J. Phys. Chem. **1984**, *88*, 3180–3182

Simulation Studies of the Dihedral Angle in Water

Mihaly Mezei

Department of Chemistry,[†] Hunter College of the City University of New York, New York, New York 10021

and Robin J. Speedy*

Center for Polymer Studies[‡] and Department of Physics, Boston University,
Boston, Massachusetts 02215 *(Received: April 10, 1984)*

We report the distribution $g(\delta)$ of the dihedral angle δ for hydrogen-bonded dimers and tetramers in liquid water, for the MCY and ST2 models. The results show a significant excess of the staggered conformation $\delta \simeq (n + {}^1/_2)2\pi/3$, $n = 0, \pm1, \pm2$, characteristic of ice-like local structures.

Introduction

At low temperature the molecules of liquid water are hydrogen bonded in a single, well-connected, three-dimensional network.[2] While the properties of the network are not well understood, it can be supposed that the conditions of connectivity, with three or four bonds per molecule, and nearly equal bond lengths, have a strong influence on the local structure. The common ices and the aqueous clathrate crystals[3] satisfy those constraints and it has long been suggested that local regions of ice-like[4] or clathrate-like[5,6] order are present in water and account for its unusual properties.[7]

The simplest signal that might indicate the presence of such structures and distinguish between them is the dihedral angle δ_2 of the water molecule dimer.[8] $\delta_2 = \delta(\mathrm{H}_{(2)}\text{–O–O–LP}_{(2)})$ is defined in Figure 1. A related but more symmetrical parameter is the dihedral angle of the hydrogen-bonded water molecule tetramer. $\delta_4 = \delta(\text{O–O–O–O})$ is the angle between the planes of the two O–O–O groups in the tetramer. We report measurements of the normalized distributions $g(\delta)$, defined such that $g(\delta)\,d\delta$ is the probability that a dimer or a tetramer be in the conformation δ to $\delta + d\delta$.

In ice Ic both δ's have the values $(n + {}^1/_2)2\pi/3$, $n = 0, \pm1, \pm2$, which corresponds to the staggered conformation. In ice Ih three quarters of the tetramers are in the staggered conformation and one quarter are eclipsed, with $\delta = n2\pi/3$. In the clathrate lattices,[3] which are characterized by a predominance of planar pentagonal rings of hydrogen-bonded water molecules, all the dimers and tetramers are close to the eclipsed conformation, $\delta = n2\pi/3$.

The conformation of a dimer or tetramer is partly determined by its own internal energy. On that account the most probable state is the one of lowest energy. However, in liquid water we expect the constraints imposed by ring formation and three-dimensional connectivity to have a strong influence on $g(\delta)$ and to examine the latter effect we have calculated $\bar{y}(\delta)$, defined by

$$g(\delta) = \bar{y}(\delta)\exp(-\beta\langle u(\delta)\rangle) \qquad \beta = 1/k_{\mathrm{B}}T \tag{1}$$

The average $\langle\ \rangle$ is over all the dimers or tetramers observed that are in the conformation δ to $\delta + d\delta$. $u(\delta)$ is the internal energy of the dimer or tetramer (i.e., the pairwise sum of the energies of interaction between the molecules that comprise it).

A more formal treatment would define $y(\delta)$ by

$$g(\delta) = \langle y(\delta)\exp(-\beta u(\delta))\rangle \tag{2}$$

but the $\bar{y}(\delta)$ defined in (1) gives a more stable average and should reveal a similar form.

Calculations

The calculations analyzed the same set of configurations of MCY[10] and ST2[11] water that were used in the previous analysis.[9] Hydrogen bonds were defined by the geometric criteria for a strong bond[9] (cutoff values O–O separation, 3.3 Å; $\mathrm{H}_{(1)}$–O–O angle, 45°; $\mathrm{LP}_{(1)}$–O–O angle, 45°; $\delta(\mathrm{H}_{(1)}\text{–O–O–LP}_{(1)})$, 90°).

For the MCY water[9] at 25 °C (1 g/cm^3, 125 molecules) results for $\delta_2 = \delta(\mathrm{H}_{(2)}\text{–O–O–LP}_{(2)})$ derive from an analysis of 13 530 configurations, each separated by 250 Monte Carlo steps. 1 778 094 hydrogen-bonded dimers were found and analyzed. For δ(O–O–O–O) 6765 configurations, separated by 500 steps, yielded 2 334 678 O–O–O–O tetramers for analysis.

Results for $\delta(\mathrm{H}_{(2)}\text{–O–O–LP}_{(2)})$ for ST2 water[9] at 10 °C (1 g/cm^3, 216 molecules) derive from the analysis of 4000 configurations, each separated by 500 steps. 1 021 024 hydrogen-bonded dimers were found and analyzed. For δ(O–O–O–O), 2099 configurations, separated by 1000 steps, yielded 1 671 403 tetramers for analysis.

Results

Figure 2 shows the forms of $g(\delta_2)$ and $\bar{y}(\delta_2)$ for the dimers. The values are normalized to unity. As in previous work[9] the ST2 results show somewhat sharper features than the MCY results, so the quantitative details are model dependent, but the general trends are similar.

The most frequency occurring dimer conformation is that with $\delta \simeq \pi/3$. This is a staggered dimer that could fit into an ice lattice but not into a clathrate lattice.

A striking feature of Figure 2 is the order of magnitude variation in $\bar{y}(\delta_2)$. In comparison, $g(\delta_2)$ is more or less constant, which shows that the strong "forces" $k_{\mathrm{B}}T(\partial \ln \bar{y}(\delta)/\partial\delta)$ and $-\partial u(\delta)/\partial\delta$, which act to twist the dimer in the opposite sense, are in a state of delicate balance. $\langle u(\delta_2)\rangle$/kcal mol^{-1} varies from -5.3 at $\delta_2 = 0$ to -3.6 at $\delta_2 = \pi$ for ST2 and from -4.5 to -3.4 for MCY.

Another feature of Figure 2 that is worth noting is the lack of symmetry in $g(\delta_2)$ with respect to the permutation of protons and lone pairs. If the protons and lone pairs could be permuted randomly over any configuration of the oxygens, subject only to the ice rules, then one would expect the symmetry $g(\delta_2) = g(\delta_2 + 2\pi/3)$. This symmetry is obviously broken.

Figure 3 and 4 show the corresponding results for $\delta_4 = \delta$(O–O–O–O). In this case the symmetry[8] $g(\delta_4) = g(\delta_4 + 2\pi/3)$ is

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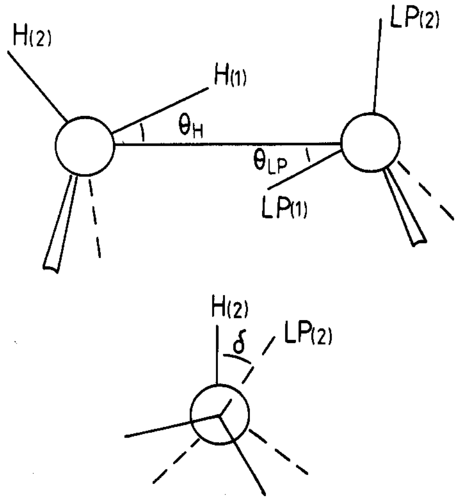

Figure 1. The hydrogen-bonded water molecule dimer. The dihedral angle δ_2 studied here is $\delta_2 = \delta(H_{(2)}\text{-O-O-}LP_{(2)})$, being the angle between the planes $H_{(2)}$-O-O and O-O-$LP_{(2)}$. This is the definition intended by Sceats and Rice.[12] Mezei and Beveridge[9] used the same figure as Sceats and Rice to define the δ_D that they report, but the figure is ambiguous and the reported values[9] refer to $\delta_D = \delta(H_{(1)}\text{-O-O-}LP_{(1)})$.

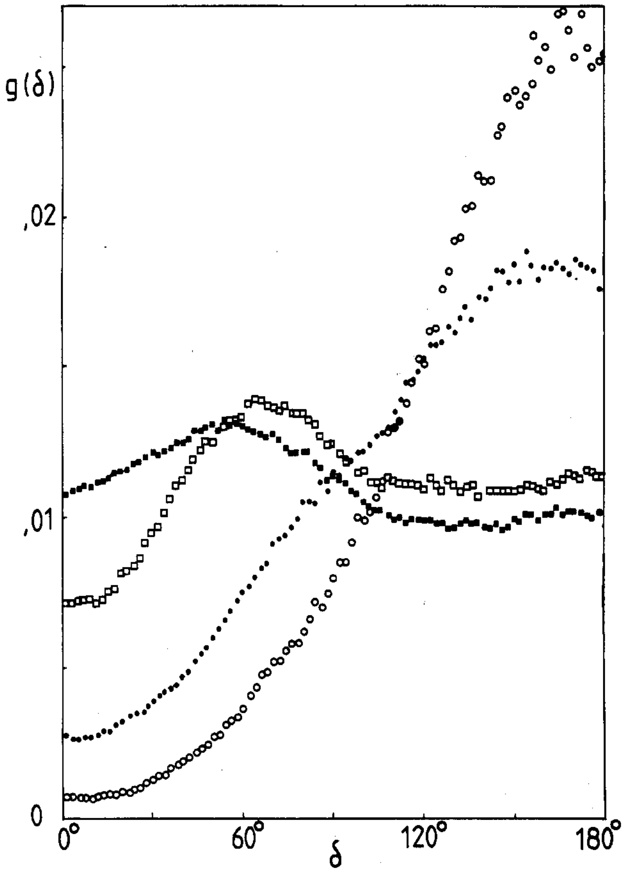

Figure 2. The normalized distributions $g(\delta_2)$ and $\bar{y}(\delta_2)$ for the dihedral angle $\delta_2 = \delta(H_{(2)}\text{-O-O-}LP_{(2)})$ in the hydrogen bonded dimer: (■) $g(\delta_2)$, MCY water at 25 °C; (□) $g(\delta_2)$, ST2 water at 10 °C; (●) $\bar{y}(\delta_2)$, MCY water at 25 °C; (○) $\bar{y}(\delta_2)$, ST2 water at 10 °C.

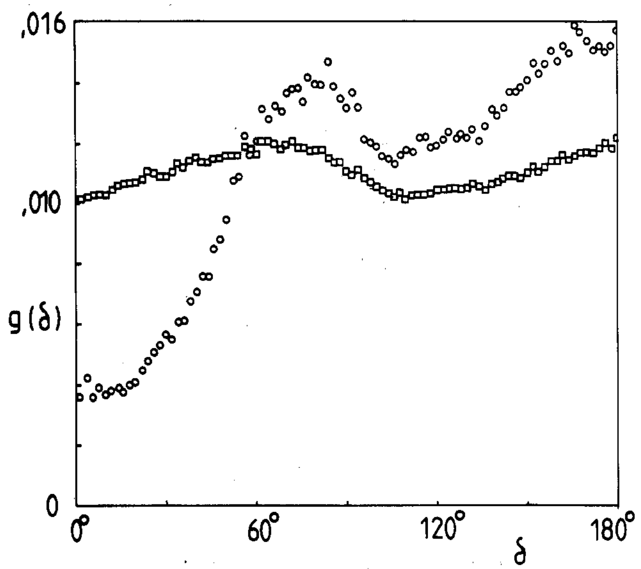

Figure 3. The normalized distribution $g(\delta_4)$ and $\bar{y}(\delta_4)$ for the dihedral angle $\delta_4 = \delta(\text{O-O-O-O})$ in the hydrogen-bonded tetramer. Data for MCY water at 25 °C: (□) $g(\delta_4)$; (○) $\bar{y}(\delta_4)$.

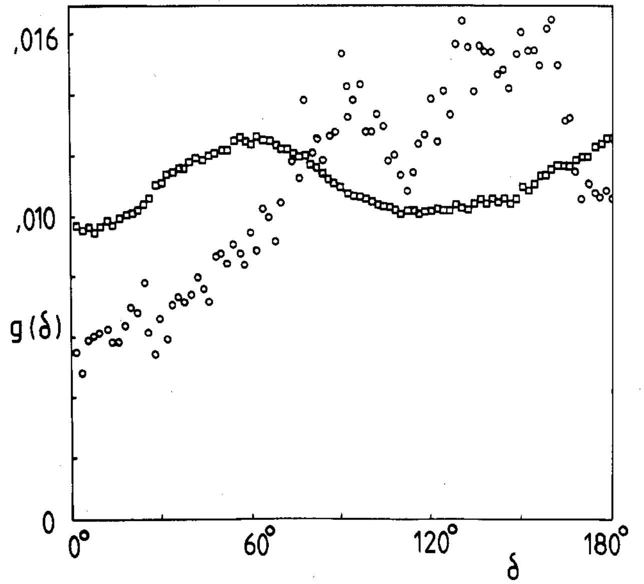

Figure 4. The normalized distributions $g(\delta_4)$ and $\bar{y}(\delta_4)$ for the dihedral angle $\delta_4 = \delta(\text{O-O-O-O})$ in the hydrogen-bonded tetramer. Data for ST2 water at 10 °C: (□) $g(\delta_4)$; (○) $\bar{y}(\delta_4)$.

evident (to within ± the dot size in the MCY case, and ± twice the dot size in the ST2 case) and the ST2 and MCY results for $g(\delta_4)$ are the same to within ± twice the dot size.

The peaks in $g(\delta_4)$ at $\delta_4 = (n + 1/2)2\pi/3$ correspond, as in the dimer case, to the staggered conformations characteristic of ice. However, the peak to trough variation is only about 25%, so there is also a substantial concentration of eclipsed tetramers.

The values of $\bar{y}(\delta_4)$ show some scatter, presumably because $u(\delta_4)$ can vary widely in the O-O-O-O cases. The troughs in $\bar{y}(\delta_4)$ occur at the eclipsed (clathrate-like) conformations, $\delta \simeq n2\pi/3$, implying that the influence of the network is to wind the tetramers away from the eclipsed state, but the peaks of $\bar{y}(\delta_4)$ do not occur precisely at the staggered conformation.

Discussion

Insofar as $g(\delta)$ serves as an indicator for structure, the results show that the local structure is somewhat more ice-like than clathrate-like. It should be noted, however, that the simulations correspond to water near room temperature and at a pressure of about 7 kbar (MCY)[9] or 800 bar (ST2).[9] That is, the results correspond to "normal" water at pressures which are likely to suppress low density states, so they do not rule out the possibility that eclipsed domains and clathrate-like structure grow as water is cooled below 0 °C at low pressure.[8] It is important to develop models that can be simulated efficiently so as to allow studies in the supercooled region.

The results give no information about the spatial correlations between eclipsed tetramers of the kind predicted in ref 8. However, in a related study,[13] we have found that pentagonal rings of

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[12] M. G. Sceats and S. A. Rice in ref 1, Vol. 7, 1983, Chapter 3.

hydrogen bonded water molecules are spatially correlated in ST2 water at 10 °C and in MCY water at 25 and 50 °C. It would be of interest, then, to study the correlation function $g_{\delta\delta}(r) = \langle \cos(3(\delta_1 - \delta_2))\rangle$, where δ_1 and δ_2 are the dihedral angles of a pair of tetramers separated by r. Since there are many more tetramers than pentagons, the statistics for $g_{\delta\delta}(r)$ should be better than those for the pentagon–pentagon correlation function $g_{55}(r)$[13] and may yield more conclusive evidence about long-range structural correlations in water.

Registry No. H_2O, 7732-18-5.

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A Time-Resolved Fluorescence Search for Intramolecular Vibrational Redistribution in S_1 *p*-Difluorobenzene Vapor

K. W. Holtzclaw and C. S. Parmenter*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405 *(Received: April 11, 1984)*

Time-resolved fluorescence spectra have been obtained after pumping each of 11 S_1 *p*-difluorobenzene vibrational levels in the range ϵ_{vib} = 1615–3310 cm^{-1}. The time resolution is acheived by collisional quenching of the S_1 state with O_2. In the absence of timing, the fluorescence spectra all contain the congestion typical of the extensive level mixing that is a prerequisite of intramolecular vibrational redistribution (IVR). When fluorescence times are limited to about 30 ps, the congestion is reduced and structure from the optically pumped level either appears or is enhanced. Such behavior indicates that a dynamic IVR is associated with the level mixing for every level studied.

Introduction

There have now been many reports describing the appearance of congested $S_1 \rightarrow S_0$ collision-free fluorescence after pumping a prominent $S_1 \leftarrow S_0$ absorption maximum in an attempt to prepare S_1 molecules in a single vibrational level.[1–3] Typically this behavior occurs as higher S_1 levels are pumped. In contrast, emission from lower levels is usually highly structured, and assignment shows that this structured emission is from the pumped S_1 level.

Some have taken the transformation from structured to congested emission as evidence for the onset and persistence of collision-free intramolecular vibrational redistribution (IVR) when higher S_1 levels are pumped. It is assumed that congested emission occurs because a fast IVR replaces the pumped S_1 vibrational identity with that of a large field of vibrational levels prior to significant fluorescence.

Others have pointed out,[1,4] however, that the fluorescence behavior can also be described on the basis of a static mixing with the dense field of states in the pumped region. This description avoids completely the concept of a time-evolving vibrational character, and there are no intrastate IVR dynamics. Thus while the collision-free spectra surely display the extensive S_1 level mixing that is a precursor to a dynamic IVR, they do not by themselves reveal whether such dynamics actually occur. It still remains an open question as to whether these indications of level mixing are also indications of a dynamic IVR.

In this report we describe a specific exploration of time-resolved emission from many levels in S_1 *p*-difluorobenzene (pDFB) in an attempt to obtain a first answer to this question. The collision-free pDFB $S_1 \rightarrow S_0$ fluorescence spectra show typical behavior. They are well structured from low S_1 levels ($\epsilon_{vib} \leq 1200$ cm^{-1}) and congested with negligible structure from high levels ($\epsilon_{vib} \geq 2500$ cm^{-1}). Structure appears superimposed on a congested background for levels of intermediate energies.

One proposes that time-resolved fluorescence spectra from higher energy regions could reveal IVR dynamics. If dynamics are present, structure from the initially pumped level will be prominent in fluorescence observed at times shorter than the IVR lifetime. At longer times, that structure will be replaced by congested emission on account of IVR.

Several reports already suggest that IVR dynamics are associated with two S_1 levels in pDFB. Most recently, Moore et al.[5,6] have observed indications of such time evolution with time scales of about 6 and 100 ps after picosecond excitation of the level $3^1 30^3$ ($\epsilon_{vib} \approx 1615$ cm^{-1}). Halberstadt and Tramer[7] earlier observed time evolution in fluorescence after pumping the level $3^1 5^1 30^1$ ($\epsilon_{vib} \approx 2190$ cm^{-1}) with the frequency doubled output of a mode-locked (500-ps pulse width) argon ion laser. The very first search in pDFB was by Dolson et al.[1,3,4,8,9] on the 2190-cm^{-1} level using the indirect method of chemical timing. Timing to about 10 ps revealed an evolution of vibrational features in the fluorescence spectrum that is consistent with IVR. The method has since been explored further, including a search for artifacts that could cloud this interpretation. None have been found in studies with pDFB or with fluorescence from *p*-fluorotoluene.[10,11]

Here we report a survey of emission from many S_1 pDFB levels in the range ϵ_{vib} = 1615–3310 cm^{-1} using chemical timing. The collision-free spectra from every level contain congestion, and from the higher levels, the congestion is to the almost complete exclusion of structure.[4,8]

The chemical timing method relies on the reduction of the fluorescence lifetime by the addition of O_2. This added gas quenches the S_1 state of pDFB with a cross section about one-third of hard sphere. This cross section is large enough so that the competing process of collision-induced vibrational redistribution does not obscure the interesting consequences of O_2 addition. In the presence of, say, 10^4 torr of O_2, fluorescence is observed (on average) only from those S_1 molecules that decay radiatively within a collision interval of about 25 ps after absorption of the pump photon. Pulsed excitation is not required. In fact, the first demonstrations of this technique used CW excitation.[8,11]

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