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Hydrogen Delocalization in Cyclic Water Clusters

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An alternative model of the dynamics in the low energy states of the water trimer is presented. In this model the dynamically averaged pseudorotational levels reflect the D_{3h} molecular symmetry group. In contrast to the currently accepted C_{3h} model, in the present model transitions through much higher energy barriers, such as clockwise to counterclockwise rearrangements, are allowed. This leads to a significantly different picture of the trimer dynamics. This paper identifies a difference between the two models which can be tested experimentally and will thereby facilitate the selection of the model that is closer to nature.

1. Introduction

The anomalous behavior of water and its importance to sustaining life make it a most intriguing compound to study. Yet, despite continuous efforts, liquid water evades a full theoretical description. This is due to its ability to form strong intermolecular hydrogen bonds. The nature of the hydrogen bond itself is a subject of much debate. There are several reports indicating that a hydrogen bond must possess partial covalent character.[1−3]

Recent progress in experimental techniques has allowed the measurement of vibrational transitions within water clusters of various sizes with great resolution. Vibrational−rotational-tunneling (VRT) experiments on small water clusters, which probe transitions between states resulting from the intermolecular interaction, are especially important for the elucidation of hydrogen bonding in liquid water. As stated by Keutsch and Saykally, these experiments lead to "Untangling the mysteries of the liquid, one molecule at a time" (see ref 4 and references therein).

A theoretical interpretation of the experimental results is necessary if we are to gain a full understanding of the dynamics in water clusters. However, the observed spectra are rather complex and their theoretical description quite difficult. In strongly anharmonic hydrogen bonded systems such as water clusters, where intra- and intermolecular degrees of freedom are strongly coupled, as evidenced for example by the substantial shift of the O−H bond stretch frequency[5,6] upon complexation, the separation of these modes is not obvious. In this case, only calculations that include all of the degrees of freedom will give a reliable picture of the dynamics. Unfortunately, such calculations are at present prohibitively expensive. Only for the smallest water cluster, the dimer, was the full 12D calculation recently performed by Leforestier et al.[7] However, to make it manageable, the authors were forced to invoke an adiabatic separation between the slow (intermonomeric) and fast (intramonomeric) modes.

For the trimer, not only the internal but also some of the intermolecular degrees of freedom must be frozen in order to make the dynamics calculations tractable.[8−13] Conclusions reached from these reduced dimensionality calculations, however, will be of limited reliability as they may lead to a distorted picture of the dynamics. The energy barriers, which on the scale of the zero point energy of a reduced problem are high, become negligible when compared to the total zero point energy of the cluster. Thus, feasible rearrangements may appear as not possible in the reduced dimensionality calculations. The numerical agreement of energetics in that case is insufficient to evaluate the feasibility of rearrangements. Such agreement is expected when the nodal structure of the reduced dimensionality wave functions coincides with that of the fully dimensional vibrational wave functions, averaged over the coordinates that are kept frozen.

Recently, Tuckerman and Marx demonstrated that quantum fluctuations of heavy atoms cannot be neglected in calculations of the free energy barrier for proton tunneling in malonaldehyde.[14] With the inclusion of the zero point energy, a system is able to access higher energy regions on the potential energy surface (see for example, Figure 3 in ref 15).

For hydrogen bonded clusters, the question arises if, and to what extent, the zero point energy of the intramolecular motion is available for intermolecular rearrangements. The zero point energy of a water trimer, calculated within the harmonic approximation, is in the range of 48 kcal/mol (16 800 cm^{-1}).[16] Taking into account the considerable strength of hydrogen bonding, including its partial covalent character, and the increased anharmonicity of the intramolecular potential induced by hydrogen bonding, one may expect that quantum fluctuations of monomers will contribute significantly to a decrease of the effective barriers for intermolecular rearrangements. In that case, the investigations of feasible rearrangements in water clusters should not be restricted to the lowest energy barriers. A barrier on the order of 100 cm^{-1} will cause a small shift of an energy level, rather than its splitting.

In this paper, an alternative interpretation of the pseudorotational component of the trimer's VRT spectrum will be presented. In this interpretation the clockwise to counterclockwise (cw-ccw) rearrangements must be taken into account to explain the low energy levels. In the first report of the VRT transition for a water trimer, Pugliano and Saykally suggested the cw-ccw rearrangement as a possible pathway.[17] However, since Wales dismissed it as not feasible,[18] it was not included in any model.

Our explanation as well as the older explanation of the origin of pseudorotational levels (briefly summarized in section 2) is

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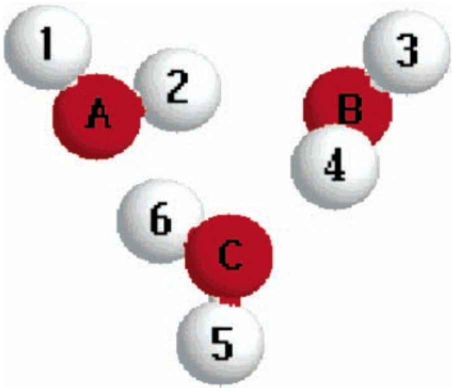

Figure 1. Minimum energy structure of a water trimer. The sense of rotation of hydrogen bonds in this figure will be referred to as clockwise (cw).

consistent with the currently available experimental evidence. However, each model yields a fundamentally different picture of the cluster dynamics. Processes that are considered slow in the old interpretation are fast in the new model. That is related to the assumption in this work that the separation of inter- and intramolecular modes in hydrogen bonded clusters is not valid. In our view, hydrogen bonding triggers significant coupling between inter- and intramolecular modes, which allows the funneling of at least some of the zero point energy of the monomers for intermolecular rearrangements. In other words, hydrogen bonded cluster should be considered as one molecule, rather than a group of interacting monomers. That should not be surprising in view of recent evidence of the partial covalent character of a hydrogen bond.[1−3]

The treatment of a cluster as one molecule changes the notion of low and high barriers and slow and fast transition processes. A barrier of few thousand of wavenumbers is small in relation to the total ZPE energy of the cluster (transition through it would be categorized as a fast process) but large when taking into account only the ZPE of one intermolecular mode (slow process).

This paper identifies a difference between the two models which can be tested experimentally and which will thereby facilitate the selection of the model that is closer to nature.

2. Pseudorotational Levels in a Water Trimer

An exhaustive summary of the theoretical and experimental work performed to date on the water trimer can be found in an excellent recent review by Keutsch et al.[19] It also provides a detailed explanation of the current understanding of the trimer dynamics.

A trimer is the smallest water cluster in which hydrogen bonds can form a cycle. Several transitions were detected and characterized for $(H_2O)_3$, and its deuterated version, $(D_2O)_3$, in the region of up to 150 cm^{-1}.[19] This permitted the construction of a manifold of the low lying intermolecular vibrational states.[12,13,20,21] There is complete agreement among ab initio calculations that the cyclic structure, represented in Figure 1, is the minimum energy conformation.[22] There are 96 equivalent minimum energy structures, differing by permutations of hydrogen and oxygen nuclei, when O−H bond breaking is not allowed. In half of the structures, O−H bonds involved in a hydrogen bonded ring are arranged in a clockwise direction (cw), and in the other half in a counterclockwise direction (ccw). In the theoretical treatment of a water trimer, the cw-ccw rearrangements were not considered feasible,[18] reducing the number of interconverting structures to 48. The rearrangements between these structures can, in general, be classified as breaking or not breaking hydrogen bonds. The transition through the lowest energy barrier (0.24−0.28 kcal/mol[16,23]), involves the flip of a non-hydrogen bonded, ‘free’ hydrogen nucleus from one side to the other of a plane formed by oxygen atoms. The barrier for the second type of rearrangement, the exchange of a hydrogen bonded hydrogen nucleus with a free one within the same monomer, requires more energy (2.04−2.34 kcal/mol[16,23]).

The observed low lying vibrational states of a trimer were attributed to the flipping (torsional) motion.[11,18] The sequential rearrangement between six equivalent structures through a flip of a ‘free’ hydrogen nucleus was named *pseudorotation*. The exchange of two hydrogen nuclei, called *bifurcation*, was considered to result in the fine-tunneling splitting detected for nearly every transition. The intensities of experimentally observed transitions to states with $K > 0$ have been consistent with spin statistics corresponding to the G_{48} permutation-inversion group[10,18,24]

The equivalent structures and their interconversions can be represented as permutations of hydrogen and oxygen nuclei. For example, to get the structure with hydrogen 3 flipped below the oxygen plane (for labels, refer to Figure 1) the atoms must be rearranged according to permutation (ACB)(153)(264)*, where the star represents the operation of inversion. In a trimer, the inversion is equivalent to a flip of all three free hydrogen nuclei to the opposite side of the oxygen plane. Permutations representing the sequential rearrangement between six equivalent structures differing by a flip of a free hydrogen nucleus form the cyclic permutation group G_6, isomorphic with the C_{3h} molecular symmetry group.[10,24] The dynamical averaging to the effective C_{3h} symmetry explains why the VRT spectra are those of a symmetric top.

Wales observed that the pseudorotational problem of tunneling between six equivalent minima is similar to that of finding benzene π-orbitals in the Hückel approximation.[18] That means that the energy levels of a trimer can be obtained in a simple perturbation treatment with one parameter. While for $(H_2O)_3$ the one parameter fit is pretty good, the spacing between the successive levels of $(D_2O)_3$ does not exactly reflect the β, 2 β, β spacing of the benzene-like problem (see the experimentally determined energy levels listed in Table 1). Recently, Keutsch et al.[25] included additional matrix elements corresponding to transitions involving double (β_{2f}) and triple (β_{3f}) flips in the Hückel-like treatment. That significantly improved the fit of $(D_2O)_3$ levels. However, the matrix elements β_{2f} and β_{3f}, obtained in the fit for $(H_2O)_3$, came out smaller than those for $(D_2O)_3$. That seems counterintuitive; one would expect larger matrix elements for the more energetic $(H_2O)_3$. While perturbative treatment leads to good numerical results, it does not definitively characterize the nature of a perturbation. Rearrangements other than a flip may be responsible for the tunneling matrix elements in the Hückel-like treatment.

The 3-D quantum mechanical calculations in torsional space of three free hydrogens (the displacement angles from the plane of oxygen atoms) in the groups of van der Avoird[10,11,26] or Bačić,[8] as well as the 2-D model calculations of Klopper and Schütz,[27] show variation in the spacing of $(D_2O)_3$ energy levels. However, they do not reproduce the magnitude of the splitting for all of the experimentally observed levels (see Table 2).

The selection rules of the C_{3h} group do not prohibit a transition that is not observed experimentally: from the $(D_2O)_3$ ground state to the state at 90.3 cm^{-1}. The 3-D quantum mechanical calculations predict a very low transition moment for the unobserved transition.[27,28] This, however, as pointed out

TABLE 1: Comparison of the Experimentally Determined Energies of ‘Pseudorotational’ States[20] to Those Calculated within the Perturbation Approach with Twelve Interacting Structures (I) and Six Interacting Structures (II)[a]

	level		$(D_2O)_3$			$(H_2O)_3$			
manifold	(C_{3h})	D_{3h}	exp.[b]	**I**	**II**	exp.[c]	**I**a	**I**b	**II**
lower	(A′)	A_1'	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	(E″)	E_1''	8.5332	7.49	10.27	22.7	21.1	21.8	21.8
	(E′)	E_1'	27.9748	26.53	30.81	65.4	64.6	65.3	65.3
	(A″)	A_2''	41.0742	41.07*	41.07*	87.1	87.1*	87.1*	87.1*
upper	(A″)	A_1''	90.3245	90.32*			2000.0	200,000	
	(E′)	E_1'	98.0380	104.86			2022.5	200,021.8	

[a] Energies, relative to the ground state, are in cm^{-1}. The asterisk denotes the levels chosen to reproduce the experimental values exactly. [b] Reference 20. [c] Reference 13.

TABLE 2: Comparison of the Experimental Energy Levels for the Deuterated Trimer with the Calculated Ones Using Various Potentials or Methods

	3D			2D	
experiment[a]	SAPT-5s[b]	DD[c]	BGLK[c]	BGLK[d]	this work
0.0	0.0	0.0	0.0	0.0	0.0
8.5332	9.4	7.68	5.15	6.4	7.49
27.9748	29.1	25.18	17.15	24.2	26.53
41.0742	41.1	36.62	24.73	40.9	41.07
90.3245	107.7	96.15	88.93	77.4	90.32
98.0380	117.0	107.51	98.27	97.8	104.86

[a] Reference 20. [b] Reference 26. [c] Reference 11. [d] Reference 27.

by Klopper and Schütz, results from the fact that the torsional potential energy surface deviates only slightly from D_{3d} symmetry,[27] in which the transition is forbidden.

3. Results

Applying the simple Hückel’s method, as proposed by Wales,[18] to twelve tunneling structures interacting in a cyclic pattern with alternating coupling constants, β_1 and β_2, it is possible to get surprisingly good agreement with experimentally observed energy levels. The structure of the resulting interaction matrix is presented below.

$$\begin{bmatrix}
0 & \beta_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta_2 \\
\beta_1 & 0 & \beta_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \beta_2 & 0 & \beta_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \beta_1 & 0 & \beta_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \beta_2 & 0 & \beta_1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \beta_1 & 0 & \beta_2 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \beta_2 & 0 & \beta_1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \beta_1 & 0 & \beta_2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta_2 & 0 & \beta_1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta_2 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta_2 & 0 & \beta_1 \\
\beta_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta_1 & 0
\end{bmatrix}$$

In Table 1, the energy levels obtained with that model (**I**), as well as with the model that includes only six structures (**II**), are presented and compared with experiment. The parameters β_1 and β_2 for **I** and β for **II** were chosen to reproduce the energy values of the levels marked with an asterisk in the table. For $(D_2O)_3$ the value of β_1 was -20.537 cm^{-1} and for $(H_2O)_3$ -43.55 cm^{-1}. Parameter β_2 for the deuterated trimer was -45.162 cm^{-1}. To get good agreement with the levels of $(H_2O)_3$, parameter β_2 must be increased significantly. In Table 1, results with $\beta_2 = -1000$ cm^{-1} (**Ia**) and $\beta_2 = -100{,}000$ cm^{-1} (**Ib**) are presented. The best agreement for $(H_2O)_3$ is obtained when β_2 is increased to infinity—the rearrangement becomes fully feasible and the interaction matrix is reduced to that of six interacting structures with $\beta = \beta_1/2$ (**II**). Thus, for $(H_2O)_3$ only one type of barrier crossing determines the low lying pseudorotational states. However, our model predicts no upper manifold of pseudorotational states below 200 cm^{-1} for $(H_2O)_3$.

For $(D_2O)_3$ the agreement is slightly better when considering twelve structures. For the lower manifold, the fitted levels differ by less than 1.5 cm^{-1} from the experimental values. In comparison, the values from the six structures model deviate from experiment by more than 1.6 cm^{-1}. In addition to the lower manifold of states, our model yields the upper manifold of states of $(D_2O)_3$ in agreement with the experimental pattern. The lower value of the experimentally observed degenerate state at 98.0 cm^{-1} can be explained by an interaction with higher energy hydrogen bond stretching states. In fact, the experimentally observed transition at 142.8 cm^{-1} was interpreted as a combination of ‘pseudorotational’ and stretching vibration.[21]

4. Discussion

In Table 2, the results of various calculations for the pseudorotational states of $(D_2O)_3$ are gathered and compared to experiment. Interestingly, the energy levels obtained in our simple perturbation treatment are closer to the experimentally observed energy levels than those obtained in 3-D quantum mechanical calculations including torsional motion.[8,10,11] Also, the 2-D calculation of Klopper and Schütz,[27] with an effective semiempirical Hamiltonian and adjustable parameters, performs quite well in comparison with a 3-D explicit treatment of torsional motion on the same PES.[11] While the potentials used for the calculations of torsional states are close to D_{3d} symmetry,[27] leading to qualitative agreement of the results with experiment, the calculated energy levels show large deviations from the experimental values in either the lower manifold (BGLK potential) or the upper manifold (DD and SAPT-5s potentials). At present, the agreement between experiment and calculation is not close enough to warrant a full acceptance of the torsional model. In addition, the calculations predict transitions to the upper manifold of $(H_2O)_3$[28] in the region of 150−200 cm^{-1} that have not yet been observed experimentally.[13] The experimental search for the presence of these transitions could vindicate one of the models. The detection of a pseudorotational transition to that manifold would strengthen the interpretation of the low lying vibrational states in terms of the torsional motion of non-hydrogen bonded hydrogens. Lack of them would support the present model.

The surprisingly good fit of the energy levels in our model, obtained with only two parameters, supports the notion that the system is in the small perturbation regime. The good agreement of the model with experiment makes it a viable alternative to the six structures model and justifies further analysis. Continued study is very important, as each model leads to a different effective symmetry of pseudorotational states and yields a fundamentally different physical picture of the cluster dynamics. The permutation-inversion group for the model of twelve structures interacting in a cyclic pattern with two alternating coupling constants is isomorphic with D_{3d} and D_{3h}. Especially interesting is the possibility that the dynamically averaged trimer's pseudorotational symmetry is D_{3h}. In that case, the rearrangements between clockwise and counterclockwise structures of the trimer must be feasible.

Unfortunately, the higher energy rearrangements, such as cw-ccw, have not drawn sufficient interest among computational chemists. Only a few papers have been devoted to, or included, high energy minima and other stationary points on the complex potential energy surface of the trimer.[29−31] At present there is insufficient information concerning the high energy rearrangements to support a tunneling pathway with certainty. Moreover, a model with a unique path may not be adequate. With the multitude of stationary points and pathways for the cw-ccw rearrangement, the β_1 and β_2 coupling constants might be multidimensional configurational averages, rather than values corresponding to a transition through a single barrier along the internal reaction coordinate, as considered for rigid systems. That, in addition to the coupling to the intramolecular degrees of freedom, may lead to significant increase of the tunneling matrix elements. The coupling constants involved in either of the proposed rearrangements are not evaluated in this work because only a multidimensional calculation can give a definitive answer about the nature of the pseudorotational states. Such calculations are at present prohibitively expensive.

A few examples of rearrangement pathways, consistent with the D_{3h} molecular symmetry group, are presented below. In the first category of rearrangements, the hydrogen nuclei in each water monomer are fixed to their oxygen atoms; the O−H bonds are not broken. However, monomers are allowed to rotate and break hydrogen bonds. One such rearrangement pattern is presented in Figure 2. The transitions represented by NW−SE arrows occur through a C_2 transition state (Figure 3a), listed as structure **14** in ref 29. That structure appears to be the lowest energy transition state for cw-ccw rearrangement. In our calculations with the GAUSSIAN98 suite of programs[32] at the B3LYP/aug-cc-pVTZ level, the transition state is 2365 cm^{-1} above the ground state. It was confirmed as the first-order stationary point through frequency calculation. The minima which it connects were obtained through minimization along the internal reaction coordinate (IRC). The transition through the C_2 structure can be represented by the permutation (BC)(12)(35)(46).

The second cw-ccw transition in this rearrangement pathway, indicated by SW−NE arrows, can be represented by the permutation (AC)(13)(24)*. The transition state for this rearrangement has not been located. However, the energy of this transition state must be less than 4331 cm^{-1}. This energy corresponds to the transition structure obtained with constrained interoxygen distances at 2.8 Å (which represent the equilibrium O−O distances in a trimer[33]). This structure is presented in Figure 3b. The calculations at the B3LYP/aug-cc-pVTZ level were done with GAUSSIAN98.[32]

Note that in Figure 2, the successive structures with the same handedness (cw or ccw) differ only by a flip and an exchange of hydrogen nuclei on one of the oxygen atoms. The bifurcated transition state for such a rearrangement lies at 2.04−2.34 kcal/mol,[16,23] which is much below the energy values for the cw-ccw transition states. However, the nodal structure will be determined by the high energy barriers.

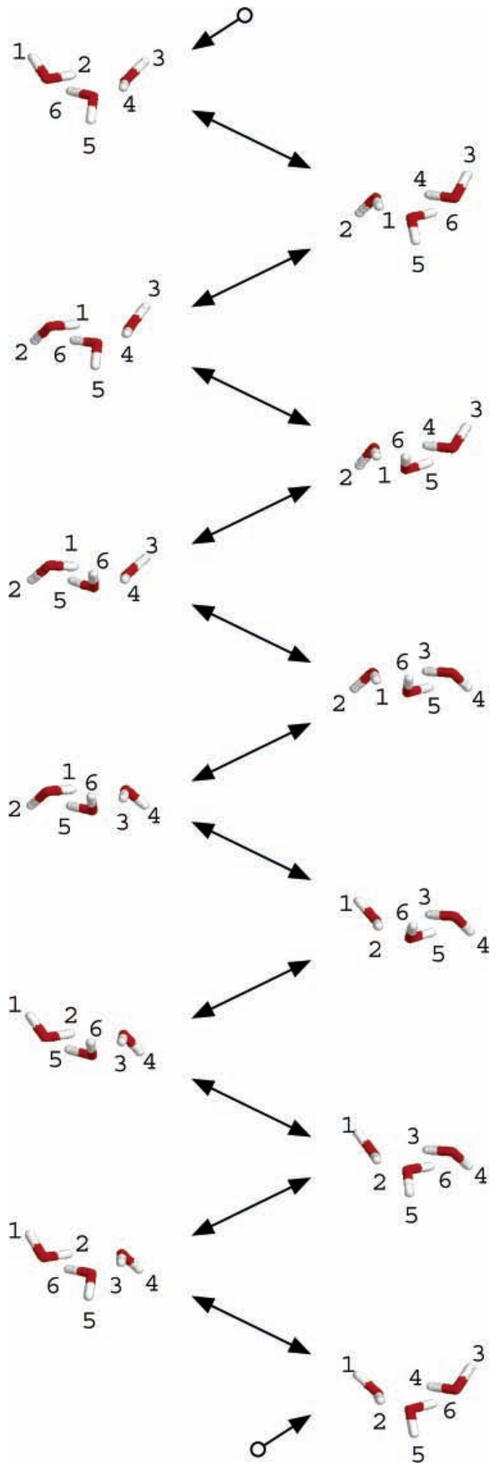

Figure 2. An example of the rearrangement pathway without breaking of O−H bonds. The hydrogen nuclei are explicitly numbered. Oxygen nuclei are kept in fixed positions as presented in Fig. 1. For the description of the transitions indicated by arrows refer to the text. Interestingly, the six successive cw (ccw) structures differ by a flip and an exchange of hydrogen nuclei on one of the oxygen atoms. Such a transition (internal rotation transition state in ref 16) requires much less energy than any of the indicated rearrangements. However, the nodal structure will be determined by the high energy barriers.

It may be interesting to examine whether the lower energy effective rearrangement, connecting structures with the same handedness, provides a better approximation for the calculation of the low energy vibrational states of a trimer, while still remaining in the low energy regions of the PES.

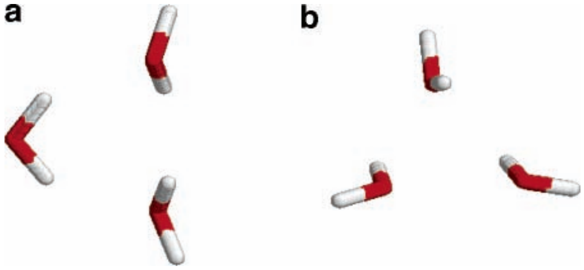

Figure 3. Transition structures for the rearrangements presented in Figure 2; (a) C_2, (b) C_s. The transition state was obtained with constrained O−O distances to 2.8 A (see text).

The second type of rearrangement pathway is more radical in the sense that it involves the breaking of covalent O−H bonds. However the word ‘broken’ in this case must be considered with care. The O−H bond is never fully dissociated, and the transition state for hydrogen transfer between the neighboring oxygen atoms occurs at much shorter O−O distances than the distances in a minimum energy structure of a trimer. Consequently, the energy for ‘breaking’ O−H bonds in a cluster is substantially lower than the energy necessary for a complete dissociation of three individual O−H bonds. In fact, as shown below, it is lower than the ZPE of $(H_2O)_3$, and this is why such a rearrangement should not be rejected without a reliable calculation that includes all of the degrees of freedom. As in the case of benzene, where Kekulé structures are supplemented by higher energy Dewar and polar ionic structures for a representation of the ground state, in a trimer the high energy rearrangements may contribute to the description of the low energy vibrational states.

One of the rearrangement pathways in this category, consistent with the D_{3h} molecular symmetry group, is presented in Figure 4. The NW−SE arrows indicate the concerted hydrogen exchange between neighboring oxygen atoms. The energy in a range of 26.36−28.11 kcal/mol (9217−9828 cm^{-1}) above the ground state was reported for the transition state for this rearrangement.[23,31] Our B3LYP/aug-cc-pVTZ calculations with GAUSSIAN98[32] yielded a similar value of 9170 cm^{-1}. That is a much lower value than the ZPE values (larger than 48 kcal/mol) obtained for $(H_2O)_3$ within the harmonic approximation at various levels of ab initio calculations by Fowler and Schaefer.[16]

The energy barrier for a concerted hydrogen transfer decreases with O−O distance and reaches a minimum (TS) for an interoxygen distance of 2.38 Å. The O−H distances at the transition state are around 1.22 Å, similar to the O−H distances observed for the proton-transfer transition state in a protonated water dimer.[34] The concerted hydrogen exchange transition is represented by the permutation (AB)(13)(46)*.

The SW−NE arrows represent a rearrangement with a flip and an exchange of hydrogen nuclei within each of the monomers. The simultaneous rearrangement on each monomer occurs through a C_{3h} structure in which all of the hydrogen bonds are bifurcated. The energy of this structure, calculated at B3LYP/aug-cc-pVTZ level with GAUSSIAN98,[32] is 3657 cm^{-1} above the ground state. The permutation corresponding to this transition is given as (12)(34)(56)*.

Overall, in the rearrangement pathway illustrated in Figure 4, hydrogen nuclei cyclically hop through free and hydrogen bonded sites on successive oxygen atoms, effectively ‘rotating’ about the central axis of the trimer. Three of the hydrogen nuclei ‘rotate’ clockwise and the other three counterclockwise. The importance of this type of rearrangement should increase with the size of a cyclic cluster. The barrier for a concerted hydrogen exchange in a tetramer is about 1300 cm^{-1} lower than that in a trimer,[31] whereas the ZPE is significantly higher.

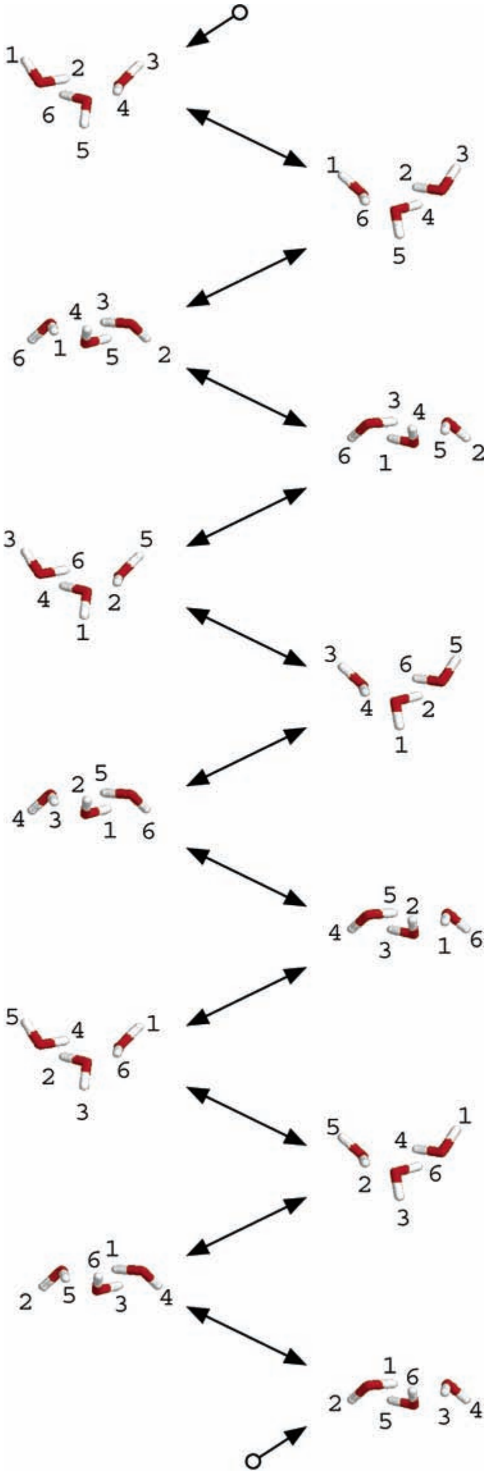

Figure 4. An example of the rearrangement pathway with breaking of O−H bonds. The hydrogen nuclei are explicitly numbered. Oxygen nuclei are kept in fixed positions as presented in Figure 1. For the description of the transitions indicated by arrows refer to the text. In this example hydrogen nuclei hop through oxygen atoms, effectively ‘rotating’ about the central axis of the trimer. Three of the hydrogen nuclei rotate clockwise and other three counterclockwise.

The effective rotation of all of the hydrogen nuclei in the same direction can be achieved by replacing the last permutation by (AB)(14)(23)(56). The contribution from this rearrangement, if present, may be important in a magnetic field. Rotating hydrogen nuclei may create a deshielding effect, like electrons in benzene. This effect should increase with the number of cycles in a cluster, being maximal for liquid water at low temperatures.

To account for the experimentally observed fine-tunneling splittings of pseudorotational levels, it is necessary to extend the symmetry considerations to the G_{96} group (or possibly larger). For the trimer, the transitions are split, in general, into four equally spaced lines.[19] The lowest and the highest energy lines are associated with transitions between nondegenerate states and the intermediate lines with transitions between triply degenerate states. This splitting can be explained by assuming that the hydrogen-bonded hydrogen nuclei move *independently* in an effective double well potential between neighboring oxygen atoms. The combination of tunneling splitting of each nucleus gives the pattern of four levels, in agreement with experimental observations. Balasubramanian and Dyke reported statistical weights for the water trimer's G_{96} group.[35] These spin statistics reproduce experimentally observed line intensities when the degeneracy of rotational states for $K > 0$ (ref 36) is taken into account.

5. Conclusions

We have presented a simple perturbation model for the cyclic water trimer which correctly reproduces the experimentally observed low energy vibrational levels. In this model the tunneling occurs between twelve degenerate structures that interact in a cyclic pattern with two alternating coupling constants. In contrast to the previously considered model, which included six degenerate structures and reflected the effective C_{3h} symmetry, this model implies the D_{3h} effective symmetry. That further implies mixing of cw and ccw structures, which can be visualized as continuous breaking and reforming of hydrogen bonds. The cw to ccw transitions may occur through rotations of monomers or a concerted hydrogen transfer. Although the high energy concerted hydrogen exchange pathways may not contribute significantly to the dynamics in a trimer, they may become more important for larger cyclic clusters or liquid water. The isotope mixing is known to occur in liquid water. It would be interesting to determine whether it occurs in small water clusters.

Much more work will be required to theoretically characterize the water trimer and to give a definitive answer as to whether hydrogen nuclei are delocalized over all of the oxygen atoms. This paper identifies a difference between the two models of pseudorotational states which can be tested experimentally and which will thereby facilitate the selection of the model that is closer to nature. Questions of the feasibility of rearrangements, the validity of the separation of intra- and intermolecular modes, the coupling strength in hydrogen bonding, and the accessibility of the internal zero point energy for intermolecular hydrogen transfer are important not only for untangling the mysteries of water, but also for understanding enzymatic or other biochemical processes, where hydrogen bonding is ubiquitous.

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