln C_{n_b}^g = (n_b/g)\ln(n_b/g) + (1 - n_b/g)\ln(1 - n_b/g)$. The combinatorial entropy ΔS_{comb} (part of the total combinatorial term P_{comb}) relates to the number of ways to select n_b bonded sites out of g total sites of the water molecules. φ_0 and φ_b denote the respective volume fraction of the free and bound solvents; $\varphi_0 = 1 - \varphi_b \equiv 1 - n_b v_b/V = 1 - n_b/g \equiv 1 - p$. ΔF_b is the local free-energy variation of a single bond formation, $\beta\Delta F_b = -\beta\Delta E_{\text{HB}} - \ln(\lambda_0/e)$. Equations (2.3a) and (2.3b) show that the free energy of a solution made up of n_b bonded and n_0 free sites is a sum of two contributions: The entropy of mixing the free and bonded sites and the free energy needed to form one hydrogen bond. Minimization of Eqs. (2.3a) or (2.3b) with respect to n_b or p results in

$$\bar{p} = \bar{n}_b/g = \frac{\lambda_s\bar{\varphi}_0}{1 + \lambda_s\bar{\varphi}_0} \quad \text{or} \quad \bar{p} = \bar{n}_b/g = \lambda_s\bar{\varphi}_0^2 = \lambda_s(1-\bar{p})^2,$$

$$(2.4)$$

with $\bar{\varphi}_0 = 1 - \bar{p}$ ($\bar{p}$ is the average equilibrium fraction of bonded water and $\bar{n}_b$ is the average number of H bonds) and $\lambda_S = \lambda_S(T) = e^{1-\beta\Delta F_b} = \lambda_0 e^{\beta\Delta E_{\text{HB}}}$ is the equilibrium constant for the bond formation. Since the entropy loss upon formation of hydrogen bonds is outweighing the gain in compositional entropy, the fraction of hydrogen bonded sites decreases with increasing temperature.[29] The degree of hydrogen bonding is thus expected to vanish when the thermal energy is exceeding the energy gain upon hydrogen bond formation ($\Delta E_{\text{HB}} \ll k_BT$). This intuitive picture is confirmed by solving the quadratic form, Eq. (2.4), with respect to $\bar{p}$,

$$\bar{p} = \bar{p}(T) = \bar{n}_b/g = \frac{\sqrt{1 + 4\lambda_s(T)} - 1}{\sqrt{1 + 4\lambda_s(T)} + 1}. \quad (2.5)$$

Equation (2.5) states the dependence of the degree of association on the temperature and the free-energy change (i.e., ΔE_{HB} and $\Delta S_{\text{HB}}^{\text{dis}}$) associated with hydrogen bond formation. $\bar{p}$ varies from 1 to 0, corresponding to completely bonded or free state, respectively. Several researchers have determined $\bar{p}$ and deduced values for ΔE_{HB} and $\Delta S_{\text{HB}}^{\text{dis}}$ by experiment and simulation.[71–76] In the following we apply Eq. (2.5) to analyze some of the existing experimental data in order to test its predictive capability. We note that a major problem in referencing to previous experimental studies are the different terminologies that are used to describe hydrogen bond formation (e.g., enthalpy/entropy are often given per H bond or per mol of water) along with different assumptions about the number of hydrogen bonds per water molecule. In the following we provide a brief overview of the various data sources that were used in our study.

Review of experimental data on ΔE_{HB} and $\Delta S_{\text{HB}}^{\text{dis}}$. Overall the reported experimental values of the enthalpy of hydrogen bond formation in water are found to vary from 1.32 to 5.58 kcal/mol. One major reason for the widely varying data is in the different assumptions of the respective authors regarding the number of H bonds that are formed per water molecule. Haggis *et al.* used a statistical method to determine the fraction of H bonds from dielectric constant and latent heat data assuming that each water molecule can exist in four-, three-, two-, one-, and zero-bonded states.[74] The obtained results are summarized in Table II of Ref. 74. Using the enthalpy of bond formation (4.5 kcal/mol) previously given by Pauling,[77] Haggis *et al.* found that the fractions of free water equal to 9% at 0 °C and ~100% at 370 °C. Earlier studies by Pauling suggesting ΔE_{HB} =4.5 kcal/mol reported the percentage of free water to be about 16% at 0 °C.[77] Eisenberg *et al.* gave values for the ΔE_{HB} determined from measurements of the sublimation enthalpy ΔH_{sub} of the ice polymorph I_h as $\Delta E_{\text{HB}} = \Delta H_{\text{sub}}/2$ =11.32/2=5.66 kcal/mol, where two bonds per water molecule have been assumed.[78] Walrafen determined the enthalpy of bond formation to be ΔE_{HB}=3.1 kcal/mol from Raman spectroscopy assuming that four H bonds are formed per water molecule.[79] In another investigation, the same author reported an entropy of $\Delta S_{\text{HB}}^{\text{dis}}$=9.5 cal/deg mol and an enthalpy of 2.8 kcal/mol mol of H bonds.[76] Similar values were also reported by Scatchard *et al.* (ΔE_{HB} =3.4 kcal/mol) (Refs. 80 and 81) as well as by Grundberg and Nissan (ΔE_{HB}=3.23–3.71 kcal/mol).[82] Suresh *et al.* developed a lattice model similar to ours in order to deduce the thermodynamic properties of H-bond formation from experimental measurements of the static dielectric constant of water. Assuming four H bonds per water molecule the authors reported values of ΔE_{HB}=5.58 kcal/mol (about twice the values given by Walrafen[76]) and $\Delta S_{\text{HB}}^{\text{dis}}$=8.89 cal/deg mol (close to Walrafen's value).[62] By evaluating the partition function for liquid water, Nemethy and Sheraga reported energies of ΔE_{HB}=3.57 kcal/mol for water molecules and ΔE_{HB}=3.57+0.24 kcal/mol for D$_2$O.[29,30] Simulation studies by Silverstein *et al.* suggested for the free energy, enthalpy, and entropy for hydrogen bond formation, ΔF_b =0.48 kcal/mol, ΔE_{HB}=1.9 kcal/mol, and $\Delta S_{\text{HB}}^{\text{dis}}/k_B$=2.4, respectively.[83–85] In a recent paper on hydrogen bonded polymer solutions, the following values have been used: $\Delta E_{\text{HB}}/k_B$=1800 K (corresponding to $\Delta E_{\text{HB}} \approx 6k_BT$ =3.58 kcal/mol at room temperature) and $\Delta S_{\text{HB}}^{\text{dis}}/k_B$=−ln((1 −cos Δ_S)/2)=2.348 (corresponding to a characteristic angle $\Delta_S = \pi/5 = 36°$).[61] For our calculations we applied the values summarized in Table I (values given per mol of H bonds) that we found to be accepted by most authors in the literature and corresponding to the assumption of two H bonds per water molecule.[29,74,76]

Temperature effect on hydrogen bond formation Figure 1 displays the variation of the average degree of hydrogen bonding between water-water molecules as a function of temperature for different values of the free energy of H-bond formation [ΔE_{HB}=5.6 kcal/mol, $\Delta S_{\text{HB}}^{\text{dis}}$=19 cal/deg mol;[76] ΔE_{HB}=3.57 kcal/mol,[29] $\Delta S_{\text{HB}}^{\text{dis}}$=11 cal/deg mol and ΔE_{HB} =4.5 kcal/mol,[74] $\Delta S_{\text{HB}}^{\text{dis}}$=7.4 cal/deg mol (Ref. 78)]. Two im-
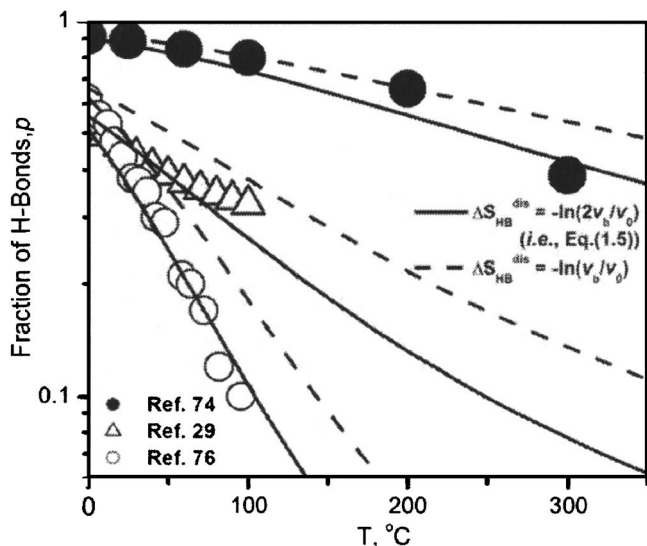
FIG. 1. Comparison between the temperature dependence of the degree of hydrogen bonding $\bar{p}$ as obtained from calculation and experiment. Calculations (shown as continuous lines) are based on Eq. (2.5) [i.e., assuming $\Delta S_{HB}^{dis}/k_B = -\ln(2v_b/v_0)$] for different values of the enthalpy and entropy needed for the H-bond formation as concluded from experiments. The experimental data are shown as symbols ($\bigcirc$, $\triangle$, $\bullet$) and correspond to, $\Delta E_{HB} = 5.6$ kcal/mol, $\Delta S_{HB}^{dis} = 19$ cal/deg mol (Ref. 76); $\Delta E_{HB} = 3.57$ kcal/mol, $\Delta S_{HB}^{dis} = 11$ cal/deg mol (Ref. 29); and $\Delta E_{HB} = 4.5$ kcal/mol (Ref. 74), $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol (Ref. 78), respectively. Dashed lines represent calculations by defining ΔS_{HB}^{dis} as $\Delta S_{HB}^{dis}/k_B = -\ln(v_b/v_0)$ and with respective thermodynamic parameters as concluded by the experiments.

portant findings can be concluded from Fig. 1: First, all experimental data are well described by Eq. (2.5) given the values for ΔE_{HB} and ΔS_{HB}^{dis} as provided by the respective authors. We thus conjecture that the deviations between the different reported data are related to different assumptions about the number of H bonds per water molecule (i.e., model based) rather than real experimental discrepancies. Second, the account of the bound order of 1/2 per H bond [i.e., defining ΔS_{HB}^{dis} as $\Delta S_{HB}^{dis}/k_B = -\ln(2v_b/v_0)$] is critical to the predictive capabilities of the lattice model. The dashed lines correspond to a calculation based on a theoretical prediction assuming $\Delta S_{HB}^{dis}/k_B = -\ln(v_b/v_0)$. The discrepancy to the experimental values demonstrates the sensitivity of the approach to proper counting analysis. For all parameter combinations, Fig. 1 confirms that the stability of H bonds decreases with increasing temperature due to the increasing influence of the entropy loss associated with the formation of bonds.

2. Temperature effect on the static dielectric constant

In order to provide further support for our predictions as well as to establish the basis for the validation of our extension to the pressure dependence (see Sec. II B) of $\bar{p}$, we introduce a relationship between the degree of hydrogen bonding $\bar{p}$ and the static dielectric constant of water ε. According to Fröhlich-Kirkwood ε is given for polar liquids by[62–64]
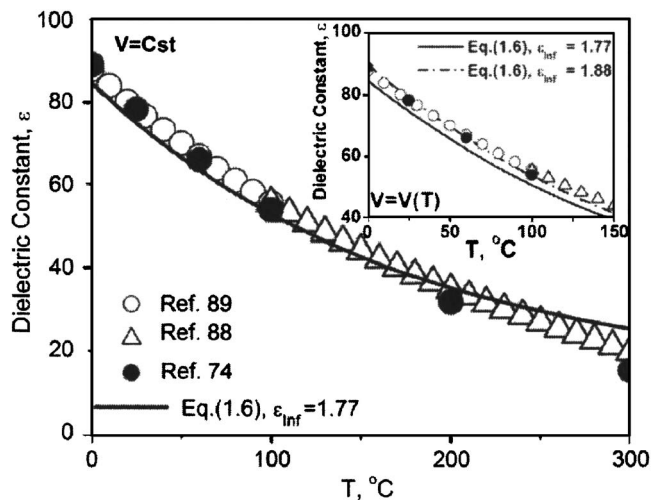

FIG. 2. Comparison between the predicted and the experimentally determined temperature dependences of the dielectric constant at zero pressure. Continuous curve corresponds to calculations based on Eqs. (2.5) and (2.6) assuming $\Delta E_{HB} = 4.5$ kcal/mol and $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol as reported by Refs. 74 and 78. The high-frequency limit of the dielectric constant is given as $\varepsilon_\infty = n^2$ and the dipolar moment as $\mu = 1.87$ D. Symbols ($\bullet$, $\triangle$, $\bigcirc$) represent experimental and calculated results as given by Refs. 74, 88, and 89. Shown in the inset is the calculated result taken into account temperature dependence of the specific volume of water (values taken from Ref. 101) demonstrating only minor effects on the predicted $\varepsilon(T)$.

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} = \frac{4\pi N_A \mu^2}{9k_B TV}g_0, \qquad (2.6)$$

where N_A, V, and μ are, respectively, the Avogadro number, the molar volume, and the dipole moment of the isolated molecule. ε_∞ denotes the high-frequency limit of the dielectric constant that results as a consequence of nuclear and electronic displacement polarizations, and which is given by $\varepsilon_\infty = n^2$, where n is the refractive index of the system. The correlation factor g_0 is a measure of the local ordering in the system in the absence of any external electric field.[86,87] Suresh et al. demonstrated that g_0 is related to the degree of hydrogen bonding via $g_0 = 1 + 4\bar{p}/(3 - \bar{p})$, which gives a value of 3 when $\bar{p} = 1$ (Ref. 87) (the original expression derived by Kirkwood $g_0 = 1 + 4\bar{p}/3$ gives a value of 2.33). Figure 2 compares the temperature dependence of the dielectric constant calculated via Eqs. (2.6) and (2.5) with experimental data reported by Haggis et al. and assuming [$\Delta E_{HB} = 4.5$ kcal/mol, $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol (Ref. 78)], $\varepsilon_\infty = n^2$ and $\mu = 1.87$ D.[1,63,64,74,87] The figure confirms the decrease in ε with increasing temperature due to the increasingly random orientation of the individual dipoles as well as the limiting value of ε_∞ at high temperatures. Note that the correction for the temperature dependence of the molar volume results in only minor changes in the predicted values, as shown in the inset of Fig. 2 (see continuous line).

3. Effect of isotopic replacement on hydrogen bonding

Many situations (for example, structural characterization methods, see below) require the use of deuterated water. The higher atomic mass of deuterium results in stronger H-bond formation, i.e., $\Delta E_{HB}^{H_2O} < \Delta E_{HB}^{D_2O}$.[72,73,90] Figure 3 presents the
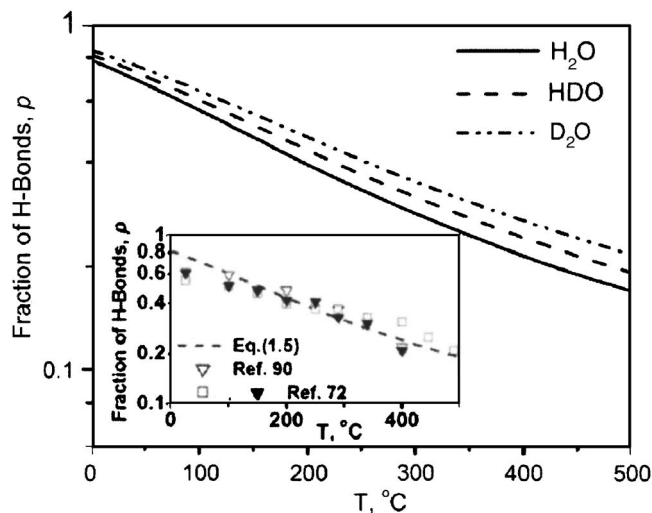
FIG. 3. Effect of isotopic replacement on the temperature dependence of the degree of hydrogen bonding $\bar{p}$ calculated for H_2O, HDO, and D_2O following Eq. (2.5). Continuous, dashed, and dashed-dot-dot lines correspond to H_2O ($\Delta E_{HB} = 3.57$ kcal/mol, $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol), HDO ($\Delta E_{HB} = 3.69$ kcal/mol, $\Delta S_{HB}^{dis} = 7.2$ cal/deg mol), and D_2O ($\Delta E_{HB} = 3.81$ kcal/mol, $\Delta S_{HB}^{dis} = 7.0$ cal/deg mol), respectively. Shown in the inset is a comparison of the model prediction with experimental data for HDO, as provided by Refs. 72 and 90. Symbols correspond to data obtained through x-ray (□) and IR absorption spectroscopies (▼,▽), respectively.

calculated temperature dependence of the degree of hydrogen bond formation $\bar{p}$ for H_2O, HDO, and D_2O based on Eq. (2.5) and assuming thermodynamic parameters for H-bond formation of H_2O ($\Delta E_{HB} = 3.57$ kcal/mol, $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol), HDO ($\Delta E_{HB} = 3.69$ kcal/mol, $\Delta S_{HB}^{dis} = 7.2$ cal/deg mol), and D_2O ($\Delta E_{HB} = 3.81$ kcal/mol, $\Delta S_{HB}^{dis} = 7.0$ cal/deg mol), respectively. The figure confirms the increasing degree of H-bond formation (at constant temperature) with increasing deuterium content, i.e., $\bar{p}(H_2O) < \bar{p}(HDO) < \bar{p}(D_2O)$ due to the larger enthalpy gain upon deuterium bond formation. The inset to Fig. 3 depicts a comparison between the calculations and experimental data on HDO (the only data available to us) that was obtained using x-ray scattering and IR spectroscopy.[72,73,90] We note that the prediction of the isotope effect on $\bar{p}$ using Eq. (2.5) is in good agreement with results obtained by Nemethy and Scheraga[30] and Marcus and Ben-Naim.[91]

The increased strength of H-bond formation in deuterated water has important implications on the behavior of solutes in aqueous systems. For example, certain proteins were found to exhibit different secondary and tertiary structures when dissolved in D_2O instead of H_2O.[92] Since deuterated solvents are routinely used in techniques such as neutron scattering or nuclear magnetic resonance experiments to enhance contrast and facilitate the structural characterization of solutes, it is important to note that Eq. (2.5) suggests the existence of an equivalence temperature T_{D_2O} for deuterated water, at which the amount of H-bond formation equals the one in water at a reference temperature T_{H_2O}, i.e., $\bar{p}_{H_2O}(T_{H_2O}) = \bar{p}_{D_2O}(T_{D_2O})$. Since the condition for equal fraction of H bonds is given by $\Delta F_{H_2O}/(k_B T_{H_2O}) = \Delta F_{D_2O}/(k_B T_{D_2O})$, one obtains for the equivalent temperature of D_2O,

$$T_{D_2O} = \frac{T_{H_2O} \Delta E_{HB}^{D_2O}}{\Delta E_{HB}^{H_2O} - T_{H_2O}(\Delta S_{HB}^{dis,H_2O} - \Delta S_{HB}^{dis,D_2O})}. \quad (2.7)$$

For the values given in Table I one can thus calculate the value for T_{D_2O} equal to $T_{D_2O} = 1.1 T_{H_2O} = 307$ K at reference temperature $T_{H_2O} = 298$ K. We note that the predicted temperature change $(T_{D_2O} - T_{H_2O}) \approx 9$ K (at room temperature) is in good agreement with recent studies by Vedamuthu *et al.* on the isotope effect on the viscosity of water, where it was shown that the viscosity of D_2O at 26.5 °C equals the one of H_2O at 20 °C. The same authors also reported that the temperature of maximum density of D_2O is 7.2 °C higher than the one of H_2O.[93–96]

B. Pressure effect on hydrogen bond formation

Pressure is the second important thermodynamic parameter to describe the phase behavior of water and water-based solutions. The implications of pressure conditions on the structure (and thus the solubilization capabilities) of water are particularly important because high pressure conditions are frequently encountered in biological and technological environments. In order to account for the coupling of pressure with the occupancy of bonded and free states, we introduce the effective number of the total sites g_{eff} given by $g_{eff} = g \psi(P)$, where $\psi(P)$ is a pressure function. In this case, the free energy reads

$$\beta F = g_{eff} \frac{v_0}{V} \left\{ 2\left(1 - \frac{p}{\delta}\right) \ln\left(1 - \frac{p}{\delta}\right) + \frac{p}{\delta} \ln\left(\frac{p}{\delta}\right) + \frac{p}{\delta} \beta \Delta F_b \right\}, \quad (2.8)$$

where $\delta = g_{eff}/g = \psi(P)$. Subsequent minimization of βF with respect to n_b (by introducing the parameter p as above) yields the fraction of H bonds as a function of the temperature T as well as the pressure P,

$$\bar{p}(T,P) = \delta(P) \bar{p}(T) = \delta(P) \frac{\sqrt{1 + 4\lambda_S(T)} - 1}{\sqrt{1 + 4\lambda_S(T)} + 1}. \quad (2.9)$$

Note that for $\delta = 1$ (i.e., at zero pressure, $g_{eff} = g$) Eq. (2.9) reduces readily to Eq. (2.5). In order to explicitly state the pressure dependence of $\bar{p}$, g_{eff} needs to be related to the change in molar volumes upon bond formation. An appropriate relationship has been introduced by Poole *et al.*, stating that the probability of bond formation for water with a given molar volume V is a normal distribution around the equilibrium molar volume of hydrogen bonded water V_{HB}.[33] We can thus write

$$\delta = e^{-((V - V_{HB})^2/\sigma)}, \quad (2.10)$$

where $\sigma = V_{HB}/4$ characterizes the width of the region around V. Using the equation of state $V - V_{HB} \approx -P \kappa_T V_{HB}$ with $\kappa_T \equiv -(1/V)(\partial V/\partial P)_T$ denoting the system's isothermal compressibility, Eq. (2.10) can be represented in the limit of small $\gamma P^2 \ll 1$ as

TABLE II. Coefficients of the Tait equation (Ref. [65]) [see Eq. (2.14)] to experimental data on the pressure dependence of the specific volume as provided by Refs. [100–104] (for details, see text). $P_0 = 1$ atm$= 1.013\,25$ bar, $\kappa_0 = \kappa(T, P_0) = V_0^{-1}(\partial V / \partial P)_{T,P_0}$, and $V_0 = V_{H_2O}(T, P_0)$ are the atmospheric pressure, the temperature-dependent isothermal compressibility, and the specific volume of the liquid at $P = P_0$. The two parameters m and n take account of the compressibility change with increasing pressure.

$0 < P < 8$ kbars	V_0 (cm^3/g)	$10^6 \kappa_0$ (bar^{-1})	m	$10^5\, n$
$T = 25\ °C$	1.003 01	45.25	3.3018	−4.2374
$T = 40\ °C$	1.007 89	44.31	3.3335	−4.7375
$T = 100\ °C$	1.043 5	47.31	3.2109	−3.9095

$$\delta = \delta(P) = e^{-\gamma P^2} \approx 1 - \gamma P^2 \tag{2.11}$$

with the coupling parameter $\gamma = (\kappa_T V_{HB} / \sigma)^2 = (4\kappa_T)^2$.[33,70] The pressure dependence of the fraction of H bonds thus results as

$$\bar{p}(T,P) = \delta(P)\bar{p}(T) = e^{-\gamma P^2} \frac{\sqrt{1 + 4\lambda_S(T)} - 1}{\sqrt{1 + 4\lambda_S(T)} + 1} \tag{2.12}$$

and in the limit of small pressures

$$\bar{p}(T,P) \approx (1 - \gamma P^2) \frac{\sqrt{1 + 4\lambda_S(T)} - 1}{\sqrt{1 + 4\lambda_S(T)} + 1}. \tag{2.13}$$

Equations (2.12) and (2.13) show a clear decrease of the fraction of hydrogen bonds with increasing the pressure. Note that at zero pressure, these equations reduce to the previous Eq. (2.5). In order to evaluate Eqs. (2.12) and (2.13) the molar volume of water needs to be estimated at the respective pressure. For our calculations we combined the experimental data reported by several authors covering a pressure range of $0 < P < 8$ kbars.[97–102] The most accurate and convenient two-constant molar volume (and consequently the compressibility) equation known as the Tait equation[65,103] has been adapted to fit experimental data for water up to 8 kbars,

$$V(T,P) = V_0 \left(1 - \frac{P - P_0}{\kappa_0^{-1} + m(P - P_0) + n(P - P_0)^2} \right), \tag{2.14}$$

where $P_0 = 1$ atm $= 1.013\,25$ bars, $\kappa_0 = \kappa(T, P_0) = -V_0^{-1}(\partial V / \partial P)_{T,P_0}$, and $V_0 = V_{H_2O}(T, P_0)$ are the atmospheric pressure, the temperature-dependent isothermal compressibility, and the specific volume of the liquid at $P = P_0$. The two parameters m and n take into account the compressibility change with increasing pressure (see Table II for the coefficients). Figure 4 displays the pressure dependence of the degree of hydrogen bonding $\bar{p}$ at the temperature $T = 25\ °C$ for different thermodynamic parameters of H-bond formation (as depicted in Table I). The pressure dependence of $\bar{p}$ at one given set of thermodynamic parameters [$\Delta E_{HB} = 4.5$ kcal/mol,[74] $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol (Ref. [78])] but at different temperatures is shown in Fig. 5. Note that the degree of hydrogen bond formation decreases (at constant pressure) with increasing temperature, while the main characteristics of the pressure dependence of $\bar{p}$ are retained.
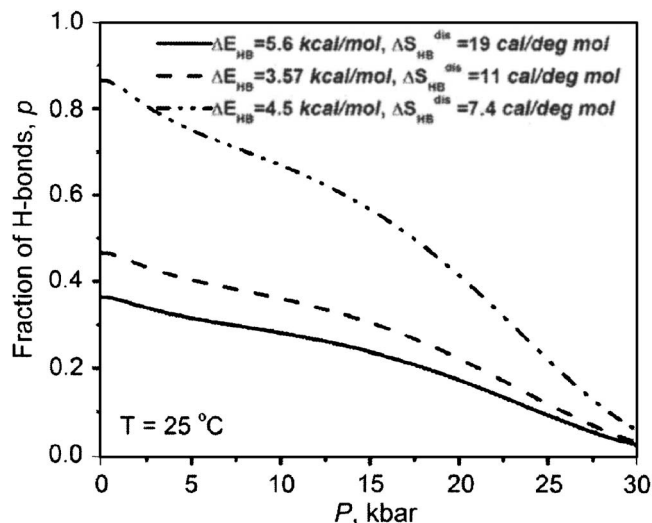

FIG. 4. Predicted pressure dependence of the degree of hydrogen bonding $\bar{p}$ at room temperature $T = 25\ °C$ calculated using Eq. (2.12) assuming different thermodynamic parameters for hydrogen bond formation: (continuous curve) $\Delta E_{HB} = 5.6$ kcal/mol, $\Delta S_{HB}^{dis} = 19$ cal/deg mol (Ref. [76]); (dashed curve) $\Delta E_{HB} = 3.57$ kcal/mol (Ref. [29]), $\Delta S_{HB}^{dis} = 11$ cal/deg mol; and (dashed-dot-dot) $\Delta E_{HB} = 4.5$ kcal/mol (Ref. [74]) $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol (Ref. [78]).

Interestingly, Eq. (2.12) predicts a sensitive dependence of the degree of H-bond formation on the applied pressure along with an effective loss of bond formations at pressures exceeding about 20 kbars.

In order to validate the predictive capabilities of Eq. (2.12), we evaluate the pressure dependence of the dielectric constant by use of Eqs. (2.12) and (2.6). As demonstrated in Fig. 6 the model captures the characteristics of $\varepsilon(T, P)$ up to pressures of about 2 kbars quantitatively and agrees qualitatively at higher pressures. Thermodynamic parameters of H-bond formation have been assumed according to Haggis et al. ($\Delta E_{HB} = 4.5$ kcal/mol, $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol).[74,78] Interestingly, despite the predicted decrease of the degree of
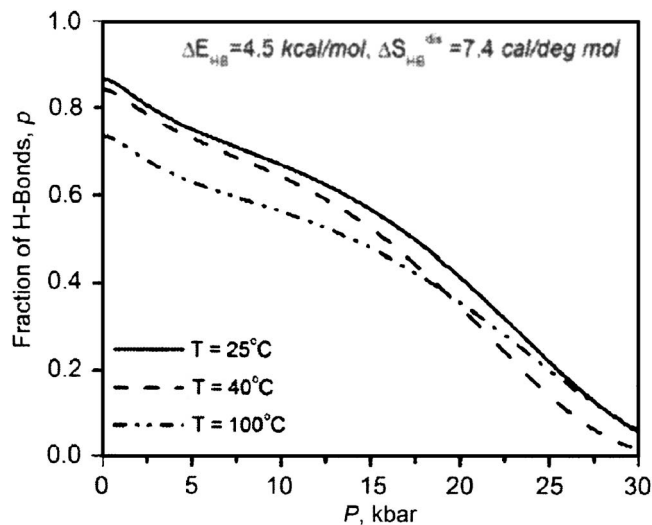

FIG. 5. Predicted pressure dependence of the degree of hydrogen bonding $\bar{p}$ at different temperatures assuming $\Delta E_{HB} = 4.5$ kcal/mol and $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol for the enthalpy and entropy of hydrogen bond formation (Refs. [74] and [78]) calculated using Eq. (2.12). Continuous, dashed, and dashed-dot-dot curves correspond to $T = 25\ °C$, $T = 40\ °C$, and $T = 100\ °C$, respectively.
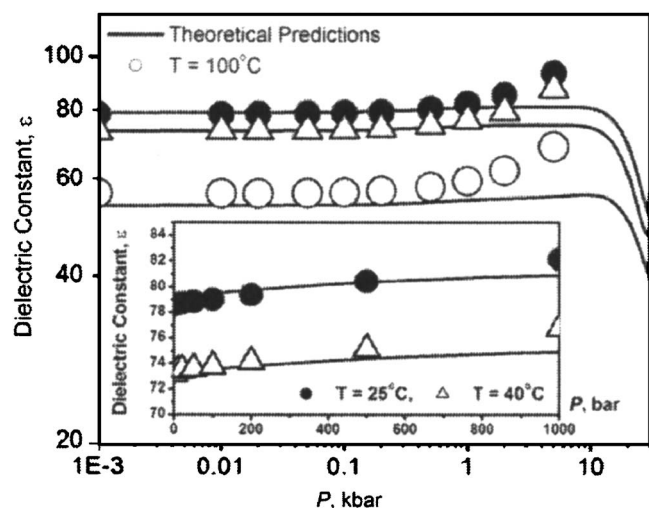
FIG. 6. Comparison of the pressure dependence of the dielectric constant at different temperatures as determined by experiment (Ref. [89]) and predicted by the model using Eqs. (2.12) and (2.6). Continuous curves represent calculated values assuming $\varepsilon_\infty = 1.88$, $\mu = 1.87$ D, and $\Delta E_{HB} = 4.5$ kcal/mol and $\Delta S_{HB}^{dis} = 7.4$ cal/deg mol for the enthalpy and entropy of hydrogen bond formation (Refs. [74] and [78]) Symbols ($\bullet$, $\triangle$, $\circ$) represent experimental results at $T = 25$ °C, $T = 40$ °C, and $T = 100$ °C, respectively (Ref. [89]). Inset shows magnified region demonstrating quantitative agreement between Eq. (2.12)/Eq. (2.6) and experimental data at moderate to high pressures.

hydrogen bonding with increasing pressure, the dielectric constant is predicted to increase in agreement with the experimental data. This behavior is contrary to the temperature effect on the dielectric constant (see Figs. 1 and 2: Increasing T results in decreasing $\bar{p}$ and ε) and is rationalized through the pronounced pressure dependence of the compressibility of water that offsets the effect of decreasing $\bar{p}$ at pressures up to 10 kbars.[65,78,89,105–107] As the pressure dependence of the compressibility levels off at high pressures, the influence of the decrease in $\bar{p}$ will eventually dominate the pressure dependence of the dielectric constant and thus the model predicts that $\varepsilon(P)$ will decrease at sufficiently high pressures, reaching values of about 40 (corresponding to polar organic solvents under normal conditions) at pressures of about 30 kbars. The model thus predicts dramatic changes in the solubilization behavior of liquid water at high pressures. Note that in the limit of infinite pressure (or temperature) ε goes to a finite value ($\varepsilon \rightarrow \varepsilon_\infty$). Unfortunately, at present the predicted change of characteristics at high pressures remains untested due to a lack of experimental data in the pressure range of interest. However, we note that Monte Carlo simulations of the pressure effect on the structure of water by Lazaridis *et al.* suggest the distortion of the water network structure at high pressures.[108]

Finally, we note that one virtue of the approach presented here is that it provides a tractable means to make available several thermodynamic quantities which are fundamental to the study of solution systems. For example, quantities such as the apparent molal enthalpy are related to the derivative of the dielectric constant with respect to temperature and pressure.[65]

Here we provide an explicit relation for $(\partial\varepsilon/\partial P)_T$,

$$\left(\frac{\partial\varepsilon}{\partial P}\right)_T = \frac{C}{V}\frac{\varepsilon}{4\varepsilon - (\varepsilon_\infty + Cg_0/V)}\left\{g_0\kappa_T + \left(\frac{\partial g_0}{\partial P}\right)_T\right\}. \tag{2.15a}$$

Using the expressions of the volume, the compressibility κ_T and the structure factor g_0 defined previously, Eq. (2.15a), becomes

$$\left(\frac{\partial\varepsilon}{\partial P}\right)_T = \frac{C}{V}\frac{\varepsilon}{4\varepsilon - (\varepsilon_\infty + Cg_0/V)}\left\{g_0\kappa_T - 2(g_0 - 1)\right.$$
$$\left.\times(g_0 + 3)\kappa_T P\left(4\kappa_T + \kappa_T^2 P - \frac{P}{V}\left(\frac{\partial^2 V}{\partial P^2}\right)_T\right)\right\}. \tag{2.15b}$$

At the atmospheric pressure ($P = P_0 = 1$ atm), Eqs. (2.15a) and (2.15b) reduce to

$$\left(\frac{\partial\varepsilon}{\partial P}\right)_{T,P_0} = \frac{C\kappa_0}{V}\frac{\varepsilon}{4\varepsilon - (\varepsilon_\infty + Cg_0^0/V_0)}\{g_0^0 - 2(g_0^0 - 1)$$
$$\times(g_0^0 + 3)\kappa_0 P_0(4 + (1 - 2m)\kappa_0 P_0)\}, \tag{2.16}$$

where $C = 4\pi N_A\mu^2(\varepsilon_\infty + 2)^2/(9k_BT)$, $g_0^0 = g_0(T, P_0)$.

III. CONCLUSION

We have presented a lattice model to describe the sensitive pressure and temperature dependence of H-bond formation in liquid water for different isotope compositions. The model correctly captures existing experimental data on the temperature dependence of the degree of hydrogen bonding as well as the dielectric constant. It accounts quantitatively for the experimentally observed pressure dependence of the dielectric constant up to pressures of 2 kbars and agrees qualitatively at higher pressures. The model predicts the existence of a—temperature dependent—pressure threshold above which hydrogen bonding rapidly decreases. The sensitive dependence of the structure of water on temperature and pressure described here rationalizes the different solubilization characteristics that have been observed in aqueous systems upon change of thermodynamic variables.

The predictive capability of a lattice model that neglects any correlations between the associated water molecules (such as next-nearest neighbor interactions or cooperativity) is surprising and likely related to the rapid exchange times of hydrogen bond that warrant the neglect of discrete cluster entities (clearly these predictions will be limited to properties that relate to sufficiently long time scales). While blending out much of the physics behind associating liquids, the approach has the advantage to be readily applicable to predict temperature and pressure effects in more complex solution scenarios (in particular, polymer solutions) as will be demonstrated in a forthcoming publication. In order to achieve a more quantitative agreement with experimental observations, we expect that one immediate improvement to our model would be to consider the temperature and pressure dependences of the energy of hydrogen bond formation that has been considered to be constant in this work.

ACKNOWLEDGMENTS

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